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A MATHEMATICAL MODEL FOR MULTICOMPONENT ION EXCHANGE UPTAKE ON CHABAZITE ZEOLITE

A Thesis

Presented for the

Master of Science

Degree

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ABSTRACT

Binary and multicomponent models for liquid ion exchange on chabazite zeolite are presented. The kinetic model assumes pore diffusion within the particle. Film mass transfer resistance is assumed to occur external to the particle. Several equilibrium models including the Langmuir, Dubinin-Polyani and a thermodynamic model are presented and utilized to complete the description of mass transport and ion exchange of strontium, cesium, calcium and/or magnesium in solution with sodium on chabazite zeolite.

A Langmuir model of the equilibrium for binary exchange, when used in the pore diffusion model, adequately predicted uptake rates of strontium and cesium. Kinetic uptake of calcium and magnesium from solution was not predicted as well, presumably because of the less accurate predictions of equilibrium by the Langmuir model.

Multicomponent uptake from solution in this system (Sr-Cs-Ca-Mg-Na) was not able to be predicted by the Dubinin-Polyani model due to instabilities encountered in the model. Kinetic multicomponent uptake for this system was predicted quite accurately by the thermodynamic model for two experimental runs taken at different total concentrations. Uptake curve variances for these two runs were found to be in the range of 1.7% to 34.2%.

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LIST OF SYMBOLS

a_i	coefficient for species i in parabolic equation
a_1	Langmuir equilibrium model constant 1
a_2	Langmuir equilibrium model constant 2
b_i	coefficient for species i in parabolic equation
b_0	Dubinin-Polyani equilibrium model constant 1
b_1	Dubinin-Polyani equilibrium model constant 2
b_2	Dubinin-Polyani equilibrium model constant 3
Bi_i	Biot number for species i , $k_{fi}R_p/D_{ei}$ (dimensionless)
c_{bi}	bulk liquid concentration of species i (meq/ml)
c_{bi}	initial bulk liquid concentration of species i (meq/ml)
c_i	liquid concentration of species i in equilibrium with solid phase (meq/ml)
c_{pi}	pore concentration of species i (meq/ml)
c_{pi}	average pore concentration of species i (meq/ml)
$c_{pi,o}$	initial pore concentration of species i (meq/ml)
C_{ptot}	total pore concentration (meq/ml)
c_{si}	surface concentration of species i (meq/ml)
d_i	coefficient for species i in parabolic equation
D_{eff}	effective pore diffusivity as defined by Robinson et al. (1993) (cm^2/s)
D_{ei}	effective diffusivity of species i (cm^2/s)
D_{mi}	molecular diffusivity of species i (cm^2/s)
D_{pi}	pore diffusivity of species i (cm^2/s)
D_{si}	surface diffusivity of species i (cm^2/s)
k_{fi}	film mass transfer coefficient (cm/s)
K_{ij}	equilibrium constant for binary pair i-j
m_t	adsorbate uptake or mass transfer rate (meq/ml/s)
r	radial position (cm)
R_p	radius of pellet (cm)
q^*	concentration on solid in equilibrium with liquid (meq/g)
q_i	adsorbed concentration of i (meq/ml particle)
q_i	average adsorbed concentration of i (meq/ml particle)
t	time (s)
V_f	volume of bulk fluid (ml)
V_s	volume of adsorbent (ml tot particle)
x	dimensionless radial distance, r/R_p
y_i	fraction of i in the solid phase
γ_i	liquid phase activity coefficient of species i
χ_i	solid phase activity coefficient of species i
δ	thickness of intraparticle concentration layer (dimensionless)
ϵ_p	porosity (ml pore space/ml particle)
Λ_{ij}	Wilson interaction parameter for binary pair i-j
σ	variance (dimensionless)
τ	time (dimensionless)
τ_p	tortuosity (dimensionless)

1. INTRODUCTION

1.1 OVERVIEW

Process waste water (PW) at Oak Ridge National Laboratory (ORNL) contains various contaminants among which are trace quantities of ^{137}Cs and ^{90}Sr. Although the concentrations of these radioisotopes are minute, they exceed allowable discharge limits. Proposed improvements to the facility which currently treats this process waste, in order to reduce secondary waste generation and improve removal of the ^{137}Cs and ^{90}Sr, include the addition of ion exchange columns.

Treatability studies were performed by Robinson and associates (Robinson and Parrott, 1988; Robinson et. al., 1991) to identify the most efficient ion exchange material capable of removing the desired radioisotopes in the presence of other ionic species in higher concentrations. In addition to achieving a specified removal rate, secondary waste generation was a concern in selecting an ion exchanger. Results from these earlier studies by Robinson et al. support the use of chabazite zeolite, an inorganic aluminosilicate molecular sieve, to remove trace quantities of ^{137}Cs and ^{90}Sr from the PW in the presence of other cations. These commercially available synthetic chabazite zeolites proved superior in tests performed by the researchers in removing cesium and strontium from PW when compared to other zeolites and resins. Secondary waste generation for this treatment process would comprise a spent zeolite which would be disposed of as a solid waste. (This is a much more desirable secondary waste form, as opposed to the current treatment process which generates a liquid secondary waste that must undergo further treatment to render it a solid radioactive waste prior to disposal.)

Zeolites are porous crystals which consist of silicon tetrahedra and aluminum tetrahedra arranged in highly structured frameworks which are permeated with channels of varying sizes and

orientations (Ruthven, 1984). This unique structure results in the "molecular sieve" properties of zeolites. The aluminum atoms present in the zeolite carry negative charges; cations, usually sodium or calcium, associated with the negative aluminum ions in the zeolite can exchange with solute cations ($^{137}Cs^{+}$ and $^{90}Sr^{2+}$ in this case) and thus give rise to the ion exchange properties of these materials.

The treatment of an aqueous stream by ion exchange on chabazite zeolite in order to remove trace amounts of ^{137}Cs and ^{90}Sr will be inhibited somewhat by the presence of other cations which will also exchange with the sodium in the zeolite. In the processing of ORNL waste water those cations are calcium, magnesium, and sodium. Typical concentrations of contaminants found in the process waste water are shown in Table 1. As seen in the table, typical concentrations of calcium, magnesium, and sodium significantly exceed the concentrations of ^{137}Cs and ^{90}Sr; and the total ionic strength of the waste stream is expected to run less than 0.01 N.

Table 1. Typical Composition of ORNL Process Waste Water

Contaminant	Concentration (N)	Contaminant	Concentration (N)
Ca^{2+}	2.0×10^{-3}	Cl^{-}	2.8×10^{-4}
Mg^{2+}	6.6×10^{-4}	NO_3^{-}	1.8×10^{-4}
Na^{+}	2.2×10^{-4}	CO_3^{2-}	2.3×10^{-4}
K^{+}	5.1×10^{-5}		
Si^{3+}	2.1×10^{-4}	^{90}Sr	1.7×10^{-11}
Al^{3+}	1.1×10^{-5}	^{137}Cs	9.1×10^{-13}
HCO_3^{-}	1.5×10^{-3}		
SO_4^{2-}	4.8×10^{-4}		

1.2 PROBLEM DEFINITION

A model of the ion exchange column would be useful in specifying system parameters such as column diameter and height and operating parameters such as flow rates. Once the behavior of the system is predictably modeled, physical and operational parameters can be optimized and the prototype can be used to predict behavior with varying inputs. In addition, this may be applied to other streams.

Robinson and coworkers (1993) examined the currently available mathematical models which are used to predict ion exchange column operation, and found that most of these models require extensive equilibrium and mass-transfer data. Thus, as the basis or first step of the prediction of column behavior, it is necessary to have the basic equilibrium and mass transfer mechanisms satisfactorily modeled for a given problem.

An examination of equilibrium and kinetic models is made in this paper. A kinetic model in combination with various equilibrium models is developed and results are presented and discussed for the corresponding binary pairs and the multicomponent system.

1.3 BACKGROUND

Previously, Robinson and coworkers (1993) modeled the binary and multicomponent systems under study in this paper using the Langmuir (for binary) and modified Dubinin-Polyani (for the multicomponent system) equilibrium relationships. Since that time Perona (1993) has developed an equilibrium relationship for these systems (both binary sets and the multicomponent system) based on thermodynamic theory. As semi-empirical relationships, the Langmuir and Dubinin-Polyani models predict the behavior of the equilibrium for the given systems competently in the concentration regions in which they were developed; however, operating outside of these concentration ranges or in the presence of competing cations in varying concentrations one would

expect the actual results to deviate from the models. As a more thermodynamically sound model, the equilibrium relationship presented by Perona is expected to predict the system behavior at equilibrium for an extended concentration range, and for a varying total concentration well outside of the concentrations within which the model parameters were developed.

Experimental data used in this study are taken from the study by Robinson and coworkers (1993). In addition, the Langmuir and Dubinin-Polyani equilibrium models which were developed by Robinson et al., as well as the model developed by Perona (1993), are analyzed as inputs to the kinetic model presented here. This kinetic model developed by Yao and Tien (1993), is a pore diffusion model; whereas the kinetic models examined by Robinson et al. (1993) assumed solid diffusion and combinations of macropore and micropore diffusion.

Below is Table 2 which lists the physical parameters of the chabazite zeolite used in the Robinson (1993) study. Robinson completed work with both zeolite crystals (Ionsiv IE-90) and zeolite pellets (Ionsiv IE-96), which are the crystals held together with a clay binder to form a larger particle. This study will deal only with the pellet form of the zeolite, IE-96, since that is the form of the zeolite that will ultimately be used in the columns.

Table 2 . Physical Properties of the Chabazite Zeolite, IE-96 (Robinson et al., 1993)

Property	Units	Value
Bulk density	g/cm^3	1.39
Real density	g/cm^3	2.05
Porosity	cm^3 pore /cm^3 total particle	0.32
Average particle radius	cm	0.02725

2. LITERATURE REVIEW

2.1 EQUILIBRIUM STUDIES

Many empirical and semi-empirical models exist to predict solid-liquid equilibrium in adsorption/ion exchange for binary systems. Among these models are the Langmuir and Freundlich equilibrium models, respectively:

$$q^* = \frac{a_1 c^*}{1 + a_2 c^*} \tag{1}$$

and

$$q^* = K(c^*)^n \tag{2}$$

where q^* is the concentration on the solid and c^* is the concentration in the liquid at equilibrium.

Both models require experimental data to predict the coefficients in the equations (a_1, a_2, K, and n). These two models appear to be the most often used equilibrium models when modeling batch and fixed bed ion exchange systems (e.g., Liapis and Rippin, 1977 and 1978; Crittenden et al., 1980; Ruthven, 1984; Yu and Wang, 1989; Gu et al., 1990); however, for the purposes of an equilibrium model for this multicomponent system neither is perfectly suitable.

The Fruendlich relationship does not reduce to Henry's Law at very low concentrations (Fritz and Schlunder, 1981), thus making it unsuitable for this system based on the expected compositions shown in Table 1. The Langmuir isotherm assumes surface homogeneity with respect to site0 energy (ibid; Wang and Tien, 1982), and although suitable for single solute adsorption (and multicomponent adsorption on sites with relatively homogeneous site energy and non-competing solutes), multicomponent adsorption would most likely not be well modeled with the competing species present in this system. In addition, the multicomponent forms of these

equilibria relationships cannot be relied on to apply over many decades of concentration ranges (Ruthven, 1984).

The ideal adsorbed solution theory (IAS) requires only single-solute data to predict multicomponent equilibrium isotherms. This theory is considered superior to the Langmuir in cases where the surface of the adsorbent is nonhomogeneous such as in the case of zeolites (Fritz and Schluender, 1981; Wang and Tien, 1982); however, the model becomes increasingly cumbersome for increasing number of solutes (Weber and Smith, 1987). In addition the IAS is based on the assumption that the adsorbed phase behaves ideally which is suitable only for some systems. The IAS has been shown to provide good estimates of experimental data for nonpolar solutes (Ruthven, 1984). Based on this information this model would not be suitable for the ionic species in this multicomponent system.

A modified Dubinin-Polyani theory was used by Robinson et al. (1993) to model the equilibrium for the multicomponent case under study. This modified version gives q_i^* , the adsorbed solid concentration at equilibrium of species i as a function of the liquid concentration of i, c_i :

$$q_i^* = \exp\left[b_0 + b_1 \ln(c_i) + b_2 [\ln(c_i)]^2\right] . \qquad (3)$$

This model was found to fit the experimental equilibrium data more accurately when tested against several other multicomponent equilibrium isotherms (Robinson et al., 1993).

The vacancy solution theory is described by Ruthven (1984) and was developed by Suwanayuen and Danner (1980). The theory is based on solution thermodynamics and assumes nonideal adsorbed phases; however it assumes an ideal liquid phase. Suwanayuen and Danner calculate the activity coefficients for the adsorbed species using the Wilson equations. Ruthven (1984) describes this model as providing a good fit in nonideal situations where other equilibrium

equations and theories break down; however, for simple systems that do not deviate far from ideality, other models may provide a better fit to the experimental data.

This theory has been taken a step further by assuming a nonideal liquid phase in addition to a nonideal solid phase (Elprince and Babcock, 1975; Smith and Woodburn, 1978; Shallcross et al., 1988; Perona, 1993). These researchers have developed ion exchange equilibrium models based on theoretical thermodynamic relationships. Each of these models is developed through the calculation and use of activity coefficients for both liquid and solid phases, thus making their predictions more accurate over a large range of concentrations (as opposed to assuming activity coefficients equal to unity for either or both phases, which implies ideality and limits the concentration range of applicability). Perona (1993) modeled the multicomponent system studied here (Cs-Sr-Ca-Mg-Na). A summary of the theory involved is given in section 3.1.3.

2.2 KINETIC STUDIES

Accounting for the transfer of the exchanging ions into and out of the zeolite pellets is the second step in modeling an adsorption/ion exchange phenomena. Kinetic modeling of multicomponent adsorption/ion exchange can be described by mass balance equations written for each species which vary with time. Thus these rate equations become partial differential equations (PDE) involving time and spatial independent variables. The actual rate (kinetics) at which components are adsorbed onto the solid is primarily dependent upon the assumed mechanisms with which the species diffuse and are adsorbed and exchanged, (such as solid diffusion, pore diffusion, surface diffusion, or a combination of these pathways) whereas the steady state solution is dependent upon the equilibrium model used. Based upon the assumptions made regarding the controlling rate mechanism(s), the calculation of mass transfer coefficients and/or diffusion coefficients must be completed.

Diffusion of a species prior to adsorption/ion exchange can be considered in two areas: (1) in the media outside the particle, and (2) within the particle. Transport outside of the particle, external particle mass transfer, is usually assumed to occur only in the laminar film surrounding the particle and is referred to as film diffusion. For a batch reactor, the bulk liquid is assumed to be well mixed, and the concentration of species *i* is assumed constant at any one time throughout the reactor. Usually, diffusion is assumed to occur through the "film layer" as a result of the difference in the particle surface concentration and the bulk liquid concentration, resulting in the classic Linear Driving Force (LDF) model proposed by Glueckauf (1955) which requires the estimation of a film mass transfer coefficient.

Diffusion of species *i* within the particle, or intraparticle diffusion, is much more complicated and can be assumed to occur by various mechanisms as mentioned previously — solid diffusion, pore diffusion, surface diffusion or a combination of these (Ruthven, 1984). Mass transfer within a porous pellet (such as chabazite zeolite) can take place at several levels, and can be modeled more simplistically by assuming a nonporous solid (homogeneous) absorber, which requires a single solid-phase diffusion coefficient (the homogeneous diffusion model) (Prazniak and Byers, 1987; Smith and Weber, 1988; Cornel et al., 1986; Robinson et al., 1993). This assumption however, works better for homogeneous particles with smooth surfaces of which the zeolite pellets are not a subset. Zeolite crystals would be expected to be much more amenable to this type of model. Robinson et al. (1993) showed this to be the case. Their homogeneous diffusion model satisfactorily modeled single crystal uptake rates of single solutes, but failed to model single or multicomponent uptake for zeolite pellets.

The next step in complexity would be to assume diffusion through the pores (pore diffusion) or diffusion along the surface of the pores (surface diffusion) is the rate limiting mechanism. In pore diffusion, the liquid in the pores is considered to be in equilibrium with the

adsorbed solid phase. The pore diffusion model is considered more accurate (as opposed to a surface diffusion model) if, in a multicomponent system, some species are more strongly adsorbed than other species. Surface diffusion modeling is usually used when weakly adsorbed species are not present (Friedman, 1984). A combination of pore and surface diffusion is sometimes referred to as heterogeneous diffusion (e.g. Fettig and Sontheimer, 1987; Merk et al., 1980), and should not be confused with "heterogeneous" diffusion as described in the next paragraph.

For a porous solid, the most accurate model would assume mass transfer occurs (a) in the pores of the material, macropore diffusion (pore and/or surface diffusion), and (b) in the solid crystals, micropore diffusion. Both of these diffusional fluxes are taken into account in the heterogeneous diffusion model (Fritz et al., 1981; Crittenden et al., 1987; Fettig and Sontheimer, 1987; Robinson et al., 1993). These mechanisms (micropore and macropore diffusion) can be assumed to occur in parallel or in series with each other (Robinson et al., 1993). The heterogeneous structure of the zeolites make the diffusion models which assume macropore (pore and/or surface diffusion which always occur in parallel) and micropore (solid diffusion) internal resistances (heterogeneous diffusion models) most realistic; however, they are also much more complicated (Ruthven, 1984; Doong and Yang, 1987; Nagel et al., 1987; Sun and Meunier, 1991; Robinson et al., 1993).

Doong and Yang (1987) modeled pressure swing adsorption on zeolite for both macropore and micropore diffusion, assuming parabolic concentration profiles in both the crystals and pellets. The model compared well with the experimental data. Nagel and coworkers (1987) modeled nonisothermal, multicomponent adsorption of gases with both macropore and micropore diffusional resistance occurring in parallel for a nonspecific case. Sun and Meunier (1991) modeled nonisothermal, multicomponent, macropore and micropore diffusion for adsorption on porous pellets in a fixed bed using a finite difference method in which the grid points were

adapted according to the steepness of the solution. They used several finite difference methods to show the expected improvement with improved modeling techniques for a nonspecific case.

Robinson et al. (1993) modeled the multicomponent system under study in this paper using macropore-micropore diffusion models in parallel and series; results were most promising with the model which assumed these diffusional mechanisms occurred in series.

Pore diffusion and/or surface diffusion models are frequently used to predict ion exchange and carbon adsorption phenomena (Kim et al., 1978; Friedman, 1984; Do and Rice, 1986; Smith and Weber, 1988; Yu and Wang, 1989; Yao and Tien, 1993). Most often, these models are solved using numerical methods such as finite difference or finite element analysis (particularly orthogonal collocation, which is a subset of finite element analysis). Various assumptions can lead to simpler equations and thus reduce calculation time. Many authors have solved adsorption problems assuming a parabolic concentration profile within the particle. This assumption simplifies the mathematics by allowing the PDEs describing the adsorption processes to be easily reduced to ODEs.

Do and Rice (1986) determined the validity of assuming a parabolic profile based on system parameters such as diffusivity, mass transfer coefficient, and particle size. In general, the researchers determined that the parabolic profile in the case of pore diffusion is valid for dimensionless time greater than 0.05, whereas the LDF model is valid for dimensionless time greater than 0.10 (Glueckauf, 1955). The smaller the particle, the more quickly the parabolic concentration profile develops; and the higher the tortuosity of a particle, the longer the concentration profile takes to develop. For the multicomponent system under consideration in this paper, based on the diffusion coefficients and mass transfer coefficients reported by Robinson et al. (1993), intraparticle pore fluid concentration profiles, assuming a parabolic fit, would be valid for $t > 1.0$ second.

In addition to studying the parabolic intraparticle profiles, Do and Rice (1986) assumed a quartic concentration profile and reduced the beginning time interval in which the assumption is not valid by approximately a factor of three. The increased complexity of such a solution would not, in most cases, be justified.

Other researchers have studied adsorption/ion exchange phenomena assuming intraparticle concentration profiles of various polynomial functions. For example, Do and Mayfield (1987) assumed an intraparticle concentration profile of the form:

$$\frac{q}{q^*} = a_0 + a_n\left(\frac{r}{R_p}\right)^n \tag{4}$$

where n is a complex function of q/q^* which improved the limit of validity for dimensionless time greater than 0.003 (where r is the radial coordinate; R_p the particle radius). Researchers Tomida and McCoy (1987) presented the following intraparticle concentration profile for pore diffusion, where for n=1, it reduces to a parabolic profile:

$$C_i(r,t) = \sum_{n=0}^{N} a_{2n}(t) r^{2n} \ . \tag{5}$$

Buzanowski and Yang (1989) assumed, for the case of solid diffusion, an intraparticle profile of the form:

$$q = A_0 + \sum_{i=2}^{N} A_i r^i . \tag{6}$$

Liaw et al. (1979), assuming a parabolic concentration within the solid particle (solid diffusion), arrived at an equation equivalent to the LDF model of Glueckauf. Doong and Yang (1987) also assumed parabolic expressions for both macropore and micropore diffusion for pressure swing adsorption using zeolite sorbent.

Yao and Tien (1993) assumed a parabolic intraparticle concentration profile for separate cases of pore and surface diffusion control. In their models, a "boundary layer" is defined within the pore of the particle in which the parabolic concentration profile is assumed. From the center of the particle to this "layer" the concentration is assumed to be the initial concentration within the pores (usually zero). The PDEs describing pore (surface) diffusion can then be reduced to ODEs, with the coefficients of the parabolic profile and the width of the boundary layer determined as functions of the various concentrations.

Yao and Tien compared calculations made with their pore diffusion and surface diffusion models to orthogonal collocation solutions for example cases. Their models agreed with the collocation solutions to within a few percent for the extreme cases. In addition, very significant improvement over the LDF model was shown for small time.

Pore diffusion is usually assumed to be the rate controlling intraparticle process (over surface diffusion) if, in a multicomponent system, some species are more strongly adsorbed than other species (Friedman, 1984) such as is the case here. Robinson and coworkers (1993) showed chabazite zeolite adsorbs cesium most strongly such that the order of selectivity is: Cs>Sr>Ca>Mg. Experimental data showed the magnesium is very weakly adsorbed compared to the other cations. In addition to this consideration, the surface diffusion coefficients were estimated by Robinson to be on the order of 10^{-9} cm^2/s compared with effective pore diffusion coefficients on the order of 10^{-5} cm^2/s, thus also supporting the dominance of pore diffusion (since these intraparticle mechanisms occur in parallel).

Since excellent agreement was reached by Yao and Tien (1993) with their model in comparison to the orthogonal collocation solution, and the calculational time on the computer would ultimately be lower using the less complex model compared to the heterogeneous model of Robinson et al. (1993), it was chosen to represent the kinetics for the binary and

multicomponent cases to be studied. Upon consideration of the points outlined in the previous paragraph, the pore diffusion model of Yao and Tien was chosen over the surface diffusion model to describe the kinetic phenomena. Equilibrium models presented by Robinson et al. (1993) will be integrated into the model, as well as the binary and multicomponent equilibrium model developed by Perona (1993) for the Sr-Cs-Ca-Mg-Na system.

2.2.1 External Mass Transfer

Usually liquid side diffusion (and resistance), or external mass transfer, is said to occur only within the laminar film surrounding the particle. In part this assumption is made for a batch reactor by assuming the liquid is well mixed with a resulting homogeneous bulk concentration with a homogeneous chemical potential, and thus there is no driving force in the bulk liquid. The mixing of this liquid, or hydrodynamics of the fluid in the case of columns, has a large effect on the diffusion in this laminar layer and thus the magnitude of the associated mass transfer coefficient. It follows that batch reactor mass transfer coefficients and those required to predict column operation would not necessarily be the same, whereas intraparticle mass transfer is essentially the same in batch and column operations (Ruthven, 1984).

The defining equation for the film mass transfer coefficient, k_f (cm/s), is written (Ruthven, 1984):

$$m_t = \frac{3k_f}{R_p}(c_b - c_s) \tag{7}$$

for a spherical particle, where:

m_t = mass transfer rate across the fluid pellet interface (meq/ml/s),
c_b = bulk fluid concentration (meq/ml),
c_s = surface fluid concentration (meq/ml), and
R_p = radius of the particle (cm).

Many empirical relationships exist for the calculation of film mass transfer coefficients

in batch reactors (e.g., Ruthven, 1984; Cornell et al., 1986; Smith and Weber, 1988). Most of these relationships involve the power input to the stirrer and the physical properties of the solutions. These correlations do not, however, account for the surface topography and roughness of an adsorbent which can impact the film mass transfer coefficient (Smith and Weber, 1988).

Film mass transfer coefficients can also be determined from experimental data by fitting the initial slope of the transient uptake (e.g., Fettig and Sontheimer, 1987; Weber and Wang, 1987; Smith and Weber, 1988; Robinson et al., 1993). Initial experimental points can be assumed to be unaffected by intraparticle mass transfer, and thus the film mass transfer coefficient can be found by:

$$\epsilon_p D_p \frac{\partial c_p}{\partial t} = \frac{3}{R_p} k_f (c_b - c_s) \tag{8}$$

assuming c_p (pore concentration, meq/ml) equals zero as t approaches zero.

For multicomponent systems, film mass transfer coefficients must be determined experimentally, because correlations do not account for the decreased rates due to component interactions (Smith and Weber, 1988).

2.2.2 Intraparticle Diffusion

Diffusion of a species in a given media is the result of two basic driving forces: (1) the gradient of chemical potential (this driving force is attributed to the concentration gradient by some), and (2) self-diffusion, the migration of a species in a solution at equilibrium (Ruthven, 1984). In the presence of a large gradient due to chemical potential such as exists initially in the zeolitic systems, self-diffusion becomes insignificant. Intraparticle diffusion in zeolites occurs in the macropores and micropores. Diffusion in the micropores is commonly modeled as solid diffusion; whereas macropore diffusion takes place within the pore liquid. Both of these

diffusional processes can exist simultaneously and operate in series or in parallel, as explained previously; however, often the diffusion process is modeled assuming diffusion in the pores is rate controlling (pore diffusion).

For liquid systems, several transport mechanisms have been identified which contribute to macropore diffusion. Two of these mechanisms are present in liquid diffusion, and operate in parallel: molecular (or bulk liquid) diffusion - transport through the center of the pores - and surface diffusion - transport through the adsorbed layer on the surface of the pores. (Others, which may become significant in gaseous systems, are Knudsen and Poiseuille diffusion.) An overall macropore diffusion coefficient, D_p, is defined as the sum of the diffusion coefficients when they operate in parallel (where D^{-1} is the resistance to mass transfer) (Ruthven, 1984):

$$D_p = \frac{D_m}{\tau_p} + D_s \tag{9}$$

where D_m is the molecular diffusion coefficient (molecular diffusivity) and D_s is the surface diffusivity. The molecular diffusivity is divided by the tortuosity, τ_p , which accounts for the random orientation of the pores, variation in pore diameter, and a reduced concentration gradient in the direction of flow for a porous solid when compared to a straight cylindrical pore path. Tortuosity factors generally fall in the range of 2-6 for zeolites (Ruthven, 1984). A tortuosity factor of less than 2 indicates that pore diffusion is significantly affected by surface diffusion, as well as molecular diffusion.

