DEVELOPMENT OF GENERALIZED EQUILIBRIUM AND RATE MODELS TO PREDICT ION EXCHANGE COLUMN PERFORMANCE

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PREFACE

Generalized models to predict ion exchange column performance are developed in this work. An equilibrium model is developed to predict the initial leakages from an ion exchange column. The equilibrium model can handle both the hydrogen and the amine cycle. The effect of various factors on the initial leakages from a column are studied using this model. A generalized rate model is developed which can predict column effluent for a multicomponent system of ions with arbitrary valences. This model can also handle partially dissociative species like monovalent amines and carbonates.

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TABLE OF CONTENTS

Chapter Page

APPENDIXES

LIST OF TABLES

Table Page

LIST OF FIGURES

NOMENCLATURE

A_i	parameter of ion i
a_s	interfacial area (L^2/L^3)
B_i	parameter of ion i
C_i	concentration of species i (meq/L^3)
C_i^*	concentration of species i at the surface of the resin (meq/L^3)
C_i^*	concentration of species i in the bulk solution (meq/L^3)
C_T	total equivalent concentration (meq/L^3)
C_{Ta}	total amine concentration (meq/L^3)
C_{Tc}	total carbonic species concentration (meq/L^3)
d_p	particle diameter (L)
D_i	self-diffusivity of species i (L^2/T)
D_e	effective diffusivity (L^2/T)
F	Faraday's constant (coulombs/mole)
FAR	fraction of anionic resin
FCR	fraction of cationic resin
J_i	flux of species i in the film $(meq/T.L^2)$
k	reaction rate constant (T^{-1})
K	representative mass transfer coefficient (L/T)
K_A^B	resin selectivity coefficient for ion B in solution compared to A in the resin
K_a	dissociation constant of amine

K_W	water dissociation equilibrium constant
K_1	first dissociation constant of CO_2
K_2	second dissociation constant of CO_2
m	number of coions
N_i	relative valence of ion i
n	number of counterions
P	exponent
q_i	concentration of species i in the resin (meq/L^3)
Q	capacity of the resin (meq/L^3)
r	radius of the film (L^{-1})
R_e	particle Reynolds number
Sc	Schmidt number
T	temperature (°C)
t	time (T)
u_s	superficial velocity in axial flow packed bed (L/T)
V	volume of the packed resin (L^3)
X_i	concentration fraction in liquid phase
Y_i	concentration fraction in the resin phase
Z_i	charge on species i
Z_j	charge on species j
Z_Y	mean coion valence

Greek Letters

δ	film thickness (L)
ε	bed void fraction
τ	dimensionless time coordinate
ξ	dimensionless space coordinate
ϕ	electric potential (ergs/coulomb)

μ	solution viscosity (cp)
ω	+1 for cations; -1 for anions
ρ	solution density (M/L^3)

Superscripts

bar	refers to resin phase
*	interfacial equilibrium condition
f	column feed condition
o	bulk phase condition

Subscripts

c	reference ion
i	counterion species
j	coion species
p	resin particle
T	total concentration

CHAPTER I

INTRODUCTION

Ion exchange is a process in which the ions in a solution can be selectively replaced by other ionic species. An ion exchange reaction may be defined as a reversible and stoichiometric exchange of ions between a solution and a solid phase. The solid phase which is insoluble and contains charged species that are permanently attached to a polymeric support is called an ion-exchanger.

The fixed attached groups in the ion-exchanger attract oppositely charged exchangeable ions to achieve electroneutrality. These ions can be exchanged for a stoichiometrically equivalent amount of other ions. If the exchangeable ion is a cation then the ion-exchanger is a cationic exchanger (or resin) and if the exchangeable ion is an anion then the exchanger is called an anionic exchanger (or resin). The total number of exchangeable ions per specified amount of an ion exchanger is defined as its capacity, usually expressed in milliequivalents per gram or milliliter (meq/g or meq/ml) of the exchanger.

The most important features characterizing an ideal exchanger are (Grimshaw and Harland, 1975):

(i) A hydrophilic structure of regular and reproduceable form.

(ii) Controlled and effective ion-exchange capacity.

(iii) Rapid rate of exchange.

(iv) Chemical stability.

(v) Physical stability in terms of mechanical strength and resistance to attrition.

(vi) Thermal stability.

(vii) Consistent particle size and effective surface area compatible with hydraulic design requirements for larger scale plant.

Ion exchange has a wide variety of applications in the fields of water purification, recovery of precious metals, production of pharmaceuticals, and medicine. Water treatment is the largest and most common industrial application of ion-exchange due to the increased demand for ultra-pure water. Water with ionic impurity levels less than one part per billion (ppb) and correspondingly low levels of particulate and microbial contaminants is referred to as 'ultra-pure water' (Sadler, 1993). A comparison of the impurity levels between typical city water and ultra-pure water used in the semiconductor industry is reported by Bulusu (1994). Large amounts of ultra-pure water is essential in many industries producing electronic components, medicinal agents and electrical power. This increased demand for ultra-pure water is leading to new innovations in ion exchangers and ion-exchange process techniques.

The power industry uses ultra-pure water to prevent corrosion in the boilers and scaling on other critical components. Another industry which requires large quantities of ultra-pure water is the semi-conductor industry. The water quality requirements of the semi-conductor industry is increasing steadily with the demand for more efficient electronic components. During the production of silicon chips, large quantities of water is used to clean the chemical residues from the surface of the wafers. The water used during this process should be pure enough to avoid the deposition of any contaminants on the surfaces being cleaned. A comparison of the water quality requirements for silicon chips of different densities is reported by Sadler (1993). Manufacturing a higher density silicon chip without increasing its size requires higher water purity levels. Ion exchange columns are commonly used to produce such high purity water.

Monobed ion exchange columns consist of either cationic or anionic resin. Cationic ion exchange columns remove only cationic impurities in the feed stream resulting in a highly acidic product stream. Anionic ion exchange columns remove only anionic impurities producing a highly basic product stream. Mixed bed ion exchange can be used to remove both cationic and anionic impurities in the same column to produce a near neutral product stream.

Mixed Bed Ion Exchange

A mixed bed ion exchange (MBIE) column consist of a mixture of anionic and cationic resin. An MBIE column can be operated in different cycles. In the hydrogen cycle (HOH cycle), the cationic resin is in the hydrogen form and the anionic resin is in the hydroxyl form at the start of operation. After exchange, the excess hydrogen and hydroxide are consumed by the water equilibrium reaction. Hydrogen cycle produces the purest form of water. Another common cycle of operation is the amine cycle. This cycle is operated either by adding amines to the feed water or using the cationic resin which is in the amine form. The amine cycle is preferred when corrosion is a problem, since it produces alkaline water.

Mixed Bed Ion Exchange Modeling

Haub and Foutch (1986 a, b) modeled mixed bed ion-exchange systems at ultra-low concentrations. Their model involved water equilibrium rather than assuming an irreversible reaction. They incorporated separate material balance considerations for the cationic and anionic resin. They considered a binary system with two monovalent ions. Divekar and Foutch (1987) extended this model to incorporate temperature effects. Zecchini (1990) extended the above models to handle a ternary system of monovalent ions. Pondugula (1995) extended this model to handle divalent ions. Bulusu (1994) developed an MBIE column model to handle multicomponent system of ions.

Objective

This research addresses specific problems related to mixed bed ion-exchange modeling. An equilibrium model to predict initial leakage from an ion-exchange column and a rate model to predict ion-exchange breakthrough are developed. The format followed in this thesis is to present the development of each model in a separate chapter. Detailed developments will be presented in the appropriate appendix.

Chapter 3 focuses on the development of a model to predict initial leakages in an ion exchange column. The effects of kinetic leakage have also been incorporated into the model. This model can handle multicomponent system of ions with arbitrary valences. The model can handle both the hydrogen and amine cycles. Initial leakage in a mixed-bed or a mono-bed ion exchange column can be predicted using this model. The model allows the user to know if resin fouling impacts the bed performance. The regeneration efficiency of an ion exchange bed can also be predicted using this model.

The development of a generalized rate model to predict the performance of a mixed bed ion exchange column is presented in Chapter 4. This model predicts the effluent concentration profiles of the impurities from an ion exchange column. This is a general model which can handle an arbitrary number of completely dissociative ions. Among the partially dissociative species, only monovalent amines and carbonates can be handled by the model. Effluent breakthrough curves for real plant conditions are predicted using this model. The effect of resin fouling on column performance is also studied.

CHAPTER II

LITERATURE REVIEW

An extensive literature review on ion exchange and ion exchange modeling has been done by Haub (1984), Yoon (1990), Zecchini (1990) and Bulusu (1994). This review focuses on the literature related to the objectives of this thesis.

Introduction

Most ion exchange operations are performed in columns. Unfortunately there is no universal theory to evaluate the ion exchange column performance because of the complexity of column kinetics (Helfferich, 1962). The theories that are commonly used to evaluate ion exchange column performance are equilibrium and rate theories. Equilibrium models assume a local equilibrium between the resin particles and the surrounding fluid. Equilibrium models are widely used in the study of mixed bed ion exchange. Equilibrium is also used to design ion exchange processes (Tondeur and Bailly, 1986). Most ion exchange processes are defined using rate theories because local equilibrium is not usually attained (Helfferich, 1962). Rate models are based on kinetic or rate laws. Different equilibrium isotherms and kinetic law expressions lead to different rate models. Depending on the situation one of these two theories can be used to model ion exchange columns.

Equilibrium Models

When an ion exchange resin is placed in an electrolyte solution, equilibrium will be attained between the two phases after a certain time. At equilibrium, all the counterions are present in both the liquid and resin phases. However, the concentration ratio of the ions between the two phases will be different. The equilibrium distribution of the ions between the solution and the resin phases can be explained by means of ion exchange isotherms, distribution coefficients or selectivity coefficients (Helfferich, 1962). Equilibrium in ion exchange modeling is usually described by means of a selectivity coefficient. For an ion exchange reaction

$$Z_A C_B + Z_B \bar{C}_A \Leftrightarrow Z_A \bar{C}_B + Z_B C_A \qquad (2\text{-}1)$$

where Z_A , Z_B are ionic valences, C's represent the concentrations and the bar indicates the resin phase, the expression for the selectivity coefficient is

$$K_A^B = \left(\frac{\bar{C}_B}{C_B}\right)^{Z_A} \left(\frac{C_A}{\bar{C}_A}\right)^{Z_B} \qquad (2\text{-}2)$$

The selectivity coefficient depends on the nature of counterions, the nature of fixed charges in the resin matrix, resin loading, solution concentration, temperature and pressure.

But the selectivity coefficient may be assumed to be constant in certain cases for engineering purposes (Pieroni and Dranoff, 1963). An ion exchanger prefers counterions that have higher valence, smaller equivalent volume, greater polarity and stronger association with fixed groups in the matrix (Helfferich, 1962).

Dranoff and Lapidus (1957) first introduced equilibrium theory to analyze ternary ion exchange systems. They assumed that the influence of the third ion was negligible and expressed the equilibrium relationships for three binary pairs. Klein et al. (1967) developed an equilibrium theory for multicomponent ion exchange in fixed beds. They assumed equilibrium operation, uniform presaturation and constant feed compositions in their analysis. Their model predicted the number of composition changes between zones of constant composition. Helfferich (1967) presented a general analytical solution for multicomponent ion exchange in fixed beds using local equilibrium. The model required uniform presaturation and constant separation factors to obtain a solution.

Tondeur (1970) showed that multicomponent heterovalent systems governed by mass action equilibria are not always ordered. The order of affinities of various components for the resin may depend on composition, even with constant equilibrium constants. Kataoka and Yoshida (1980) proposed a model that considered non idealities in the liquid phase. They corrected the selectivity coefficients by using the activity coefficients of different species in the liquid phase. Klein et al. (1984) developed a model to handle variable initial and feed compositions in multicomponent fixed bed sorption systems. Helfferich (1984) proposed a model to illustrate the concept of concentration waves and their interferences in multicomponent ion exchange systems.

Lopez et al. (1992) studied the binary exchange of anions on Amberlite IRA-400 and Amberlite IRA-410. They obtained the equilibrium data using batch methods and fitted that data to ion exchange isotherm equations. They found that the Langmuir isotherm was most suitable for both correlation of equilibrium data and prediction and interpretation of breakthrough curves. Garcia et al. (1992) made a theoretical analysis of multicomponent ion exchange in fixed beds. Wolf Gang et al. (1993) applied the surface complex formation model to exchange equilibria on ion exchange resins. Binary equilibria are described by a logarithmic equilibrium parameter and multicomponent equilibria are considered as a superposition of several binary equilibria.

Clifford and Majano (1993) developed a computer program to predict ion exchange column performance based on equilibrium multicomponent chromatography theory (EMCT) with constant separation factors. Their model assumes instantaneous equilibrium, homogeneous resin presaturation and constant feed composition. Jansen et al. (1996b) developed a thermodynamics based equilibrium model to describe ion exchange equilibria of strong and weak electrolytes. Their model is applicable to binary and multicomponent systems, using selectivity coefficients for all ion pairs and distribution coefficients for all neutral species as parameters. Jansen et al. (1996a) also studied the effect of pH and concentration on column dynamics of weak electrolyte ion exchange.

Rate Models

The kinetic or rate models are based on different rate controlling steps such as particle diffusion control or film diffusion control. Helfferich (1962) gave the criteria to identify whether the rate determining step is film diffusion or particle diffusion. Apart from these, the chemical reactions, neutralization and dissociation occurring during the ion exchange process also influence the ion exchange rate. The effects of chemical reactions are not considered in the early ion exchange kinetic theories.

The linear driving force approximation and the Nernst-Planck model are useful in developing rate models. Thomas (1944) developed the most general model using rate theory to evaluate the column performance under non-equilibrium conditions. He assumed reversible second order reaction kinetics as an approximation to the actual diffusion process which was difficult to solve. Gluekauf (1947) first suggested the linear driving force approximation used in the ion exchange model developments later. In this method the rate of ion exchange of an ion into the resin is written as the product of the surface area of the resin, an effective mass transfer coefficient, and a driving force. The driving force is usually the difference between the bulk average concentration in the resin and the concentration on the surface of the resin. The linear driving force approximations are easy to handle and obtain a solution but they do not take the effect of electric potential of the ions during the exchange process into consideration. These effects are included in the Nernst-Planck model developed later.

Schlogl and Helfferich (1957) were the first to apply Nernst-Planck equations to film diffusion controlled ion exchange. They compared ionic fluxes with and without considering the electric field in their work. However, their work was limited to binary systems with monovalent ions. Omatete et al. (1980a,b) developed a model for multicomponent film diffusion controlled ion exchange. They compared the Nernst-Planck model and Fick's law to describe the ion exchange process. They also evaluated the column performance for ternary exchange experimentally (1980b).

Kataoka et al. (1987) derived ionic flux expressions for a ternary system of ions with equal and arbitrary valences using Nernst-Planck equations. Their solutions were exact for equal valence cases and approximate for the cases of arbitrary valences. However, their solutions could not be extended to the general multicomponent case. Franzreb et al. (1993) developed a more general solution for a multicomponent case. Most of the earlier models combine the Nernst-Planck equations with the condition of no net current flow and integrate the resulting equations to obtain flux expressions. Unlike the earlier models, they differentiated the resulting equations to obtain a homogeneous second order differential equation. Bulusu and Foutch (1994) developed a column model to predict mixed bed ion exchange breakthrough using the flux expression developed by Franzreb et al. (1993).

In this thesis, the model developed by Bulusu and Foutch has been generalized and extended to a multicomponent case. Also, unlike the previous models, the ions continue to exchange with the resin until the resin is completely saturated with the most selective ion in the feed. In other words, the exchange process is continued until the cationic resin is saturated with the most selective cation and anionic resin is saturated with the most selective anion in the feed. The model is capable of handling any number of completely dissociative species. Among weak electrolytes only monovalent amines and carbonates are handled.

CHAPTER III

DEVELOPMENT OF A COLUMN MODEL TO PREDICT INITIAL LEAKAGES IN MULTICOMPONENT SYSTEMS

Abstract

A model for predicting initial leakages from an ion exchange column is developed. The model can handle both hydrogen cycle (neutral pH) and amine cycle (equal influent and effluent amine concentrations). The model can handle an arbitrary number of species with arbitrary valences. Initial leakages in both mixed-bed and mono-bed ion exchange columns can be predicted using this model. This model can also be used to determine the regeneration efficiency of an ion exchange column.

Introduction

An ion exchange column can be visualized in terms of zones that move through the bed (Chowdiah, 1996). The ion concentrations change as the zones move through the bed from which breakthrough curves can be generated. The different zones in an ion-exchange column are shown in Figure 1.

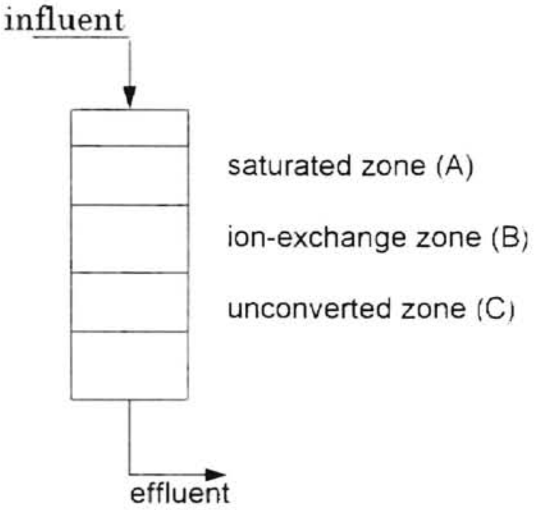

Figure 1. Schematic of a Fixed Bed with Different Exchange Zones

The zone near the inlet is the saturated zone. In this zone, the resin is fully loaded with the ionic impurities. The feed solution attains equilibrium with the resin and no further exchange takes place for the same feed conditions. If the feed conditions are changed the resin loading will either increase or decrease depending on the new equilibrium.

The second zone is the ion-exchange zone. Most of the exchange from the liquid phase to the resin phase takes place in this zone. The bottom zone is the unconverted zone. The feed concentrations reduce to very low levels by the time the feed reaches this zone. If the resin phase concentrations in this zone are greater than the feed concentrations, ions leach out of the resin into the bulk phase to attain equilibrium. The ion concentrations leaving the column under these conditions are referred to as equilibrium leakage.

In some situations there will be no unconverted zone and the ion-exchange zone extends to the bottom of the bed. The ionic concentrations leaving the bed under these conditions are referred to as kinetic leakage. This situation may arise due to:

1. Poor mass transfer characteristics of the resin.
2. High flow rate.

Sadler (1993) described various mechanisms responsible for the leakage of ionic impurities from ion exchange columns. They are:

- Equilibrium Leakage: Leakage due to the release of impurities from the resin to achieve an equilibrium between the resin and bulk phase concentrations.
- Kinetic Leakage: Leakage due to incomplete ion exchange of influent impurities so that a portion of them pass through the bed.
- Residual Regenerant Leakage: Leakage from the resin due to the slow release of traces of chemicals used during regeneration.
- Organic Impurity Leakage: Leakage arising from the low level release of organic impurities from the resins themselves.

Most of these leakages can be controlled or minimized by improving the resin regeneration and/or management techniques. Sadler (1993) discussed various methods to minimize the leakages.

In this thesis the focus is mainly on developing a model to predict equilibrium and kinetic leakages. The model is developed to handle both the hydrogen and amine cycles. In hydrogen cycle the ion exchange column is operated with the cationic resin in hydrogen form. In the amine cycle the cationic resin is in the amine form.

TABLE I

Model Assumptions

---

1. Uniform resin phase concentrations.
2. Uniform initial loading throughout the bed.
3. Neutral feed with constant feed concentrations.
4. Selectivity coefficients are temperature and concentration independent.
5. Binary selectivity coefficients can be used for multicomponent ion exchange.
6. Activity coefficients are constant and unity.
7. Bulk phase neutralization.
8. No coion flux across the particle surface.
9. No net current flow.
10. Isothermal and isobaric operation.
11. Plug flow.
12. Uniform resin bead diameters.
13. Fick's law can be used to calculate the fluxes during the initial phase of ion exchange column operation.

Model Development

Ion exchange equilibrium can be described in terms of separation factor, selectivity coefficient, or distribution coefficient (Helfferich, 1962). In this thesis selectivity coefficient is used to describe the equilibrium.

Equilibrium

For the ion exchange reaction

$$Z_A C_B + Z_B \bar{C}_A \Leftrightarrow Z_A \bar{C}_B + Z_B C_A \tag{3-1}$$

where,

C_A - Bulk phase concentration of ion A

C_B - Bulk phase concentration of ion B

$\bar{C}_A$ - Resin phase concentration of ion A

$\bar{C}_B$ - Resin phase concentration of ion B

Z_A - Valence of ion A

Z_B - Valence of ion B

the selectivity expression is

$$K_A^B = \left(\frac{\bar{C}_B}{C_B^*}\right)^{Z_A} \left(\frac{C_A^*}{\bar{C}_A}\right)^{Z_B} \tag{3-2}$$

where C^* represents the interfacial concentration and the bar represents the resin phase. Since interfacial concentrations are equal to the bulk phase concentrations at equilibrium, we can write the above equation in terms of bulk concentrations as

$$K_A^B = \left(\frac{\bar{C}_B}{C_B}\right)^{Z_A} \left(\frac{C_A}{\bar{C}_A}\right)^{Z_B} \tag{3-3}$$

The above equation can be rearranged to express the concentration of ion B in the bulk phase as,

$$C_B = \bar{C}_B \cdot \left(\frac{C_A}{\bar{C}_A}\right)^{Z_B/Z_A} \cdot \left(\frac{1}{K_A^B}\right)^{1/Z_A} \tag{3-4}$$

So, the concentration of any ion ' i ' in the bulk phase exchanging for the ion 'A' in the resin phase can be expressed as

$$C_i = \bar{C}_i \cdot \left(\frac{C_A}{\bar{C}_A}\right)^{Z_i/Z_A} \cdot \frac{1}{{K_A^i}^{1/Z_A}} \tag{3-5}$$

Charge Balance

The Charge Balance Equation is:

$$\sum Z_i C_i + \sum Z_j C_j = 0 \tag{3-6}$$

where subscript ' i ' denotes cations and ' j ' denotes the anions.

Initially, the anionic resin is in the hydroxyl form and anions in the bulk phase exchange with the hydroxyl ions in the resin phase. The selectivities of anions are usually expressed with respect to hydroxyl ion. So the bulk phase concentration of any anion can be expressed in terms of the hydroxyl ion concentration in the bulk phase using Equation (3-5) as

$$C_j = \bar{C}_j \cdot \left(\frac{C_{OH^-}}{\bar{C}_{OH^-}} \right)^{z_j / z_{OH^-}} \cdot \frac{1}{K_{OH^-}^{j} {}^{1/z_{OH^-}}} \tag{3-7}$$

Since all other variables on the right hand side of the above equation are known except the hydroxyl ion concentration in the bulk phase, concentrations of all anions can be expressed as a function of hydroxyl ion concentration as

$$C_j = f\big([\mathrm{OH}^-] \tag{3-8}$$

The cationic resin is in the hydrogen form in hydrogen cycle and in the amine form in amine cycle. We use the selectivities of cations with respect to the hydrogen ion in the hydrogen cycle and with respect to the amine ion in the amine cycle. So, depending on the cycle of operation we can express the bulk-phase cation concentrations in terms of either hydrogen ion concentration or the amine ion concentration. For the hydrogen cycle we have,

$$C_i = \bar{C}_i \cdot \left(\frac{C_{H^+}}{\bar{C}_{H^+}} \right)^{z_i / z_{H^+}} \cdot \frac{1}{K_{H^+}^{i} {}^{1/z_{H^+}}} \tag{3-9}$$

$$(\text{ or }) \quad C_i = f([H^+]) \tag{3-10}$$

similarly, for the amine cycle we can express the concentration as

$$C_i = f([\mathrm{Amine}^+]) \tag{3-11}$$

Hence, the charge balance equation can be expressed as a function of just two variables.

$$f([H^+]) + f([OH^-]) = 0 \qquad \text{(Hydrogen cycle)} \qquad (3\text{-}12)$$

$$(\text{ or }) \quad f([\text{Amine}^+]) + f([OH^-]) = 0 \qquad \text{(Amine cycle)} \qquad (3\text{-}13)$$

In order to solve Equations (3-12) and (3-13), we must simplify them to have only one unknown variable (i.e., only $[H^+]$ or $[\text{Amine}^+]$ or $[OH^-]$).

We accomplish this by making use of the following :

(i) For Hydrogen cycle, the dissociation constant of water Kw can be used to relate $[H^+]$ and $[OH^-]$ as below.

$$K_W = [H^+][OH^-] \qquad (3\text{-}14)$$

$$\text{or} \qquad [OH^-] = \frac{K_W}{[H^+]} \qquad (3\text{-}15)$$

Using this relation the number of variables in Equation (3-12) can be reduced to one (i.e, either $[H^+]$ or $[OH^-]$). In this thesis $[OH^-]$ has been replaced with $[H^+]$ to reduce the whole equation in terms of $[H^+]$.

(ii) For Amine cycle, the relationship between $[\text{Amine}^+]$ and $[OH^-]$ is derived from the amine equilibrium in water. The equilibrium reaction between amine and water is

$$\text{Amine} + H_2O \Leftrightarrow \text{Amine}^+ + OH^- \qquad (3\text{-}16)$$

The dissociation constant for the above reaction can be written as:

$$K_a = \frac{[Amine^+][OH^-]}{[Amine]} \tag{3-17}$$

But the total concentration of amine should be

$$C_{Ta} = [Amine] + [Amine^+] \tag{3-18}$$

From Equations (3-17) and (3-18) we can derive the relationship between $[Amine^+]$ and $[OH^-]$ as

$$[Amine^+] = \frac{Ka.C_{Ta}}{Ka + [OH^-]} \tag{3-19}$$

This relation can be used to eliminate $[Amine^+]$ from the charge balance Equation (3-13) to write it in terms of only $[OH^-]$.

TABLE II

Solution Strategy to Calculate Equilibrium Concentrations in the Hydrogen Cycle

1. Substitute Equation (3-15) in Equation (3-12) to express the charge balance as a function of $[H^+]$.
2. Solve the charge balance equation using Newton-Raphson method for the hydrogen ion concentration.
3. Calculate the hydroxyl ion concentration from Equation (3-15).
4. Calculate the bulk phase concentrations of the remaining anions using Equation (3-7).
5. Calculate the bulk phase concentrations of the remaining cations using Equation (3-9).

TABLE III

Solution Strategy to Calculate Equilibrium Concentrations in the Amine Cycle

---

1. Substitute Equation (3-19) in Equation (3-13) to express the charge balance as a function of [OH^-].
2. Solve the charge balance equation using Newton-Raphson method for the hydroxyl ion concentration.
3. Calculate the amine ion concentration from Equation (3-19).
4. Calculate the bulk phase concentrations of the remaining anions using Equation (3-7).
5. Calculate the bulk phase concentrations of the remaining cations using Equation (3-11).

Column Material Balances

The final form of the dimensionless column material balance equations derived in Appendix D are

$$\frac{\partial x_i}{\partial \xi_c} + (FCR)\frac{\partial y_i}{\partial \tau_c} = 0 \qquad \text{(for cations)} \qquad (3\text{-}20)$$

$$\frac{\partial x_i}{\partial \xi_c} + (FAR)\frac{\partial y_i}{\partial \tau_c} = 0 \qquad \text{(for anions)} \qquad (3\text{-}21)$$

where,

x_i - Concentration fraction of ion 'i' in the bulk phase

y_i - Concentration fraction of ion 'i' in the resin phase

ξ_c - Dimensionless space coordinate

τ_c - Dimensionless time coordinate

FCR - Fraction of cationic resin

FAR - Fraction of anionic resin

Substituting $x_i = \frac{C_i}{C_T^f}$, $y_i = \frac{q_i}{Q_c}$ and $y_i = \frac{q_i}{Q_a}$

where,

C_i - Concentration of ion 'i' in the bulk phase

C_T^f - Total feed concentration

q_i - Concentration of ion 'i' in the resin phase

Q_c - Cationic resin capacity

Q_a - Anionic resin capacity

we have

$$\frac{\partial C_i}{\partial \xi_c} + (\mathrm{FCR})\frac{C_T^f}{Q_c}\frac{\partial q_i}{\partial \tau_c} = 0 \qquad \text{(for cations)} \qquad (3\text{-}22)$$

$$\frac{\partial C_i}{\partial \xi_c} + (\mathrm{FAR})\frac{C_T^f}{Q_a}\frac{\partial q_i}{\partial \tau_c} = 0 \qquad \text{(for anions)} \qquad (3\text{-}23)$$

Rate Equations

The rate equations derived in Appendix D are

$$\frac{\partial y_i}{\partial \tau_c} = \frac{-6J_i}{K_i C_T^f}\frac{K_i}{K_c}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c} \qquad \text{(for cations)} \qquad (3\text{-}24)$$

$$\frac{\partial y_i}{\partial \tau_c} = \frac{-6J_i}{K_i C_T^f} \frac{K_i}{K_c} \qquad \text{(for anions)} \qquad (3\text{-}25)$$

where K_i is the mass transfer coefficient of ion 'i' and K_C is the mass tranfer coefficient of the reference ion.

Substituting $y_i = \frac{q_i}{Q_c}$ for cations and $y_i = \frac{q_i}{Q_a}$ for anions we have

$$\frac{\partial q_i}{\partial \tau_c} = \frac{-6J_i}{K_i C_T^f} \frac{K_i}{K_c} \frac{d_{pa}}{d_{pc}} Q_a \qquad \text{(for cations)} \qquad (3\text{-}26)$$

$$\frac{\partial q_i}{\partial \tau_c} = \frac{-6J_i}{K_i C_T^f} \frac{K_i}{K_c} Q_a \qquad \text{(for anions)} \qquad (3\text{-}27)$$

where d_{pa} and d_{pc} are the anionic and cationic resin bead diameters respectively.

Substituting these rate equations in the material balance equations we have

$$\frac{\partial C_i}{\partial \xi_c} = \frac{6(FCR)}{K_c} \frac{d_{pa}}{d_{pa}} \frac{Q_a}{Q_c} J_i \qquad \text{(for cations)} \qquad (3\text{-}28)$$

$$\frac{\partial C_i}{\partial \xi_c} = \frac{6(FAR)}{K_c} J_i \qquad \text{(for anions)} \qquad (3\text{-}29)$$

The flux expression based on Fick's law is

$$J_i = K_i (C_i^{eq} - C_i^{bulk}) \qquad (3\text{-}30)$$

where K_i is the mass transfer coefficient of ion 'i' and the driving force is the difference between the equilibrium and actual bulk phase concentrations.

TABLE IV

Solution Strategy to Calculate Equilibrium Leakages

1. Read the input data (Resin parameters, Bed parameters, Feed Conditions of the ions, Initial resin loadings, Ion property data).
2. Calculate the theoretical mass transfer coefficients using Carberry and Kataoka's correlations.
3. Calculate the dimensionless column height and the number of slices down the column. The solution of the problem requires the column to be divided into slices.
4. Calculate the equilibrium concentrations using the solution strategies given in Table II or Table III depending on the cycle of operation.
5. Initialize the bulk concentration in the first slice to the feed concentrations.
6. Calculate the fluxes using Equation (3-30).
7. Calculate the bulk concentrations entering the next slice from Equations (3-28) and (3-29) using Euler's method.
8. Calculate the hydroxyl and hydrogen/amine concentrations entering the next slice from the charge balance.
9. If the last slice is not reached, go to step 6.

The features and limitations of the computer code which implements the above strategy to calculate the initial leakages are discussed below.

Program Features

The program can handle an arbitrary number of completely dissociative species with arbitrary valences. Both the hydrogen and amine cycles can be handled by the code. The theoretical mass transfer coefficients are calculated from the correlations and notified to the user. The user can also see the results based on the experimental mass transfer coefficients to know if resin fouling impacts the bed performance. The code can be used to predict leakages in mono-bed ion exchange columns also. For cation beds FCR (volume fraction of cationic resin) is set very close to 1.0 (i.e, about 0.999). For anion beds FAR (volume fraction of anionic resin) is set close to 1.0. The program can also be used to predict the regeneration efficiency of an ion exchange by varying the initial loading fractions in the resin to match the predicted leakages with the observed leakages.

Program Limitations

The program cannot handle any partially dissociative species in the hydrogen cycle. In amine cycle, no other dissociative species can be handled except a monovalent amine. This is because, different partially dissociative species have different equilibrium chemistry and it is difficult to develop a general code to handle all the dissociative species. Effluent predictions with time are not addressed in this model. No ionic generation terms from the resin are included. Selectivity and diffusivity data are required in the input data.

Results and Discussion

The model was used to predict the initial leakages from a mixed bed ion exchange column. The effect of various factors on the initial leakages has been studied. These factors include cation to anion resin ratio, flow rate, temperature, initial resin loading, resin fouling, column length, column diameter, and void fraction. A base case was defined with respect to which all the comparisons were made. The input parameters for the base case are given in Table V.

TABLE V

Input Data for the Base Case

Property	Value
Bed diameter (cms)	335.28
Resin depth (cms)	100.0
Cation-to-anion exchange resin (volumetric ratio)	1:1
Resin bead diameter (cm)	
Cation (Dowex Monosphere 650C)	0.06
Anion (Dowex Monosphere 550A)	0.055
Resin capacity (meq/ml)	
Cation	1.9
Anion	1.1
Temperature (°C)	65.55
Influent concentration (meq/ml)	
sodium	8.80E-08
calcium	1.12E-07
chloride	8.80E-08
sulfate	1.12E-07
Initial loading on the resin (%)	
sodium	1%
calcium	1%
chloride	1%
sulfate	1%
Bed void fraction	0.35
Influent flow rate	3.05E+5 cm^3/s (50.95 gpm/ft^2)

Effect of Initial Resin Loading

The initial leakages have been predicted for three different percentage loadings of the ions on the resin. The loadings of all the ions are assumed to be equal although not required by the program. All other parameters are maintained at the base case. The results are presented in Table VI.

TABLE VI

Effect of Initial Loadings on Initial Leakages

%Loading	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
0.1	0.4155E-02	0.5652E-09	0.8609E-03	0.6160E-10
1.0	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09
10.0	0.5021E+00	0.2965E-07	0.1109E+00	0.1022E-07

The initial leakage of sodium was one order of magnitude less when the percentage loading was reduced from 1% to 0.1%. On the other hand, there was a one order increase in magnitude of leakage when the loading was increased from 1% to 10%. Calcium also showed a similar trend. There was an order of magnitude increase in the initial leakage for an order of magnitude increase in the initial loading. The percentage initial loading had a similar effect on chloride and sulfate also. The above results show that the initial loading of the ions on the resin has a significant effect on the initial leakage.

Higher initial loading implies a higher concentration of the ion in the resin. If the observed leakage is kinetic then higher concentrations in the resin lead to a lower flux into the resin in the exchange zone resulting in even higher kinetic leakages. If the leakage is equilibrium leakage then higher concentrations in the resin lead to a higher flux out of the resin in the unconverted zone resulting in higher equilibrium leakages. So higher initial loadings always results in higher equilibrium and kinetic leakages.