Diffusivities are concentration dependent for all but the most ideal solutions; however this dependence varies for different systems. In liquid systems the surface diffusivities are generally quite concentration dependent, while the molecular diffusivities are much less so. Also, as Ruthven (1984) points out, surface diffusion in macropores is usually significant only when Knudsen diffusion occurs (gas adsorption). Adsorbed phases, micropore solid diffusion, would

show a much higher dependence on concentration than would macropore diffusion (Ruthven, 1984). Since this study is not concerned with either macropore surface diffusion or micropore solid diffusion, the effective pore diffusivities will assumed to be constant. This is a valid assumption for the low concentrations being used in this study (Fettig and Sontheimer, 1987).

In most cases intraparticle diffusion coefficients are determined by fitting experimental data (Crittenden, 1980; Weber and Wang, 1987; Smith and Weber, 1988); however, empirical and semiempirical correlations do exist but must be used with caution (Weber and Liu, 1980; Ruthven, 1984). As with the calculation of film mass transfer coefficients, the interactions in multicomponent systems are not accounted for by correlations used to estimate intraparticle diffusivities (Liang and Weber, 1985). Robinson and coworkers (1993) determined intraparticle diffusion coefficients for this zeolite ion exchange system. The results reported by Robinson are discussed in detail in Section 3.2.3.

3. MODEL DEVELOPMENT

3.1 EQUILIBRIUM MODELS

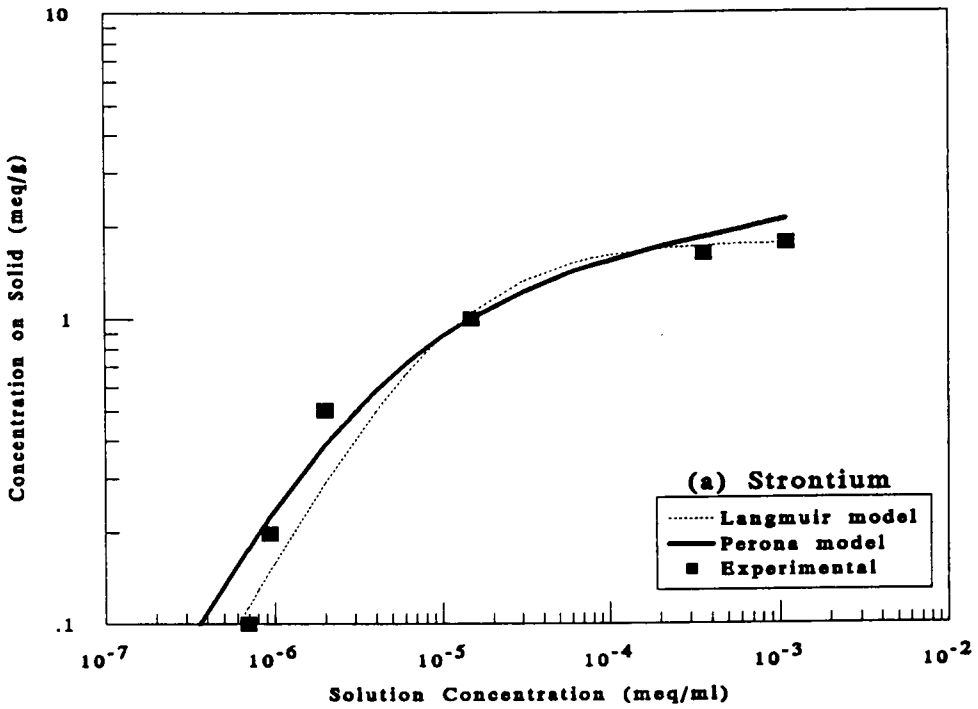
Various equilibrium models will be used with the kinetic model developed by Yao and Tien (1993). These equilibrium models are the two presented by Robinson et al. (1993): (a) the Langmuir for binary pairs, and (b) the modified Dubinin-Polyani for the multicomponent system, and the thermodynamic model developed by Perona (1993) for the binary and multicomponent systems. The coefficients determined by the researchers are given in the next sections, along with the graphical results of their work.

3.1.1 Langmuir Model

Robinson et al. (1993) found the best fit for the binary pair data to be predicted by the Langmuir equilibrium model given in equation (1). They obtained excellent results for the strontium-sodium and cesium-sodium exchanging pairs, with R^2 close to one. Figure 1 shows the predicted equilibrium isotherms curves for the binary pairs, compared to the experimental results. Calcium and magnesium equilibriums were not predicted quite as well, as seen from the R^2 values in Table 3 and from the resulting curves in Figure 1. Also included in the figure are

Table 3. Langmuir Isotherm Parameters for the Binary Pairs (Robinson et al., 1993)

Coefficient	Units	Sr-Na	Cs-Na	Ca-Na	Mg-Na
a_1	ml/g	173,702	157,009	456,942	481,696
a_2	ml/meq	98,176	68,574	221,015	610,790
R^2	---	0.95	0.94	0.67	0.78



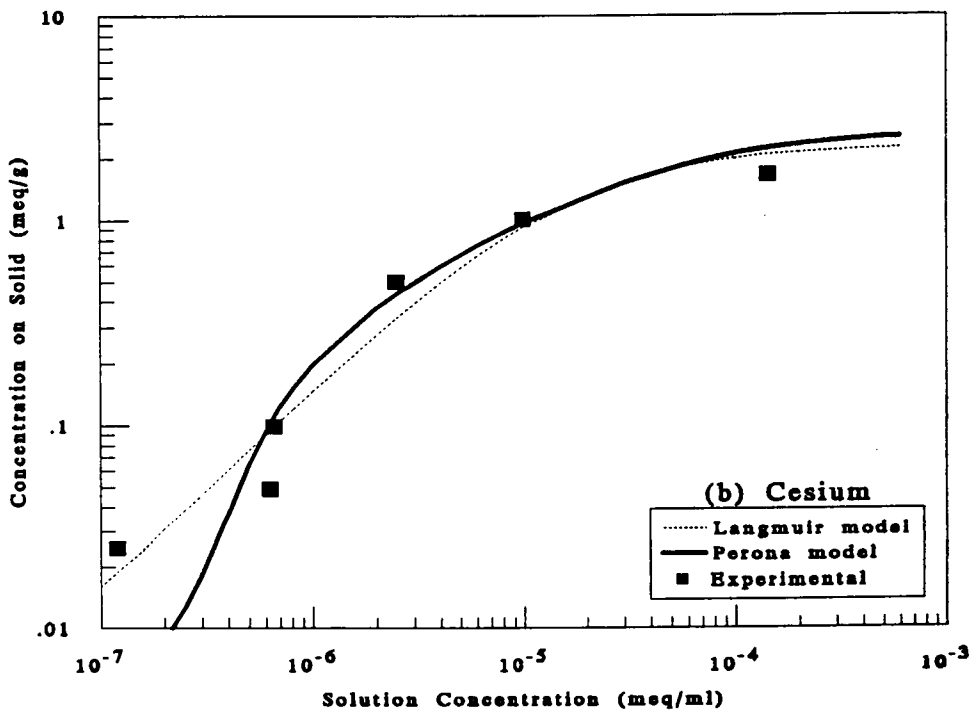
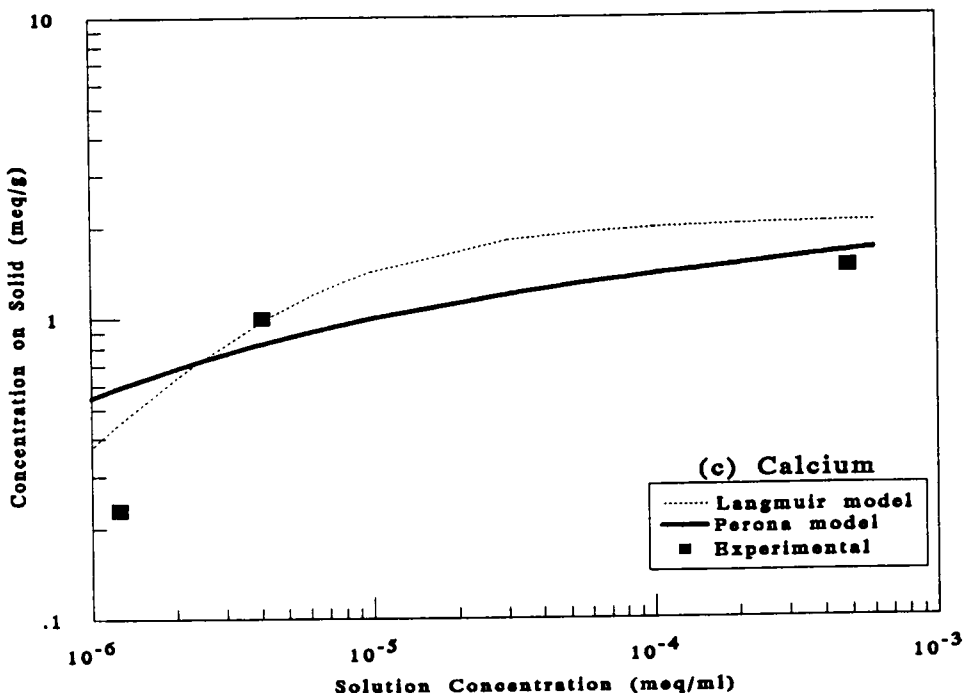


Figure 1. Binary equilibrium isotherms for (a) strontium, (b) cesium, (c) calcium and (d) magnesium.



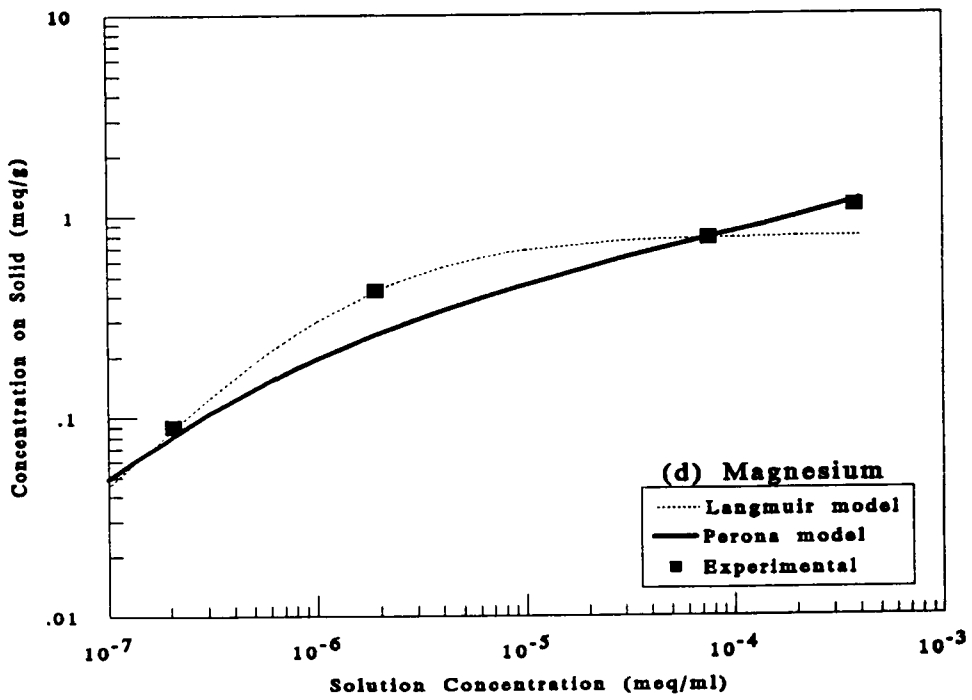


Figure 1. (Continued).

the binary equilibrium isotherms as predicted by the Perona (1993) equilibrium model. This model is discussed further in section 3.1.3; comparison of the models is made in section 3.1.4.

3.1.2 Dubinin-Polyani Model

Robinson et al., (1993) determined the best fit for the multicomponent system to be predicted by the modified Dubinin-Polyani given in equation (3). The researchers tried several other empirical equilibrium predictors, including the multicomponent Langmuir and Fruendlich models, however these relationships did not predict the experimental data as well as the Dubinin-Polyani model. Table 4 contains the resulting coefficients determined by Robinson for equation (3). In addition, the model predictions are shown against experimental data for each species in the multicomponent system in Figure 2. Also shown in Figure 2 are the Perona model (Perona, 1993) predicted equilibrium points for the given experimental points. Further discussion of the Perona model is included in section 3.1.3. Comparison of the models is made in section 3.1.4.

Table 4. Dubinin-Polyani Isotherm Parameters for Multicomponent System (Robinson et al., 1993)

Coefficient	Strontium isotherm	Cesium isotherm	Calcium isotherm	Magnesium isotherm
b_0	-4.742	-1.532	-4.212	-17.28
b_1	-1.157	-0.5890	-0.8560	-3.345
b_2	-0.07507	-0.05002	-0.04703	-0.1818
R^2	0.99	0.99	1.00	0.93

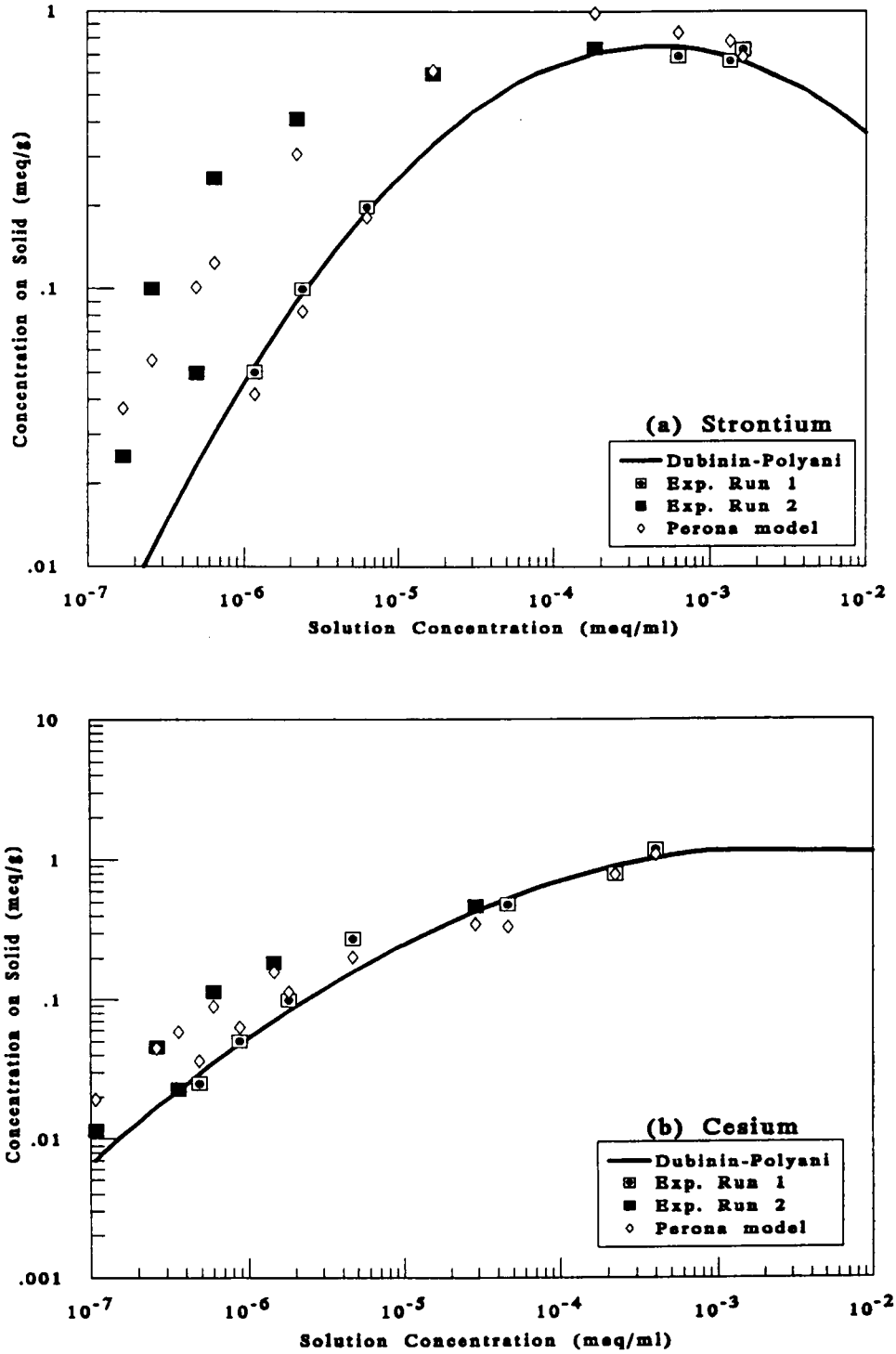
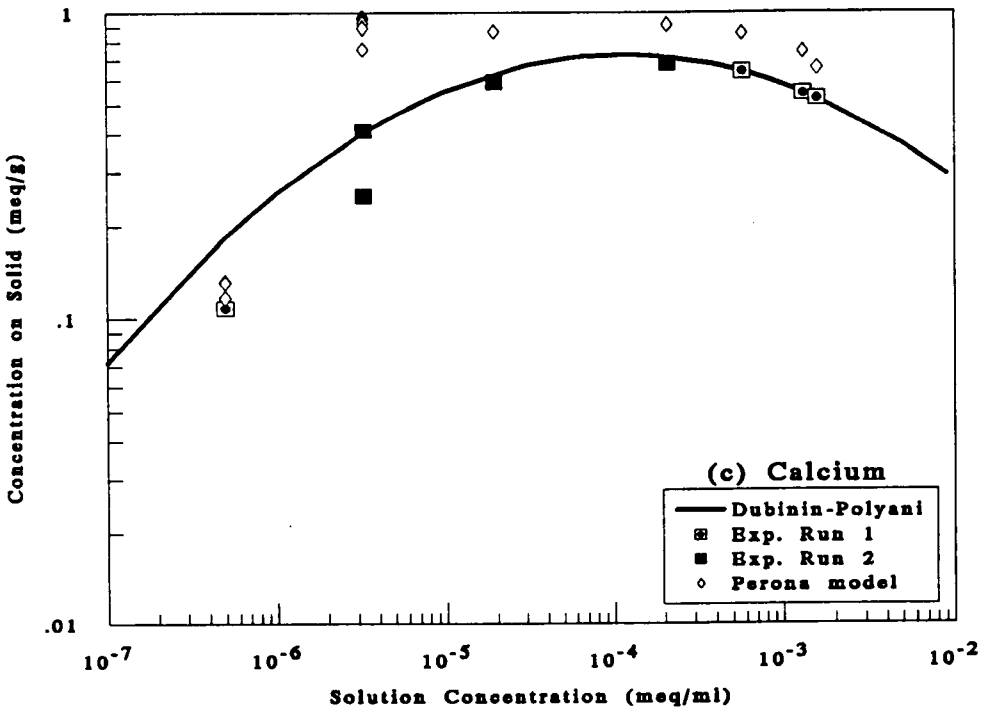


Figure 2. Multicomponent equilibrium isotherms for (a) strontium, (b) cesium, (c) calcium and (d) magnesium.



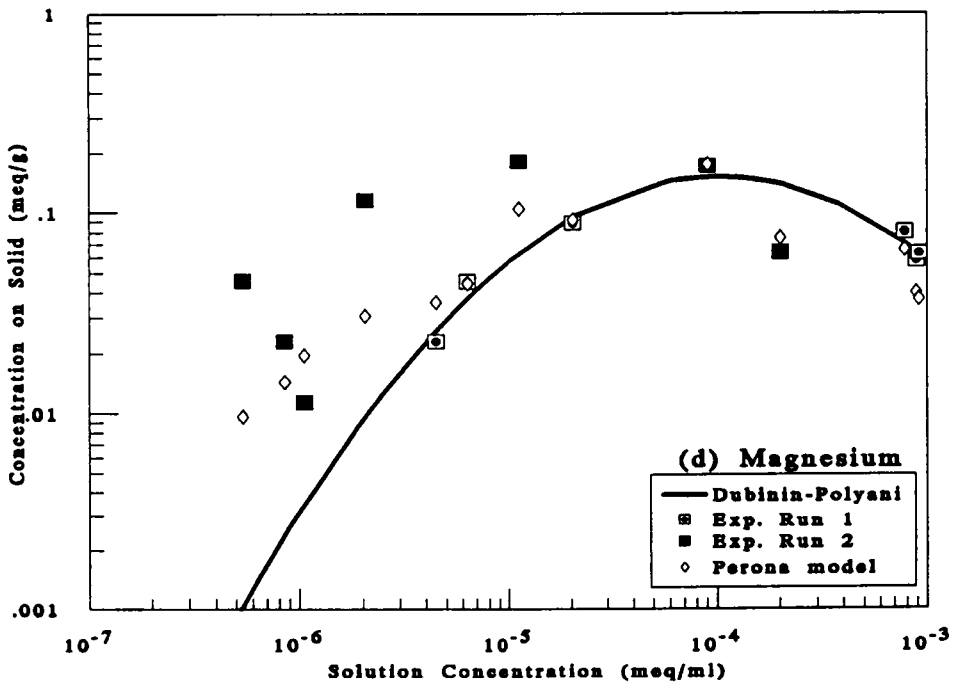


Figure 2. (Continued).

3.1.3 Thermodynamic Model

The adsorption-equilibrium model for the multicomponent system Cs-Sr-Ca-Mg-Na was developed by Perona (1993) based on fundamental thermodynamic relationships. Following is a brief discussion of the theory involved.

An ion exchange reaction between a species in solution, A, and the ion in the solid phase, $\underline{B}$, can be expressed as:

$$bA^{+a} + a\underline{B}^{+b} \leftrightarrows b\underline{A}^{+a} + aB^{+b} \ .$$

The equilibrium constant, $K_{A\text{-}B}$ for the above reaction is written:

$$K_{A-B}=\left(\frac{\Upsilon_A y_A}{\gamma_A c_A}\right)^b\left(\frac{\gamma_B c_B}{\Upsilon_B y_B}\right)^a \qquad (10)$$

where

y_i = equivalents fraction of i in the solid phase,
c_i = normality of i in the liquid phase, meq/ml,
γ_i = activity coefficient of i in the liquid phase,
Υ_i = activity coefficient of i in the solid phase.

In Perona's model, the Pitzer equation is used to calculate the liquid phase activity coefficients. The Wilson equation is used to calculate solid phase activity coefficients. This relationship relates the solid phase fraction to the solid phase activity coefficients, and is based on the Gibbs-Duhem equation. Wilson's equation for a multicomponent system is written:

$$\ln\underline{\gamma}_i=1-\ln\left(\sum_{j=1}^{m} y_j\Lambda_{ij}\right)-\sum_{k=1}^{m}\left(\frac{y_k\Lambda_{ki}}{\sum_{j=1}^{m} y_j\Lambda_{kj}}\right) \qquad (11)$$

where the Λ terms are the interaction parameters that are found by fitting experimental binary data for the multiple pairs (where all $\Lambda_{ij} = 1$). In turn, for the multicomponent system these binary interaction parameters are used in this same Wilson equation. Through the use of the equilibrium

relationship in equation (10), the Pitzer and the Wilson equations, and binary pair equilibrium data, the multicomponent isotherms are predicted. These equilibrium expressions can then be used in the rate equations to completely model the kinetics of the system. Table 5 contains the Wilson binary interaction parameters for the multicomponent system studied here as determined by Perona (1993).

Figures 1 and 2 show the model predictions for binary pairs Sr-Na, Cs-Na, Ca-Na and Mg-Na as determined by the Perona (1993) model, and multicomponent experimental points for each species: the equilibrium adsorbed concentrations on the solid as calculated by the Perona model given the experimental liquid concentrations at equilibrium.

Table 5. Wilson Binary Interaction Parameters and Equilibrium Constants (Perona, 1993)

Components		Wilson interaction parameters		Equilibrium constant
A	*B*	$\Lambda_{A\text{-}B}$	$\Lambda_{B\text{-}A}$	$K_{A\text{-}B}$
Sr	Cs	0.001	2.0	
	Ca	25	4.0	
	Mg	0.03	42	
	Na	7.96	0.112	0.159
Cs	Ca	4.8	0.2	
	Mg	2.0	100	
	Na	0.01	3.95	51
Ca	Mg	52	92	
	Na	86	2.0	0.022
Mg	Na	20	4.0	0.0005

3.1.4 Comparison of Equilibrium Models

Figures 1 and 2 show the comparisons for binary and multicomponent equilibrium models for each species. In Figure 1 the Langmuir equilibrium isotherm equation is used to predict loading for binary ion exchange with sodium for each of the four components. Also shown are the solid loadings for each species as predicted by the Perona equilibrium model. The Langmuir equations predict the loading more accurately than the Perona model for all the binary pairs in the given concentration ranges with the exception of the high range liquid concentrations (10^{-4} to 10^{-3} meq/ml) of calcium and magnesium. The Perona thermodynamic model predicts the loading in this concentration range for Ca and Mg more accurately.

Figure 2 shows the equilibrium models fit to experimental data for the multicomponent case (each species is shown separately). Two equilibrium runs were made with different total concentrations. The two experimental runs give quite obviously different loadings at concentrations below approximately 10^{-4} meq/ml for all but the calcium run; the calcium loading appears to be unaffected by total concentration.

Robinson's (1993) Dubinin-Polyani model was derived from the experimental run no. 1 as seen in the figure. The experimental data, regardless of the total concentration, appear to converge for higher liquid concentrations to the same loading results, and therefore the Dubinin-Polyani model would predict well at higher concentrations. At lower solution concentrations (under 10^{-4} meq/ml), the equilibrium loadings for each species are different for varying total concentrations, as seen in the figure.

The Perona model accounts for interactions between components, and thus more accurately predicts the changes in loading for a single species due to the varying concentrations of the remaining ions, as seen in Figure 2. Two distinct curves result from the Perona model (and follow the experimental data) for the equilibrium solid loadings of strontium, cesium and

magnesium in the two data sets. The varying solid loadings, which appear to be dependent on total solution concentration in a multicomponent system (and thus other species concentrations), are accurately modeled by the Perona model, whereas the empirical Dubinin-Polyani model is not able to account for the different total solution concentration and the presence of competing species.

3.2 KINETIC MODEL

Several important assumptions were made in developing the kinetic model described herein. These assumptions include: (a) the local ion-exchange rate is much faster than the rate of diffusion and is therefore not limiting, (b) the system is assumed isothermal because of the dilute concentrations, (c) local equilibrium is assumed to exist between the liquid and solid at all interfaces, that is, the macropore liquid and the particle surfaces, and (d) the liquid concentration is uniform throughout the reactor in the bulk liquid phase.

3.2.1 Pore Diffusion Model

As discussed in Section 2, researchers have made various assumptions regarding the intraparticle pore fluid concentration profile in adsorption phenomena. Parabolic, cubic, and quartic concentration profiles have been assumed, and the partial differential equations for adsorption within the particle subsequently modified. Yao and Tien (1993) assumed a boundary layer within the particle of depth, δ , in which the pore concentration follows a parabolic profile. From the center of the particle to the boundary layer the pore concentration for adsorbate i is c_{pio}, which, for the case of adsorption, is usually assumed to be zero at time zero. The model of Yao and Tien is developed here for a multicomponent system.

Beginning with the intraparticle mass balance for pore diffusion of species, i :

$$\epsilon_p \frac{\partial c_{pi}}{\partial t} + \frac{\partial q_i}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \epsilon_p D_{pi} \frac{\partial c_{pi}}{\partial r}\right) \tag{12}$$

where:

c_{pi}	= pore concentration of i (meq/ml pore),
q_i	= adsorbed concentration of i (meq/ml particle),
ϵ_p	= porosity of adsorbent (ml pore/ml particle),
r	= radial position (cm),
D_{pi}	= overall pore diffusion coefficient (cm^2/s), and
t	= time (sec).