Effect of Resin Fouling

The effect of resin fouling on the initial leakages has been studied by predicting the leakages for different degrees of resin fouling. Initial leakages were predicted for 20%, 40% and 60% resin fouling and compared against the base case (no fouling). The results are shown below.

TABLE VII

Effect of Resin Fouling on Initial Leakages

%Fouling	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
0	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09
20	0.4221E-01	0.3515E-07	0.8789E-02	0.6420E-09
40	0.4221E-01	0.3003E-05	0.8789E-02	0.6980E-09
60	0.4221E-01	0.2721E-03	0.8790E-02	0.2571E-06

There was no significant effect of resin fouling on sodium leakage. This is because the ion-exchange zone for sodium did not extend to the end of the bed in spite of the resin fouling. The ion exchange zone for sodium reached to about 95% of the column length at 60% fouling. Resin fouling showed a significant effect on calcium leakage. The leakage increased by an order of magnitude for 20% fouling. There was an increase of three orders of magnitude for 40% fouling and an increase of five orders of magnitude for 60% resin fouling. Like sodium, there was no significant effect of resin fouling on chloride. Sulfate leakages were not affected at 20% fouling. There was an 8.7% increase in the sulfate leakage at 40% fouling and an increase of three orders of magnitude at 60% resin fouling. An increase in resin fouling results in poor mass transfer characteristics which lead to higher initial leakages.

Effect of Flow Rate

Three different flow rates are selected to study the effect of flow rate on initial leakages. Flow rates of 40 gpm/ft^2, 50 gpm/ft^2 and 60 gpm/ft^2 are used. All other parameters were kept constant. The results are presented in Table VIII.

TABLE VIII

Effect of Flow Rate on Initial Leakages

Flow rate (gpm/ft^2)	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
40	0.4221E-01	0.2089E-08	0.8789E-02	0.6420E-09
50	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09
60	0.4221E-01	0.4194E-08	0.8789E-02	0.6420E-09

There was no change in the initial leakage of sodium with flow rate. This suggests that the observed leakages are equilibrium leakages. Higher flow rates could not extend the exchange zone for sodium to the end of the bed. There was a 16% increase in calcium leakage at 50 gpm/ft^2 compared to the leakage at 40 gpm/ft^2. At 60 gpm/ft^2 a 98%

increase in calcium leakage was predicted. The leakage observed for calcium at 40 gpm/ft^2 was kinetic leakage. Further increase in flow rate resulted in lesser contact time of feed water with the resin giving even higher kinetic leakages. Like sodium, leakages of chloride and sulfate also did not change with flow rate.

Effect of Resin Ratio

Initial leakages were predicted for three different cation to anion resin volume ratios.

Case1: 30% cationic resin, 70% anionic resin

Case2: 50% cationic resin, 50% anionic resin(base case)

Case3: 70% cationic resin, 30% anionic resin

The results are shown in Table IX.

TABLE IX

Effect of Resin Ratio on Initial Leakages

FCR/FAR	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
0.3/0.7	0.4221E-01	0.3097E-05	0.8789E-02	0.6420E-09
0.5/0.5	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09
0.7/0.3	0.4221E-01	0.2070E-08	0.8789E-02	0.7044E-09

Equilibrium leakages of sodium were not affected by the change in the resin ratios. There was a significant effect of resin ratios on calcium leakages. When the column had only 30% cationic resin the calcium leakage increased by three orders of magnitude. The increase in calcium leakage is because of the kinetic leakage due to low cationic resin fraction. For the case of 70% cationic resin there was a 15% decrease in the initial leakage of calcium. This decrease is because higher volumetric fraction of cationic resin results in more calcium exchanging into the resin. As in the case of sodium, the resin ratios did not have any affect on initial leakage of chloride. Increasing the anionic resin fraction to 70% did not have any effect on the initial leakage of sulfate. This suggests that the leakage observed at 50% anionic resin fraction is equilibrium leakage and further increase in the anionic resin fraction would not have any effect on sulfate leakages. However, decreasing the anionic resin fraction to 30% increased the initial leakage of sulfate by 10%. Higher FCR results in lower cation leakages and higher FAR results in lower anion leakages.

Effect of Temperature

The temperature sensitive parameters in the model are viscosity, diffusivities, selectivities and dissociation constants. The viscosity of water decreases with an increase in temperature. The diffusivity of ions increase with temperature due to an increase in their mobility. Selectivities and dissociation constants also usually increase with temperature.

Three different temperatures were considered to evaluate the effect of temperature on initial leakages. The temperatures selected are 30°C, 50°C and 65°C. Diffusivities of the ions under consideration are calculated at these temperatures using the correlations reported by Bulusu (1994). They are tabulated in Table X. Initial leakages from the column are calculated using the above temperatures and diffusivities. All other parameters are maintained at the base case. The results are tabulated in Table XI.

TABLE X

Diffusivities at Different Temperatures

Temperature (°C)	Sodium	Calcium	Chloride	Sulfate
30	1.568E-05	0.955E-05	2.285E-05	1.328E-05
50	2.439E-05	1.472E-05	3.392E-05	2.016E-05
65	3.238E-05	1.913E-05	4.391E-05	2.602E-05

TABLE XI

Effect of Temperature on Initial Leakages

Temperature (°C)	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
30	0.1459E-01	0.7887E-05	0.3040E-02	0.3139E-09
50	0.2784E-01	0.3649E-07	0.5797E-02	0.3793E-09
65	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09

There was an increase in the initial leakage of sodium with temperature. Initial leakage increased by 91% when the operating temperature was increased from 30°C to 50°C. There was a further increase of 52% when the temperature was increased to 65°C. This is due to the increase in the diffusivity of sodium with temperature. Unlike sodium, the initial leakages of calcium decreased with increasing temperature. There was a decrease of two orders of magnitude when the temperature was increased from 30°C to 50°C. There was a further decrease of one order when the temperature was increased to 65°C. This decrease may be due to the effect of temperature on equilibria.

Chloride showed a similar trend as that of sodium. There was a 91% increase in the chloride leakage when the temperature is increased from 30°C to 50°C. The leakage increased further by 52% at 65°C. Sulfate also showed a similar trend. Sulfate leakage increased by 21% when the temperature was increased to 50°C and it increased by 105% when the temperature was increased to 65°C.

Effect of Column Length

The effect of column length for the case under consideration was determined by choosing five different column lengths. The column lengths considered are 30cm, 50cm, 80cm, 100cm and 150cm. The results are tabulated in Table XII.

TABLE XII

Effect of Column Length on Initial Leakages

Column Length (cm)	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
30	0.4229E-01	0.2593E-02	0.8796E-02	0.1735E-04
50	0.4221E-01	0.2858E-04	0.8789E-02	0.4431E-08
80	0.4221E-01	0.3515E-07	0.8789E-02	0.6420E-09
100	0.4221E-01	0.2434E-08	0.8789E-02	0.6420E-09
150	0.4221E-01	0.2070E-08	0.8789E-02	0.6420E-09

There was very little effect of column length on sodium leakage. There was an increase of 0.17% in the leakage when the column length was reduced to 30cm from the base case column length of 100cm. The initial leakage of sodium at all other column lengths was the same as the base case indicating that it is the equilibrium leakage.

Column length showed a significant effect on calcium leakage. There was a six orders of magnitude difference when the column length was reduced by 70cm from the base case. There was a significant effect on calcium leakage when the column length was reduced from the base case. The effect was not very significant when the column length was increased from the 100cm to 150cm. There was only a 15% increase in the leakage for this increase in column length. This is because, for small column lengths there would be less resin surface and time for the exchange which may result in an incomplete exchange leading to kinetic leakage. Once the column length exceeds the required length of ion-exchange zone for complete exchange, there will be very less effect of column length on the initial leakages. Any column length greater than the minimum required length for complete exchange gives equilibrium leakage.

Like sodium, initial leakage of chloride also showed very little change with column length. There was a 0.1% increase in the initial leakage of chloride when the column length was reduced to 30cm. For all other column lengths the predicted leakage was equal. Column length had a significant effect on sulfate leakage. There was a significant effect when the column length is varied between 30cm and 80cm. There was no change in the sulfate leakage when the column length was increased further. This suggests that the minimum column length required to achieve equilibrium leakage of sulfate in the effluent is around 80cms. The above study shows how this code can be used to find the optimum length of an ion exchange column to achieve the required initial leakages.

Effect of Void Fraction

Initial leakages were predicted for three different bed void fractions to find the effect of void fraction on the initial leakages. Bed void fractions of 0.35, 0.45 and 0.55 were used to predict the effluent leakages. All other parameters are kept constant. Table XIV shows the results for these three cases.

TABLE XIII

Effect of Void Fraction on Initial Leakages

Void Fraction	Sodium (ppb)	Calcium (ppb)	Chloride (ppb)	Sulfate (ppb)
0.35	0.4221E-01	0.2435E-08	0.8789E-02	0.6420E-09
0.45	0.4221E-01	0.2648E-05	0.8789E-02	0.6863E-09
0.55	0.4222E-01	0.5792E-03	0.8791E-02	0.1053E-05

An increase in void fraction implies less resin volume for the same bed depth (i.e, a reduction in capacity). So higher void fractions may result in higher initial leakages. But initial leakage of sodium was not affected by the change in void fraction. This may be because the volume of the resin available at higher void fraction was sufficient to remove most of the sodium present in the influent stream giving equilibrium leakage concentration at the effluent. Any further increase in the resin volume would give the same concentration at the effluent. So, void fraction did not show significant effect on sodium leakage.

Unlike sodium, there was a significant effect of void fraction on calcium leakages. There was a three order increase in the initial leakage of calcium when the void fraction was increased from 0.35 to 0.45. The leakage increased further by two orders when the void fraction was increased to 0.55. This is because the resin volume available at higher void fractions was not sufficient to achieve equilibrium concentrations at the outlet. Increasing the void fraction would increase the resin volume resulting in lower concentrations till equilibrium leakage concentrations are achieved at the effluent.

As in the case of sodium, void fraction did not have a significant effect on chloride leakage. Sulfate leakage did not have a very significant effect when the void fraction was increased from 0.35 to 0.45. There was a only a 7% increase in the initial leakage. There was a significant increase in the leakage when the void fraction was increased to 0.55. This suggests that the volume of resin available when the void fraction is 0.45 was sufficient to achieve almost equilibrium leakage concentrations at the effluent.

Conclusions

A model for predicting the initial leakages from an ion exchange column has been presented. A computer code implementing this model is attached in the appendix. The model was used to study the effect of various parameters like initial loadings, resin fouling, flow rate, resin ratio, temperature, column length, column diameter and void fraction on the initial leakages. The above study was based on hydrogen cycle operation of the bed. However, the model can handle amine cycle also.

Initial resin loadings showed a significant effect on the initial leakages of all the ions considered in this study (Na^+, Ca^{+2}, Cl^- & SO_4^{-2}). Resin fouling did not have any effect on the initial leakages of monovalent ions (Na^+ & Cl^-). Among the divalent ions, calcium leakages were significantly affected by resin fouling. Sulfate leakages were affected at fouling levels above 40%. Flow rate did not have any significant on the leakages of all the ions. Temperature had a significant effect on the initial leakages of all the ions.

In general, higher initial resin loadings and temperatures always result in higher initial leakages, whether they are due to equilibrium or kinetics. All other parameters considered in this study may or may not affect the initial leakages depending on the type of leakages observed. If the leakages observed are kinetic then a decrease in resin fouling, flow rate and void fraction results in lower initial leakages. If the leakages observed are from equilibrium then any further decrease in flow rate, void fraction and resin fouling will not affect the observed leakages, however, an increase in these variables may result in higher leakages. Increasing the column length results in lower kinetic leakages but do not affect equilibrium leakages.

CHAPTER IV

DEVELOPMENT OF A GENERALIZED COLUMN MODEL TO PREDICT ION EXCHANGE BREAKTHROUGH

Abstract

A general model is developed to predict multicomponent mixed bed ion exchange breakthrough. The model is capable of handling an arbitrary number of completely dissociative species with arbitrary valences. Monovalent amines and carbonates can also be handled by this model. The model is used to predict the effluent concentrations using real plant conditions. The effect of resin fouling on the breakthrough curves is also studied.

Introduction

Many researchers have investigated binary and ternary ion exchange systems. However, there were very limited studies involving multicomponent systems. Researchers like Helfferich (1967), Klein et al. (1967), Tondeur (1970) and Garcia et al. (1992) have developed equilibrium models to predict column effluents for multicomponent systems. These models are good at low flow rates when equilibrium plays an important role. But in power industries and semiconductor industries, ion exchange columns are operated at very high flow rates. At high flow rates kinetics, rather than equilibrium, plays an important role. Hence rate models are more appropriate to simulate these units.

Haub and Foutch (1986 a,b) modeled mixed bed ion exchange columns taking ion exchange kinetics into consideration. They considered a binary system consisting of completely dissociative univalent ions in their study. Zecchini and Foutch (1990) extended this work to ternary univalent system. Pondugula and Foutch (1995) extended it further to include one divalent species. Bulusu and Foutch (1994) developed a model to handle a partially dissociative species. The partially dissociative species in their work is carbonate.

The objective of this work is to develop a generalized model which can handle any number of completely dissociative species with arbitrary valences. The model also included monovalent amines and carbonate which are the partially dissociative species.

Model Development

The model addresses the exchange of a multicomponent system of ions in an ion exchange column. The ionic system may include any number of completely dissociative ions, monovalent amines and carbonates. The film diffusion fluxes are described using the Nernst-Planck model. The interfacial concentrations are determined from the selectivity expressions. The equilibrium relationships of amines and carbonic species are taken into account during bulk phase neutralization. The final effluent concentrations are determined by solving the column material balance equations along with the rate expressions numerically. Only the equations relevant for the discussion are presented here. Detailed derivations are presented in the Appendices A through D.

Assumptions

The number of simplifying assumptions have been kept to a minimum to develop a general model. The most important assumption is that the ion exchange process is film diffusion controlled. The ions with higher valency are assumed to be preferred to the ions with lower valency by the ion-exchange resin. Between the ions with same valency, the ion with higher selectivity is preferred by the resin. The concentration of dissolved CO_2 is assumed to be negligible compared to that of carbonate and bicarbonate in developing carbonate equilibrium equations. Table XIV lists all the assumptions that are used in this model.

Amine Equilibrium

Amines are weak electrolytes. They do not dissociate completely in water. Depending on its type, an amine can exist in two or more forms in water. Monovalent amines exist in water in two forms and divalent amines exist in three forms. In this model only monovalent amines are considered to reduce the complexity. Monovalent amines exist in water in both ionic (dissociated) and molecular (undissociated) forms.

TABLE XIV

Model Assumptions

1. Film diffusion control.
2. The Nernst-Planck model incorporates all interactions between diffusing ionic species.
3. An ion with a higher valence is preferred to an ion with a lower valence by the ion-exchange resin.
4. Between the ions with same valence, the ion with higher selectivity is preferred to the ion with lower selectivity by the ion-exchange resin.
5. Pseudo steady state exchange (variations of concentration with space are much more important than with time).
6. No net current flow and no net coion flux within the film.
7. No coion flux across the particle surface.
8. Local equilibrium at solid-film interface.
9. Curvature of the film is negligible.
10. Selectivity coefficients are constant and temperature independent.
11. Binary selectivity coefficients can be used for multicomponent ion exchange.
12. Bulk phase neutralization.
13. Uniform concentrations across the resin bead.
14. Uniform bulk phase concentrations.
15. Reactions are instantaneous when compared with the rate of exchange.
16. Activity coefficients are constant and unity.
17. Negligible axial dispersion and plug flow.
18. Isothermal, isobaric operation.
19. Concentration of dissolved CO_2 is negligible compared to that of HCO_3^-/CO_3^{2-}.

TABLE XV

Correlations for Temperature Dependent Parameters

Ionic Diffusion Coefficients (cm^2/s) (Bulusu, 1994)

Hydrogen $D_H = 8.931*10^{-10}(T+273.16)(221.71+5.52T-0.0144T^2)$

Hydroxide $D_{OH} = 8.931*10^{-10}(T+273.16)(104.74+3.807T^2)$

where T is temperature in °C.

Dissociation Constants

Water $pK_w = -6.0875 + 0.0176T + \frac{4470.99}{T}$

CO_2 1st. dissociation(*) $pK_1 = \frac{17052}{T} + 215.21LOG(T) - 0.12675T - 545.56$

CO_2 2nd. dissociation(*) $pK_2 = \frac{2902.39}{T} + 0.02379T - 6.498$

where T is temperature in °K.

Solution Properties

Viscosity(cp) $\mu = 1.5471 + 0.0317T + 2.334E-04T^2$

Density(g/cc)

$$\rho = \left[\frac{1 + 0.134248*SS2 - 3946263*10^{-3}*SS1}{3.1975 - 0.3151548*SS2 - 1.203374*10^{-3}*SS1 + 7.48908*10^{-13}*SS1^4}\right]^{1/2}$$

where $SS1 = 374.11 - T$

$SS2 = SS1^{1/3}$

T is temperature in °C in the above correlations

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* Loewenthal and Marias (1982)

The two forms of amine exist in equilibrium according to the following reaction:

$$\text{Amine} + H_2O \Leftrightarrow \text{Amine}^+ + OH^- \tag{4-1}$$

The dissociation constant for the above reaction can be written as

$$K_a = \frac{[\text{Amine}^+][OH^-]}{[\text{Amine}]} \tag{4-2}$$

Chowdiah (1996) reported the values of dissociation constants for various amines. He also discussed the mass transfer of amines in ion exchange in detail. The equations relating the concentrations of both the amine forms with the hydrogen ion concentration are derived for equilibrium conditions in the Appendix A.

Carbonate Equilibrium

Carbonic species dissolved in water exist in four different forms: dissolved CO_2, carbonic acid H_2CO_3, and the ions HCO_3^- and CO_3^{2-}. The sum of these concentrations in the solution is the total carbonic species concentration (TCC). The carbonic species together with hydrogen and hydroxyl ions of the water exist in a state of dynamic equilibrium described by the following reactions:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \tag{4-3}$$

$$H_2CO_3 \xleftrightarrow{K_1} H^+ + HCO_3^- \tag{4-4}$$

$$HCO_3^- \xleftrightarrow{K_2} H^+ + CO_3^{2-} \tag{4-5}$$

K_1 and K_2 are the first and second dissociation constants of carbonate equilibrium, respectively. These two constants are temperature dependent. The temperature correlations for these constants are give in Table XV. The temperature correlation for K_1 was determined for the range of 0°C to 38°C, while that for K_2 was determined for 0°C to 50°C. Plots of pK_1 and pK_2 for temperatures between 0°C and 90°C were reported by Bulusu (1994).

Equations relating the concentrations of each of the carbonic species with the hydrogen ion concentration are derived for equilibrium conditions in Appendix A. Using the known total carbonic species concentration and the electroneutrality condition, the concentrations of the individual species can be calculated.

Interfacial Concentrations

Interfacial concentrations (solid-film interface) of the ions are determined using ion exchange equilibria. It is assumed that there is a local equilibrium at the solid-film interface. The selectivity coefficient expression for a general case, can be written using a mass action law, as follows:

$$K_A^B = \left(\frac{q_B}{C_B^*}\right)^{Z_A}\left(\frac{C_A^*}{q_A}\right)^{Z_B} \tag{4-6}$$

where q's are the concentrations in the resin phase while C^*'s are the interfacial concentrations. The above equation can be written in terms of equivalent fractions, total resin capacity and total interfacial concentration as follows:

$$K_A^B = \left(\frac{Y_B}{X_B^*}\right)^{Z_A}\left(\frac{X_A^*}{Y_A}\right)^{Z_B} Q^{(Z_A-Z_B)} C_T^{*(Z_B-Z_A)} \tag{4-7}$$

Generalizing the above equation for an ion 'i' we have

$$X_i^* = Y_i \left(K_A^i\right)^{-1/Z_A} \left(\frac{X_A^*}{Y_A}\right)^{Zi/Z_A} \left(\frac{Q}{C_T^*}\right)^{1-Zi/Z_A} \tag{4-8}$$

For 'n' counterions in the bulk liquid replacing ion A in the resin, we can write 'n' such expressions. However, given the resin loadings, resin capacity and total interfacial concentration, we will have n+1 unknown interfacial fractions. The extra equation needed to completely specify the system is obtained from material balance at the solid-film interface.

$$\sum_{i=1}^{n+1} X_i^* = 1.0 \tag{4-9}$$

From the Equation (4-9) it is evident that for an arbitrary valence case, the ion exchange equilibrium depends on the resin capacity and total interfacial concentration. This leads to an iterative solution to determine the interfacial concentrations. However, before we can determine these individual interfacial concentrations, we need to have an expression for the total interfacial concentration, C_T^*. This is discussed in the following section. The detailed equations for calculation of interfacial concentrations are presented in Appendix B.

Flux Expression

The flux expression in this work is developed according to a method proposed by Franzreb et al.(1993). The Nernst-Planck equation, which is the basis of the flux expression is

$$J_i = -D_i\left(\frac{\partial C_i}{\partial r} + \frac{C_i Z_i F}{RT}\frac{\partial \phi}{\partial r}\right) \quad (4\text{-}10)$$

The first term on the right hand side of Equation (4-10) is the concentration gradient term and the second term is the electric potential term. The electric potential term in the Nernst-Planck equation is eliminated using the assumption of no net coion flux in the film. With the introduction of total equivalent concentration, C_T, the electric potential term can be written as

$$\frac{d\phi}{dr} = \frac{-RT}{Z_Y F}\frac{1}{C_T}\frac{dC_T}{dr} \quad (4\text{-}11)$$

where Z_Y is the mean coion valence (Appendix C). Substituting of Equation (4-11) in Equation (4-10) and assuming a pseudo steady state exchange we have

$$J_i = -D_i\left(\frac{dC_i}{dr} - \frac{C_i Z_i}{C_T Z_Y}\frac{dC_T}{dr}\right) \quad (4\text{-}12)$$

After a series of mathematical manipulations, the final form of the flux expression is as follows:

$$J_i = \frac{D_i}{\delta}\left((1-\frac{N_i}{P})(C_i^* - C_i^o) + N_i A_i (1+\frac{1}{P})(C_T^* - C_T^o)\right) \quad (4\text{-}13)$$

where $N_i = -\frac{Z_i}{Z_Y}$ (4-14)

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^* - X_i^\circ \right)}{\sum_{i=1}^{n} D_i \left(X_i^* - X_i^\circ \right)} \tag{4-15}$$

$$C_T^* = \left(\frac{\sum_{i=1}^{n} (1+N_i) D_i X_i^\circ}{\sum_{i=1}^{n} (1+N_i) D_i X_i^*} \right)^{\frac{1}{P-1}} C_T^\circ \tag{4-16}$$

From Equations (4-8) and (4-16) we know that the total interfacial concentration (C_T^*) and the individual interfacial equivalent fractions (X_i^*) are not independent. Thus, an iterative solution had to be used to determine these quantities and subsequently the ionic fluxes. The solution strategy adopted in the computer code to determine the ionic fluxes is presented in Table XVI.

TABLE XVI

Solution Strategy for Calculation of Ionic Fluxes

1. Assume $C_T^* = C_T^o$.
2. Calculate X_i^*'s using Equations (4-8) and (4-9).
3. Calculate C_T^* using Equation (4-16).
4. If the difference between new and old C_T^* exceeds the chosen tolerance, repeat steps 2 and 3.
5. Calculate the ionic fluxes using Equation (4-13) and other necessary equations given in Appendix C.

Equation (4-13) is used to determine the overall effective diffusivity defined as:

$$D_e = \frac{\sum_{i=1}^{n} \left| J_i \delta \right|}{\sum_{i=1}^{n} \left| C_i^{*} - C_i^{0} \right|} \qquad (4\text{-}17)$$

The film thickness in Equation (4-13) is eliminated using the relation

$$\delta = D_e / K \qquad (4\text{-}18)$$

where K is a mass transfer coefficient calculated from Dwivedi and Upadhyay's correlation (Chowdiah, 1996) or experimental value provided by the user.

Particle Rates

The rate of exchange is related to the flux of the species by:

$$\frac{d < C_i >}{dt} = -J_i a_s \qquad (4\text{-}19)$$

The resin phase concentration $< C_i >$ can be represented as:

$$< C_i > = y_i Q \qquad (4\text{-}20)$$

Now Equation (4-19) can be written as

$$\frac{dy_i}{dt} = \frac{-J_i a_s}{Q} \qquad (4\text{-}21)$$

The rate of ion loadings into the resin can be determined using the above equations once the individual ionic fluxes are known.

Column Material Balances

The form of the material balance equations does not change from those used earlier. The final form of the dimensionless material balance equations derived in Appendix D is

$$\frac{\partial x_i}{\partial \xi} + \frac{\partial y_i}{\partial \tau} = 0 \qquad (4\text{-}22)$$

The dimensionless form of the rate equations are derived in Appendix D. The final form of the dimensionless rate equations are:

$$\frac{\partial y_i}{\partial \tau_c} = \left(-\frac{6J_i}{K_i C_f}\right)\frac{K_i}{K_c}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c} \qquad \text{(Cations)} \qquad (4\text{-}23)$$

$$\frac{\partial y_i}{\partial \tau_c} = \left(-\frac{6J_i}{K_i C_f}\right)\frac{K_i}{K_c} \qquad \text{(Anions)} \qquad (4\text{-}24)$$

The effluent concentrations from the column are determined by solving the above set of equations. The method of characteristics is employed to solve this system of equations. The resin and bulk phase fraction equations are then solved using first order Eulers method and fourth order Gears method.

Resin Loading Process

An ion exchange column is divided into several slices to predict the effluent concentrations with time. Most of the discussion in this section is with respect to the resin in a single slice at a fixed time. Initially most of the exchange sites in a cationic resin are occupied by the hydrogen ions. Similarly most of the exchange sites in an anionic resin are occupied by the hydroxyl ions. Apart from the hydrogen and hydroxyl ions, the resin may also contain traces of other ions. The fraction of an ion initially present in the resin is referred to as its initial loading. As the ion exchange process proceeds, the hydrogen and hydroxyl ions in the resin are replaced by their counter-ions in the bulk liquid surrounding the resin according to the following criteria:

1. An ion with a higher valence is preferred to an ion with a lower valence by the ion-exchange resin.
2. Between the ions with the same valency, the ion with higher selectivity is preferred by the resin.

In order to implement the above criteria for cationic resin loading in the computer code, the cations are arranged in the descending order of their valences. The cations with same valency are arranged in the descending order of their selectivities. Let us say there are 'n' cations in the list. So initially all the cations replace the 'n'th cation, usually hydrogen, in the list. When almost all of the 'n'th cation in the cationic resin is replaced i.e., when the sum of the resin loadings of the first 'n-1' cations become greater than 0.999, then the top 'n-2' cations now start replacing the 'n-1'th cation. This process continues till the resin is completely loaded with the top most cation in the list i.e., the cation with the highest valency and selectivity. The same method is followed for anionic resin loading also.

The concentration of an ion in the bulk phase also plays an important role in the resin loading process, especially if there is a few orders of difference between the concentrations of the ions in the feed stream. An ion present in significantly high concentrations can replace an ion present in lower concentrations even if the valence and selectivity of the former are less than that of the latter.

Solution Strategy

The system of equations developed earlier in this chapter is solved by the method of characteristics. In this method the ion exchange column is considered to be a grid defined by lines of constant τ and constant ξ as shown in Figure 2. Each point of intersection of a vertical line with a horizontal line is a grid point. Each grid point represents a slice in the ion exchange bed at a fixed time. In the following discussion the dimensionless bulk phase concentration is referred to as 'X' and the dimensionless resin phase concentration is referred to as 'Y'.

The resin phase concentrations at the grid points along the line $\tau = 0$ (initial loadings) and the bulk phase concentrations at the grid points along the line $\xi = 0$ (feed concentrations) are given as the initial and boundary conditions i.e., the values of X at the grid points along the line $\tau = 0$ and the values of Y at the grid point along the line $\xi=0$ are known. If the values of X and Y are known at a grid point (τ, ξ) then the rate of the ion exchange into the resin at that point can be calculated. Now using the finite difference approximations for the Equations (4-22), (4-23) and (4-24) the values of Y at ($\tau+\Delta\tau$, ξ) and the value of X at (τ, $\xi+\Delta\xi$) can be calculated. Since the values of X and Y are known at the grid point (1,1) initially, the rates are calculated at that point first. Using the finite difference approximations of the Equations (4-22), (4-23) and (4-24) the values of

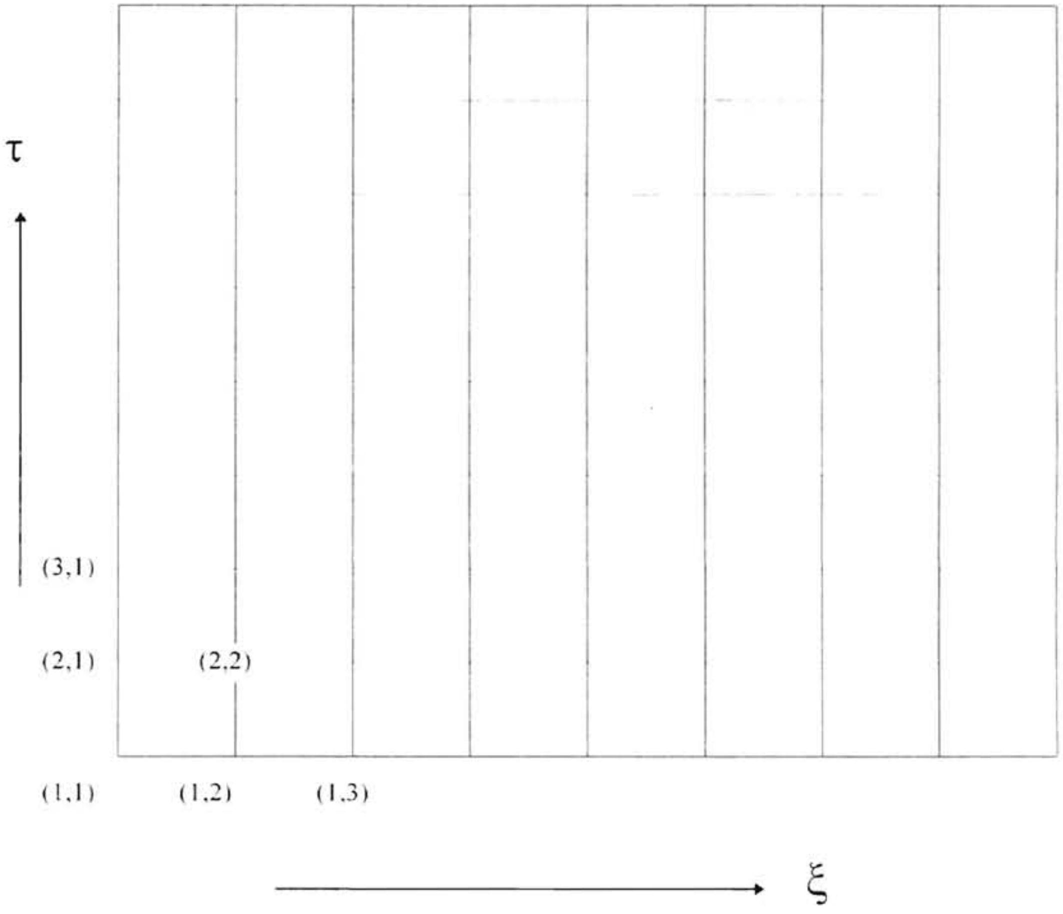

Figure 2. Solution Grid Illustrating the Method of Characteristics

Y at (2,1) and the values of X at (1,2) are calculated from the values of X, Y and rates at (1,1). Now since the values of X and Y are known at point (1,2) the values of Y at (2,2) and the values of X at (1,3) are calculated. This way the calculation proceeds from left to right across an entire row of the grid before τ is incremented. The bulk concentrations at the last grid point in a row are the effluent concentrations. The effluent concentrations at different values of τ yield a breakthrough curve.

The accuracy of the value predicted by a finite difference method depends upon its order. A first order finite difference method estimates the value at a point using the data at the previous point. A second order method uses the data at previous two points. Similarly a fourth order method uses the data at previous four points to estimate the value at a particular point. All these points should be equi-distant. First order Euler's method was used to estimate the values of X at the second, third and the fourth points in all rows. A fourth order gears method was used to estimate X values at all subsequent points of a row since the values at the previous four points will be available for these points. All the Y values are estimated using first order Eulers method.

Bulusu (1994) used constant step sizes for both the distance and time steps. Since a first order Euler's method was being used for the first three steps, a small distance step was necessary to estimate the X values for the first three steps with reasonable accuracy. A large step size for the first three steps used to result in run time errors. Since constant step sizes were being used, the same small step size was being used for the remaining distance steps also. In other words, more distance steps were being taken. This resulted in huge run times of the computer code developed by Bulusu (1994).

A variable step size method as shown in Figure 3 is used in this code to improve the run time. Two different step sizes are used for each pass down the ion exchange column i.e., for each row of the grid. A very small step size is used to calculate the values at the second, third and fourth points, represented by thick lines, to be used in the fourth order method with a higher step size. A relatively higher step size is used for the subsequent steps in a row. For example, if the smaller step is 0.01 and the bigger step is 0.1 then the values at $\xi = 0.01, 0.02, 0.03$ are calculated using a first order eulers method. The values from $\xi = 0.04$ to $\xi = 0.3$ are calculated using a fourth order method with the smaller step size (0.01 in this case). All the values starting from $\xi = 0.4$ are calculated using a fourth order method with a bigger step size (0.1 in this case). The values at $\xi = 0.0$, $\xi = 0.1$, $\xi = 0.2$ and $\xi = 0.3$ are used to calculate the value at $\xi = 0.4$. Similarly, all the subsequent values are calculated from the values at the previous three equidistant points. This method increased the stability and decreased the runtime of the computer code considerably compared to the previous codes.