The effective diffusivity for adsorbate i, D_{ei} , will be defined as:

$$D_{ei} \equiv \epsilon_p D_{pi}. \tag{13}$$

Boundary and initial conditions for the above case, adsorption of n, i-species into a spherical particle are:

$$\text{at } r = 0 \qquad \frac{\partial c_{pi}}{\partial r} = 0, \tag{14}$$

$$\text{at } t = 0 \qquad c_{pi} = c_{pi_0}, \text{ and} \tag{15}$$

$$\text{at } r=R_p \qquad D_{ei}\frac{\partial c_{pi}}{\partial r}\Big|_{r=R_p} = k_{fi}\left(c_{bi} - c_{pi}\big|_{r=R_p}\right). \tag{16}$$

Where the following variables are defined as:

c_{pio}	= initial pore concentration of species i (meq/ml pore),
R_p	= particle radius (cm), and
k_{fi}	= film mass transfer coefficient for species i (cm/s).

The equations are then written in terms of the following dimensionless independent variables:

$$\tau \equiv \frac{D_{ei}t}{R_p^2} \qquad \text{and} \qquad x \equiv \frac{r}{R_p}, \tag{17}$$

and the dimensionless Biot number for component i,

$$Bi_i \equiv \frac{kR_p}{D_{ei}} . \tag{18}$$

Assuming a constant diffusivity, the mass balance for pore diffusion becomes:

$$\left(\epsilon_p + f'(c_{pi})\right)\frac{\partial c_{pi}}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial c_{pi}}{\partial x}\right), \tag{19}$$

where $f'(c_{pi})$ is the equilibrium relationship. The initial and boundary conditions in terms of the independent variables are:

$$\text{at} \quad \tau = 0 \qquad c_{pi} = c_{pi_0} , \tag{20}$$

$$\text{at} \quad x = 0 \qquad \frac{\partial c_{pi}}{\partial x} = 0 , \quad \text{and} \tag{21}$$

$$\text{at} \quad x = 1 \qquad D_{ei}\frac{\partial c_{pi}}{\partial x}\Big|_{x=1} = Bi_i(c_{bi} - c_{si}) , \tag{22}$$

where c_{si} is the surface concentration of i in meq/ml. For a multicomponent system the equilibrium adsorbed phase concentration is dependent on the local concentration of all adsorbable components (Ruthven, 1984):

$$f'(c_{pi}) = \frac{dq_i}{dc_{pi}} = \frac{\partial q_i}{\partial c_{pi}}\Big|_{c_{pi+1}\cdots c_{pn}} + \frac{\partial q_i}{\partial c_{pi+1}}\frac{\partial c_{pi+1}}{\partial c_{pi}}\Big|_{c_{pi}c_{pi+2}\cdots c_{pn}} + \cdots\cdots + \frac{\partial q_i}{\partial c_n}\frac{\partial c_n}{\partial c_{pi}}\Big|_{c_{pi}\cdots c_{pn-1}} \tag{23}$$

Assuming, at any one time, τ ,

$$C_{ptot} = c_{pi} + c_{pi+1} + \cdots\cdots + c_{pn} \tag{24}$$

and assuming constant total pore concentration, C_{plot} , equation (23) reduces to:

$$f'(c_{pi}) = \frac{dq_i}{dc_{pi}} = \frac{\partial q_i}{\partial c_{pi}}\bigg|_{c_{pi+1}\cdots c_{pn}} - \frac{\partial q_i}{\partial c_{pi+1}}\bigg|_{c_{pi},c_{pi+2}\cdots c_{pn}} - \cdots\cdots - \frac{\partial q_i}{\partial c_n}\bigg|_{c_{pi}\cdots c_{pn-1}} . \tag{25}$$

Defining the adsorbate uptake rate, m, as the amount of material transported into the particle per unit time per unit of total particle volume one writes:

$$m = \epsilon_p \frac{d\bar{c}_{pi}}{dt} + \frac{d\bar{q}_i}{dt} = \frac{d}{dt}\left(\epsilon_p \bar{c}_{pi} + \bar{f}(c_{pi})\right) \tag{26}$$

or, in terms of dimensionless time τ ,

$$m = \frac{D_{ei}}{R_p}\frac{d}{d\tau}\left(\epsilon_p \bar{c}_{pi} + \bar{f}(c_{pi})\right) . \tag{27}$$

where the overbar denotes the average of the function over the entire volume or, for a sphere:

$$\bar{c}_{pi} = \frac{\int_0^1 c_{pi}x^2 dx}{\int_0^1 x^2 dx} = 3\int_0^1 c_{pi}x^2 dx \tag{28}$$

By requiring the average residual error in equation (19) to vanish, the following equation may be derived (Yao and Tien 1993):

$$\frac{d}{d\tau}\left(\epsilon_p \bar{c}_{pi} + \bar{f}(c_{pi})\right) = 3\frac{\partial c_{pi}}{\partial x}\bigg|_{x=1} . \tag{29}$$

Substitution of equation (22) gives:

$$m = \frac{3D_{ei}B_i}{R_p}\left(c_{bi} - c_{si}\right) . \tag{30}$$

Yao and Tien (1993) define a parabolic concentration layer within the pore of the particle. Figure 3 depicts this assumption for pore fluid concentration versus dimensionless radial distance. As shown in the figure, the initial pore concentration of component i is c_{pio} for x=0 to x=1-δ .

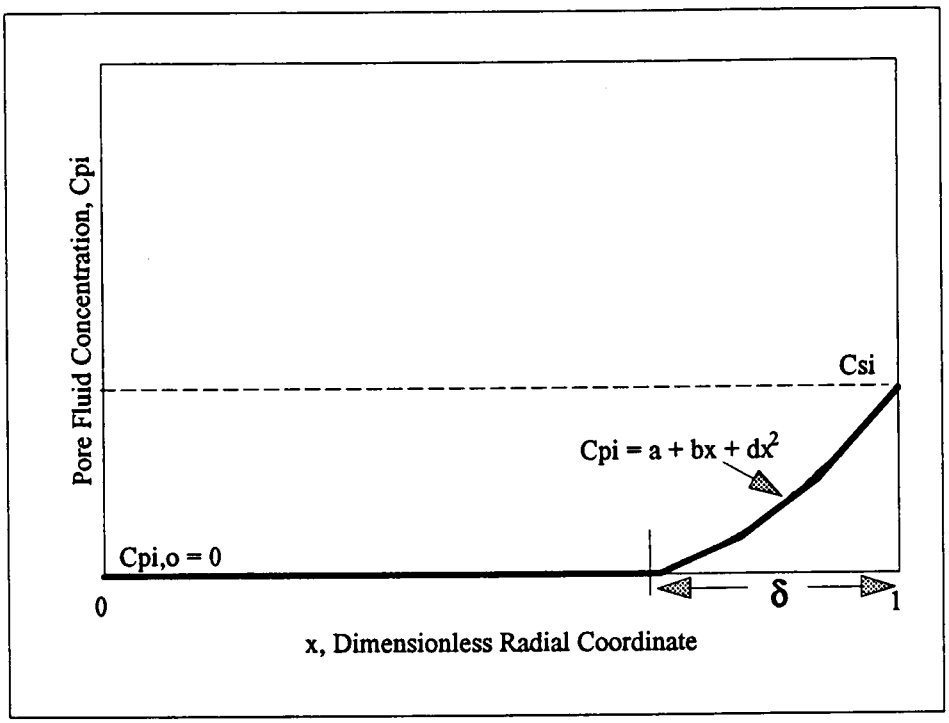


Figure 3. Pore fluid concentration as a function of dimensionless radial distance for the Yao and Tien (1993) model.

For x=1-δ to x=1 the pore concentration of species i is assumed to follow a parabolic profile, thus:

$$\begin{aligned} c_{pi} &= a_i + b_i x + c_i x^2 \qquad \text{for} \quad 1-\delta \le x \le 1 \\ c_{pi} &= c_{pi_0} \qquad\qquad\qquad\quad \text{for} \quad 0 \le x \le 1-\delta . \end{aligned} \tag{31}$$

Given this assumption and the continuity requirement which gives:

$$c_{pi} = c_{pi_0} \quad \text{and} \quad \frac{\partial c_{pi}}{\partial x} = 0 \quad \text{at} \quad x = 1-\delta , \tag{32}$$

Yao and Tien solve for the constants a_i, b_i, and d_i in terms of the concentration layer thickness, δ, and surface pore concentration of i, c_{si}:

$$a_i = \frac{(c_{si} - c_{pi_0})(1-\delta)^2}{\delta^2} \tag{33}$$

$$b_i = -\frac{2(c_{si} - c_{pi_0})(1-\delta)}{\delta^2} \tag{34}$$

$$d_i = \frac{c_{si} - c_{pi_0}}{\delta^2} , \tag{35}$$

thus δ is found to be:

$$\delta = \frac{\bar{c}_{pi} - c_{pi_0}}{c_{si} - c_{pi_0} - \left(\frac{\bar{c}_{pi} - c_{pi_0}}{2}\right)} . \tag{36}$$

Continuous functions for $\frac{\partial c_{pi}}{\partial x}$ through the pore space can be written and substitutions for a_i, b_i, d_i and δ_i are made to give:

$$\left.\frac{\partial c_{pi}}{\partial x}\right|_{x=1} = \frac{2\left(c_{si} - c_{pi_0}\right)\left(c_{si} - c_{pi_0} - \dfrac{\bar{c}_{pi} - c_{pi_0}}{2}\right)}{\bar{c}_{pi} - c_{pi_0}} \quad . \tag{37}$$

Yao and Tien introduce an approximation:

$$\bar{f}\left(c_{pi}\right) \approx f\left(\bar{c}_{pi}\right) \tag{38}$$

which is exact for a linear isotherm. The deviation of this assumption from real behavior depends on the extent of nonlinearity of the isotherm. With this assumption, and combining equations (29) and (37),Yao and Tien arrive at:

$$\left(\epsilon_p + f'(\bar{c}_{pi})\right)\frac{d\bar{c}_{pi}}{d\tau} = \frac{6\left(c_{si} - c_{pi_0}\right)\left(c_{si} - c_{pi_0} - \dfrac{\bar{c}_{pi} - c_{pi_0}}{2}\right)}{\bar{c}_{pi} - c_{pi_0}} \tag{39}$$

and

$$Bi_i\left(c_{bi} - c_{si}\right) = \frac{2\left(c_{si} - c_{pi_0}\right)\left(c_{si} - c_{pi_0} - \dfrac{\bar{c}_{pi} - c_{pi_0}}{2}\right)}{\bar{c}_{pi} - c_{pi_0}} \tag{40}$$

which are both valid for small τ, but not for large τ. A further approximation, that

$$\text{for small } \tau, \quad \bar{c}_{pi} << c_{si} \quad \text{and} \quad \text{large } \tau, \quad \bar{c}_{pi} \rightarrow c_{si} \tag{41}$$

results in Yao and Tien's Model 1 for intracrystalline pore diffusion:

$$\left(\epsilon_p + f'(\bar{c}_{pi})\right)\frac{d\bar{c}_{pi}}{d\tau} = 6\left[\frac{c_{si} - c_{pi_0}}{\bar{c}_{pi} - c_{pi_0}} + \frac{1}{2}\right]\left(c_{si} - \bar{c}_{pi}\right) \tag{42}$$

and

$$Bi_i\left(c_{bi} - c_{si}\right) = 2\left[\frac{c_{si} - c_{pi_0}}{\bar{c}_{pi} - c_{pi_0}} + \frac{1}{2}\right]\left(c_{si} - \bar{c}_{pi}\right). \tag{43}$$

These two equations can be equated to give:

$$\frac{d\bar{c}_{pi}}{d\tau} = \frac{3Bi_i\left(c_{bi} - c_{si}\right)}{\left(\epsilon_p + f'(\bar{c}_{pi})\right)} \tag{44}$$

which can be solved numerically. For this study, equation (44) was solved using a fourth order Runga-Kutta routine.

The values for c_{bi} and c_{si} in the above equation are found by writing an overall mass balance:

$$V_f\left(c_{bi_0} - c_{bi}\right) = V_s\left(\epsilon_p\bar{c}_{pi} + \bar{q}_i\right) \tag{45}$$

and again from equation (43), assuming $c_{pi0} = 0$ at $\tau = 0$:

$$2\left(\frac{c_{si}}{\bar{c}_{pi}} + \frac{1}{2}\right)\left(c_{si} - \bar{c}_{pi}\right) = Bi_i\left(c_{bi} - c_{si}\right) \tag{46}$$

which upon rearrangement gives:

$$\frac{2}{\bar{c}_{pi}}c_{si}^2 + \left(Bi_i - 1\right)c_{si} - \left(1 + Bi_i\frac{c_{bi}}{\bar{c}_{pi}}\right) = 0 \tag{47}$$

which can be solved by the quadratic equation to obtain c_{si}.

3.2.2 Film Mass Transfer Coefficients

Film mass transfer coefficients were determined by Robinson et al. (1993) for the binary and multicomponent systems using various semi-empirical correlations and by fitting the experimental data. The correlations used by the researchers included the Treybal, Gilliland-Sherwood, Froessling, and Ranz and Marshall correlations. Results obtained by Robinson and coworkers are shown in Table 6. For all binary cases with the exception of magnesium, the film mass transfer coefficients calculated by Robinson from the experimental data were higher than those found by Robinson using the aforementioned correlations. Multicomponent film mass transfer coefficients were estimated by Robinson through fitting the experimental data to the initial uptake slope for each component.

The film mass transfer coefficients determined by fitting the pore diffusion model of this study to the initial uptake rates are shown in the second half of the table. Binary film mass transfer coefficients found by fitting the initial slope of the uptake curve fell within the range of those predicted by correlations, as seen in Table 6, and were somewhat lower (about a factor of two) than the binary film mass transfer coefficients calculated by Robinson et al. (1993). The multicomponent film mass transfer coefficients (also found by fitting the initial slope of the pore diffusion model) were also approximately a factor of two lower than those calculated by Robinson. However, Robinson et al. did not include film mass transfer resistance in the heterogeneous model they developed, so direct comparison of this parameter as it predicts the uptake behavior of the zeolite is not possible.

For a multicomponent system, individual film mass transfer coefficients would be expected to be lower than those calculated for a binary system (Smith and Weber, 1988), as is shown by the experimentally determined k_f's. This is explained by the competition present with multiple diffusing and counterdiffusing species. As the concentrations of the species decrease in a

Table 6. Film Mass Transfer Coefficients for Binary and Multicomponent Systems

Component	Binary system		Multicomponent
	Range of k_f (cm/s) from correlations	k_f (cm/s) experimental	k_f (cm/s) experimental
Strontium [a]	0.001 — 0.018	0.018	0.0039
Cesium [a]	0.0015 — 0.024	0.026	0.0064
Calcium [a]	0.0011 — 0.018	0.021	0.0039
Magnesium [a]	0.001 — 0.017	0.010	0.0075
Film mass transfer coefficients found by fitting the initial experimental data with the pore diffusion model for binary cases and multicomponent cases for experimental data run SK-34.			
Strontium		0.009	0.002
Cesium		0.021	0.004
Calcium		0.006	0.0018
Magnesium		0.004	0.0025
Film mass transfer coefficients found by fitting the initial experimental data for the lower concentration multicomponent run (SK-24) with the pore diffusion model.			
Strontium			.01
Cesium			.006
Calcium			.006
Magnesium			.004

[a] As calculated by Robinson et al., (1993).

multicomponent situation, one would expect the film mass transfer coefficients to approach the values estimated for the single components. This was demonstrated in modeling the more dilute multicomponent experimental data for which slightly higher values for k_f's were required to fit the initial uptake curves (see Table 6).

The dimensionless Biot number (defined in equation (18)) is the ratio of the external phase mass transfer rate to the intraparticle phase mass transfer rate. As the Biot number increases (generally over 30), the intraparticle mass transfer rate is reduced and thus controls the overall exchange rate, while a smaller Biot number (< 0.5) signals an external (film) mass transfer rate controlled process (Crittenden, 1980; Friedman, 1984). For this system Biot numbers for each component — in both binary exchange and multicomponent exchange — are about 2.5. This value signals neither external or internal mass transfer dominance. The sensitivity of this pore diffusion model to the film mass transfer coefficient and intraparticle diffusivities is discussed in section 4.1.1.

3.2.3 Diffusion Coefficients

Robinson et al. (1993) determined the diffusion coefficients for the exchanging species in the binary pairs and the multicomponent system (Sr-Cs-Ca-Mg-Na); Table 7 lists the values the researcher obtained for these systems. The researchers estimated molecular diffusivities using the Nernst-Haskell equation, and found surface diffusivities to be on the order of 10^{-9} cm^2/s through fitting a heterogeneous series diffusion model. The calculated diffusivities are well within the ranges expected for ion exchange uptake (Ruckenstein et al., 1971: Ruthven, 1984; Friedman, 1986). The molecular, surface, and effective pore diffusivities are related through equation (9). For both the binary and multicomponent cases, assuming a tortuosity of 2 (typical for zeolites), the effective diffusivities should be much smaller than they are. This suggests a lower resistance

Table 7. Diffusivities Calculated for the Sr-Cs-Ca-Mg Multicomponent System and Each Binary System by Robinson et al. (1993)

Component	D_m [a] (cm^2/s)	D_s (cm^2/s)	*Binary* $D_{p,eff}$ (cm^2/s)	*Multicomponent* $D_{p,eff}$ (cm^2/s)
Sr	1.2 E-5	6.0 E-9	2.8 E-4	5.0 E-5
Cs	1.9 E-5	4.0 E-9	9.0 E-4	1.5 E-4
Ca	1.3 E-5	3.0 E-9	2.0 E-4	6.0 E-5
Mg	1.3 E-5	3.5 E-9	1.4 E-4	1.0 E-3

[a] Molecular diffusivities calculated by using the Nernst-Haskell equation (Robinson et al., 1993).

and subsequently mass transfer is faster than might otherwise be expected. Robinson and coworkers explained that surface diffusion was contributing to mass transfer, and thus the effective diffusivities were larger than expected based on the values of the molecular diffusivities. Possibly the calculated molecular diffusivities are not very accurate, and this would account for the higher than expected effective diffusivities.

3.3 INTEGRATION OF EQUILIBRIUM AND KINETIC MODELS

Integration of the equilibrium model and the kinetic model is shown in equation (19). The calculation of the derivative of the equilibrium model, $f'(\bar{c}_{pi})$, for the Langmuir and modified Dubinin-Polyani equilibrium equations is relatively uncomplicated. Both are simple equations where the average solid phase adsorbed concentration is given as a function of the average liquid concentration for a single species, and these derivatives can be expressed as a single function. For the Perona model (Perona, 1993) the concentration of species i in the solid phase that is in

equilibrium with the liquid concentration of all *n*-components requires an iterative routine. A change in the liquid concentration of a single component would be expected to elicit a change in the loading of all components. Equation (23) demonstrates this interdependence for a multicomponent system. A finite difference technique was used to calculate the change in the solid loading of species *i* for small step changes, ξ, in *each* solute (average) pore concentration $\bar{c}_{pi}$ while holding all other average pore concentrations constant ($\bar{c}_{pi+1,\ldots,n}$ (Lapidus and Pinder, 1982):

$$\left.\frac{\partial q_i}{\partial \bar{c}_{pi}}\right|_{\bar{c}_{pi+1,\ldots,n}} = \frac{q_i|_{\bar{c}_{pi}+\xi} + q_i|_{\bar{c}_{pi}-\xi}}{2\xi} \tag{48}$$

The total derivative for a solute was then calculated as a combination of the partial derivatives with respect to the change in each liquid phase solute as in equation (25).

An additional assumption was necessary in order to utilize the Perona model. In order to predict solid loading, the equilibrium model requires the liquid concentrations of all exchanging components, including sodium. The initial sodium concentration in the pores was assumed to be equal to the bulk liquid concentration, representing no net charge difference (and thus no electrical driving force) between bulk and pore liquids. Assuming electroneutrality, the total pore concentration in terms of total positive charges was considered to be constant for all time. Thus the iterative technique for converging upon equilibrium solution concentrations included the additional constraint that the sodium concentration equal the total concentration less the concentrations of the other species.

3.4 MAXIMUM LOADING OF CHABAZITE ZEOLITE

The maximum loading of the IE-96 chabazite zeolite was found by Robinson and coworkers (1993) to be 3.2 meq/g in the presence of cesium, and 2.8 meq/g without cesium in the

solution. Researchers Dyer and Keir (1989) found the maximum loading of chabazite zeolite IE-96 to be 2.22 meq/g. An intermediate value of 2.6 meq/g was used in the Perona equilibrium model, as it predicted the loading for all cases (binary and multicomponent) with the least error.

4. RESULTS AND DISCUSSION

Uptake curves for binary and multicomponent systems were predicted using the Yao and Tien (1993) pore diffusion model in conjunction with various equilibrium models. Presented and discussed below are the results for: (1) binary pairs using a– the Langmuir isotherm (Robinson et al., 1993), and b– the thermodynamic model (Perona, 1993); and (2) multicomponent system using a– the Dubinin-Polyani equilibrium model, and b– the thermodynamic model of Perona (1993).

4.1 BINARY SYSTEMS

4.1.1 Langmuir Model

Figures 4 through 7 show the uptake curves for strontium, cesium, calcium, and magnesium binary ion exchange on chabazite zeolite in a batch reactor using the Langmuir equilibrium model. Chabazite shows a strong affinity for both strontium and cesium, and both are modeled quite well in binary uptake with the Langmuir model (Figures 4 and 5), while the calcium and magnesium uptake from solution was not modeled as satisfactorily (Figures 6 and 7). The isotherm fit to the equilibrium data using the Langmuir model (see Figure 1) for both of these components was also not as good as the fit for Sr and Cs, as demonstrated by the R^2 factors for the isotherms as listed in Table 3. Several factors may contribute to this: cesium and strontium concentrations in solution are much more accurately measured than calcium and magnesium and thus would result in more accurate experimental curves, and chabazite zeolite has a lower affinity for calcium and magnesium possibly resulting in less accurate solution concentration measurements.

The film mass transfer coefficients were altered to fit the initial part of the uptake curve,

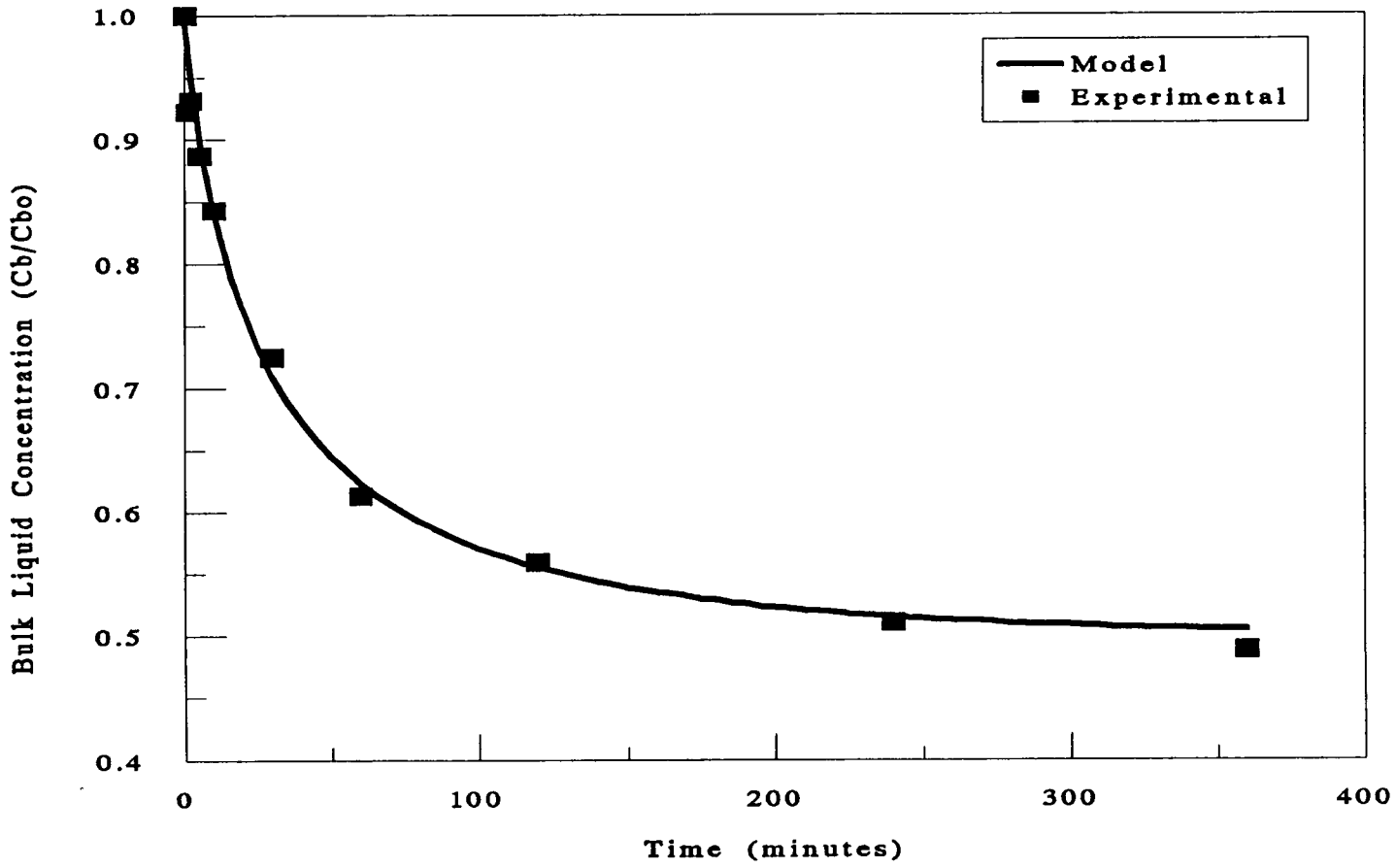


Figure 4. **A pore diffusion model of transient strontium-sodium exchange on chabazite zeolite modeled using a Langmuir equilibrium model.**