Exception Handling

The computer code is divided into different subroutines. Each subroutine returns a "flag" to its calling routine. The value of this flag is set to "0" initially in the main routine. The main program calls the appropriate subroutines wherever necessary. These subroutines may call other subroutines to perform their tasks. If a subroutine has to exit abnormally due to an unexpected input from the calling routine, a divide by zero etc., it

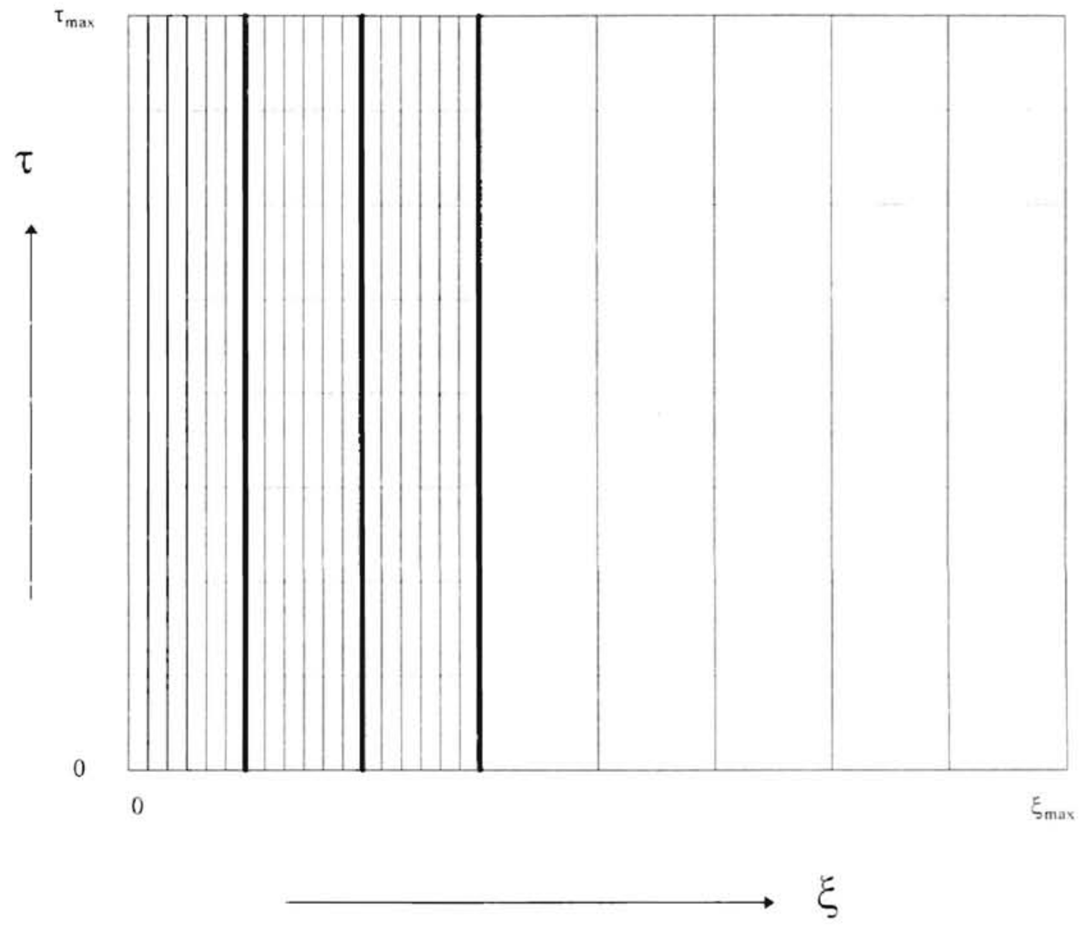

Figure 3. Solution Grid Illustrating the Modified Method

prints the appropriate error message and sets the value of the flag equal to "1" and returns, else it executes normally and restores the value of the flag. So, whenever a subroutine is called, the value of the flag is tested and if it is equal to "1", the calling routine also exits with an appropriate error message. This way the computer program exits with appropriate error messages in case of a problem and will not crash. No special checks have been incorporated to check the validity of the input. The following situations might arise while running the code.

1. The program exits with error messages. Most of these error messages are either due to unacceptable input data or large step sizes.
2. Instability: Sometimes the breakthrough curves might show instability. This is mainly due to a large step sizes. Using smaller step sizes will eliminate the problem. But this might result in longer run times.

Desulphonation of Cationic Resins

Sulfate is a common ionic impurity encountered in the industry. One of the main sources of sulfate is the desulphonation of strongly acidic cationic resin. Various investigators have studied the release of sulfur molecules into water by the strongly acidic cationic resins. This desulphonation is a function of temperature. Pondugula (1995) derived the following expression for the rate constant for desulphonation as a function of temperature based on the data provided by Fisher (1993) and others.

$$k = 7.5 \times 10^{6} e^{\frac{-10278.6}{T+273.16}}$$

where k is a first order rate constant (hr^{-1}) and T is temperature in ^{o}C.

The above equation is used in the computer code to account for the desulphonation effect. The user is given an option whether or not to include the desulphonation effect.

Results and Discussion

The model developed in the previous sections was used to predict the breakthrough curves for the following two cases.

Case I : No dissociative species in the feed.

Case II: Partially dissociative species present in the feed.

The model was also used to study the effect of resin fouling and resin heels on the column performance.

Case I: The input parameters for this case are presented in Table XVII. The feed stream consisted of six completely dissociative cations (two monovalent, two divalent, two trivalent ions) and five completely dissociative anions (one divalent and four monovalent ions). The selectivities of the ions considered in this case are presented in Table XVIII.

TABLE XVII

Input Data for Case I

Property	Value
Bed diameter (cms)	150.0
Resin depth (cms)	100.0
Cation-to-anion exchange resin (volumetric ratio)	1:1
Resin bead diameter (cm)	
Cation (Amberlite - IR 120 Plus)	0.065
Anion (Amberlite - IRA 440)	0.060
Resin capacity (meq/ml)	
Cation	1.8
Anion	1.1
Feed pH	7.0
Temperature (°C)	25
Influent concentration (ppb)	
Cations:	
Sodium (Na^+)	36.8
Potassium (K^+)	62.4
Calcium (Ca^{+2})	32.0
Magnesium (Mg^{+2})	19.2
Aluminum (Al^{+3})	14.4
Chromium (Cr^{+3})	27.7
Anions:	
Sulfate (SO_4^{-2})	92.16
Nitrate (NO_3^-)	119.04
Bromide (Br^-)	153.6
Chloride (Cl^-)	68.16
Fluoride (F^-)	36.48
Initial loading on the resin (%)	
Cations:	0.1
Sodium	0.1
Potassium	0.1
Calcium	0.1
Magnesium	0.1
Aluminum	0.1
Chromium	0.1
Anions:	
Sulfate	0.1
Nitrate	0.1
Bromide	0.1
Chloride	0.1
Fluoride	0.1
Bed void fraction	0.35
Influent flow rate (cm^3/s)	2.56E+4 (4.28 gpm/ft^2)

TABLE XVIII

Selectivities of the Ions in Case I

Ion	Selectivity with respect to Hydrogen
Cations:	
Sodium (Na^+)	1.5
Potassium (K^+)	2.5
Calcium (Ca^{+2})	3.9
Magnesium (Mg^{+2})	2.5
Aluminum (Al^{+3})	5.62
Chromium (Cr^{+3})	5.86
Anions:	
Sulfate (SO_4^{-2})	60
Nitrate (NO_3^-)	65
Bromide (Br^-)	50
Chloride (Cl^-)	22
Fluoride (F^-)	1.6

Figure 4 shows the breakthrough curves for cations in this case. As expected, the breakthrough of low valence ions was observed prior to the breakthrough of the ions with higher valence. The breakthrough of the two monovalent ions, sodium and potassium, occurred at about 20 days of column operation. The divalent cations, calcium and magnesium, were seen to breakthrough at about 30 days. The trivalent cations, aluminum and chromium, started to breakthrough at around 80 days of column operation. Sodium started to breakthrough prior to potassium because the selectivity of sodium is less than that of potassium. Among the two divalent cations, magnesium started to breakthrough first because of its lower selectivity. There was no significant difference between the breakthrough times of aluminum and chromium because the difference between their selectivities is very small.

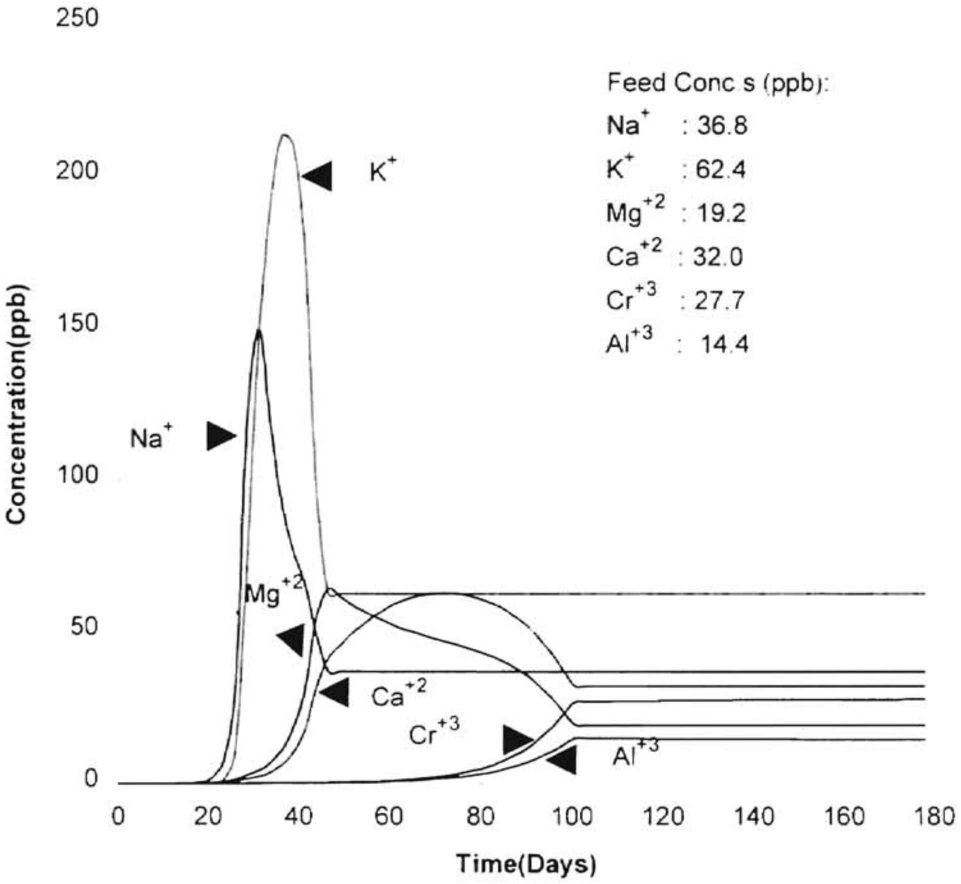

Figure 4. Breakthrough Curves for Cations - Case I

The peaks observed in the breakthrough curves of sodium, potassium, calcium, and magnesium are due to the ion throw. Initially, when the cationic resin is in the hydrogen form, all the ions replace hydrogen. When all the hydrogen in the cationic resin is replaced, the next weakest cation i.e., the ion with the next lowest valence and selectivity, sodium in this case, gets replaced by the remaining cations. When all the sodium is replaced, the next weakest cation, which is potassium in this case, starts getting replaced. This process continues until the resin is saturated with the ion with highest valence and selectivity.

The sodium peak is observed first because it is the weakest among the six cations considered. The peaks in breakthrough curves follow the same order as the breakthroughs. The strongest ion, chromium in this case, did not show any peak as expected. Aluminum throw was not seen because its selectivity is almost the same as that of chromium. The peaks of sodium and potassium are steeper than those of magnesium and calcium. This is because sodium and potassium are replaced by more number of ions and hence replaced faster.

The effluent concentrations of sodium and potassium reached their feed concentrations at about 46 days and remained constant. This is because, after 46 days the resin would have been filled with calcium, magnesium, aluminum, and chromium. Magnesium and calcium throw was observed between 46 and 100 days. At about 100 days, the effluent concentrations of calcium and magnesium reached their feed concentrations.

The breakthrough curves of anions for this case are shown in Figure 5. As expected, the breakthrough of monovalent ions occurred before the divalent ion. Fluoride started to breakthrough at around 23 days. Chloride started to breakthrough around 28 days. The breakthroughs of bromide and nitrate were observed at 34 days and 36 days, respectively. Sulfate breakthrough was seen at around 120 days.

All the anions except sulfate showed ion throw. Fluoride throw was seen first because it is the weakest among the five anions considered. As expected, the fluoride peak was followed by the chloride and bromide peaks respectively. Flat plateau's were observed in the breakthrough curves of fluoride, chloride, bromide, and nitrate. Fluoride showed a plateau between 35 and 120 days. Chloride plateau was seen between 45 and 120 days. Bromide and nitrate showed plateau's between 70 and 120 days. This may be because the ions thrown out of the resin in the top portion of the bed enter back into the resin, some place down the bed, before reaching the effluent by replacing the remaining hydroxide. When the sulfate started to breakthrough around 120 days, the effluent concentrations of all the remaining ions started falling down and reached their feed concentrations.

Figure 6 shows the pH curve for this case. The pH is constant till 20 days since no breakthrough occurred. A huge fluctuation in the pH can be seen between 20 and 40 days. This is because most of the ions started to breakthrough in this period. Whenever an ion breaks through, it disturbs the charge balance in the effluent stream. The charge balance is restored by the H^+ and OH^- ions formed from the dissociation of water. This results in a pH fluctuation. The pH increases when an anion breaks through and decreases

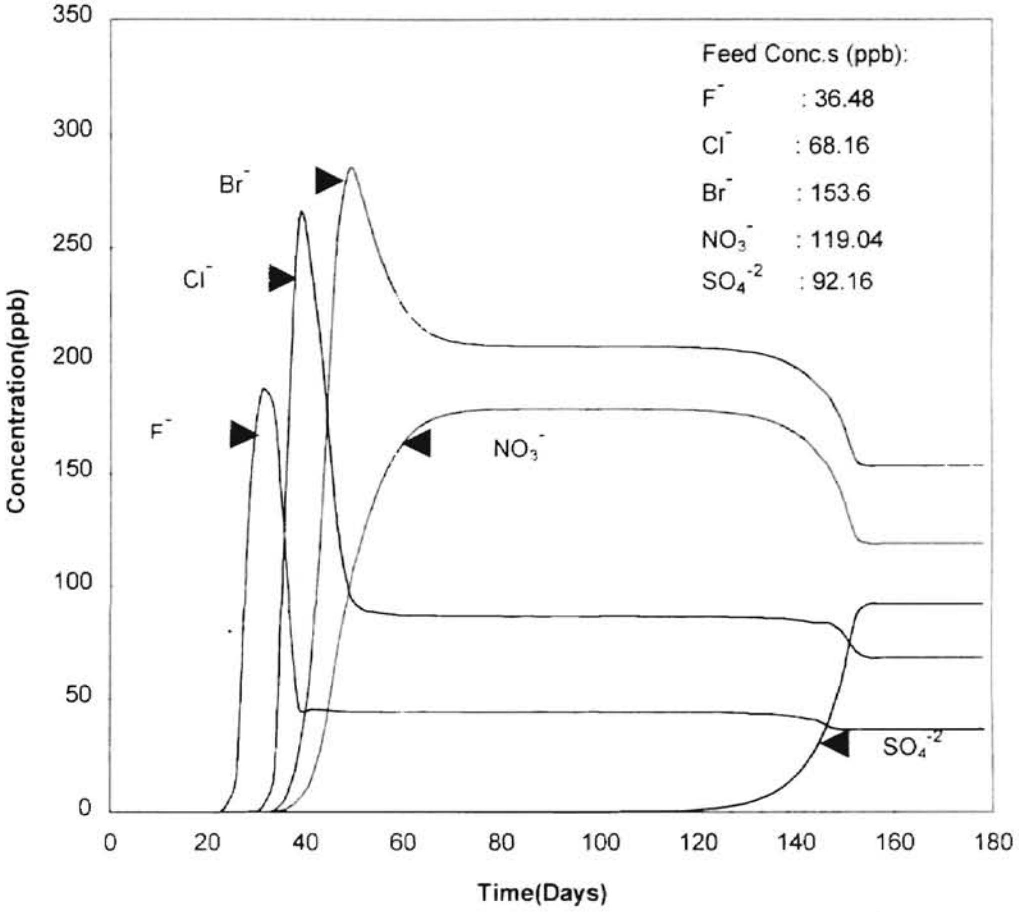

Figure 5. Breakthrough Curves for Anions - Case I

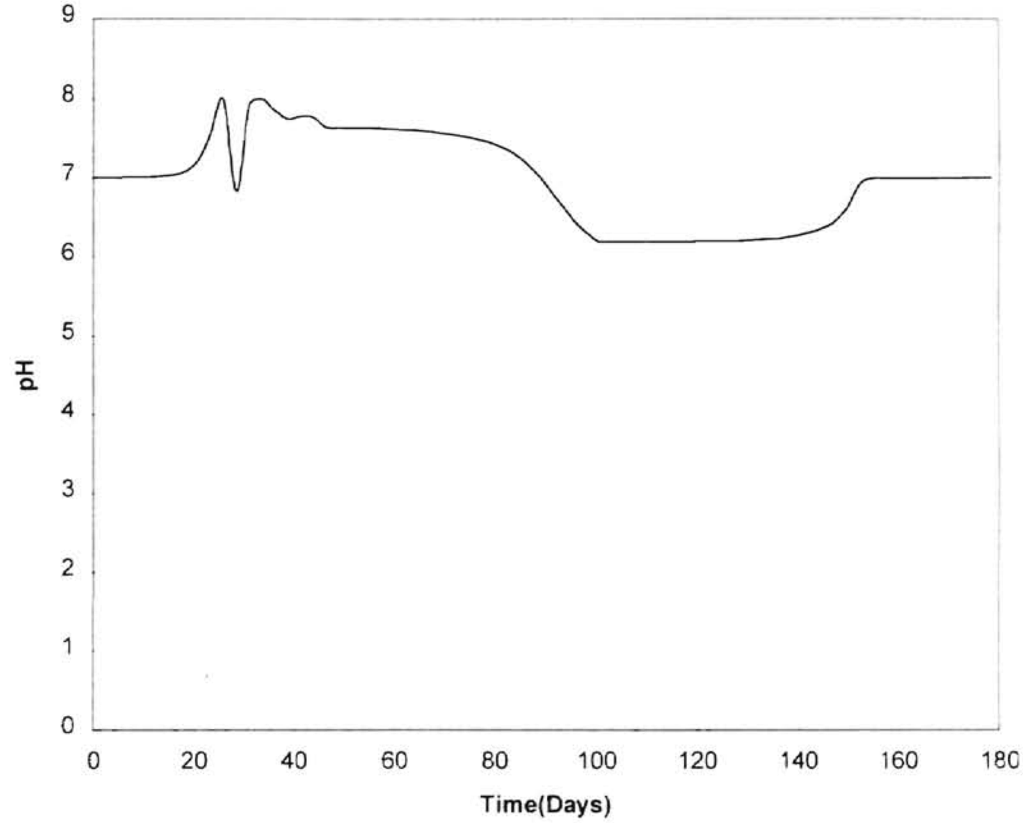

Figure 6. pH Profile for Case I

when a cation breaks through. If there is no change in the effluent concentrations pH remains constant. The pH is relatively constant between 40 and 80 days because of no major change in the effluent concentrations. The pH drop between 80 and 100 days corresponds to the breakthrough of chromium and aluminum. The pH surge between 140 and 160 days corresponds to the sulfate breakthrough.