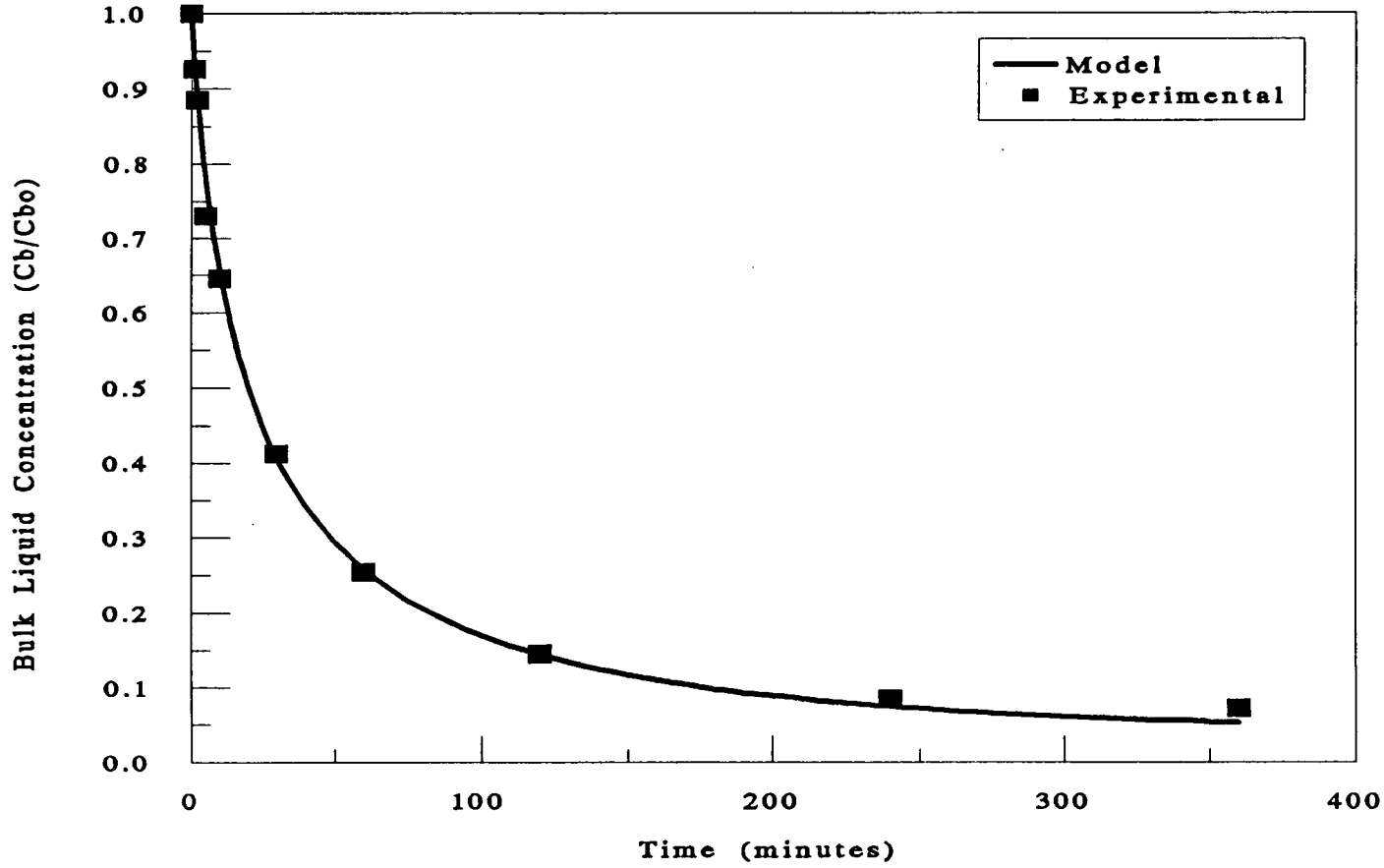


Figure 5. **A pore diffusion model of transient cesium-sodium exchange on chabazite zeolite modeled using a Langmuir equilibrium model.**

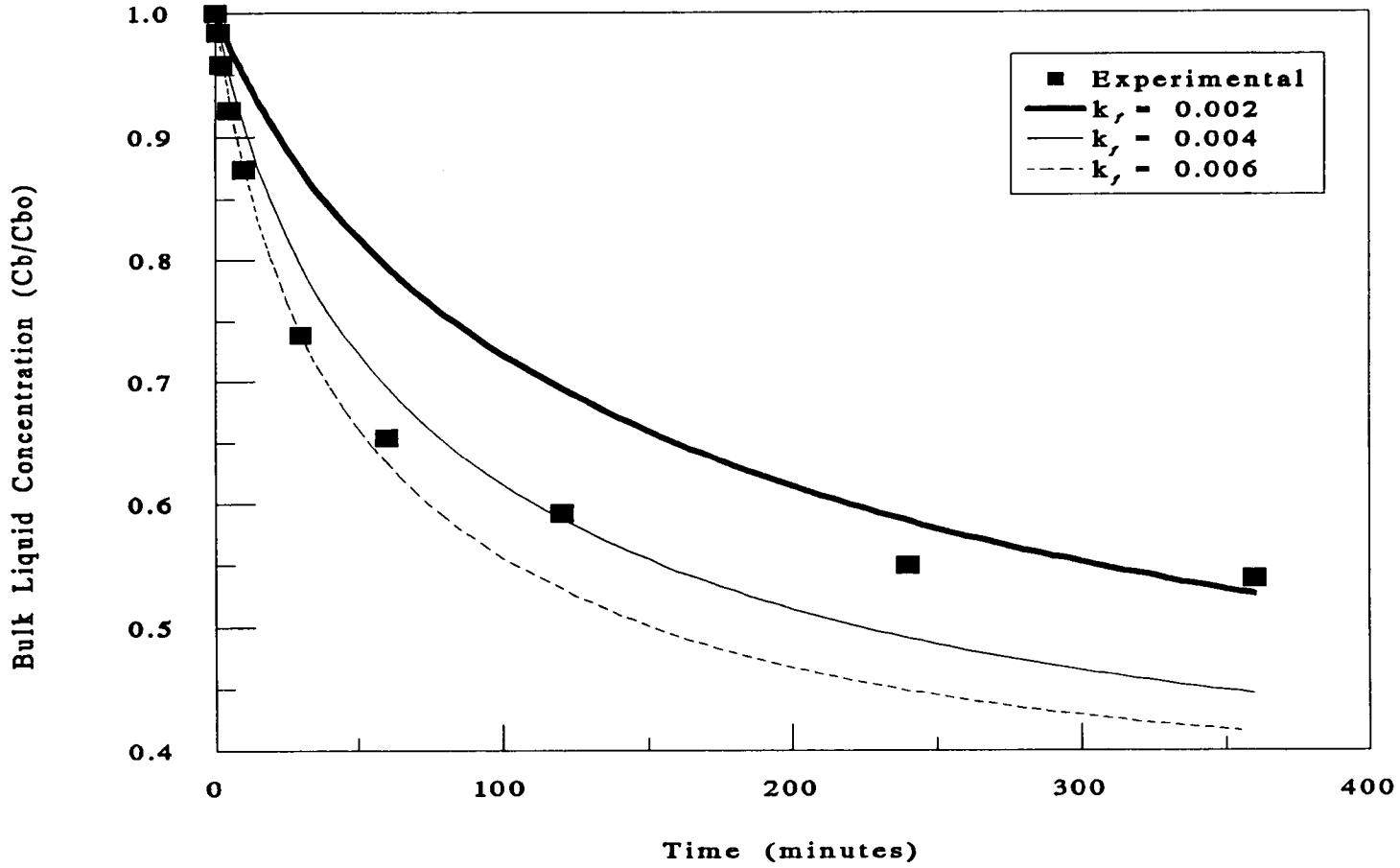


Figure 6. **A pore diffusion model of transient calcium-sodium exchange on chabazite zeolite modeled using a Langmuir equilibrium with varying film mass transfer coefficient, k_f.**

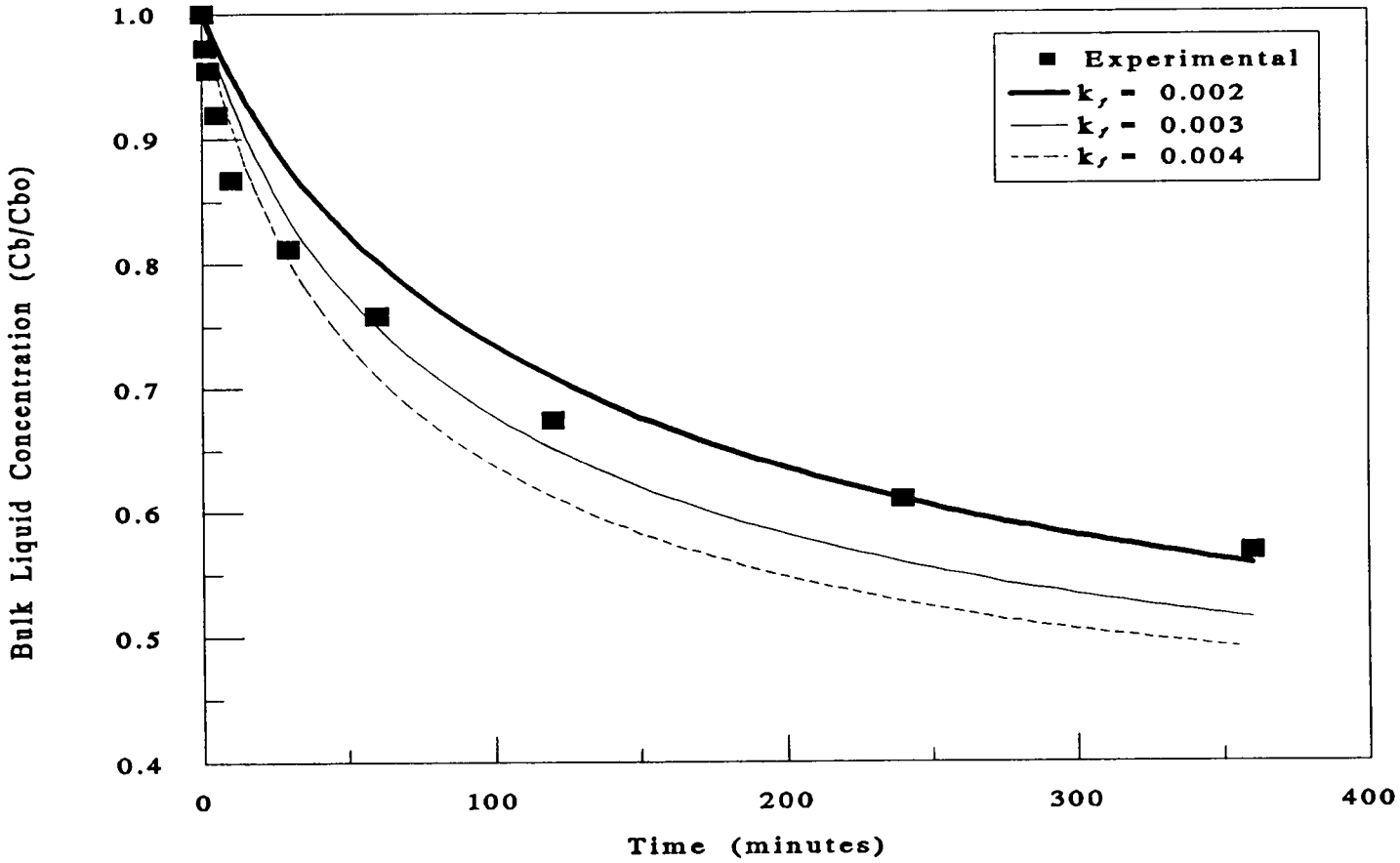


Figure 7. **A pore diffusion model of transient magnesium-sodium exchange on chabazite zeolite modeled using a Langmuir equilibrium with varying film mass transfer coefficient, k_f.**

and the resulting values for k_f are shown in Table 6. All k_f values are within the ranges predicted by Robinson et al. (1993) using several correlations. The sensitivity of the pore diffusion model to the film mass transfer coefficient is demonstrated in Figures 6 and 7. Biot numbers calculated for each binary pair from equation (18) were within the range 2 to 2.7. Higher Biot numbers (over 30) indicate resistance to intraparticle diffusion controls the rate of exchange, while lower Biot numbers (less than 0.5) indicate film diffusion control (Friedman, 1984). Ruthven (1984) indicates that intraparticle resistance significantly contributes to the rate of diffusion provided the Biot number exceeds 1. The Biot numbers for this case indicate that film mass transfer and intraparticle diffusion both act as diffusional resistances and thus control the rate of diffusion. In addition, the dependence of the uptake curves on the film mass transfer coefficient supports its significance in controlling the rate of exchange. The k_f's found by fitting the model were intermediate in the range of possible film mass transfer coefficients as calculated by Robinson et al. (1993), also suggesting intraparticle diffusional resistance is significant, whereas had the film mass transfer coefficients been lower it would have suggested intraparticle resistance was less significant.

The macropore diffusion coefficients (listed in Table 7) as determined by Robinson et al. (1993) were used in this pore diffusion model. The diffusion coefficients for each binary pair were varied in either direction, but were not found to affect the uptake rate as significantly as the film mass transfer coefficients. A decrease in the diffusion coefficient raised the intraparticle resistance, thereby lowering the rate of loading and ultimately raising the uptake curve slightly i.e., reducing the amount removed from solution (until equilibrium was reached). Since variation in the pore diffusion coefficients did not appear to cause significant changes in the exchange rate, the values as estimated by Robinson and coworkers were used with confidence.

4.1.2 Thermodynamic Model

An attempt was made to model the binary exchange of calcium using the Perona equilibrium model. Initial results showed that the prediction of the experimental uptake of calcium from solution would have been superior to the predictions using the Langmuir model; however, stability problems were encountered when equilibrium was approached. Figure 8 shows the model predictions for uptake of calcium from solution through a time of 150 minutes. Excellent agreement was obtained with experimental results up to this time using a mass transfer coefficient of 0.009 cm/s and an effective diffusivity of $2.x10^{-6}$ cm^2/s. The stability of the model seems to be affected by the time step. Further investigation into adjusting this parameter is recommended.

4.2 MULTICOMPONENT SYSTEMS

The multicomponent exchange of strontium, cesium, calcium, and magnesium with sodium on chabazite zeolite was modeled using the empirical Dubinin-Polyani equilibrium model and the Perona thermodynamic equilibrium model. Results are discussed below.

4.2.1 Dubinin-Polyani Model

Predictions of multicomponent uptake using the pore diffusion model in conjunction with the Dubinin-Polyani equilibrium model were unable to be made. The model became unstable after a short time (approximately dimensionless time of 8) when run with the initial bulk liquid concentrations given in the experimental data. When several orders of magnitude lower bulk liquid concentrations were assumed, the model was able to predict uptake curves through to equilibrium. The equilibrium isotherms for each component in a multicomponent system using the Dubinin-Polyani model were given in Figure 2. The isotherms go through a maximum, at

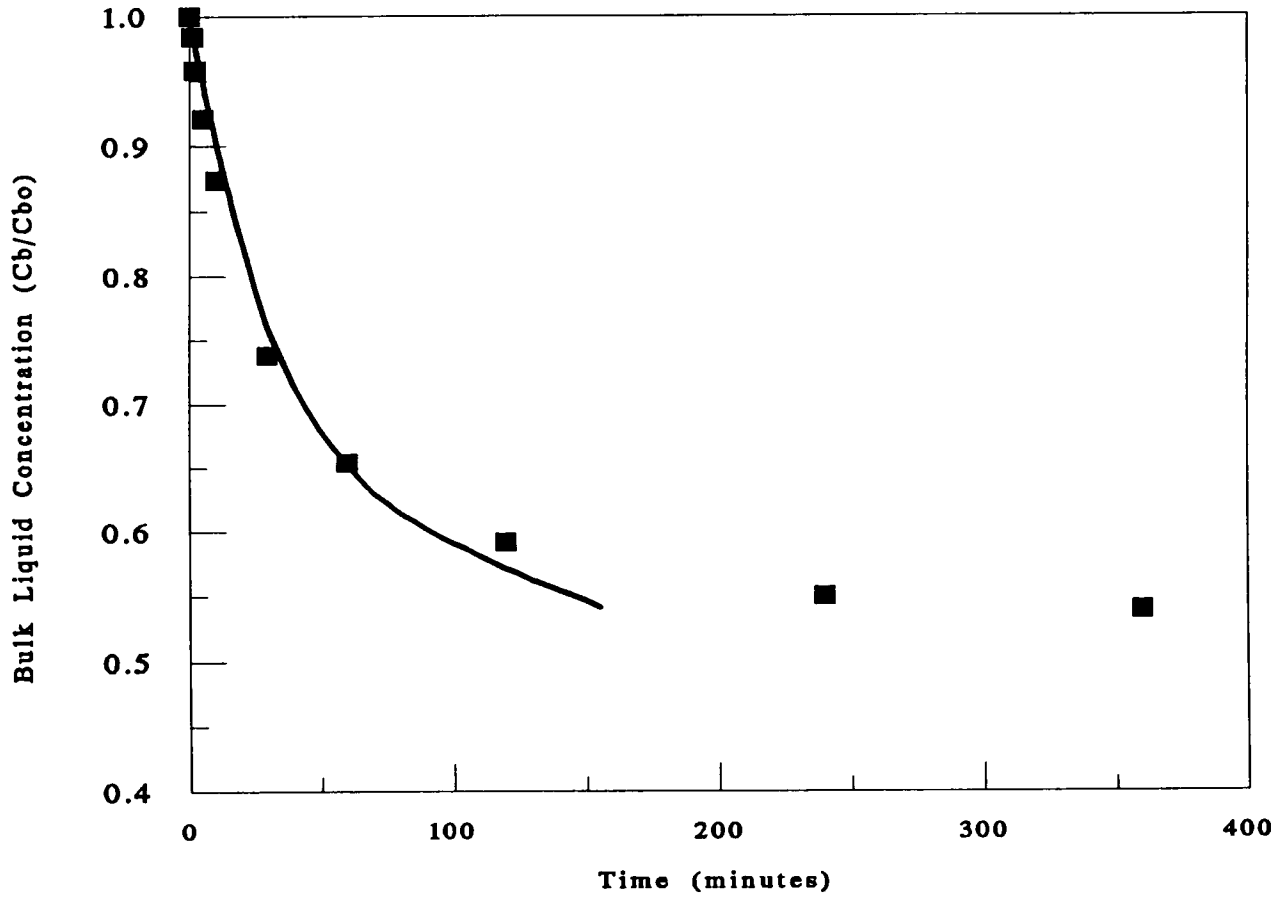


Figure 8. **A pore diffusion model of transient calcium-sodium exchange on chabazite zeolite modeled using Perona thermodynamic equilibrium model.**

which the derivative is zero. Assuming initial concentrations to the left of the curve (positive slope) enabled convergence and allowed predictions to be made in the transient uptake from solution for each component. However, initial concentrations which required passage through the maximum caused the model to become unstable.

Desorption occurs in a multicomponent system when ions for which the exchanger has a high affinity are exchanged with those ions that are lower in the selectivity order. This phenomena is demonstrated in the down turn of the isotherms for Sr, Ca, and Mg at higher concentrations in the presence of cesium. Since the Dubinin-Polyani model is empirical, and the equilibrium of each component is modeled independent of the other, the desorption shown in the isotherm is not compensated by uptake in another component. In the interest of time, further investigation into why the pore diffusion model did not proceed through the maximum was not made, although possible solutions such as smaller time steps or a different numerical method might have succeeded.

4.2.2 Thermodynamic Model

The Perona (1993) thermodynamic equilibrium model was used in the pore diffusion model to predict multicomponent ion exchange on chabazite zeolite from a batch reactor for two sets of experimental data provided by Robinson et al. (1993).

The first set of kinetic data, SK-34, was run at higher initial experimental concentrations for each component (on the order of 10^{-3} meq/ml). Figures 9 through 12 show the experimental values for the transient uptake from solution of strontium, cesium, calcium, and magnesium versus that predicted by the multicomponent model. The uptake of each component was predicted quite well, with percent variances of 1.7%, 3.3%, 3.3%, and 2.6% for strontium, cesium, calcium, and magnesium, respectively.

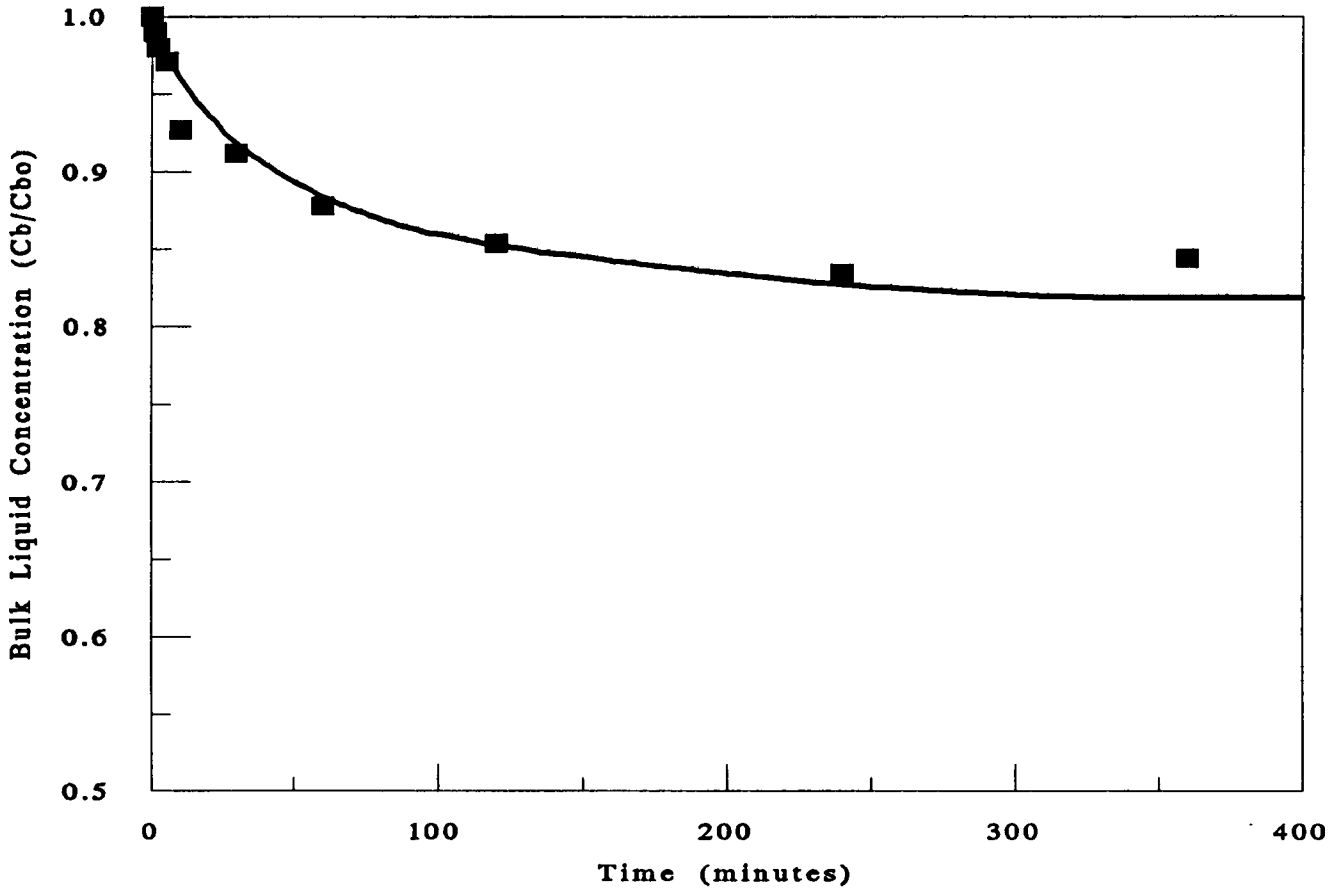


Figure 9. **Strontium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-34.**

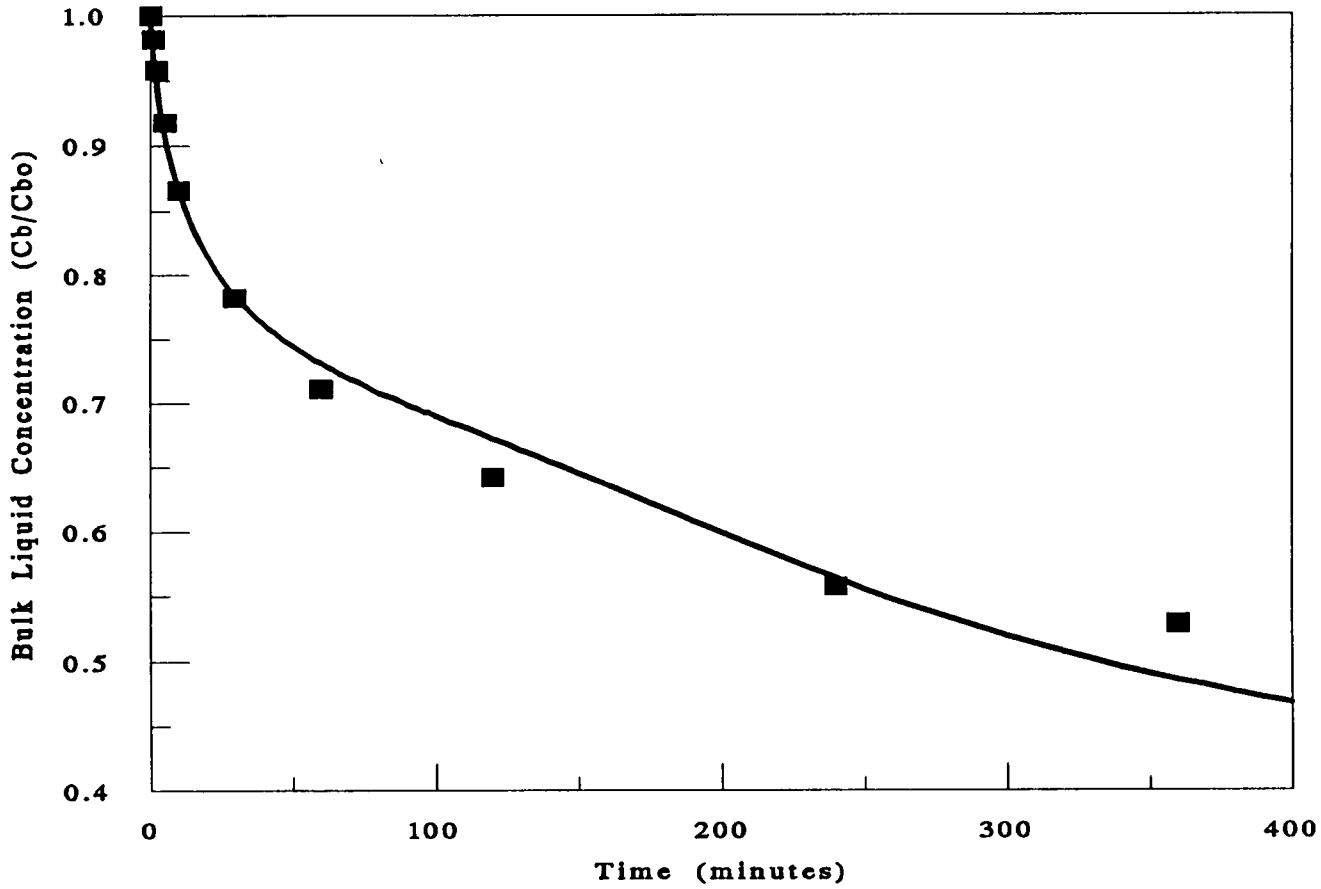


Figure 10. **Cesium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-34.**

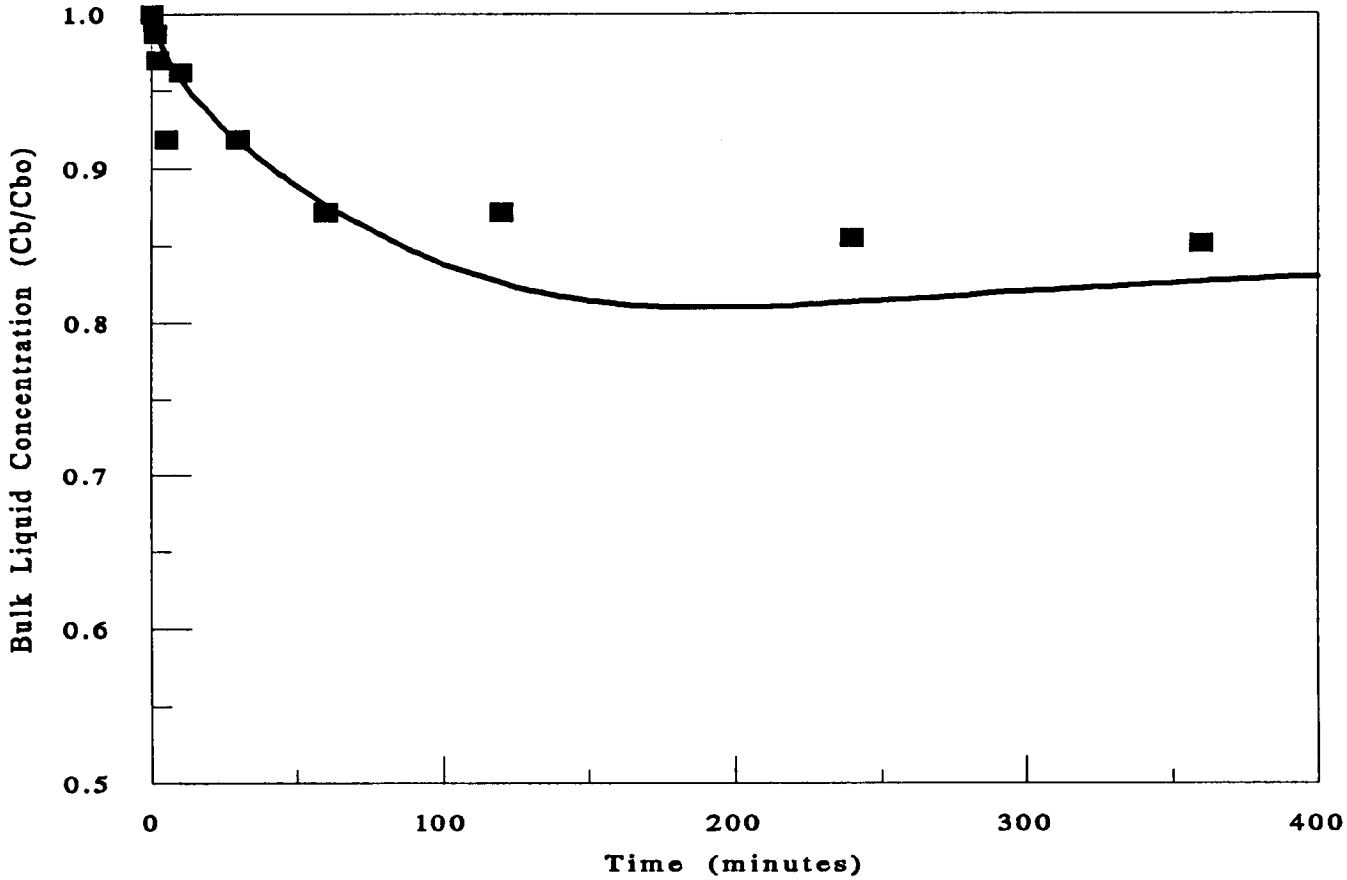


Figure 11. **Calcium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-34.**

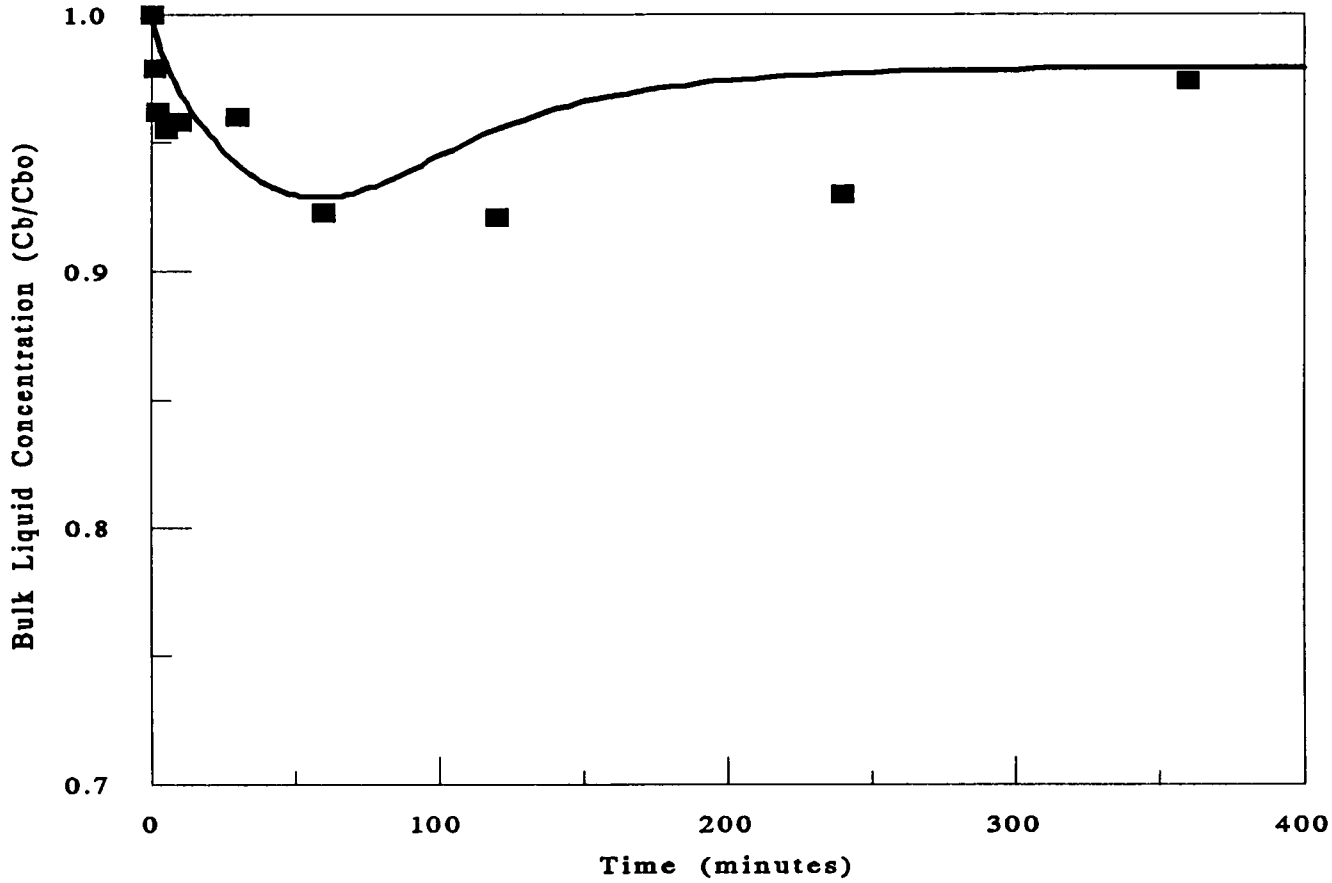


Figure 12. **Magnesium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-34.**

The variance was calculated by:

$$\sigma = \left(\frac{1}{n} \sum_{i=1}^{n} \left(\frac{experimental - theoretical}{experimental} \right)^2 \right)^{0.5} . \qquad (49)$$

Film mass transfer coefficients were found by fitting the initial experimental uptake curve with the model. Table 6 contains the values as calculated by this technique. Multicomponent film mass transfer coefficients are somewhat lower than those calculated for binary systems, as expected due to the competition resulting from multiple species diffusing and counterdiffusing through the film layer (Smith and Weber, 1988). Again, as with the binary examples, the uptake curves were sensitive to changes in the mass transfer coefficients.

Effective pore diffusivities used in the model were those listed in Table 7. Robinson and coworkers (1993) calculated these diffusivities by fitting the experimental data with a heterogeneous series diffusion model. Only the effective diffusivity of calcium (in the multicomponent system) was changed somewhat to give a better fit to the experimental data using the pore diffusion model. This change was justified further by achieving a better fit for calcium in two sets of experimental data. Overall effective diffusivities were then calculated from equation (13). The effective diffusivities were varied somewhat, and as with the binary model, significant changes in the uptake curves were seen only for large (one order of magnitude) changes in diffusivities. However, since this is multicomponent exchange where the equilibrium model predicts loading for each species as a function of the concentration of *all* species, a change in the uptake of one component would result in a change in all component uptake rates to a lesser degree. Optimization of this dependence between the species to better predict uptake rates by adjusting diffusivities accordingly would be desirable.

The utility of a model may be judged by the accuracy with which it predicts system behavior outside the bounds in which it was observed and developed. A second set of

experimental kinetic uptake data (run SK-24 having an order of magnitude lower initial concentration for each component than the previous SK-34 data run) was predicted using the pore diffusion model in conjunction with the Perona thermodynamic equilibrium model in order to further test the program. Transient uptake curves for strontium, cesium, calcium, and magnesium in a multicomponent system were predicted as shown in Figures 13 through 16. Results were good, but not as accurate as at the higher concentrations (SK-34) based on the respective variances of 14.8%, 34.2%, 6.9% and 4.6% for strontium, cesium, calcium and magnesium uptake. This is to be expected, however, based on the results of the equilibrium model when tested alone as seen in Figure 2. The equilibrium model slightly underpredicts the solid loading of strontium, cesium, and magnesium, and over predicts the loading of calcium at lower concentrations.

Film mass transfer coefficients were adjusted to fit the initial slope of the uptake curve, as was done for the previous binary and multicomponent experimental data sets. Since the total concentration (and the concentration of each species) was lower in the SK-24 experimental data than the SK-34 data, the film mass transfer coefficients would be expected to be higher due to the decreased diffusion and counterdiffusion of competing and like species. The individual film mass transfer coefficients approached the values obtained in the binary exchanges, as would be expected. Diffusion coefficients were not changed from the previous example.

The results from fitting both experimental data sets support the fact that film mass transfer is a significant rate determining step in this system, as is the intraparticle diffusion which is suitably modeled assuming macropore diffusion. The Perona equilibrium model accurately modeled the multicomponent uptake for both experimental cases.

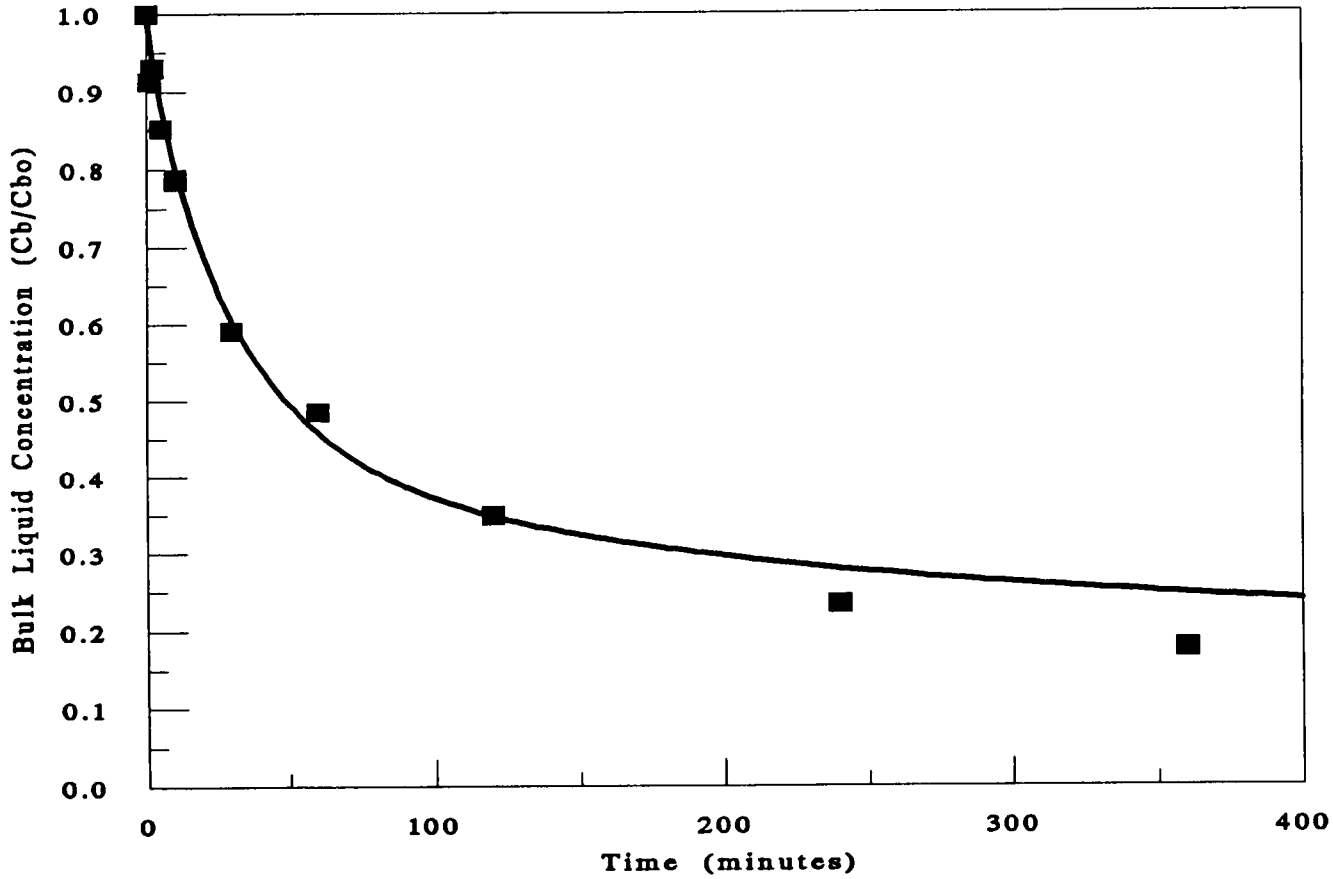


Figure 13. **Strontium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-24.**

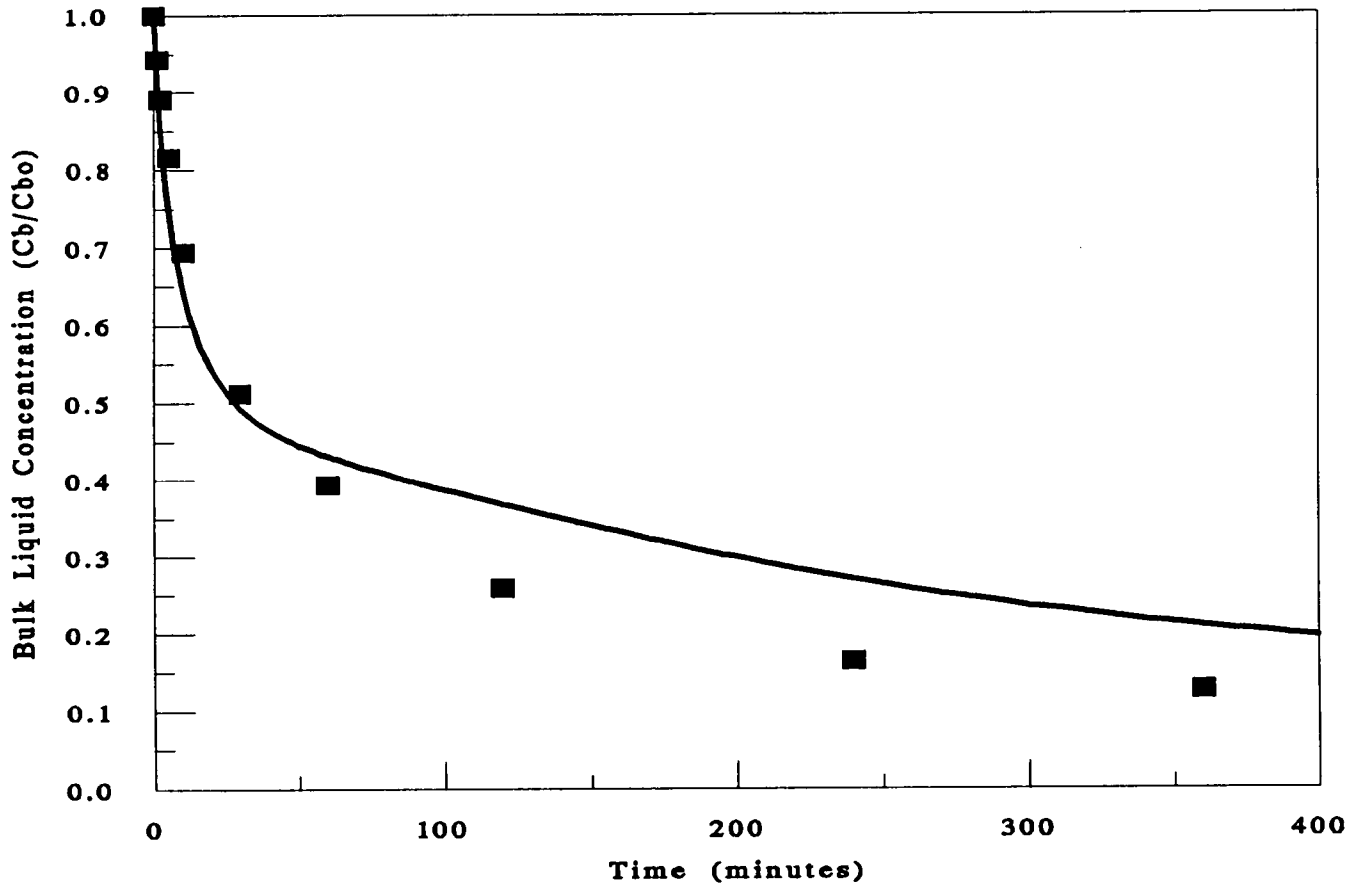


Figure 14. **Cesium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-24.**

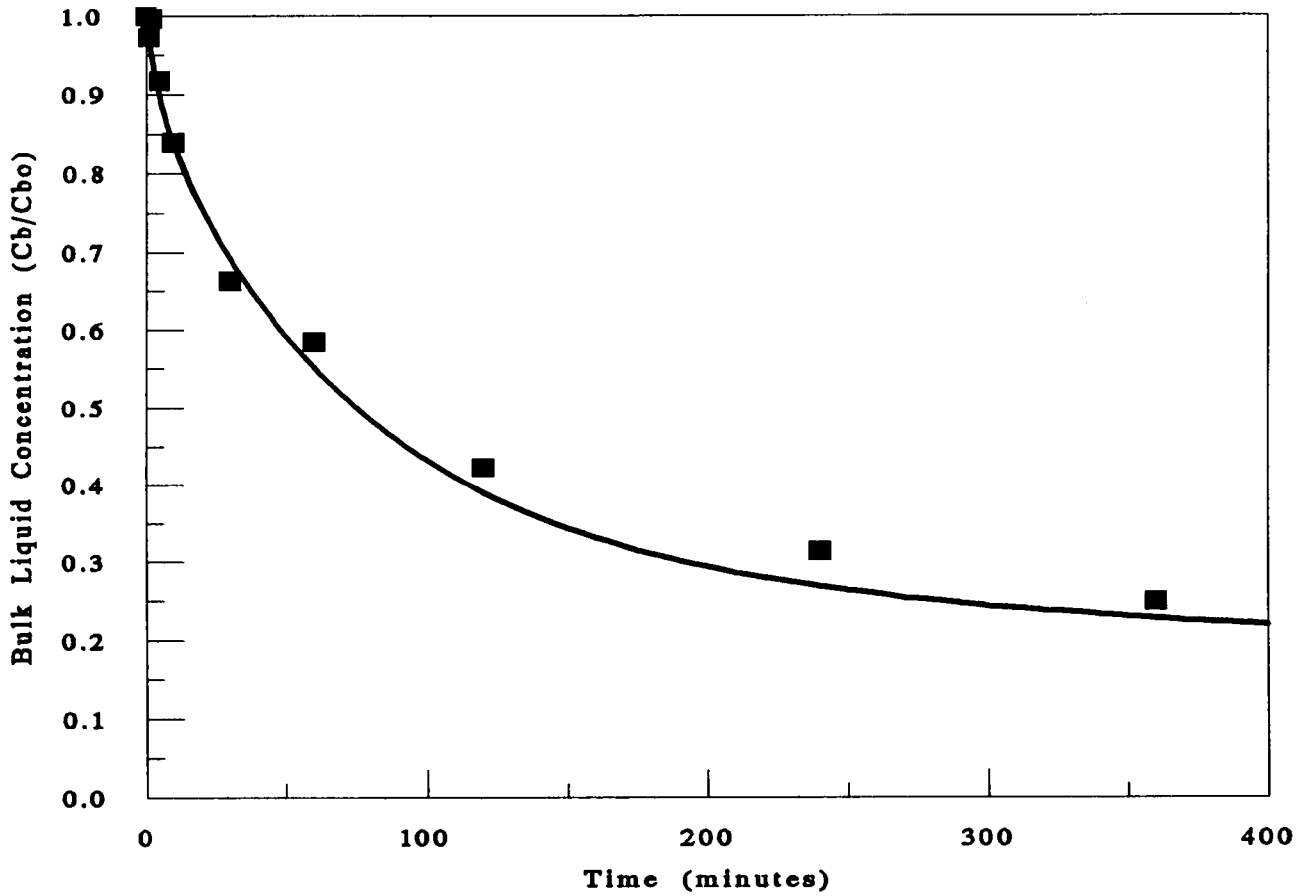


Figure 15. **Calcium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion exchange for experimental run SK-24.**

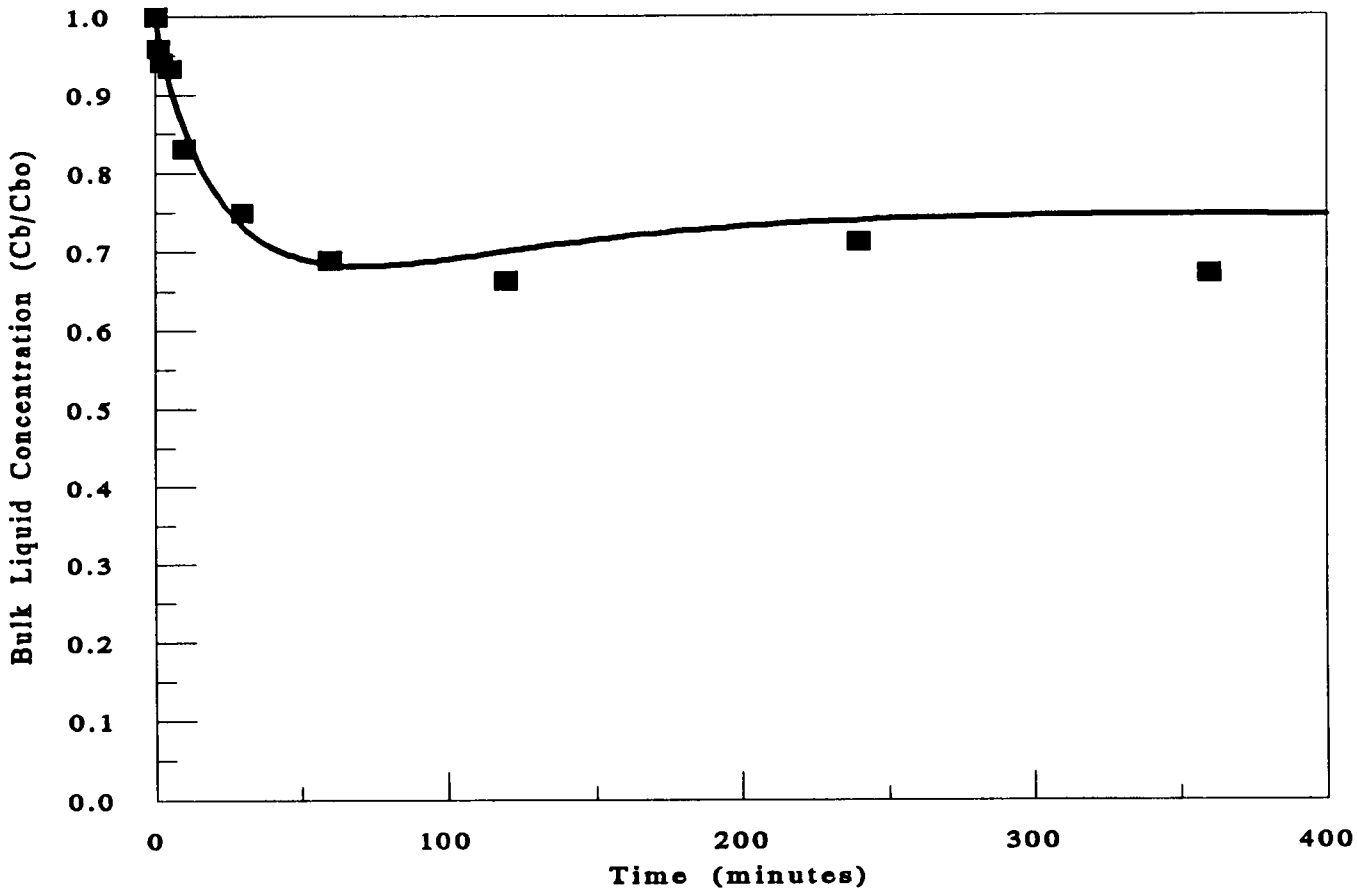


Figure 16. **Magnesium uptake on chabazite zeolite in Sr-Cs-Ca-Mg-Na multicomponent ion for experimental run SK-24.**

5. CONCLUSIONS AND RECOMMENDATIONS

The model of Yao and Tien (1993) for calculating transient uptake in a spherical porous particle assuming external film mass transfer and intraparticle macropore diffusion was employed with various equilibrium models to accurately predict uptake rates in binary and multicomponent ion exchange on chabazite zeolite. The following conclusions have been reached regarding this model and its use with several equilibrium models.

(1) The Langmuir equilibrium model in combination with the pore diffusion model satisfactorily predicted the uptake of strongly held species, strontium and cesium, in binary ion exchange. Calcium and magnesium uptake on chabazite zeolite was not predicted as well, because the Langmuir equilibrium model did not predict the solid-liquid equilibrium concentrations as accurately for these components. Results show that the Perona equilibrium model would predict the calcium uptake better than the Langmuir model, when combined with the pore diffusion model; however the mathematical routine became unstable just prior to reaching equilibrium. Employing a smaller time step within the algorithm would probably allow equilibrium to be attained.

(2) The pore diffusion calculations for the binary case were quite sensitive to changes in the film mass transfer coefficient as displayed by variations in the uptake curve, thus supporting the dependence of the rate of mass transfer on external fluid resistance. Film mass transfer coefficients on the order of 10^{-3} cm/s were obtained; these values agree well with reported literature values. The dimensionless Biot number was estimated to be approximately 2.5 for each binary exchange system, indicating that intraparticle diffusion also is significant in controlling the rate of exchange. Variations in the effective pore diffusivities for the binary pairs altered the uptake curves somewhat, however film mass

transfer coefficient variations more significantly affected the uptake curves. Model predictions employing effective pore diffusivities on the order of 10^{-5} cm^2/s matched the experimental data accurately. These values for effective diffusivities agree well with those reported in the literature.

(3) The Dubinin-Polyani equilibrium relationship, when used in the pore diffusion model, causes the resulting uptake curve for the multicomponent system to become unstable. This is probably because of the maximum in the curve, where the derivative is equal to zero.

(4) Based on the resulting isotherms for species in a multicomponent system, it appears that at liquid concentrations of 10^{-4} meq/ml and less the solid loading of each species is affected by the remaining species (and thus total concentration). At higher concentrations (10^{-4} and up) the solid loading converges for each species (i.e. becomes independent of other component concentrations), and predictably at very low concentrations the loadings would converge. Therefore, a true multicomponent equilibrium model is needed to predict the equilibrium solid loading changes anticipated for varying concentrations.

(5) The Perona equilibrium model was shown to accurately predict shifting equilibrium isotherms for a species with varying total solution concentrations, thus showing the interaction between species in a multicomponent system. The model would therefore be expected, when used in the kinetic pore diffusion model, to predict multicomponent transient uptake and equilibrium outside of the concentration ranges in which the model was developed and for a variety of initial conditions.