Case II: The input for this case consists of two completely dissociative cations (sodium and calcium), two completely dissociative anions (chloride and sulfate), and two partially dissociative species (ammonia and carbonate). The input parameters for this case are presented in Table XIX.

The breakthrough curves for the cations for this case are shown in Figure 7. The breakthrough of sodium and ammonia occurred before the calcium breakthrough. The monovalent ions, sodium and ammonia, started to breakthrough around 6 days of column operation. Calcium started to breakthrough around 10 days of column operation. The breakthrough times of the cations were earlier because of the high concentrations in the feed. The breakthrough curves of sodium and ammonia show ion throw. This is because they are replaced by calcium when all the hydrogen in the resin is replaced.

The anion breakthrough curves for this case are shown in Figure 8. Chloride started to breakthrough around 10 days. Sulfate breakthrough started around 21 days. The initial leakage of carbonate was very high. The carbonate effluent concentration consists of the monovalent bicarbonate (HCO_3^-), the divalent carbonate (CO_3^{2-}) and the undissociated carbonate. The effluent concentration of carbonate is expressed in terms of

TABLE XIX

Input Data for Case II

Property	Value
Bed diameter (cms)	150.0
Resin depth (cms)	50.0
Cation-to-anion exchange resin (volumetric ratio)	1:1
Resin bead diameter (cm)	
Cation	0.08
Anion	0.06
Resin capacity (meq/ml)	
Cation	2.1
Anion	1.0
Feed pH	6.76
Temperature (°C)	60
Influent concentration (ppb)	
Cations:	
Sodium (Na^+)	92.0
Calcium (Ca^{+2})	80.0
Ammonia (total)	25.5
Anions:	
Sulfate (SO_4^{-2})	192.0
Chloride (Cl^-)	142.0
Carbonate (total)	93.0
Initial loading on the resin (%)	
Cations:	
Sodium	0.1
Calcium	0.1
Ammonia	0.1
Anions:	
Sulfate	0.1
Chloride	0.1
Carbonate	0.1
Bed void fraction	0.35
Influent flow rate (cm^3/s)	2.56E+4 (4.28 gpm/ft^2)

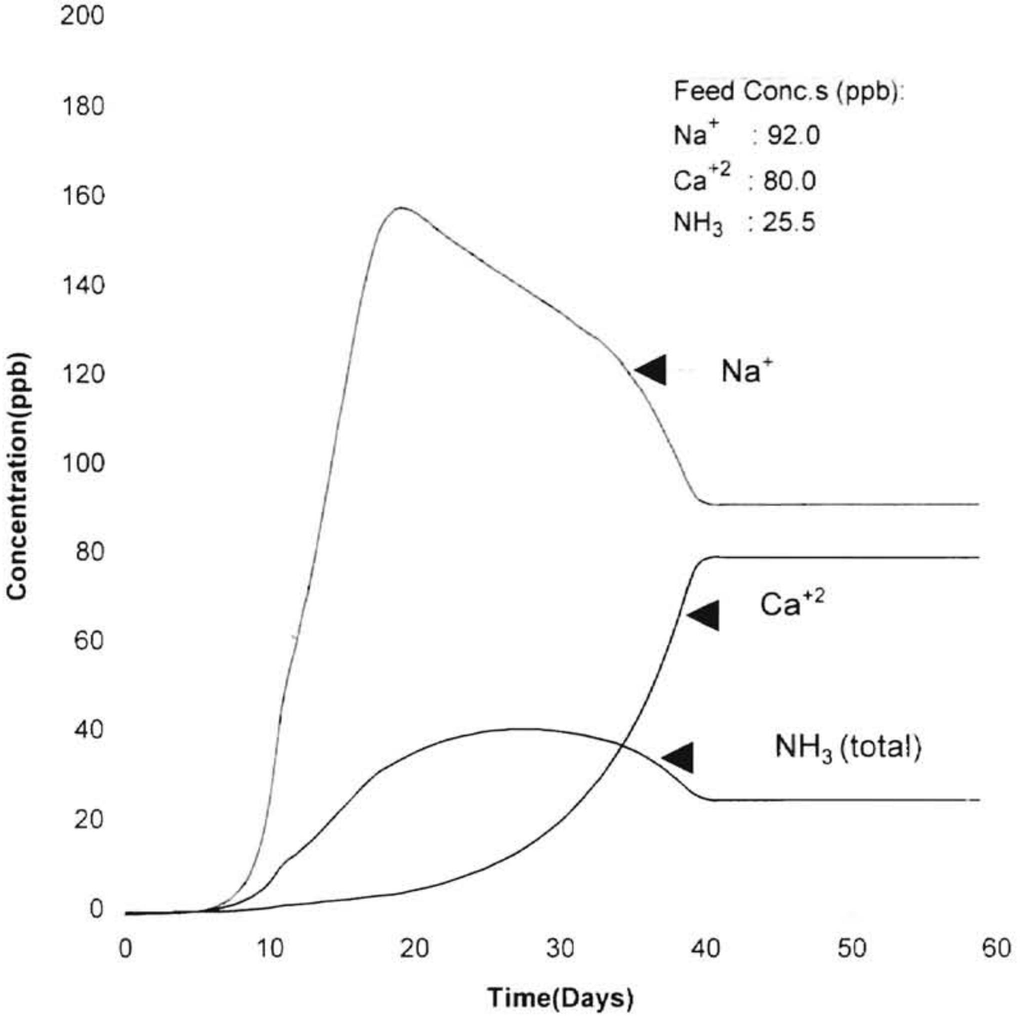

Figure 7. Breakthrough Curves for Cations - Case II

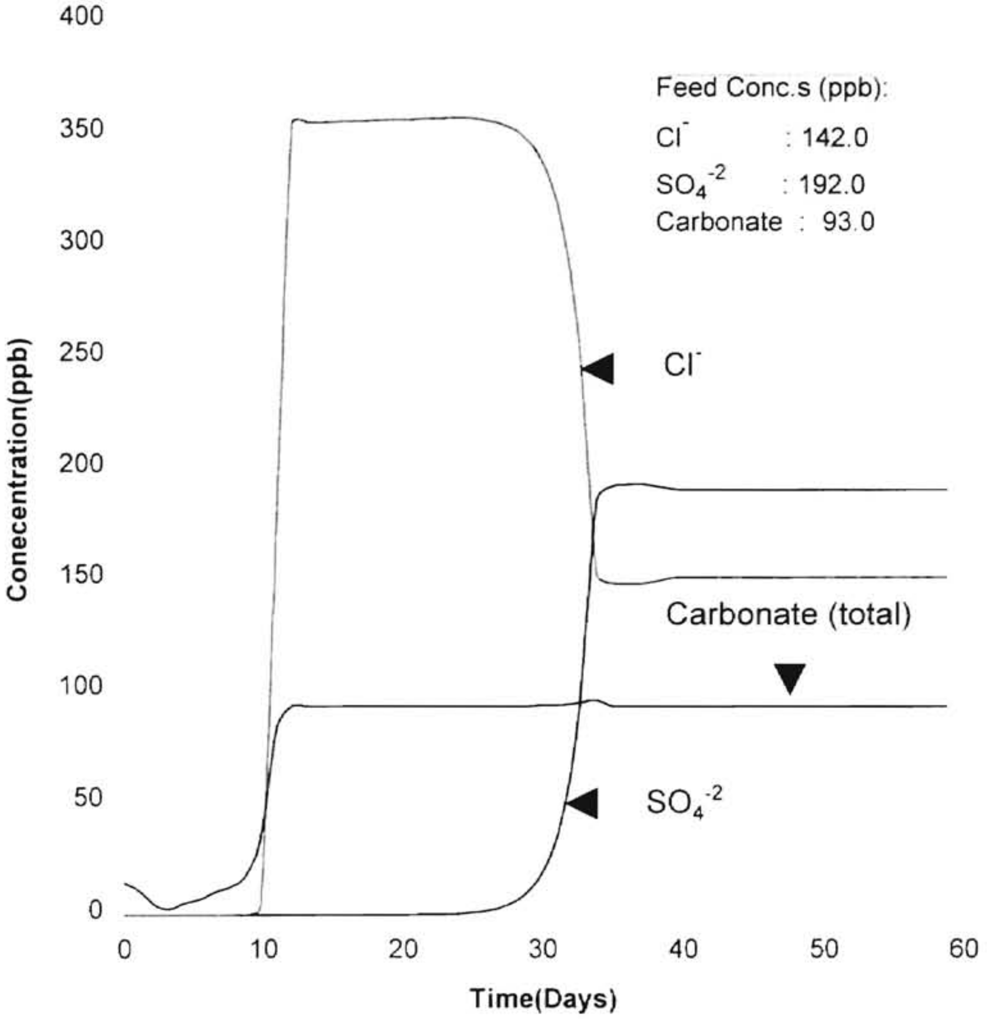

Figure 8. Breakthrough Curves for Anions - Case II

the parts per billion of the undissociated carbonate (H_2CO_3). Carbonate started to breakthrough with chloride. This may be because of the dominant effect of bicarbonate, which is a monovalent, in the total carbonate concentration.

Effect of Resin Fouling

Resin fouling is a very common phenomenon in ion exchange. Resin fouling effects the mass transfer of the ions during the ion exchange process. The effect of resin fouling on the performance of a mixed bed ion exchange column was studied using the model. The percentage resin fouling is simulated by multiplying the theoretical mass transfer coefficients with a fouling factor. The breakthrough curves of the ions for 20% fouling, 40% fouling , and 60% fouling are compared against a base case with no fouling. The input parameters for the base case are presented in Table XX.

The effect of resin fouling on the initial leakages of cations considered in this case is shown in Table XXI. There was no significant effect of resin fouling on sodium leakage at 20% and 40% fouling. At 60% fouling, the initial leakage of sodium increased by two orders in magnitude. Resin fouling did not have a significant effect on the initial leakage of potassium for 20% and 40% fouling. There was a 98% increase at 60% resin fouling. Resin fouling showed a significant effect on calcium leakage. The initial leakage of calcium increased by an order of magnitude for every 20% increase in fouling.

Table XXII shows the initial leakages of anions for different values of resin fouling. Resin fouling did not have any effect on the initial leakages of chloride and nitrate. This indicates that the leakages of chloride and nitrate are the equilibrium

TABLE XX

Input Data for the Base Case of Resin Fouling

Property	Value
Bed diameter (cm)	152.4
Resin depth (cm)	91.6
Cation-to-anion exchange resin (volumetric ratio)	0.34 : 0.66
Resin bead diameter (cm)	
Cation (Ambersep UP132)	0.06
Anion (Ambersep UP440)	0.05
Resin capacity (meq/ml)	
Cation	2.0
Anion	1.0
Temperature (°C)	60
Influent concentration (ppb)	
Cations:	
Sodium (Na^+)	160.0
Potassium (K^+)	20.0
Calcium (Ca^{+2})	10.0
Anions:	
Chloride (Cl^-)	60.0
Nitrate (NO_3^-)	80.0
Carbonate (total)	682.0
Initial loading on the resin (%)	
Cations:	
Sodium (Na^+)	0.1
Potassium (K^+)	0.1
Calcium (Ca^{+2})	0.1
Anions:	
Chloride (Cl^-)	0.1
Nitrate (NO_3^-)	0.1
Carbonate (total)	0.1
Bed void fraction	0.35
Influent flow rate (cm^3/s)	1.325E+4 (10.7 gpm/ft^2)

leakages. The initial leakages of carbonate were affected by resin fouling. There was a 44% increase in the initial leakage of carbonate at 60% resin fouling.

TABLE XXI

Effect of Resin Fouling on Initial Leakages of Cations

%Fouling	Sodium (ppb)	Potassium (ppb)	Calcium (ppb)
0	4.69E-04	4.8E-04	1.59E-05
20	4.75E-04	4.83E-04	2.04E-04
40	7.38E-04	4.91E-04	1.57E-03
60	2.02E-02	9.72E-04	3.14E-02

TABLE XXII

Effect of Resin Fouling on Initial Leakages of Anions

%Fouling	Chloride (ppb)	Nitrate (ppb)	Carbonate (ppb)
0	4.7E-05	2.8E-05	3.11
20	4.7E-05	2.8E-05	3.26
40	4.7E-05	2.8E-05	3.58
60	4.7E-05	2.8E-05	4.47

Figure 9 shows the sodium breakthrough curves for different resin fouling percentages. Sodium started to breakthrough around 28 days when there was no fouling. The breakthrough time decreased to 25 days at 20% fouling and to 21 days at 40% fouling. Sodium started to break around 13 days of column operation at 60% resin

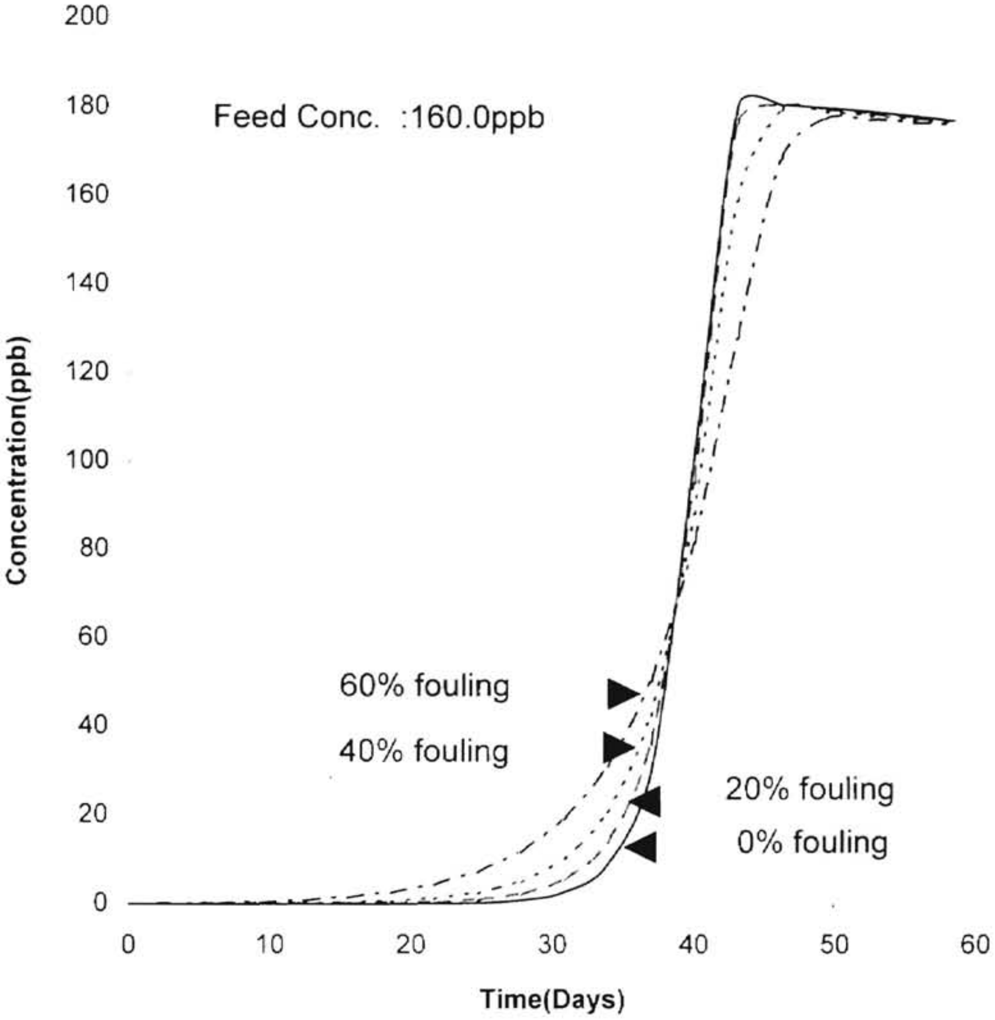

Figure 9. Effect of Resin Fouling on Sodium Breakthrough

fouling. A comparison of the potassium breakthrough curves is shown in Figure 10. Potassium breakthrough was around 37 days when there was no fouling. The breakthrough time for potassium was around 33 days at 20% fouling and around 30 days at 40 % fouling. At 60% fouling potassium started to breakthrough around 27 days.

A comparison of the calcium breakthrough curves predicted for the four different levels of fouling is shown in Figure 11. Calcium started to breakthrough around 350 days when there was no fouling. At 20% fouling the breakthrough time was 300 days and at 40% fouling it was 200 days. Calcium breakthrough started around 150 days at 60% fouling. Unlike sodium and potassium, resin fouling had a significant effect on the calcium breakthrough.

The effect of resin fouling on chloride breakthrough can be seen in Figure 12. Chloride started to breakthrough around 12 days when there was no fouling. There was no significant effect on the breakthrough time of chloride at 20% and 40 % fouling. There was a slight decrease in breakthrough time of chloride at 60% fouling. Figure 13 shows the effect of resin fouling on nitrate breakthrough. There was no significant difference in the breakthrough time of nitrate at 0% fouling, 20% fouling, and 40% fouling. Nitrate started to breakthrough around 300 days in all the above three cases. Nitrate breakthrough started around 260 days at 60% fouling. As shown in Figure 14, carbonate breakthrough was not affected by the resin fouling. This may be due to carbonate starting to breakthrough only after two days of column operation even at 0% fouling due to its high feed concentration.