(6) The Perona equilibrium model was used in combination with the pore diffusion model to accurately predict multicomponent experimental uptake curves for two runs with different total concentrations. As with the binary uptake curves, external film mass transfer and

intraparticle diffusion were both shown to control the rate of exchange.

The pore diffusion model in combination with the Perona equilibrium model accurately predicts multicomponent ion exchange for the Sr-Cs-Ca-Mg-Na system. Incorporation of this particle mass transfer model into a transient column model is recommended to completely define the chabazite zeolite ion exchange columns and predict system behavior with varying input conditions. In addition, this work emphasizes the importance of the equilibrium model in defining ion exchange uptake in a transient system. In order to accurately predict transient and equilibrium loading of a component for varying input conditions such as might exist in a multicomponent system, one must be assured that the equilibrium model is able to accomodate these changes.

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APPENDIXES

APPENDIX A

EQUILIBRIUM DATA

Table A.1. Binary Equilibrium Data, Langmuir Model and Experimental Data (Robinson et al., 1993)

Strontium			Cesium			Calcium			Magnesium		
(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)
3.00E-07	0.051		1.00E-07	0.016		1.00E-06	0.374		1.00E-07	0.045	
4.00E-07	0.067		1.20E-07	0.019	0.025	1.25E-06	0.448	0.230	2.06E-07	0.088	0.090
6.95E-07	0.113	0.100	1.50E-07	0.023		2.00E-06	0.634		3.00E-07	0.122	
7.00E-07	0.114		2.00E-07	0.031		2.48E-06	0.732		5.00E-07	0.185	
8.00E-07	0.129		2.50E-07	0.039		4.00E-06	0.970		6.30E-07	0.219	
9.00E-07	0.144		3.00E-07	0.046		4.06E-06	0.978	1.000	6.58E-07	0.226	
9.36E-07	0.149	0.197	5.00E-07	0.076		6.00E-06	1.179		7.00E-07	0.236	
1.00E-06	0.158		6.30E-07	0.095	0.049	8.00E-06	1.321		8.00E-07	0.259	
2.00E-06	0.290	0.502	6.58E-07	0.099	0.099	9.93E-06	1.420		9.00E-07	0.280	
4.00E-06	0.499		7.00E-07	0.105		1.00E-05	1.423		1.00E-06	0.299	
6.00E-06	0.656		8.00E-07	0.119		3.00E-05	1.797		1.92E-06	0.426	0.427
8.00E-06	0.778		9.00E-07	0.133		6.00E-05	1.922		2.00E-06	0.434	
1.00E-05	0.877		1.00E-06	0.147		8.00E-05	1.957		2.48E-06	0.475	
1.49E-05	1.051	1.000	2.00E-06	0.276		1.00E-04	1.978		4.00E-06	0.560	
3.00E-05	1.321		2.48E-06	0.333	0.499	1.43E-04	2.004		6.00E-06	0.620	
6.00E-05	1.513		4.00E-06	0.493		2.00E-04	2.022		8.00E-06	0.655	
8.00E-05	1.569		6.00E-06	0.667		4.00E-04	2.044		9.93E-06	0.677	
1.00E-04	1.606		8.00E-06	0.811		4.87E-04	2.048	1.460	1.00E-05	0.678	
2.00E-04	1.684		9.93E-06	0.928	1.010	6.00E-04	2.052		3.00E-05	0.748	
3.63E-04	1.721	1.630	1.00E-05	0.931					6.00E-05	0.768	
4.00E-04	1.725		3.00E-05	1.541					7.62E-05	0.772	0.780
6.00E-04	1.740		6.00E-05	1.842					8.00E-05	0.773	
8.00E-04	1.747		8.00E-05	1.937					1.00E-04	0.776	
1.00E-03	1.751		1.00E-04	1.998					1.43E-04	0.780	
1.10E-03	1.753	1.760	1.43E-04	2.078	1.660				2.00E-04	0.782	
			2.00E-04	2.134					3.81E-04	0.785	1.120
			4.00E-04	2.209					4.00E-04	0.785	
			6.00E-04	2.235							

Table A.2. Binary Equilibrium Data, Perona Equilibrium Model and Experimental Data

Strontium			Cesium			Calcium			Magnesium		
(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)
3E-07	0.0838		1E-07	0.00329		1E-06	0.546		1E-07	0.049	
4E-07	0.109		1.2E-07	0.00414	0.025	1.25E-06	0.59	0.230	2.06E-07	0.0812	0.090
6.95E-07	0.175	0.100	1.5E-07	0.00559		2E-06	0.683		3E-07	0.103	
7E-07	0.176		2E-07	0.00861		2.48E-06	0.726		5E-07	0.137	
8E-07	0.196		2.5E-07	0.0127		4E-06	0.821		6.3E-07	0.155	
9E-07	0.216		3E-07	0.0184		4.06E-06	0.824	1.000	6.58E-07	0.158	
9.36E-07	0.223	0.197	5E-07	0.0641		6E-06	0.9		7E-07	0.163	
1E-06	0.234		6.3E-07	0.103	0.049	8E-06	0.955		8E-07	0.174	
2E-06	0.386	0.502	6.58E-07	0.111	0.099	9.93E-06	0.996		9E-07	0.184	
4E-06	0.583		7E-07	0.123		1E-05	0.997		1E-06	0.194	
6E-06	0.711		8E-07	0.149		3E-05	1.19		1.92E-06	0.257	0.427
8E-06	0.805		9E-07	0.174		6E-05	1.31		2E-06	0.261	
1E-05	0.878		1E-06	0.197		8E-05	1.35		2.48E-06	0.284	
1.49E-05	1.01	1.000	2E-06	0.372		0.0001	1.39		4E-06	0.339	
3E-05	1.22		2.48E-06	0.436	0.499	0.000143	1.44		6E-06	0.389	
6E-05	1.42		4E-06	0.594		0.0002	1.49		8E-06	0.426	
8E-05	1.49		6E-06	0.748		0.0004	1.6		9.93E-06	0.455	
0.0001	1.54		8E-06	0.869		0.000487	1.63	1.460	1E-05	0.456	
0.0002	1.71		9.93E-06	0.966	1.010	0.0006	1.67		3E-05	0.618	
0.000363	1.84	1.630	1E-05	0.969					6E-05	0.735	
0.0004	1.86		3E-05	1.52					7.62E-05	0.778	0.780
0.0006	1.95		6E-05	1.88					8E-05	0.787	
0.0008	2.02		8E-05	2.01					0.0001	0.831	
0.001	2.08		0.0001	2.11					0.000143	0.905	
0.0011	2.11	1.760	0.000143	2.24	1.660				0.0002	0.984	
			0.0002	2.34					0.000381	1.18	1.120
			0.0004	2.49					0.0004	1.2	
			0.0006	2.55							

Table A.3. Multicomponent Equilibrium Data, Dubinin-Polyani Model and Experimental Data (Robinson et al., 1993)

Strontium			Cesium			Calcium			Magnesium		
(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)	(meq/mL)	Model (meq/g)	Exp. (meq/g)
1.69E-07	7.06E-03		1.07E-07	6.98E-03		1.00E-07	7.19E-02		1.00E-07	2.50E-05	
2.58E-07	1.15E-02		1.20E-07	7.84E-03		4.99E-07	1.84E-01	1.08E-01	2.06E-07	1.40E-04	
3.00E-07	1.36E-02		1.50E-07	9.79E-03		9.00E-07	2.44E-01		3.00E-07	3.19E-04	
4.95E-07	2.31E-02		2.00E-07	1.29E-02		1.00E-06	2.56E-01		5.38E-07	1.03E-03	
6.47E-07	3.02E-02		2.60E-07	1.66E-02		3.24E-06	4.04E-01		6.30E-07	1.39E-03	
9.00E-07	4.14E-02		3.58E-07	2.22E-02		4.06E-06	4.35E-01		6.58E-07	1.50E-03	
1.17E-06	5.27E-02	5.02E-02	4.86E-07	2.90E-02	2.51E-02	6.00E-06	4.87E-01		7.00E-07	1.68E-03	
2.21E-06	9.02E-02		5.98E-07	3.46E-02		8.00E-06	5.25E-01		8.53E-07	2.39E-03	
2.39E-06	9.60E-02	1.00E-01	8.78E-07	4.76E-02	5.02E-02	9.93E-06	5.53E-01		9.00E-07	2.62E-03	
4.00E-06	1.41E-01		1.00E-06	5.28E-02		1.00E-05	5.54E-01		1.00E-06	3.13E-03	
6.24E-06	1.90E-01	1.98E-01	1.82E-06	8.33E-02	9.93E-02	3.00E-05	6.72E-01		1.92E-06	8.66E-03	
8.00E-06	2.22E-01		4.00E-06	1.44E-01		6.00E-05	7.15E-01		2.06E-06	9.57E-03	
1.69E-05	3.35E-01	5.96E-01	4.68E-06	1.59E-01	2.75E-01	8.00E-05	7.25E-01		2.48E-06	1.24E-02	
3.00E-05	4.34E-01		7.00E-06	2.04E-01		1.00E-04	7.28E-01		4.49E-06	2.58E-02	2.28E-02
6.00E-05	5.55E-01		9.00E-06	2.37E-01		1.43E-04	7.26E-01		6.37E-06	3.75E-02	4.54E-02
8.00E-05	6.02E-01		1.00E-05	2.51E-01		2.00E-04	7.17E-01		8.00E-06	4.67E-02	
1.86E-04	7.10E-01		2.00E-05	3.62E-01		4.00E-04	6.75E-01		9.93E-06	5.66E-02	
4.00E-04	7.52E-01		2.90E-05	4.32E-01		5.75E-04	6.42E-01	6.42E-01	1.00E-05	5.69E-02	
6.27E-04	7.47E-01	6.92E-01	4.67E-05	5.31E-01	4.80E-01	6.00E-04	6.38E-01		2.05E-05	9.48E-02	8.86E-02
8.50E-04	7.30E-01		7.00E-05	6.22E-01		8.00E-04	6.07E-01		6.00E-05	1.43E-01	
1.35E-03	6.88E-01	6.64E-01	9.00E-05	6.80E-01		1.31E-03	5.48E-01	5.44E-01	7.62E-05	1.48E-01	
1.63E-03	6.65E-01	7.30E-01	1.00E-04	7.04E-01		1.58E-03	5.23E-01	5.25E-01	9.10E-05	1.50E-01	
4.00E-03	5.26E-01		2.25E-04	8.93E-01	7.88E-01	5.00E-03	3.69E-01		1.00E-04	1.51E-01	
6.00E-03	4.55E-01		4.03E-04	1.02E+00	1.17E+00	9.00E-03	2.94E-01		1.43E-04	1.47E-01	
9.00E-03	3.84E-01		6.00E-04	1.09E+00					2.02E-04	1.38E-01	
1.00E-02	3.66E-01		8.00E-04	1.13E+00					3.81E-04	1.09E-01	
			1.00E-03	1.16E+00					7.83E-04	7.03E-02	7.94E-02
			1.00E-02	1.13E+00					8.88E-04	6.38E-02	5.74E-02
									9.14E-04	6.23E-02	6.25E-02

Table A.4. Multicomponent Batch Equilibrium Data, Perona Model and Experimental Data

Solution concentration (meq/mL)				Model solid concentration (meq/g)				Experimental solid concentration (meq/g)			
Strontium	Cesium	Calcium	Magnesium	Strontium	Cesium	Calcium	Magnesium	Strontium	Cesium	Calcium	Magnesium
1.69E-07	1.07E-07	3.24E-06	1.06E-06	3.72E-02	1.92E-02	9.64E-01	1.95E-02	2.50E-02	1.14E-02	2.49E-02	1.14E-02
2.58E-07	2.60E-07	3.24E-06	5.38E-07	5.53E-02	4.45E-02	9.49E-01	9.65E-03	9.99E-02	4.54E-02	9.94E-02	4.58E-02
4.95E-07	3.58E-07	3.24E-06	8.53E-07	1.01E-01	5.83E-02	9.25E-01	1.43E-02	4.97E-02	2.26E-02	4.95E-02	2.28E-02
6.47E-07	5.98E-07	3.24E-06	2.06E-06	1.24E-01	8.90E-02	8.92E-01	3.08E-02	2.52E-01	1.14E-01	2.51E-01	1.15E-01
1.17E-06	4.86E-07	4.99E-07	4.49E-06	4.19E-02	3.60E-02	1.32E-01	3.59E-02	5.02E-02	2.51E-02	4.64E-02	2.28E-02
2.21E-06	1.46E-06	3.24E-06	1.13E-05	3.08E-01	1.60E-01	7.60E-01	1.04E-01	4.11E-01	1.87E-01	4.11E-01	1.80E-01
2.39E-06	8.78E-07	4.99E-07	6.37E-06	8.28E-02	6.33E-02	1.31E-01	4.45E-02	1.00E-01	5.02E-02	9.28E-02	4.54E-02
6.24E-06	1.82E-06	4.99E-07	2.05E-05	1.82E-01	1.14E-01	1.17E-01	9.16E-02	1.98E-01	9.93E-02	1.84E-01	8.86E-02
1.69E-05	4.68E-06	1.94E-05	9.10E-05	6.14E-01	2.03E-01	8.67E-01	1.74E-01	5.96E-01	2.75E-01	5.94E-01	1.71E-01
1.86E-04	2.90E-05	2.10E-04	2.02E-04	9.84E-01	3.50E-01	9.12E-01	7.41E-02	7.38E-01	4.68E-01	6.81E-01	6.31E-02
6.27E-04	4.67E-05	5.75E-04	7.83E-04	8.39E-01	3.37E-01	8.53E-01	6.49E-02	6.92E-01	4.80E-01	6.42E-01	7.94E-02
1.35E-03	2.25E-04	1.31E-03	8.88E-04	7.83E-01	7.85E-01	7.46E-01	3.96E-02	6.64E-01	7.88E-01	5.44E-01	5.74E-02
1.63E-03	4.03E-04	1.58E-03	9.14E-04	6.88E-01	1.08E+00	6.59E-01	3.71E-02	7.30E-01	1.17E+00	5.25E-01	6.25E-02

APPENDIX B

KINETIC DATA

Table B.1. Batch Reactor Operating Conditions for Ionsiv-96 (Robinson et al., 1993)

Run number	Solution volume (g/mL)	Solids weight (g)	Stirrer speed (rpm)	Initial solution concentration (meq/L)				Solids loading (meq/g)
				Strontium	Cesium	Calcium	Magnesium	
Binary data runs								
SK-16	80.46	0.0473	750	2.04				1.773
SK-18	80.36	0.0472	750		1.01			1.591
SK-41	79.84	0.0468	750			1.92		1.516
SK-19	80.52	0.0473	750				0.82	0.599
Multicomponent data run								
SK-34	79.74	0.0471	750	2.05	1	2.35	0.89	1.965
SK-24	80.24	0.0474	750	0.55	0.25	0.57	0.21	1.968

Table B.2. Experimental Single Component Data for Ionsiv IE-96 (Robinson et al., 1993)

Time (min)	Strontium: (meq/mL)	Run SK-16 Cb/Cbo	Cesium: (meq/mL)	Run SK-18 Cb/Cbo	Calcium: (meq/mL)	Run SK-41 Cb/Cbo	Magnesium: (meq/mL)	Run SK-19 Cb/Cbo
0	2.04E-03	1.00E+00	1.01E-03	1.00E+00	1.91E-03	1.00E+00	8.13E-04	1.00E+00
1	1.88E-03	9.22E-01	9.35E-04	9.26E-01	1.88E-03	9.84E-01	7.90E-04	9.72E-01
2	1.90E-03	9.31E-01	8.94E-04	8.85E-01	1.83E-03	9.58E-01	7.76E-04	9.54E-01
5	1.81E-03	8.87E-01	7.37E-04	7.30E-01	1.76E-03	9.21E-01	7.47E-04	9.19E-01
10	1.72E-03	8.43E-01	6.52E-04	6.46E-01	1.67E-03	8.74E-01	7.05E-04	8.67E-01
30	1.48E-03	7.25E-01	4.16E-04	4.12E-01	1.41E-03	7.38E-01	6.60E-04	8.12E-01
60	1.25E-03	6.13E-01	2.57E-04	2.54E-01	1.25E-03	6.54E-01	6.16E-04	7.58E-01
120	1.14E-03	5.59E-01	1.46E-04	1.45E-01	1.13E-03	5.92E-01	5.48E-04	6.74E-01
240	1.04E-03	5.10E-01	8.58E-05	8.50E-02	1.05E-03	5.50E-01	4.96E-04	6.10E-01
360	9.96E-04	4.88E-01	7.31E-05	7.24E-02	1.03E-03	5.39E-01	4.61E-04	5.67E-01
480					1.03E-03	5.39E-01		

Table B.3. Multicomponent Data for Ionsiv IE-96, Run SK-24 (Robinson et al., 1993)

Time (min)	Strontium (meq/mL)	Cb/Cbo	Cesium (meq/mL)	Cb/Cbo	Calcium (meq/mL)	Cb/Cbo	Magnesium (meq/mL)	Cb/Cbo
0	5.53E-04	1.000	2.52E-04	1.000	5.68E-04	1.000	2.10E-04	1.000
1	5.05E-04	0.913	2.37E-04	0.943	5.53E-04	0.973	2.02E-04	0.959
2	5.14E-04	0.930	2.24E-04	0.891	5.66E-04	0.997	1.98E-04	0.942
5	4.71E-04	0.852	2.05E-04	0.816	5.21E-04	0.917	1.96E-04	0.933
10	4.34E-04	0.786	1.75E-04	0.694	4.76E-04	0.839	1.75E-04	0.831
30	3.27E-04	0.591	1.29E-04	0.512	3.76E-04	0.663	1.58E-04	0.750
60	2.68E-04	0.485	9.93E-05	0.394	3.32E-04	0.585	1.45E-04	0.689
120	1.93E-04	0.349	6.52E-05	0.259	2.40E-04	0.422	1.39E-04	0.663
240	1.29E-04	0.234	4.13E-05	0.164	1.78E-04	0.314	1.50E-04	0.712
360	9.80E-05	0.177	3.16E-05	0.126	1.41E-04	0.249	1.41E-04	0.671

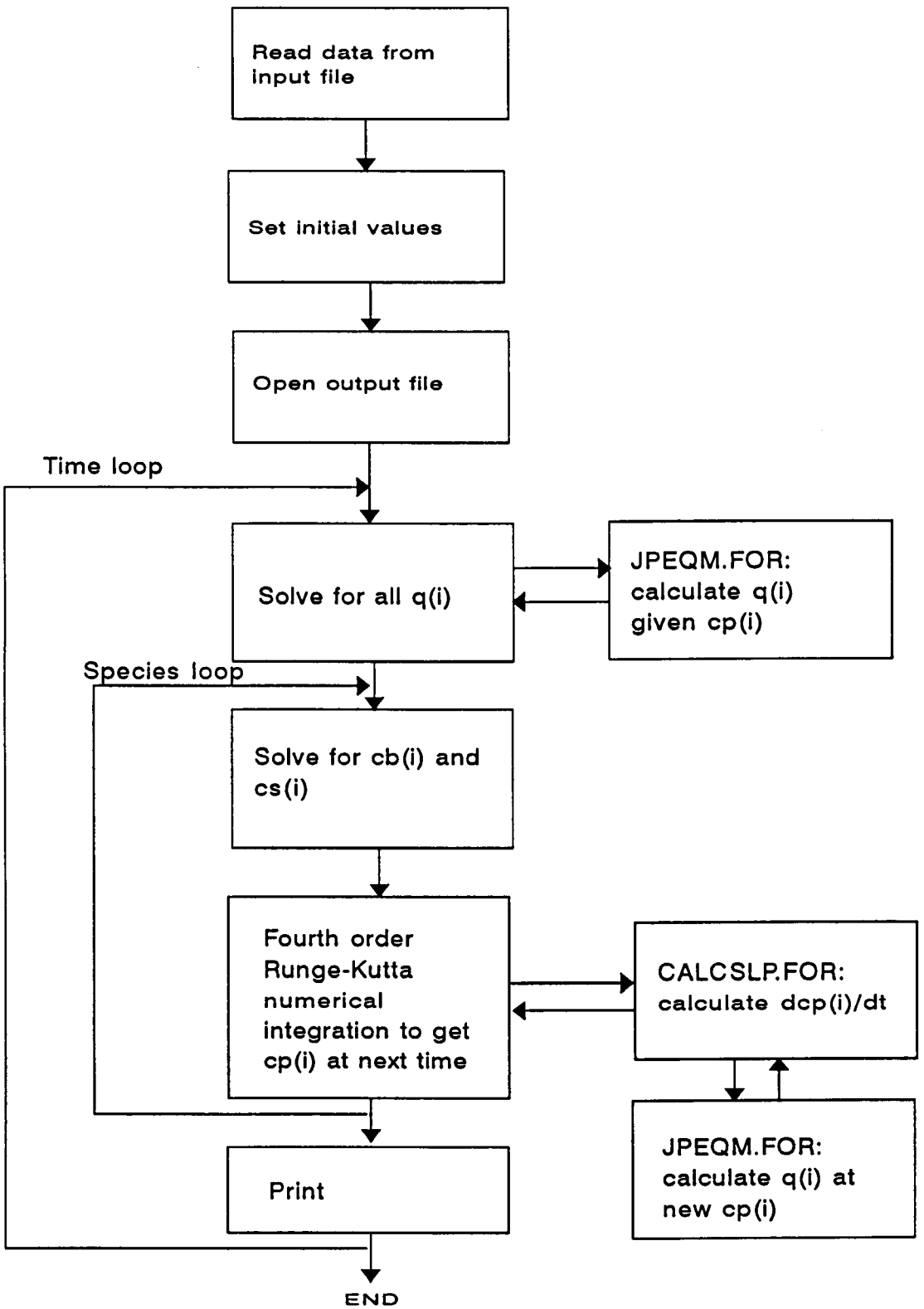
Table B.4. Experimental Multicomponent Data for Ionsiv IE-96, Run SK-34 (Robinson et al., 1993)

Time	Strontium		Cesium		Calcium		Magnesium	
(min)	(meq/mL)	Cb/Cbo	(meq/mL)	Cb/Cbo	(meq/mL)	Cb/Cbo	(meq/mL)	Cb/Cbo
0	2.05E-03	1.00E+00	1.00E-03	1.00E+00	2.35E-03	1.00E+00	8.91E-04	1.00E+00
1	2.03E-03	9.90E-01	9.82E-04	9.82E-01	2.32E-03	9.87E-01	8.72E-04	9.79E-01
2	2.01E-03	9.80E-01	9.58E-04	9.58E-01	2.28E-03	9.70E-01	8.57E-04	9.62E-01
5	1.99E-03	9.71E-01	9.18E-04	9.18E-01	2.16E-03	9.19E-01	8.51E-04	9.55E-01
10	1.90E-03	9.27E-01	8.66E-04	8.66E-01	2.26E-03	9.62E-01	8.54E-04	9.58E-01
30	1.87E-03	9.12E-01	7.82E-04	7.82E-01	2.16E-03	9.19E-01	8.55E-04	9.60E-01
60	1.80E-03	8.78E-01	7.11E-04	7.11E-01	2.05E-03	8.72E-01	8.22E-04	9.23E-01
120	1.75E-03	8.54E-01	6.42E-04	6.42E-01	2.05E-03	8.72E-01	8.21E-04	9.21E-01
240	1.71E-03	8.34E-01	5.57E-04	5.57E-01	2.01E-03	8.55E-01	8.29E-04	9.30E-01
360	1.73E-03	8.44E-01	5.28E-04	5.28E-01	2.00E-03	8.51E-01	8.68E-04	9.74E-01
480	1.74E-03	8.49E-01	5.12E-04	5.12E-01	2.07E-03	8.81E-01	8.67E-04	9.73E-01

APPENDIX C

PROGRAM FLOWSHEET

Program Flowsheet for YPMULT.FOR



APPENDIX D

PROGRAMS

PROGRAM: EQBINARY.FOR

PURPOSE: CALCULATES THE EQUILIBRIUM SOLID CONCENTRATIONS GIVEN THE LIQUID CONCENTRATIONS FOR A BINARY SYSTEM USING THE PERONA MODEL

```
c
c*************************************************************************
c                                 eqbinary.for
c                             by j. j. perona
c                          modified by s. m. depaoli
c
c*************************************************************************
c     this program calculates the solid phase compositions given the
c      liquid phase compositions for a binary system -
c      sr-na, cs-na, ca-na, mg-na, on chabazite zeolite.
c
c*************************************************************************
c     #  1 = strontium
c        2 = cesium
c        3 = calcium
c        4 = magnesium
c        5 = sodium
c     wp## = wilson parameter for binary components # and #
c     ak## = equilibrium constant for binary components # and #
c     z#   = ionic charge on each component
c     c#   = liquid phase concentration for component # [mol/l, m]
c
c     ctot = total solution normality [eq/l, n]
c     y#   = fraction equivalent of each component in absorbed phase
c     streni = ionic strength of solution
c     gam# = liquid phase activity coefficient of component #
c
c*************************************************************************
      implicit real*8 (a-h,o-z)
      dimension wp(5,5),ak(5,5),z(5),conc(5),c(5),gam(5),sgam(5),
     ,fac(5),sgamx(5),f(5),y(5),qconc(5)
c
c  input the wilson parameters (wp) where #s refer to components
c  e.g. wp15 is the wilson parameter for the strontium-sodium binary
c  system
c
      open(unit=6,file='eqbinout.dat',status='new')
      wp(1,1)=1.00
      wp(2,2)=1.00
      wp(3,3)=1.00
      wp(4,4)=1.00
      wp(5,5)=1.00
      wp(1,5)=7.96
      wp(5,1)=0.112
      wp(2,5)=0.01
      wp(5,2)=4.0
      wp(3,5)=86.0
      wp(5,3)=2.0
      wp(4,5)=20.0
      wp(5,4)=4.0
      wp(1,2)=0.001
      wp(2,1)=2.0
      wp(1,3)=25.
      wp(3,1)=4.0
      wp(1,4)=0.03
      wp(4,1)=42.0
```

```
      wp(2,3)=4.8
      wp(3,2)=0.2
      wp(2,4)=2.0
      wp(4,2)=100.0
      wp(3,4)=52.0
      wp(4,3)=92.0
c
c
c  the equilibrium constants for the binary pairs were calculated from
c  experimental data
c
      ak(1,5) = 0.159
      ak(2,5) = 51.1
      ak(3,5) = 0.022
      ak(4,5) = 0.0005
c
c  charge on each component
c
      z(1)=2.
      z(2)=1.
      z(3)=2.
      z(4)=2.
      z(5)=1.
c
c  input the normality (eq/l) of each cation in solution
c
      open(unit=5,file='eqbinary.dat',status='old')
      read(5,*) sgamx(1),sgamx(2),sgamx(3),sgamx(4),sgamx(5),nin
      read(5,*) cistr,qmax
      do 3 mm=1,nin
        read(5,*) conc(1),conc(2),conc(3),conc(4)
        conc(5)=cistr-conc(1)-conc(2)-conc(3)-conc(4)
c
c  calculate the total solution normality, ctot, eq/l
c
        ctot=0.0
        do 15 i=1,5
          ctot=ctot + conc(i)
 15     continue
c
c  units of molarity needed to calculate ionic strength, change units
c  on solution conc.
c
        do 20 i=1,5
          c(i)=conc(i)/z(i)
 20     continue
c
c  total concentration of anion needed, anion is cl, so ctot is also
c  molarity of cl (z=1)
c
c  calculate the ionic strength of solution: (add on the anion conc)
c
        streni=0.0
        do 25 i=1,5
          streni= streni + z(i)**2*c(i)
 25     continue
        streni=(streni+ctot)*0.5
c
c  calculate the liquid phase activity coefficients from the pitzer
c  equation assuming low concentrations so the pitzer equations are
c  truncated at the first term
c
        ai = sqrt(streni)
```

```
      bi = 1. + 1.2*ai
c
      fgam=-0.3915 * (ai/bi + (log(bi))/0.6)
c
c  the liquid phase activity coefficients are calculated using the
c  first term in the pitzer eqns
c
      do 30 i=1,5
        if (conc(i).eq.0.0) goto 30
        gam(i)=exp((z(i)**2)*fgam)
 30   continue
c
c  calculate the solid-phase activity coefficients from the wilson
c  equations
c
c
      do 19 k=1,20
c
c  if the first time through loop, skip these steps (go to line 66)
        if(k.eq.1) go to 66
c
c  if second or more times through, set solid activity coeff. to
c  previous solid activity coeff. values
c
        do 40 i=1,5
          sgam(i)=sgamx(i)
 40     continue
c
c  calculate the summation terms that are in the wilson equations
c  (for i, sum over j: y(j)*wp(ij))(where wp(ii) = 1):
c
        sum=0.0
        do 45 i=1,5
          do 50 j=1,5
            if (conc(j).eq.0.0) goto 50
            sum=y(j)*wp(i,j)+sum
 50       continue
          if (conc(i).eq.0.0) goto 43
          fac(i)=sum
 43       continue
          sum=0.0
 45     continue
c
c  using  summation terms from above in wilson equations, calculate
c  new solid phase activity coeff
c
        sum=0.0
        do 55 i=1,5
          do 60 j=1,5
            if (conc(j).eq.0.0) goto 60
            sum=y(j)*wp(j,i)/fac(j) + sum
 60       continue
          if (conc(i).eq.0.0) goto 53
          sgamx(i)=exp(1.-log(fac(i))- sum)
 53       continue
          sum=0.0
 55     continue
c
c  calculate new solid phase activity coefficients as follows:
c
        do 65 i=1,5
          sgamx(i)=0.5*sgamx(i)+0.5*sgam(i)
 65     continue
```

```
c
  66      continue
c
c  using the initial guess for (or new adjusted) solid phase activity
c  coefficients, calculate the solid phase equivalent fractions
c  (y1,y2,...) using the expressions for the equilibrium quotient:
c
          do 70 i=1,4
            if (conc(i) .eq. 0.0) goto 70
            f(i)=(gam(i)*conc(i)*ak(i,5)*sgamx(5)**z(i))/
     ,      (sgamx(i)*(gam(5)*conc(5))**z(i))
  70      continue
c
c  with 2 equations, f1.. or f4, and yi+y(na)=1.0, solve for
c  y1,y2,y3,or y4 and y5...
c
          a=f(1)+f(3)+f(4)
          b=f(2)+1.
          if (a.eq.0.0) then
           y(5)=1./b
          else
           y(5)=(-b+sqrt(b**2+4.*a))/(2.*a)
          endif
c
          do 80 i=1,4
            if (conc(i) .eq. 0.0) goto 80
            y(i)=f(i)*y(5)**z(i)
  80      continue
c
  19    continue
c
        write( *, 24) y(1),y(2),y(3),y(4),y(5),ctot
  24    format(2x,'y1=',e8.3,1x,'y2=',e8.3,1x,'y3='e8.3,
     ,  1x,'y4=',e8.3,1x,'y5=',e8.3,'ctot=',e8.3)
        do 85 i=1,4
          qconc(i)=y(i)*qmax
          if (conc(i).ne.0.0) then
            write(6,26) conc(i),qconc(i)
          endif
  85    continue
  26    format(5e12.3)
  27    continue
   3  continue
      end
```

PROGRAM: EQMULT.FOR

PURPOSE: CALCULATES THE EQUILIBRIUM SOLID CONCENTRATIONS GIVEN THE LIQUID CONCENTRATIONS FOR A MULTICOMPONENT SYSTEM USING THE PERONA EQUILIBRIUM MODEL

```
c*************************************************************************
c                              eqmult.for
c                           by j. j. perona
c                        modified by s. m. depaoli
c
c*************************************************************************
c     this program calculates the solid phase compositions given the
c      liquid phase compositions for a multicomponent system -
c      sr-cs-ca-mg-na, on chabazite zeolite.
c
c*************************************************************************
c     #  1 = strontium
c        2 = cesium
c        3 = calcium
c        4 = magnesium
c        5 = sodium
c     wp## = wilson parameter for binary components # and #
c     ak## = equilibrium constant for binary components # and #
c     z#   = ionic charge on each component
c     c#   = liquid phase concentration for component # [mol/l, m]
c     conc# = liquid phase concentration for component # [meq/ml, n]
c     ctot = total solution normality [meq/ml, n]
c     y#   = fraction equivalent of each component in absorbed phase
c     streni = ionic strength of solution
c     gam# = liquid phase activity coefficient of component #
c     qmax = maximum loading on zeolite, [meq/ml particle]
c
c*************************************************************************
      implicit real*8 (a-h,o-z)
      dimension wp(5,5),ak(5,5),z(5),conc(5),c(5),gam(5),sgam(5),
     ,fac(5),sgamx(5),f(5),y(5),qconc(5)
c
c  input the wilson parameters (wp) where #s refer to components
c  e.g. Wp15 is the wilson parameter for the strontium-sodium binary
c  system
c
      wp(1,1)=1.00
      wp(2,2)=1.00
      wp(3,3)=1.00
      wp(4,4)=1.00
      wp(5,5)=1.00
      wp(1,5)=7.96
      wp(5,1)=0.112
      wp(2,5)=0.01
      wp(5,2)=4.0
      wp(3,5)=86.0
      wp(5,3)=2.0
      wp(4,5)=20.0
      wp(5,4)=4.0
      wp(1,2)=0.001
      wp(2,1)=2.0
      wp(1,3)=25.
      wp(3,1)=4.0
```

```
      wp(1,4)=0.03
      wp(4,1)=42.0
      wp(2,3)=4.8
      wp(3,2)=0.2
      wp(2,4)=2.0
      wp(4,2)=100.0
      wp(3,4)=52.0
      wp(4,3)=92.0
c
c
c  the equilibrium constants for the binary pairs were calculated from
c  experimental data
c
      ak(1,5) = 0.159
      ak(2,5) = 51.1
      ak(3,5) = 0.022
      ak(4,5) = 0.0005
c
c  charge on each component
c
      z(1)=2.
      z(2)=1.
      z(3)=2.
      z(4)=2.
      z(5)=1.
c
C
      open(unit=5,file='eqmultin.dat',status='old')
      read (5,*) qmax,noin
      open(unit=6,file='eqmult.dat',status='new')
c
      do 99 ixx=1,noin
        read (5,*) totistr,conc(1),conc(2),conc(3),conc(4)
        totcon=conc(1)+conc(2)+conc(3)+conc(4)
        conc(5)=totistr-totcon
c  calculate the total solution normality, ctot, eq/l
c
        ctot=0.0
        do 15 i=1,5
        ctot=ctot + conc(i)
  15    continue
c
c  units of molarity needed to calculate ionic strength, change units
c  on solution conc.
c
        do 20 i=1,5
          c(i)=conc(i)/z(i)
  20    continue
c
c  total concentration of anion needed, anion is cl, so ctot is also
c  molarity of cl (z=1)
c
c  calculate the ionic strength of solution: (add on the anion conc)
c
        streni=0.0
        do 25 i=1,5
          streni= streni + (z(i)**2)*c(i)
  25    continue
        streni=(streni+ctot)*0.5
c
c  calculate the liquid phase activity coefficients from the pitzer
c  equation assuming low concentrations so the pitzer equations are
c  truncated at the first term
```

```
c
      ai = sqrt(streni)
      bi = 1. + 1.2*ai
c
      fgam=-0.3915 * (ai/bi + (log(bi))/0.6)
c
c  the liquid phase activity coefficients are calculated using the
c  first term in the pitzer eqns
c
      do 30 i=1,5
        gam(i)=exp((z(i)**2)*fgam)
 30   continue
c
c  calculate the solid-phase activity coefficients from the wilson
c  equations
c
c  first, assume trial values for solid-phase equivalent fractions
      sgamx(1)=0.5
      sgamx(2)=0.5
      sgamx(3)=0.005
      sgamx(4)=0.003
      sgamx(5)=0.98
c
      do 19 k=1,100
c
c  if the first time through loop, skip these steps (go to line 66)
      if(k.eq.1) go to 66
c
c  if second or more times through, set solid activity coeff. to
c  previous solid activity coeff. values
c
      do 40 i=1,5
        sgam(i)=sgamx(i)
 40   continue
c
c  calculate the summation terms that are in the wilson equations
c  (for i, sum over j: y(j)*wp(ij))(where wp(ii) = 1):
c
      do 45 i=1,5
        do 50 j=1,5
          sum=y(j)*wp(i,j)+sum
 50     continue
        fac(i)=sum
        sum=0.0
 45   continue
c
c  using  summation terms from above in wilson equations, calculate
c  new solid phase activity coeff
c
      do 55 i=1,5
        do 60 j=1,5
           sum=y(j)*wp(j,i)/fac(j) + sum
 60     continue
        sgamx(i)=exp(1.-log(fac(i))- sum)
        sum=0.0
 55   continue
c
c  calculate new solid phase activity coefficients as follows:
c
      do 65 i=1,5
        sgamx(i)=0.5*sgamx(i)+0.5*sgam(i)
 65   continue
c
```

```
  66    continue
c
c  using the initial guess for (or new adjusted) solid phase activity
c  coefficients, calculate the solid phase equivalent fractions
c  (y1,y2,...) using the expressions for the equilibrium quotient:
c
        do 70 i=1,4
          f(i)=sgamx(i)*(gam(5)*conc(5))**z(i)/
     ,    (gam(i)*conc(i)*ak(i,5)*sgamx(5)**z(i))
  70    continue
c
c  with 4 equations, f1.. .. F4, and yi+y(na)=1.0, solve for
c  y1,y2,y3,y4 and y5...
c
        a=1./f(1)+1./f(3)+1./f(4)
        b=1./f(2)+1.
        y(5)=(-b+sqrt(b**2+4*a))/(2*a)
        do 75 i=1,4
          y(i)=1/f(i)*y(5)**z(i)
  75    continue
c
  19    continue
c
        write( *, 24) y(1),y(2),y(3),y(4),y(5)
  24    format(2x,'y1=',e8.3,1x,'y2=',e8.3,1x,'y3='e8.3,
     ,  1x,'y4=',e8.3,1x,'y5=',e8.3)
        write( *, 26) ctot
  26    format(2x,'ctot=',e8.3)
        if (y(5).gt.1.00) then
           y(5)=1.-Y(1)-y(2)-y(3)-y(4)
        endif
c
c  calculate qconc (meq/ml) solid phase compositions to return
c  where qmax is the max. loading on zeolite
        do 100 i=1,4
          qconc(i)=y(i)*qmax
  100   continue
        write(6,27) qconc(1),qconc(2),qconc(3),qconc(4)
   27   format (4e12.3)
c
   99 continue
c
      end
```

PROGRAM : LANGXX.FOR

PURPOSE: CALCULATES UPTAKE OF SINGLE COMPONENT USING LANGMUIR EQUILIBRIUM ISOTHERM

```
c*********************************************************************
c                              langxx
c
c       model for calculation of batch adsorption in a finite
c       bath with fresh adsorbent, pore diffusion controlling,
c       langmuir isotherm, and finite film mass transfer resistance.
C       for xx binary case, xx being cs, sr, ca, or mg
c       assumes favg'(c) ~ f'(cavg)
c       model from yao and tien
c       (chem. engr. science, 48, 1993)
c       programmed by s.m.depaoli
c
c
c*********************************************************************
c                                 variables
c                          (input variables preceeded by *)
c
c         *a1        =constant in langmuir equil isotherm,
c                      ml liq/g solid
c         *a2        =constant in langmuir equil isotherm,
c                      ml liq/g solid
c         alpha      =dimensionless constant, vs/vf
c         b          =dimensionless constant, rp*trank/dp
c         cb         =bulk liquid concentration, meq/ml
c         *cb0       =initial concentration in bulk, meq/ml
c         cnorm      =normalized bulk liq conc, cb/cbo
c         cs         =surface concentration, meq/ml
c         dcdt()     =dc/dt, function at given () conc.
C         *den       =density of particle, g/ml tot particle
c         *dp        =pore diffusion coefficient, cm2/s
c         de         =effective diffusivity, ep*dp
c         dqdc()     =dq/dc, function at given () conc.
C         *ep        =porosity of particle
c         *grams     =mass of adsorbent, g
c         k          =number of time steps to take between printing
c         *n         =number of real time steps to take
c         *rp        =radius of particle, cm
c         rtime      =real time, s
c         tau        =dimensionless time, dp*time/rp^2
c         taustp     =dimensionless time step
c         *trank     =mass transfer coefficient, cm/s
c         *tstep     =real time step, s
c         timet      =total time, s
c         vf         =volume of bulk fluid, ml (vtot - vs)
c         vs         =volume of adsorbent, ml tot particle
c         *vtot      =volume of solution, ml
c
c
c*********************************************************************
        implicit real*8 (a-h,o-z)
        character title1*28
        common/const1/alpha,b,cb0,ep,cs
        common/const2/a1,a2
        tau = 0.0D0
        m=0
c
```

```
c       read input parameters
c
        open(unit=5,file='langmg.dat',status='old')
        rewind 5
        read (5,11) title1
   11   format (a28)
        read (5,*) vtot,den,ep,rp
        read (5,*) dp,trank
        read (5,*) cb0,grams
        read (5,*) tstep,n
        read (5,*) a1,a2
c
        open(unit=6,file='mg1.dat',status='new')
c
c       assume an initial value for cavg of 1e-15
c       because 0.0 is not allowed
c       Also, a1 units are changed to ml liq/ml tot particle
c       in order to change units of q to meq/ml tot particle
c
        a1=a1*den
        de=ep*dp
        cavg=1.0e-15
        Cb=cb0
        vs=grams/den
        vf=vtot-vs
        alpha=vs/vf
        b=rp*trank/de
        taustp=tstep*de/rp**2
        icount=1
        k=30/tstep
c
        write (6,12) title1
   12   format (x,a28)
        write (6,16) trank
   16   format (' mass trans coeff, cm/s =',e12.3)
c
c
        Do 50 i=1,n
c
c         solve for cs using quadratic formula
c
          unsq=(b-1.)**2-8./Cavg*((b*alpha*(ep+a1/(1.+A2*cavg))-1.)*
     ,    Cavg-b*cb0)
          cs=(-(b-1.)+(Unsq)**0.5)/(4./Cavg)
c
c         fourth order runge-kutta, solve for cavg at next tau
c
          x1=taustp*dcdt(cavg)
          newtau=tau+taustp/2.0D0
          cmid=cavg+x1/2.0D0
          x2=taustp*dcdt(cmid)
          cmid=cavg+x2/2.0D0
          x3=taustp*dcdt(cmid)
          newtau=tau+taustp
          cmid=cavg+x3
          x4=taustp*dcdt(cmid)
          cavg=cavg+(x1+2.0D0*(x2+x3)+x4)/6.0D0
          tau=tau+taustp
          m=m+1
          l=l+1
c
c         print results
c
```

```
            if (m.lt.k) goto 50
            cb=cb0-alpha*cavg*(ep+a1/(1.+A2*cavg))
            cnorm=cb/cb0
            rtime=((tau-taustp)*rp**2/de)/60.
            Write(6,200) rtime,cnorm
  200       format (1e12.3,',',1e12.3)
C
c
            if ((l.eq.k*10).and.(icount.eq.1)) Then
              k=k*2
              icount=2
              l=0
            endif
            if ((l.eq.k*15).and.(icount.eq.2)) Then
              k=k*5
              icount=3
              l=0
            endif
            m=0
c
    50    continue
          end
c
c
          function dcdt(cavg)
          implicit real*8 (a-h,o-z)
          common/const1/alpha,b,cb0,ep,cs
          common/const2/a1,a2
          dcdt=(3.0D0*b*(cb0-alpha*cavg*(ep+a1/(1.+A2*cavg))-cs))/
       ,  (ep+dqdc(cavg))
          return
          end
c
c
          function dqdc(cavg)
          implicit real*8 (a-h,o-z)
          common/const2/a1,a2
          dqdc=a1/(1.0D0+a2*cavg)+(a1*a2*cavg)/(1.0D0+a2*cavg)**2
          return
          end
```

PROGRAM: JPBINARY.FOR

PURPOSE: CALCULATES THE BINARY UPTAKE USING THE PERONA EQUILIBRIUM MODEL

```
c**********************************************************************
c                              jpbinary
c
c  model for calculation of batch adsorption in a finite
c  bath with fresh adsorbent, pore diffusion controlling,
c  perona isotherm, and finite film mass transfer resistance.
c  for xx binary case, xx being cs, sr, ca, or mg
c  assumes favg'(c) ~ f'(cavg)
c  model from yao and tien
c  (chem. engr. science, 48, 1993)
c  binary equil model by jj perona
c  programmed by s.m.depaoli
c
c
c**********************************************************************
c                                 variables
c                         (input variables preceeded by *)
c
c       alpha     =dimensionless constant, vs/vf
c       b         =dimensionless constant, rp*trank/dp
c       cb        =bulk liquid concentration, meq/ml
c       *cb0      =initial concentration in bulk, meq/ml
c       cnorm     =normalized bulk liq conc, cb/cbo
c       cs        =surface concentration, meq/ml
c       dcdt()    =dc/dt, function at given () conc.
c       *den      =density of particle, g/ml tot particle
c       *dp       =pore diffusion coefficient, cm2/s
c       de        =effective diffusion coefficient, cm2/s*
c                  ml pore/ml part
c       dqdc()    =dq/dc, function at given () conc.
c       *ep       =porosity of particle
c       *grams    =mass of adsorbent, g
c       k         =number of time steps to take between printing
c       *n        =number of real time steps to take
c       *rp       =radius of particle, cm
c       rtime     =real time, s
c       tau       =dimensionless time, de*time/rp^2
c       taustp    =dimensionless time step
c       *trank    =mass transfer coefficient, cm/s
c       *tstep    =real time step, s
c       timet     =total time, s
c       vf        =volume of bulk fluid, ml (vtot - vs)
c       vs        =volume of adsorbent, ml tot particle
c       *vtot     =volume of solution, ml
c
c
c**********************************************************************
      implicit real*8 (a-h,o-z)
      character title1*28
      common/varb1/b(4),de(4),cb0(4),cs(4),qavg(5),cavg(5)
      common/const1/den,qmax,ep,rp,alpha,pistr,ncomp
      common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
      dimension trank(4),dp(4),cnorm(4),cb(5)
      tau = 0.0d0
      m=0
      icount=1
```

```
      ncomp=4
      bistr=0.0
      pistr=0.0
      do 10 i=1,ncomp
         sgamx(i)=0.0
 10   continue
c
c  assign values for equilibrium calculations
      wp(1,1)=1.0
      wp(2,2)=1.0
      wp(3,3)=1.0
      wp(4,4)=1.0
      wp(5,5)=1.0
      wp(1,5)=7.96
      wp(5,1)=0.112
      wp(2,5)=0.01
      wp(5,2)=4.0
      wp(3,5)=86.0
      wp(5,3)=2.0
      wp(4,5)=20.0
      wp(5,4)=4.0
      wp(1,2)=0.001
      wp(2,1)=2.0
      wp(1,3)=25.0
      wp(3,1)=4.0
      wp(1,4)=0.03
      wp(4,1)=42.0
      wp(2,3)=4.8
      wp(3,2)=0.2
      wp(2,4)=2.0
      wp(4,2)=100.0
      wp(3,4)=52.0
      wp(4,3)=92.0
      ak(1,5)=0.159
      ak(2,5)=51.1
      ak(3,5)=0.022
      ak(4,5)=0.0005
      z(1)=2.
      z(2)=1.
      z(3)=2.
      z(4)=2.
      z(5)=1.
c
c  read input parameters
c
      open(unit=5,file='jpbinin.dat',status='old')
      rewind 5
      read (5,11) title1
 11   format (a29)
      read (5,*) icomp
      read (5,*) qmax,sgamx(icomp),sgamx(5)
      read (5,*) vtot,den,ep,rp
      read (5,*) dp(icomp),trank(icomp)
      read (5,*) cb0(icomp),grams
      read (5,*) tstep,n
c
      do 20 i=1,4
        de(i)=ep*dp(i)
        if (i.eq.icomp) goto 20
        cb0(i)=0.0
        trank(i)=0.0
        dp(i)=0.0
        de(i)=0.0
```

```
          cavg(i)=0.0
          b(i)=0.0
 20     continue
c
        bistr=cb0(icomp)
c
        open(unit=6,file='jpbinout.dat',status='unknown')
c  assume an initial value for cavg of 1e-15
c  because 0.0 is not allowed
c
        cavg(icomp)=1.0e-10
        cb(icomp)=cb0(icomp)
        vs=grams/den
        vf=vtot-vs
        alpha=vs/vf
        b(icomp)=rp*trank(icomp)/de(icomp)
        icount=1
        k=30/tstep
        qmax=qmax*den
        pistr=bistr
c
c  assume pore and bulk ionic strength the same, calculate
c  na concentration in the pore
        cavg(5)=pistr-cavg(icomp)
c
        write (6,12) title1
 12     format ('  ',a29)
c
        do 50 j=1,n
c
c  solve for qavg,i
        call jpeqb(cavg,qavg)
c
        do 60 i=1,ncomp
c
c  jump out of loop if not dealing with icomp
          if (i.ne.icomp) goto 60
c
c  solve for cb,i
          cb(i)=cb0(i)-alpha*(ep*cavg(i)+qavg(i))
c
c  solve for cs using quadratic formula
          unsq=(b(i)-1.)**2+8.*(1.+b(i)*cb(i)/cavg(i))
          cs(i)=(-(b(i)-1.)+(unsq)**0.5)/(4./cavg(i))
c
c  fourth order runge-kutta, solve for cavg at next tau
c
          cpore=cavg(i)
          call calcslp(i,cpore,dcdt)
          x1=tstep*dcdt
          cpore=cavg(i)+x1/2.0d0
          call calcslp(i,cpore,dcdt)
          x2=tstep*dcdt
          cpore=cavg(i)+x2/2.0d0
          call calcslp(i,cpore,dcdt)
          x3=tstep*dcdt
          cpore=cavg(i)+x3
          call calcslp(i,cpore,dcdt)
          x4=tstep*dcdt
          cavg(i)=cavg(i)+(x1+2.0d0*(x2+x3)+x4)/6.0d0
c
 60     continue
c
```

```
      cavg(5)=pistr-cavg(icomp)
      tau=tau+tstep
      m=m+1
      ll=ll+1
c
c  print results
c
      if (m.lt.k) goto 50
      do 70 l=1,ncomp
        if (l.ne.icomp) goto 70
        cnorm(l)=cb(l)/cb0(l)
 70   continue
      rtime=(tau-tstep)/60.
      write(6,200) rtime,cnorm(icomp)
 200  format (2e12.3)
c
c
      if ((ll.eq.k*10).and.(icount.eq.1)) then
        k=k*2
        icount=2
        ll=0
      endif
      if ((ll.eq.k*15).and.(icount.eq.2)) then
         k=k*5
         icount=3
         ll=0
      endif
      m=0
c
 50   continue
      end
c
c
c**********************************************************************
      subroutine calcslp(i,cpore,dcdt)
      implicit real*8 (a-h,o-z)
      common/varb1/b(4),de(4),cb0(4),cs(4),qavg(5),cavg(5)
      common/const1/den,qmax,ep,rp,alpha,pistr,ncomp
      common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
      dimension cavgr(5),cavgl(5),qavgr(5),qavgl(5)
     c  ,cavgx(5),qavgx(5),cavglx(5),cavgrx(5),qavglx(5),qavgrx(5)
c
c
c  subroutine to calculate dc/ct at various c's, but first need
c  to calculate dq/dc by finite difference method
c
      do 100 k=1,ncomp
        if (k.eq.i) then
          cavgx(k)=cpore
          cavgl(k)=cpore-0.000001*cpore
          cavglx(k)=cpore
          cavgl(5)=pistr-cavgl(k)
          cavgx(5)=pistr-cavgx(k)
          cavglx(5)=pistr-cpore-0.000001*(pistr-cpore)
          else
          cavgx(k)=cavg(k)
          cavgl(k)=cavg(k)
          cavglx(k)=cavg(k)
        endif
 100  continue
c
      call jpeqb(cavgl,qavgl)
      call jpeqb(cavglx,qavglx)
```

```
c
c
      do 200 k=1,ncomp
        if (k.eq.i) then
          cavgx(k)=cpore
          cavgr(k)=cpore+0.000001*cpore
          cavgrx(k)=cpore
          cavgr(5)=pistr-cavgr(k)
          cavgx(5)=pistr-cavgx(k)
          cavgrx(5)=pistr-cpore+0.000001*(pistr-cpore)
          else
          cavgx(k)=cavg(k)
          cavgr(k)=cavg(k)
          cavgrx(k)=cavg(k)
        endif
 200  continue
c
      call jpeqb(cavgr,qavgr)
      call jpeqb(cavgrx,qavgrx)
c
c
      delta=0.000001*cpore
      dqdna=(qavgrx(i)-qavglx(i))/(2.*delta)
      dqdc=(qavgr(i)-qavgl(i))/(2.*delta)-dqdna
c
c
      call jpeqb(cavgx,qavgx)
      cbx=cb0(i)-alpha*(ep*cpore+qavgx(i))
      unsq=(b(i)-1.)**2+8.*(1.+b(i)*cbx/cpore)
      csx=((-b(i)-1.)+sqrt(unsq))/(4./cpore)
      dcdt=(3.*b(i)*de(i)*(cbx-csx))/(rp**2*(ep+dqdc))
c
      return
      end
c
c**********************************************************************
       subroutine jpeqb(conc,qconc)
c
c
c                perona model for binary equilibrium
c                by j. j. perona
c                modified by s. m. depaoli 7/1994
c
c**********************************************************************
c    this program calculates the solid phase compositions given the
c     liquid phase compositions for a binary system -
c     sr-na, cs-na, ca-na, mg-na, on chabazite zeolite.
c
c**********************************************************************
c    #  1 = strontium
c       2 = cesium
c       3 = calcium
c       4 = magnesium
c       5 = sodium
c    wp## = wilson parameter for binary components # and #
c    ak## = equilibrium constant for binary components # and #
c    z# = ionic charge on each component
c    c# = liquid phase concentration for component # [mol/l, m]
c    conc# = liquid phase concentration for component # [eq/l, n]
c    ctot = total solution normality [eq/l, n]
c    y# = fraction equivalent of each component in absorbed phase
c    streni = ionic strength of solution
c    gam# = liquid phase activity coefficient of component #
```

```
c
c*************************************************************************
      implicit real*8 (a-h,o-z)
      common/const1/den,qmax,ep,rp,alpha,pistr,ncomp
      common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
      dimension conc(5),c(5),gam(5),sgam(5),fac(5),f(5),y(5),qconc(5)
c
c  calculate the total solution normality, ctot, eq/l
c
      ctot=0.0
      do 15 iz=1,5
        ctot=ctot + conc(iz)
 15   continue
c
      do 17 iz=1,5
        sgam(iz)=0.0
 17   continue
c
c  units of molarity needed to calculate ionic strength, change units
c  on solution conc.
c
      do 20 iz=1,5
        c(iz)=conc(iz)/z(iz)
 20   continue
c
c  total concentration of anion needed, anion is cl, so ctot is also
c  molarity of cl (z=1)
c
c  calculate the ionic strength of solution: (add on the anion conc)
c
      streni=0.0
      do 25 iz=1,5
        streni= streni + z(iz)**2*c(iz)
 25   continue
      streni=(streni+ctot)*0.5
c
c  calculate the liquid phase activity coefficients from the pitzer
c  equation assuming low concentrations so the pitzer equations are
c  truncated at the first term
c
      ai = sqrt(streni)
      bi = 1. + 1.2*ai
c
      fgam=-0.3915 * (ai/bi + (log(bi))/0.6)
c
c  the liquid phase activity coefficients are calculated using the
c  first term in the pitzer eqns
c
      do 30 iz=1,5
       if (conc(iz).eq.0.0) goto 30
         gam(iz)=exp((z(iz)**2)*fgam)
 30   continue
c
c  calculate the solid-phase activity coefficients from the wilson
c  equations
c
c
      do 19 k=1,40
c
c  if the first time through loop, skip these steps (go to line 66)
        if(k.eq.1) go to 66
c
c  if second or more times through, set solid activity coeff. to
```

```
c  previous solid activity coeff. values
c
         do 40 iz=1,5
            sgam(iz)=sgamx(iz)
 40      continue
c
c  calculate the summation terms that are in the wilson equations
c  (for i, sum over j: y(j)*wp(ij))(where wp(ii) = 1):
c
         sum=0.0
         do 50 iz=1,5
           do 43 j=1,5
             if (conc(j).eq.0.0) goto 43
             sum=y(j)*wp(iz,j)+sum
 43        continue
           if (conc(iz).eq.0.0) goto 45
           fac(iz)=sum
 45        continue
           sum=0.0
 50      continue
c
c  using  summation terms from above in wilson equations, calculate
c  new solid phase activity coeff
c
         sum=0.0
         do 70 iz=1,5
           do 60 j=1,5
             if (conc(j).eq.0.0) goto 60
             sum=y(j)*wp(j,iz)/fac(j) + sum
 60        continue
           if (conc(iz).eq.0.0) goto 65
           sgamx(iz)=exp(1.-log(fac(iz))- sum)
 65        continue
           sum=0.0
 70      continue
c
c  calculate new solid phase activity coefficients as follows:
c
         do 72 iz=1,5
           sgamx(iz)=0.5*sgamx(iz)+0.5*sgam(iz)
 72      continue
c
 66      continue
c
c  using the initial guess for (or new adjusted) solid phase activity
c  coefficients, calculate the solid phase equivalent fractions
c  (y1,y2,...) using the expressions for the equilibrium quotient:
c
         do 75 iz=1,4
           if (conc(iz) .eq. 0.0) goto 75
           f(iz)=(gam(iz)*conc(iz)*ak(iz,5)*sgamx(5)**z(iz))/
     ,     (sgamx(iz)*(gam(5)*conc(5))**z(iz))
 75      continue
c
c  with 2 equations, f1.. or F4, and yi+y(na)=1.0, solve for
c  y1,y2,y3,or y4 and y5...
c
         a=f(1)+f(3)+f(4)
         b=f(2)+1.
         if (a.eq.0.0) then
           y(5)=1./b
         else
           y(5)=(-b+sqrt(b**2+4.*a))/(2.*a)
```

```
          endif
c
          do 80 iz=1,4
            if (conc(iz) .eq. 0.0) goto 80
            y(iz)=1.-y(5)
 80       continue
c
          sgamsum=0.0
          sgamtot=0.0
          do 85 iz=1,4
            sgamsum=sgamsum+sgam(iz)
            sgamtot=sgamtot+sgamx(iz)
 85       continue
          if (abs(sgamsum-sgamtot).lt.(0.001*sgamsum)) goto 90
c
 19     continue
c
 90     continue
        do 95 iz=1,4
          qconc(iz)=y(iz)*qmax
 95     continue
c
        return
        end
```