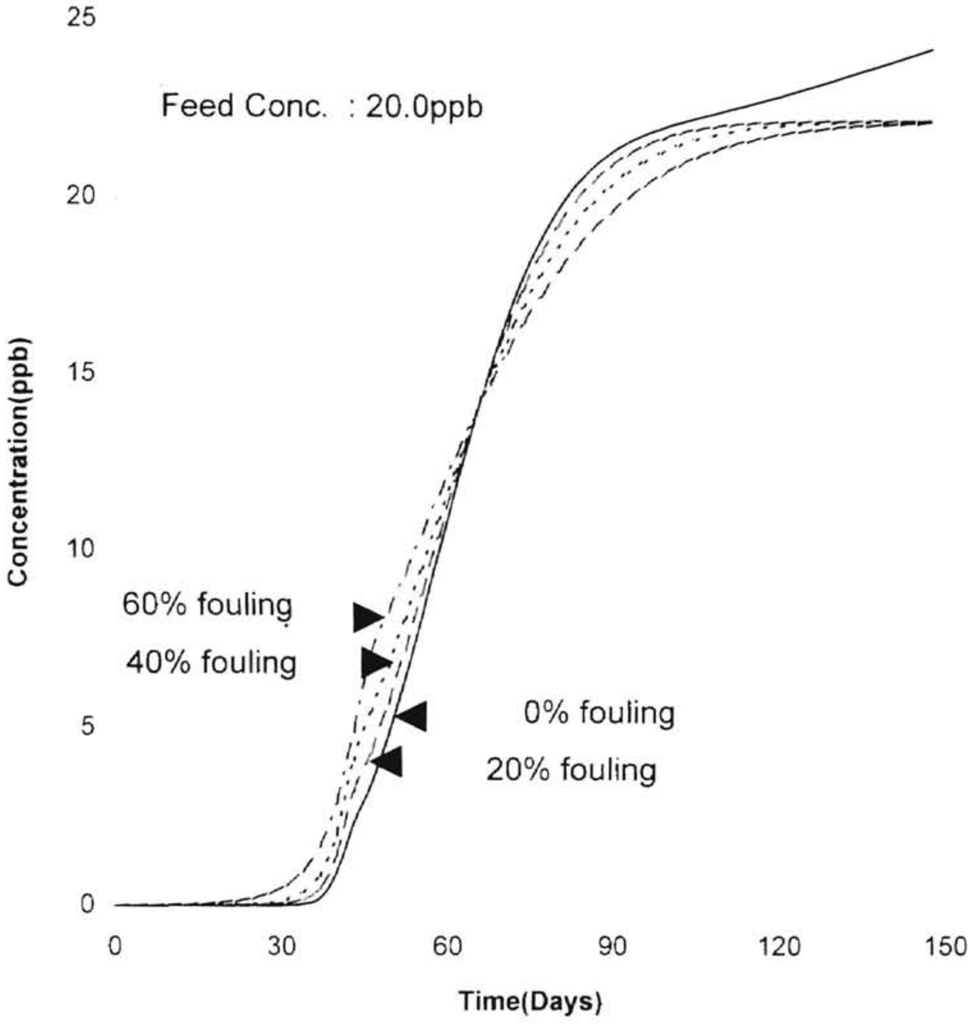

Figure 10. Effect of Resin Fouling on Potassium Breakthrough

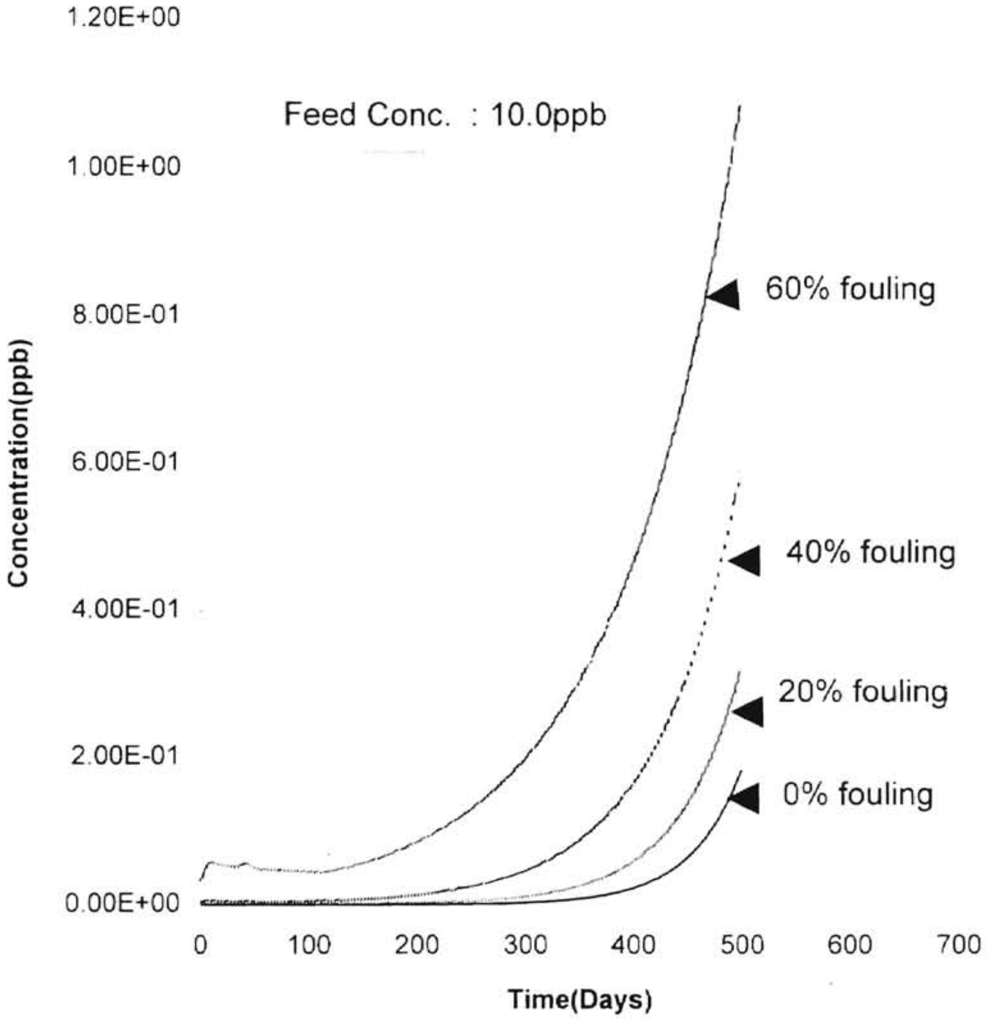

Figure 11. Effect of Resin Fouling on Calcium Breakthrough

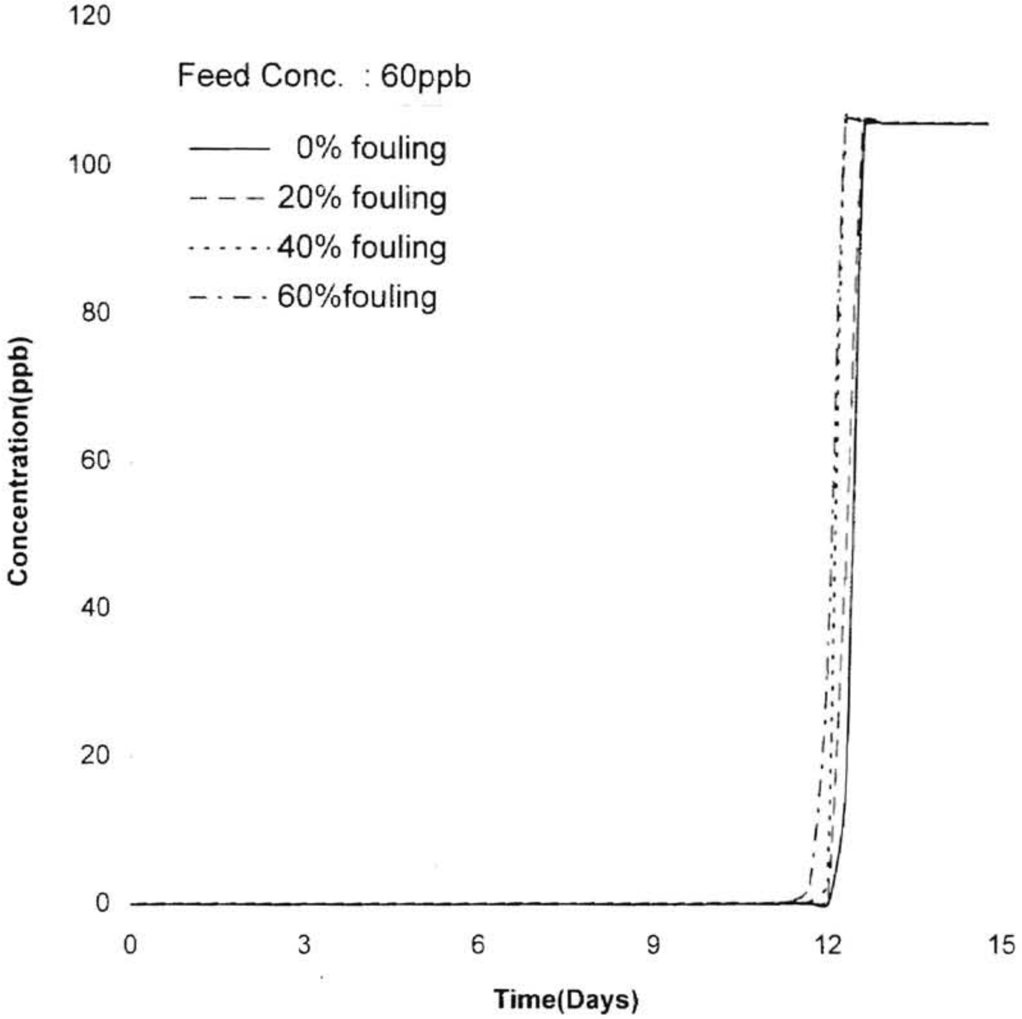

Figure 12. Effect of Resin Fouling on Chloride Breakthrough

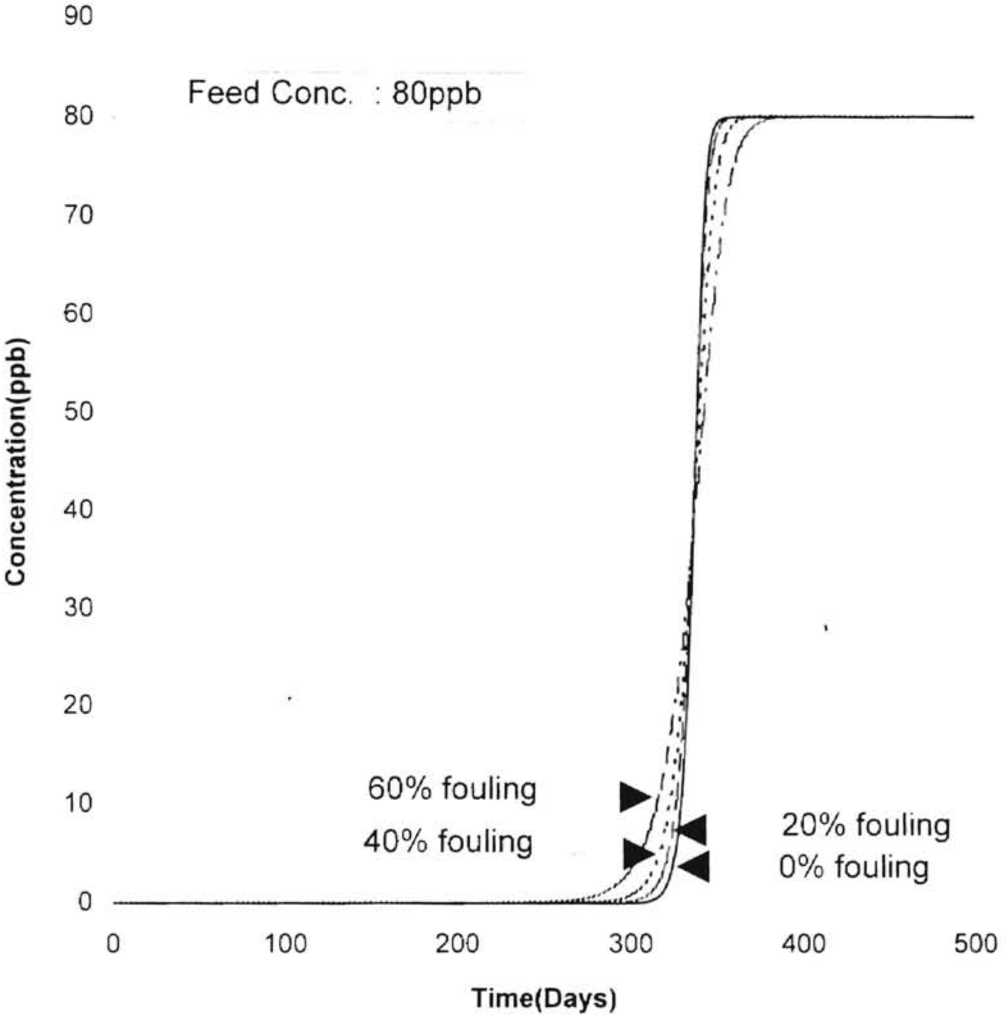

Figure 13. Effect of Resin Fouling on Nitrate Breakthrough

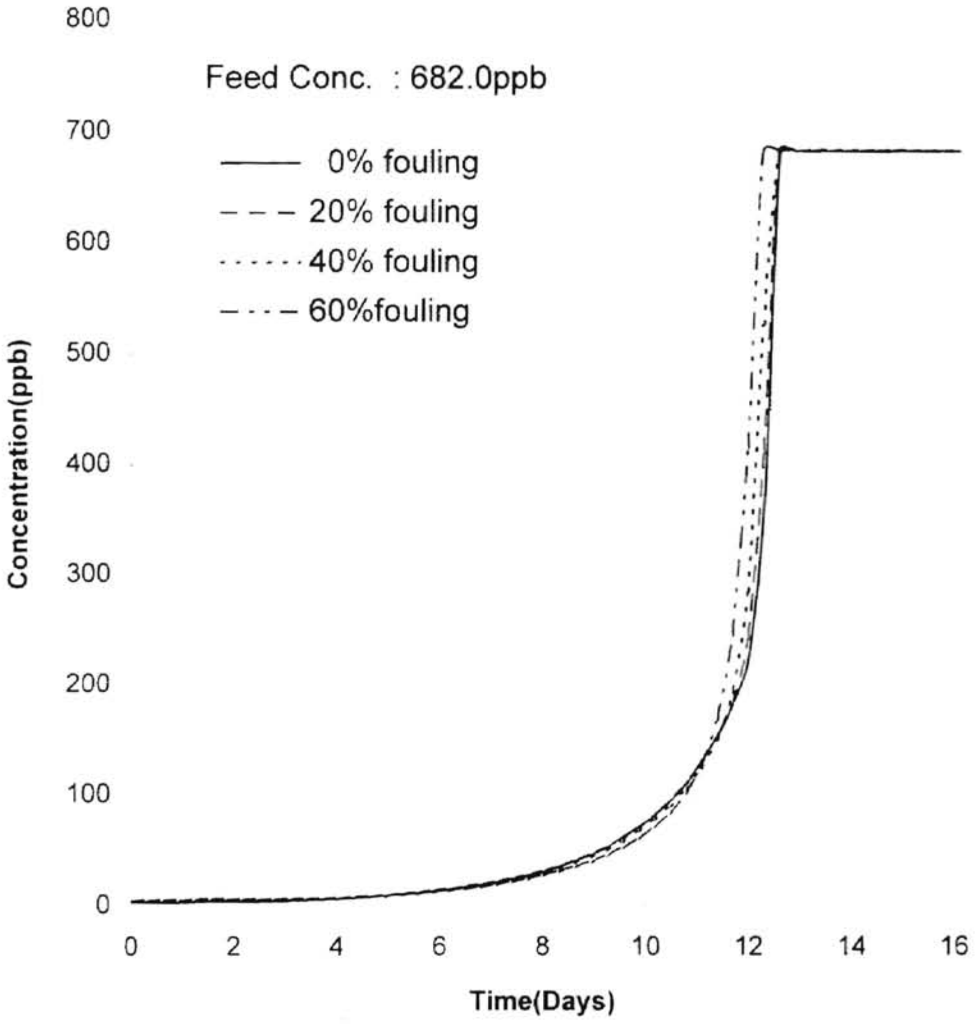

Figure 14. Effect of Resin Fouling on Carbonate Breakthrough

Conclusions and Recommendations

A model to predict the effluent breakthrough curves from a mixed-bed ion exchange column was developed. The model is used to predict the breakthrough curves using real plant conditions. The results predicted by this model agree conceptually with what would be expected. Due to the lack of experimental data for multicomponent systems at ultra-low concentrations, the model's quantitative capabilities could not be evaluated. Since industrial data is difficult to find, the model has to be evaluated by generating experimental data in the laboratory.

In the test cases run using this model, ions with lower valency started to breakthrough earlier than the ions with higher valency. Among the ions with same valence, ions with lower selectivity started to breakthrough earlier. Also, all the ions except the ion with highest valency and selectivity showed ion throw. Resin fouling resulted in higher initial leakages and earlier breakthrough times for most of the ions considered in the study.

Among the partially dissociative species only monovalent amines and carbonates are handled in the model. A generalized model could not be developed to handle all the partially dissociative species because of their varied chemistry. However, the current model can be modified to handle additional partially dissociative species.