PROGRAM: DPMULT.FOR

PURPOSE: CALCULATES UPTAKE RATE FOR MULTICOMPONENT SYSTEM USING THE DUBININ-POLYANI MULTICOMPONENT EQUILIBRIUM ISOTHERM MODELS

```
c*************************************************************
c                              dpmult
c
c        model for calculation of batch adsorption in a
c        finite bath with fresh adsorbent, pore diffusion
c        controlling,
c        dubinin-polyani isotherm, and finite film mass
c        transfer resistance.
C        assumes favg'(c) ~ f'(cavg)
c        model from yao and tien
c        (chem. engr. science, 48, 1993)
c        programmed by s.m.depaoli
c
c
c*************************************************************
c                         variables
c              (input variables preceeded by *)
c
c     *db0       =constant in dubinin-polyani equil equation
c     *db1       =constant in dubinin-polyani equil equation
c     *db2       =constant in dubinin-polyani equil equation
c     alpha      =dimensionless constant, vs/vf
c     b          =dimensionless constant, rp*trank/dp
c     cavg       =average pore concentration, meq/ml particle
c     cb         =bulk liquid concentration, meq/ml liquid
c     *cb0       =initial concentration in bulk, meq/ml liquid
c     cnorm      =normalized bulk liq conc, cb/cbo
c     cs         =surface concentration, meq/ml
c     dcdt()     =dc/dt, function at given () conc.
C     *den       =density of particle, g/ml particle
c     *dp        =pore diffusion coefficient, cm2/s
c     de         =effective diffusivity, ep*dp
c     dqdc()     =dq/dc, function at given () conc.
C     *ep        =porosity of particle
c     *grams     =mass of adsorbent, g
c     k          =number of time steps to take between printing
c     *n         =number of real time steps to take
c     ncomp      =number of components:1=sr,2=cs,3=ca,4=mg
c     *rp        =radius of particle, cm
c     rtime      =real time, s
c     *trank     =mass transfer coefficient, cm/s
c     *tstep     =real time step, s
c     timet      =total time, s
c     vf         =volume of bulk fluid, ml (vtot - vs)
c     vs         =volume of adsorbent, ml tot particle
c     *vtot      =volume of solution, ml
c     #1         =strontium
c      2         =cesium
c      3         =calcium
c      4         =magnesium
c      5         =sodium
c
c*************************************************************************
       implicit real*8 (a-h,o-z)
```

```
      character title1*34
      common/const1/alpha,b(4),de(4),cb0(4),ep,rp,cs,qavg
      common/const2/db0(4),db1(4),db2(4),den
      dimension trank(4),cnorm(4),cavg(4),dp(4)
      tau = 0.0D0
      m=0
      icount=1
      ncomp=4
c
c     read input parameters
c
      open(unit=5,file='dpmultin.dat',status='old')
      rewind 5
      read (5,11) title1
   11 format (a34)
      read (5,*) den,ep,rp
      read (5,*) vtot,grams
      read (5,*) tstep,n
      do 25 i=1,ncomp
        read (5,*) cb0(i)
        read (5,*) dp(i),trank(i)
        read (5,*) db0(i),db1(i),db2(i)
        de(i)=dp(i)*ep
   25 continue
c
c
      vs=grams/den
      vf=vtot-vs
      alpha=vs/vf
      k=30/tstep
c
      open(unit=6,file='dpmult.dat',status='new')
      write (6,12) title1
   12 format (x,a34)
c
c     assume an initial value for cavg of 1e-10
c     because 0.0 is not allowed
      Do 30 i=1,ncomp
        cavg(i)=1.0e-10
        B(i)=rp*trank(i)/de(i)
   30 continue
c
c
      do 60 j=1,n
c
      do 50 i=1,ncomp

c  solve for qavg,i
      qavg=den*dexp(db0(i)+db1(i)*log(cavg(i))+
     ,   db2(i)*(log(cavg(i)))**2)
c
c       solve for cb,i
        cb=cb0(i)-alpha*(ep*cavg(i)+qavg)
c
c       solve for cs,i using quadratic formula
        unsq=(b(i)-1.)**2+8.*(1.+B(i)*cb/cavg(i))
        cs=(-(b(i)-1.)+(Unsq)**0.5)/(4./Cavg(i))
c
c       fourth order runge-kutta, solve for cavg at next tau
c
        cpore=cavg(i)
        x1=tstep*dcdt(cpore,i)
        newtau=tau+tstep/2.0D0
```

```
          cmid=cavg(i)+x1/2.0D0
          x2=tstep*dcdt(cmid,i)
          cmid=cavg(i)+x2/2.0D0
          x3=tstep*dcdt(cmid,i)
          newtau=tau+tstep
          cmid=cavg(i)+x3
          x4=tstep*dcdt(cmid,i)
          cavg(i)=cavg(i)+(x1+2.0D0*(x2+x3)+x4)/6.0D0
c
c
   50   continue
c
        tau=tau+tstep
        m=m+1
        ll=ll+1
c
c       print results
c
        if (m.lt.k) goto 60
        do 40 l=1,ncomp
          qavg=den*dexp(db0(l)+db1(l)*log(cavg(l))+
     ,    db2(l)*(log(cavg(l)))**2)
          cb=cb0(l)-alpha*(cavg(l)*ep+qavg)
          cnorm(l)=cb/cb0(l)
   40   continue
c
        rtime=(tau-tstep)/60.
        Write(6,200) rtime,cnorm(1),cnorm(2),cnorm(3),cnorm(4)
  200   format (5e12.3)
C
        if ((ll.eq.k*10).and.(icount.eq.1)) Then
          k=k*2
          icount=2
          ll=0
        endif
        if ((ll.eq.k*15).and.(icount.eq.2)) Then
          k=k*5
          icount=3
          ll=0
        endif
        m=0
c
c
   60   continue
        end
c
c
         function dcdt(cpore,i)
         implicit real*8 (a-h,o-z)
         common/const1/alpha,b(4),de(4),cb0(4),ep,rp,cs,qavg
         common/const2/db0(4),db1(4),db2(4),den
         dcdt=(3.*b(i)*de(i)*(cb0(i)-alpha*(ep*cpore+qavg)-
     ,   cs))/(rp**2*(ep+dqdc(cpore,i)))
         return
         end
c
         function dqdc(cpore,i)
         implicit real*8 (a-h,o-z)
         common/const2/db0(4),db1(4),db2(4),den
         dqdc=den*exp(db0(i)+db1(i)*log(cpore)+db2(i)*log(cpore)*
     ,   log(cpore))*(db1(i)/cpore+db2(i)*2.*Log(cpore)/cpore)
         return
         end
```

PROGRAM: YPMULT.FOR

PURPOSE: CALCULATES THE UPTAKE FOR A MULTICOMPONENT SYSTEM USING THE PERONA MULTICOMPONENT EQUILIBRIUM MODEL

```
c**********************************************************************
c                              ypmult
c
c       model for calculation of batch adsorption in a finite
c       bath with fresh adsorbent, pore diffusion controlling,
c       perona equilibrium isotherm, and finite film mass transfer
c       resistance.
c       assumes favg'(c) ~ f'(cavg)
c       kinetic model from yao and tien;
c       (chem. engr. science, 48, 1993)
c       programmed by s.m.depaoli
c
c
c**********************************************************************
c                                  variables
c                          (input variables preceeded by *)
c
c         alpha      =dimensionless constant, vs/vf
c         b          =dimensionless constant, rp*trank/dp
c         bistr      =bulk ionic strength, meq/ml fluid
c         bnorm      =bulk solution normality, meq/ml
c         cavg       =average pore concentration, meq/ml pore
c         cb         =bulk liquid concentration, meq/ml fluid
c         *cb0       =initial concentration in bulk, meq/ml fluid
c         cna        =conc of sodium in pores, meq/ml pore
c         cnorm      =normalized bulk liq conc, cb/cbo
c         cs         =surface concentration, meq/ml fluid
c         dcdt()     =dc/dt, function at given () conc.
c         *den       =density of particle, g/ml particle
c         *dp        =pore diffusion coefficient, cm2/s
c         de         =effective diffusivity,ep*dp
c         dqdc()     =dq/dc, function at given () conc.
c         *ep        =porosity of particle, ml pore/ml particle
c         *grams     =mass of adsorbent, g
c         k          =number of time steps to take between printing
c         *n         =number of real time steps to take
c         ncomp      =number of components:1=sr,2=cs,3=ca,4=mg
c         pistr      =pore ionic strength, meq/ml pore
c         *rp        =radius of particle, cm
c         rtime      =real time, s
c         *trank     =film mass transfer coefficient, cm/s
c         *tstep     =real time step, s
c         timet      =total time, s
c         vf         =volume of bulk fluid, ml (vtot - vs)
c         vs         =volume of adsorbent, ml particle
c         *vtot      =volume of solution, ml
c         #1         =strontium
c          2         =cesium
c          3         =calcium
c          4         =magnesium
c          5         =sodium
c
c**********************************************************************
```

```
      implicit real*8 (a-h,o-z)
      character title1*34
      common/varb1/b(5),dex(5),cb0(5),cs(5),qavg(5),cavg(5)
      common/const1/qmax,ep,rp,alpha,pistr,ncomp
      common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
      dimension trank(5),dp(5),cnorm(5),cb(5)
     c ,cpore(5),x1(5),x2(5),x3(5),x4(5),dcdt(5)
      tau = 0.0d0
      m=0
      icount=1
      ncomp=4
      bistr=0.0
      bnorm=0.0
      pistr=0.0
      sgamx(1)=0.5
      sgamx(2)=0.5
      sgamx(3)=0.015
      sgamx(4)=0.015
      sgamx(5)=0.98
c
c  assign values for equilibrium calculation
      wp(1,1)=1.0
      wp(2,2)=1.0
      wp(3,3)=1.0
      wp(4,4)=1.0
      wp(5,5)=1.0
      wp(1,5)=7.96
      wp(5,1)=0.112
      wp(2,5)=0.01
      wp(5,2)=4.0
      wp(3,5)=86.0
      wp(5,3)=2.0
      wp(4,5)=20.0
      wp(5,4)=4.0
      wp(1,2)=0.001
      wp(2,1)=2.0
      wp(1,3)=25.0
      wp(3,1)=4.0
      wp(1,4)=0.03
      wp(4,1)=42.0
      wp(2,3)=4.8
      wp(3,2)=0.2
      wp(2,4)=2.0
      wp(4,2)=100.0
      wp(3,4)=52.0
      wp(4,3)=92.0
      ak(1,5)=0.159
      ak(2,5)=51.1
      ak(3,5)=0.022
      ak(4,5)=0.0005
      z(1)=2.
      z(2)=1.
      z(3)=2.
      z(4)=2.
      z(5)=1.
c
c  read input parameters
c
      open(unit=5,file='ypmultin.dat',status='old')
      rewind 5
      read (5,11) title1
 11   format (a34)
      read (5,*) den,ep,rp
```

```
      read (5,*) qmax
      read (5,*) vtot,grams
      read (5,*) tstep,n
      do 25 i=1,ncomp
         read (5,*) cb0(i)
         read (5,*) dp(i),trank(i)
 25   continue
c
      do 26 i=1,ncomp
         dex(i)=ep*dp(i)
         bistr=bistr+cb0(i)
         bnorm=bnorm+cb0(i)
 26   continue
c
      rtime=0.0
      vs=grams/den
      vf=vtot-vs
      alpha=vs/vf
      k=1*60/tstep
      cavg1t4=0.0
      qmax=qmax*den
c
c
      open(unit=6,file='ypmult.dat',status='unknown')
      write (6,12) title1
 12   format (1x,a34)
c
      write (6,13) dp(1),dp(2),dp(3),dp(4)
 13   format ('  the diffusion coeffs..',4e12.3)
c  assume an initial value for cavg,i=1,4 of 1e-10
c  because 0.0 is not allowed
      do 30 i=1,ncomp
         cavg(i)=1.0d-10
         b(i)=rp*trank(i)/dex(i)
         cavg1t4=cavg1t4+cavg(i)
 30   continue
c
c  calculate ionic strength in meq, to apply to initial pore
c  concentration of na (assumption of constant ionic strength
c  in pore and bulk gives na initial pore conc)
      pistr=bistr
      cavg(5)=pistr-cavg1t4
c
c
      do 60 j=1,n
         xtime=tau/60.
c
         if ((xtime.gt.10.).and.(xtime.le.100)) then
           k=2*60/tstep
         endif
         if ((xtime.gt.100).and.(xtime.le.200)) then
           tstep=0.04
           k=5*60/tstep
         endif
        if (xtime.gt.200) then
          tstep=0.08
          k=10*60/tstep
        endif
c  solve for qavg,i
        call jpeqm(cavg,qavg)
c
c
        do 50 i=1,ncomp
```

```
c
c  solve for cb,i and cs,i and set cpore=cavg
          cb(i)=cb0(i)-alpha*(ep*cavg(i)+qavg(i))
          unsq=(b(i)-1.)**2+8.*(1.+b(i)*cb(i)/cavg(i))
          cs(i)=(-(b(i)-1.)+dsqrt(unsq))/(4./cavg(i))
          cpore(i)=cavg(i)
 50     continue
        cpore(5)=cavg(5)
c
c  fourth order runge-kutta, solve for all cavg at next tau
c
c
        call calcslp(cpore,dcdt)
        cportot=0.0
        do 100 i=1,ncomp
          x1(i)=tstep*dcdt(i)
          cpore(i)=cavg(i)+x1(i)/2.0d0
          cportot=cportot+cpore(i)
 100    continue
        cpore(5)=pistr-cportot
c
        call calcslp(cpore,dcdt)
        cportot=0.0
        do 110 i=1,ncomp
          x2(i)=tstep*dcdt(i)
          cpore(i)=cavg(i)+x2(i)/2.0d0
          cportot=cportot+cpore(i)
 110    continue
        cpore(5)=pistr-cportot
c
        call calcslp(cpore,dcdt)
        cportot=0.0
        do 120 i=1,ncomp
          x3(i)=tstep*dcdt(i)
          cpore(i)=cavg(i)+x3(i)
          cportot=cportot+cpore(i)
 120    continue
        cpore(5)=pistr-cportot
c
        call calcslp(cpore,dcdt)
        cportot=0.0
        do 130 i=1,ncomp
          x4(i)=tstep*dcdt(i)
          cavg(i)=cavg(i)+(x1(i)+2.0d0*(x2(i)+x3(i))+x4(i))/6.0d0
          cportot=cportot+cavg(i)
 130    continue
        cavg(5)=pistr-cportot
c
c
        m=m+1
        ll=ll+1
c
c  print results
c
        if (m.lt.k) goto 59
        do 40 l=1,ncomp
          cnorm(l)=cb(l)/cb0(l)
 40     continue
c
        rtime=tau/60.
        write(6,200) rtime,cnorm(1),cnorm(2),cnorm(3),cnorm(4),noiter
 200    format (5e12.3,1i4)
        m=0
```

```
c
c
 59      continue
c
         tau=tau+tstep
c
 60    continue
 999   continue
       end
c
c**********************************************************************
       subroutine calcslp(cpore,dcdt)
       implicit real*8 (a-h,o-z)
       common/varb1/b(5),dex(5),cb0(5),cs(5),qavg(5),cavg(5)
       common/const1/qmax,ep,rp,alpha,pistr,ncomp
       common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
       dimension cavgr(5),cavgl(5),cpore(5),qavgr(5),qavgl(5)
      c ,pqpc(5,5),ql(5,5),qr(5,5),dqdc(5),delta(5),dcdt(5)
      c ,cbx(5),csx(5),qavgx(5)
c
c
c  subroutine to calculate dc/dt(i) at various c's, but first need
c  to calculate dq/dci(i) by finite difference method
c
       call jpeqm(cpore,qavgx)
       do 100 k=1,ncomp+1
          cavgl(k)=cpore(k)
          cavgr(k)=cpore(k)
 100   continue
c
       do 200 m=1,ncomp+1
c
          cavgl(m)=cpore(m)-.0001*cpore(m)
          call jpeqm(cavgl,qavgl)
          cavgl(m)=cpore(m)
          do 300 n=1,ncomp+1
            ql(n,m)=qavgl(n)
 300      continue
c
c
          cavgr(m)=cpore(m)+0.0001*cpore(m)
          call jpeqm(cavgr,qavgr)
          cavgr(m)=cpore(m)
          do 400 n=1,ncomp+1
            qr(n,m)=qavgr(n)
 400      continue
c
c
          delta(m)=0.0001*cpore(m)
c
          do 500 n=1,ncomp
            pqpc(n,m)=(qr(n,m)-ql(n,m))/(2.*delta(m))
 500      continue
c
 200   continue
c
c
       do 600 m=1,ncomp+1
         dqdc(m)=0.0
         do 700 n=1,ncomp
           if (n.eq.m) then
             dqdc(m)=dqdc(m)+pqpc(n,m)
           else
```

```
            dqdc(m)=dqdc(m)-pqpc(n,m)
          endif
 700    continue
c
        cbx(m)=cb0(m)-alpha*(ep*cpore(m)+qavgx(m))
c
        unsq=(b(m)-1.)**2+8.*(1.+b(m)*cbx(m)/cpore(m))
        csx(m)=(-(b(m)-1.)+dsqrt(unsq))/(4./cpore(m))
c
        dcdt(m)=3.*b(m)*dex(m)*(cbx(m)-csx(m))/(rp**2*(ep+dqdc(m)))
 600  continue
c
c
      return
      end
c
c**********************************************************************
        subroutine jpeqm(conc,qconc)
c
c
c                              eqmulti.for
c                           by j. j. perona
c                       modified by s. m. depaoli 7/1994
c
c**********************************************************************
c  this program calculates the solid phase compositions given the
c  liquid phase compositions for a multicomponent system -
c  sr-na, cs-na, ca-na, mg-na, on chabazite zeolite.
c
c**********************************************************************
c  #  1 = strontium
c     2 = cesium
c     3 = calcium
c     4 = magnesium
c     5 = sodium
c    Wp## = wilson parameter for binary components # and #
c    ak## = equilibrium constant for binary components # and #
c    z# = ionic charge on each component
c    c# = liquid phase concentration for component # [mol/l, m]
c    conc# = liquid phase concentration for component # [meq/ml, n]
c    ctot = total solution normality [meq/ml, n]
c    y# = fraction equivalent of each component in absorbed phase
c    streni = ionic strength of solution
c    gam# = liquid phase activity coefficient of component #
c    qmax = maximum loading on zeolite, [meq/ml particle]
c
c**********************************************************************
      implicit real*8 (a-h,o-z)
      common/const1/qmax,ep,rp,alpha,pistr,ncomp
      common/equil/sgamx(5),wp(5,5),ak(5,5),z(5)
      dimension conc(5),c(5),gam(5),sgam(5),
     cfac(5),f(5),y(5),qconc(5)
      diftot=0.0
      sgamsum=0.0
      do 14 i=1,5
         sgam(i)=0.0
  14  continue
      noiter=0
c
c
c  calculate the total solution normality, ctot, eq/l
c
      ctot=0.0
```

```
      do 10 ji=1,5
        ctot= ctot + conc(ji)
 10   continue
c
c  units of molarity needed to calculate ionic strength, change units
c  on solution conc.
c
      do 20 ij=1,5
        c(ij)=conc(ij)/z(ij)
 20   continue
c
c  total concentration of anion needed, anion is cl, so ctot is also
c  molarity of cl (z=1)
c  calculate the ionic strength of solution: (add on the anion conc)
c
      streni=0.0
      do 25 ij=1,5
        streni= streni + (z(ij)**2)*c(ij)
 25   continue
      streni=(streni+ctot)*0.5
c
c  calculate the liquid phase activity coefficients from the pitzer
c  equation assuming low concentrations so the pitzer equations are
c  truncated at the first term
c
      ai = dsqrt(streni)
      bi = 1. + 1.2*ai
c
      fgam=-0.3915 * (ai/bi + (dlog(bi))/0.6)
c
c  the liquid phase activity coefficients are calculated using the
c  first term in the pitzer eqns
c
      do 30 ij=1,5
        gam(ij)=dexp((z(ij)**2)*fgam)
 30   continue
c
c  calculate the solid-phase activity coefficients from the wilson
c  equations
c
      do 19 k=1,50
        noiter=noiter+1
c
c  if the first time through loop, skip these steps (go to line 66)
        if(k.eq.1) go to 66
c
c  if second or more times through, set solid activity coeff. to
c  previous solid activity coeff. values
c
        do 40 ij=1,5
         sgam(ij)=sgamx(ij)
 40     continue
c
c  calculate the summation terms that are in the wilson equations
c  (for i, sum over j: y(j)*wp(ij))(where wp(ii) = 1):
        sum=0.0
        do 45 ii=1,5
          do 50 j=1,5
            sum=y(j)*wp(ii,j)+sum
 50       continue
          fac(ii)=sum
          sum=0.0
 45     continue
```

```
c
c  using  summation terms from above in wilson equations, calculate
c  new solid phase activity coeff
c
        do 55 ii=1,5
          do 60 j=1,5
            sum=y(j)*wp(j,ii)/fac(j) + sum
 60       continue
          sgamx(ii)=dexp(1.-dlog(fac(ii))- sum)
          sum=0.0
 55     continue
c
c  calculate new solid phase activity coefficients as follows:
c
        do 65 ii=1,5
          sgamx(ii)=0.5*sgamx(ii)+0.5*sgam(ii)
 65     continue
c
 66   continue
c
c  using the initial guess for (or new adjusted) solid phase activity
c  coefficients, calculate the solid phase equivalent fractions
c  (y1,y2,...) using the expressions for the equilibrium quotient:
c
      do 70 ii=1,4
        f(ii)=sgamx(ii)*(gam(5)*conc(5))**z(ii)/
     c  (gam(ii)*conc(ii)*ak(ii,5)*sgamx(5)**z(ii))
 70   continue
c
c  with 4 equations, f1.. .. F4, and yi+y(na)=1.0, solve for
c  y1,y2,y3,y4 and y5...
c
      a=1./f(1)+1./f(3)+1./f(4)
      b=1./f(2)+1.
      y(5)=(-b+dsqrt(b**2+4.d0*a))/(2.d0*a)
      do 75 ii=1,4
        y(ii)=1.d0/f(ii)*y(5)**z(ii)
 75   continue
      sgamold=sgamsum
      diftot=0.0
      do 80 ii=1,5
        dif=(sgamx(ii)-sgam(ii))**2
        diftot=diftot+dif
 80   continue
      diftot=diftot**0.5
      if (diftot.lt.(0.01*sgamx(3))) goto 85
c
 19   continue
 85   continue
c
      if (y(5).gt.1.00) then
        y(5)=1.0-y(1)-y(2)-y(3)-y(4)
      endif
c
c  calculate qconc (meq/ml) solid phase compositions to return
c  where qmax is the max. loading on zeolite
c
      do 100 ii=1,ncomp+1
        qconc(ii)=y(ii)*qmax
 100  continue
c
      return
      end
```

VITA

Susan Marie Mrochek DePaoli was born in Ames, Iowa on April 1, 1963. Shortly thereafter her family moved to Oak Ridge, Tennessee. She attended private and public schools in Oak Ridge. Susan began her college education at the University of Tennessee, Knoxville in March, 1981. She received her Bachelor of Science in Chemical Engineering from the University of Tennessee in March, 1986. The following October Susan began full-time employment at Oak Ridge National Laboratory. The next year she began her graduate studies with the University of Tennessee. Susan is now employed by Oak Ridge National Laboratory on a part-time basis and is a mother of two small children.