The results predicted by this model are sensitive to the input parameters like selectivities, diffusivities, and dissociation constants. All these parameters are temperature dependent and there is a lack of proper data for these input parameters for some ionic species. There is a need to find accurate data for these parameters.

The runtime of the computer code implementing this model is dependent on the input data. The computer code may take huge runtimes for certain input data, especially if the input has partially dissociative species. Sometimes very small distance and time increments may be required to avoid errors and instability in the predictions resulting in huge runtimes. This is due to the limitations of the numerical methods used in this code. There is a need to study the numerical methods that can be effectively used to handle the equations involved in this model. Also, since most of the calculations in this code are done in iterative loops the run-time can be reduced considerably by avoiding repetitive calculations in these loops.

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APPENDIX A

EQUILIBRIUM RELATIONSHIPS

I. AMINE EQUILIBRIUM EQUATIONS

The equilibrium reaction between a monovalent amine and water is

$$\text{Amine} + H_2O \Leftrightarrow \text{Amine}^+ + OH^- \tag{A-1}$$

The dissociation constant for the above reaction can be written as:

$$K_a = \frac{[\text{Amine}^+][OH^-]}{[\text{Amine}]} \tag{A-2}$$

But the total concentration of amine should be

$$C_{Ta} = [\text{Amine}] + [\text{Amine}^+] \tag{A-3}$$

From equations (A-2) and (A-3) we can derive the relationship between [Amine$^+$] and [H$^+$] as

$$[\text{Amine}^+] = \frac{Ka.C_{Ta}}{Ka + [OH^-]} \tag{A-4}$$

This relation can be used to eliminate [Amine$^+$] from the charge balance equation to write it in terms of only [H$^+$].

II. CARBONATE EQUILIBRIUM EQUATIONS

Carbonic species dissolved in water exist in four different forms: dissolved CO_2, carbonic acid H_2CO_3, and the ions HCO_3^- and CO_3^{2-} (Loewenthal and Marias, 1982). The sum of these concentrations in the solution is the total carbonic species concentration (TCC). The carbonic species together with hydrogen and hydroxyl ions of the water exist in a state of dynamic equilibrium described by the following reactions:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \tag{A-5}$$

$$H_2CO_3 \xleftrightarrow{K_1} H^+ + HCO_3^- \tag{A-6}$$

$$HCO_3^- \xleftrightarrow{K_2} H^+ + CO_3^{2-} \tag{A-7}$$

$$H_2O \xleftrightarrow{K_W} H^+ + OH^- \tag{A-8}$$

It is assumed that the concentration of dissolved CO_2 is negligible when compared to that of HCO_3^-/CO_3^{2-}. This will let us define

$$[H_2CO_3] + [CO_2] = [H_2CO_3^*] \tag{A-9}$$

This way, we would be able to eliminate one unknown quantity. Now the dissociation constants can be written as:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \tag{A-10}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{A-11}$$

$$K_W = [H^+][OH^-] \tag{A-12}$$

The total carbonic species concentration in solution , C_{Tc}, is defined as:

$$C_{Tc} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{A-13}$$

Once the total carbonic species concentration C_{Tc} of the input water is given, equations relating the concentrations of each of the individual ions with the hydrogen ion concentration can be derived for equilibrium conditions as follows:

Solving for the carbonate and carbonic acid species concentrations, we have

$$[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{K_1} \tag{A-14}$$

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} \tag{A-15}$$

Substituting equations A-14 and A-15 in equation A-13 would lead to

$$C_{Tc} = \frac{[H^+][HCO_3^-]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]} \tag{A-16}$$

Now an expression for bicarbonate concentration can be written as:

$$[HCO_3^-] = \frac{C_{Tc}}{X} \tag{A-17}$$

where X is

$$X=\frac{\left[H^{+}\right]}{K_1}+\frac{K_2}{\left[H^{+}\right]}+1 \qquad \text{(A-18)}$$

The expressions for the concentrations of other ions can now be written as:

$$\left[H_2CO_3^{\bullet}\right]=\frac{\left[H^{+}\right]C_{Tc}}{K_1X} \qquad \text{(A-19)}$$

$$\left[CO_3^{2-}\right]=\frac{K_2C_{Tc}}{\left[H^{+}\right]X} \qquad \text{(A-20)}$$

The above relations are used to express the concentrations of the carbonic species in terms of the hydrogen ion concentration in the charge balance equation.

APPENDIX B

INTERFACIAL CONCENTRATIONS

Interfacial concentrations (solid-film interface) of the ions are determined using ion exchange equilibria. Local equilibrium at the solid-film interface is assumed. The selectivity coefficient expression for a general case of ion B replacing ion A, can be written using mass action law, as

$$K_A^B = \left(\frac{q_B}{C_B^*}\right)^{Z_A}\left(\frac{C_A^*}{q_A}\right)^{Z_B} \tag{B-1}$$

where q is the resin phase concentration and C^* is the interfacial concentration.

For any ion 'i' we can express the resin phase concentration and the interfacial concentration as

$$q_i = Y_i Q \tag{B-2}$$

$$C_i^* = X_i^* C_T^* \tag{B-3}$$

Equation (B-1) can be written in terms of equivalent fractions, total resin capacity and total interfacial concentration as follows:

$$K_A^B = \left(\frac{Y_B}{X_B^*}\right)^{Z_A}\left(\frac{X_A^*}{Y_A}\right)^{Z_B} Q^{(Z_A - Z_B)} C_T^{*(Z_B - Z_A)} \tag{B-4}$$

Rearranging the above equation the interfacial fractional concentration of ion B can be expressed as

$$X_B^* = Y_B \left(K_A^B\right)^{-1/Z_A} \left(\frac{X_A^*}{Y_A}\right)^{Z_B/Z_A} \left(\frac{Q}{C_T^*}\right)^{1-Z_B/Z_A} \tag{B-5}$$

Generalizing the above expression, the interfacial fractional concentration of an ion 'i' exchanging for an ion 'A' can be written as

$$X_i^* = Y_i \left(K_A^i\right)^{-1/Z_A} \left(\frac{X_A^*}{Y_A}\right)^{Z_i/Z_A} \left(\frac{Q}{C_T^*}\right)^{1-Z_i/Z_A} \tag{B-6}$$

If we have 'n-1' ions exchanging for ion A we can write 'n-1' such equations. But we have 'n' unknowns. The extra equation needed to completely specify the system is obtained from material balance at the solid-film interface.

$$\sum_{i=1}^{n} X_i^* = 1.0 \tag{B-7}$$

Rewriting the interfacial fractional concentrations as

$$X_i^* = \lambda_i \left(X_A^*\right)^{\frac{Z_i}{Z_A}} \tag{B-8}$$

where $\lambda_i = Y_i \left(K_A^i\right)^{-1/Z_A} \left(Y_A\right)^{-Z_i/Z_A} \left(\frac{Q}{C_T^*}\right)^{1-Z_i/Z_A}$ (B-9)

and substituting these in equation (B-7) we have

$$X_A^* + \sum_{i=1}^{n-1} \lambda_i \left(X_A^*\right)^{\frac{Z_i}{Z_A}} = 1 \qquad \text{(B-10)}$$

This is a polynomial in X_A^* and could be solved using an iteration technique. Regula-Falsi method was used in this work. In the above equations, the total interfacial concentration, C_T^*, is still unknown. The expression for this is derived in Appendix C.

APPENDIX C

IONIC FLUX EXPRESSIONS

Flux expressions describing multicomponent ion exchange process are derived using Nernst-Planck model and basic principles of ion exchange. Haub and Foutch (1984) and Zecchini and Foutch (1990) successfully applied Nernst-Planck model to describe film diffusion controlled mixed bed ion exchange process. A similar approach will be followed to derive the necessary flux expressions.

The Nernst-Planck equation is used to describe the flux of a given species within the static film that is assumed around the resin bead. Neglecting the curvature of the film, this expression is:

$$J_i = -D_i\left(\frac{\partial C_i}{\partial r} + \frac{C_i Z_i F}{RT}\frac{\partial \phi}{\partial r}\right) \qquad \text{(C-1)}$$

where ϕ is the electric potential and Z_i is the ion valence. Assuming pseudo steady state allows us to replace the partial derivatives by ordinary derivatives. The flux expressions derived in this model are based on bulk-phase neutralization.

The conditions that must be satisfied within the film surrounding the resin are:

$$\sum Z_i C_i = \sum Z_j C_j \qquad \text{(Electroneutrality)} \qquad \text{(C-2)}$$

where 'i' stands for counterions and 'j' stands for coions.

$$Z_j J_j = 0 \qquad \text{(No coion flux)} \qquad \text{(C-3)}$$

$$\sum Z_i J_i = \sum Z_j J_j \qquad \text{(No net current flow)} \qquad \text{(C-4)}$$

From Equations C-3 and C-4 we have

$$\sum Z_i J_i = 0 \qquad \text{(No net current flow)} \qquad \text{(C-5)}$$

The total equivalent ion concentration can be defined as:

$$C_T = \omega \sum_{i=1}^{n} Z_i C_i = \omega_j \sum_{j=1}^{m} Z_j C_j \qquad \text{(C-6)}$$

where 'n' is the number of counterions, 'm' is the number of coions and ω =+1 for cations and -1 for anions.

Using the no coion flux condition (Equation C-3), we have

$$\frac{d\phi}{dr} = -\frac{RT}{F} \frac{Z_j \frac{dC_j}{dr}}{Z_j^2 C_j} \qquad \text{(C-7)}$$

From the no coion flux condition we have that the sum of the coion fluxes in the film is also zero. Now the electric potential term in the Nernst-Planck equation can be eliminated in terms of the total equivalent concentration as:

$$\frac{d\phi}{dr} = -\frac{RT}{F} \frac{\sum_{j=1}^{m} Z_j \frac{dC_j}{dr}}{\sum_{j=1}^{m} Z_j^2 C_j} \qquad \text{(C-8)}$$

Introducing a mean coion valence defined as

$$Z_Y = \frac{\sum_{j=1}^{m} Z_j^2 C_j}{\sum_{j=1}^{m} Z_j C_j} \tag{C-9}$$

and combining with the definition for total concentration (Equation C-6), Equation C-8 reduces to

$$\frac{d\phi}{dr} = \frac{-RT}{Z_Y F} \frac{1}{C_T} \frac{dC_T}{dr} \tag{C-10}$$

Now the Nernst-Planck expression for counterions can be written as:

$$J_i = -D_i \left(\frac{dC_i}{dr} - \frac{C_i Z_i}{C_T Z_Y} \frac{dC_T}{dr} \right) \tag{C-11}$$

Using the no net current flow condition (Equation C-5) and Equation C-11, we get

$$\sum_{i=1}^{n} Z_i D_i \frac{dC_i}{dr} + \sum_{i=1}^{n} Z_i D_i N_i \frac{C_i}{C_T} \frac{dC_T}{dr} = 0 \tag{C-12}$$

where $N_i = -\frac{Z_i}{Z_Y}$.

For monovalent system of ions or equal valence system of ions, the above equation could be easily integrated to obtain a relation between C_i and C_T. This is not possible in the case of arbitrary valences. At this point the method proposed by Franzreb (1993) is used to proceed further. In this method, Equation C-11 is differentiated to eliminate the unknown J_i. This leads to a homogeneous second order differential equation:

$$\frac{d^2C_i}{dr^2}+\frac{N_i}{C_T}\frac{dC_i}{dr}\frac{dC_T}{dr}+N_i\frac{C_i}{C_T}\left(\frac{d^2C_T}{dr^2}-\frac{1}{C_T}\left(\frac{dC_T}{dr}\right)^2\right)=0 \tag{C-13}$$

This method leads to an exact solution for the case of equal valences and only an approximation for the case of arbitrary valences. For counterions of equal valences, summation of Equation 13 for all the ions leads to

$$\sum_{i=1}^{n}\frac{d^2C_i}{dr^2}+\frac{1}{C_T}\frac{dC_T}{dr}\sum_{i=1}^{n}N_i\frac{dC_i}{dr}+\frac{1}{C_T}\frac{d^2C_T}{dr^2}\sum_{i=1}^{n}N_iC_i-\frac{1}{C_T^2}\left(\frac{dC_T}{dr}\right)^2\sum_{i=1}^{n}N_iC_i=0 \tag{C-14}$$

Substituting Equation C-6 and its derivatives in the above leads to

$$\frac{d^2C_T}{dr^2}=0 \tag{C-15}$$

From the above equation it can be understood that for the case of counterions of equal valences, the profile of the total concentration in the film is linear. Zecchini and Foutch (1990) arrived at the same conclusion in their model for univalent ternary ions. The above equation combined with Equation C-6 can be used to obtain relationships between the derivatives of C_i and C_T. Substitution of all these derivatives in Equation C-14 leads to

$$\frac{d^2C_i}{dC_T^2}+\frac{N_i}{C_T}\frac{dC_i}{dC_T}-\frac{N_iC_i}{C_T^2}=0 \tag{C-16}$$

This is the Euler's differential equation the solution of which is

$$Z_iC_i = A_iC_T + B_iC_T^{-P} \tag{C-17}$$

For the case of equal valences, we have $P = N_i$. Using the boundary conditions

$$r = 0, C_T = C_T^{\bullet}$$
$$r = \delta, C_T = C_T^{o}$$

the values of the parameters A_i and B_i can be determined as follows:

$$A_i = \frac{1}{C_T^o}\left(Z_iC_i^o - B_i\left(C_T^o\right)^{-P}\right. \tag{C-18}$$

and

$$B_i = \omega\frac{X_i^{\bullet} - X_i^o}{\left(C_T^{\bullet}\right)^{-P-1} - \left(C_T^o\right)^{-P-1}} \tag{C-19}$$

Equation C-17 gives us a relation between the individual ion concentrations, C_i and the total equivalent concentration, C_T. Substituting for C_i and its derivative in the modified Nernst-Planck Equation (C-11), we get the following flux expression:

$$J_i = -\frac{D_i}{Z_i}\frac{dC_T}{dr}\left[\left(A_i - PB_iC_T^{-P-1}\right) + N_i\left(A_i + B_iC_T^{-P-1}\right)\right) \tag{C-20}$$

For the case of arbitrary valences, Equation C-17 is only an approximation. In this case however. N_i is not the same for all the counterions and hence, P cannot be equal to N_i. Combining the above equation with the condition of no net current flow (Equation C-5) results in

$$\left(\sum_{i=1}^{n} D_i A_i + \sum_{i=1}^{n} N_i D_i A_i\right) + \left(\sum_{i=1}^{n} N_i D_i B_i - P\sum_{i=1}^{n} D_i B_i\right) C_T^{-P-1} = 0 \qquad \text{(C-21)}$$

The only way the above equation can hold true is when both the terms are equal to zero. That leads to

$$\sum_{i=1}^{n} (1 + N_i) D_i A_i = 0 \qquad \text{(C-22)}$$

Substitution of A_i (Equation C-18) in to above and some mathematical manipulations gives the desired expression for total interfacial concentration, C_T^*:

$$C_T^* = \left(\frac{\sum_{i=1}^{n} (1 + N_i) D_i X_i^{o}}{\sum_{i=1}^{n} (1 + N_i) D_i X_i^{*}} \right)^{1/P+1} C_T^{o} \qquad \text{(C-23)}$$

Equating the second parentheses term to zero and substitution of B_i would give us the expression for the exponent P as:

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^{*} - X_i^{o}\right)}{\sum_{i=1}^{n} D_i \left(X_i^{*} - X_i^{o}\right)} \qquad \text{(C-24)}$$

In an equal valance case, P is equal to Ni and in an arbitrary case, it would be in the neighborhood of Ni. The concentrations involved in this work are very low and lead to lot of numerical errors and instability. Because of numerical discrepancies, sometimes the value of P computed in the code is unusually high and leads to problems in further computations. Hence the expression for P (Equation C-24) is modified as follows:

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^{*} - X_i^{o}\right)}{\sum_{i=1}^{n} D_i \left(X_i^{*} - X_i^{o}\right)}$$

Once again substitution of the above equations into C-11 and integrating between the boundary conditions given earlier, We would get the final desired form of the ionic flux expression:

$$J_i = \frac{D_i}{\delta}\left((1-\frac{N_i}{P})(C_i^{*} - C_i^{o}) + N_i A_i (1+\frac{1}{P})(C_T^{*} - C_T^{o})\right) \qquad \text{(C-25)}$$

Particle Rates

The rate of exchange is related to the flux of the species by:

$$\frac{d < C_i >}{dt} = -J_i a_s \qquad \text{(C-26)}$$

The resin phase concentration $< C_i >$can be represented as:

$$< C_i >= y_i Q \qquad \text{(C-27)}$$

Now Equation 3-17 can be written as

$$\frac{dy_i}{dt} = \frac{-J_i a_s}{Q} \qquad \text{(C-28)}$$

The rate of ion loadings in to the resin can be determined using the above equation once the individual ionic fluxes are known.

The effective diffusivity is defined as:

$$D_e = \frac{\sum_{i=1}^{n} \left| J_i \delta \right|}{\sum_{i=1}^{n} \left| C_i^{*} - C_i^{O} \right|} \tag{C-29}$$

The film thickness in Equation C-25 is eliminated using the relation

$$\delta = D_e/K \tag{C-30}$$

where K is a mass transfer coefficient found from Dwivedi and Upadhyay's correlation.

$$K = \frac{D_i}{d_p} Sc^{1/3} \, Re \left[\frac{0.765}{(\varepsilon \, Re)^{0.82}} + \frac{0.365}{(\varepsilon \, Re)^{0.386}} \right] \tag{C-31}$$

In the above Equation, D_i is the diffusivity of ion 'i', d_p is the particle diameter , Re is Reynolds number, Sc is Schmidt number and ε is void fraction.

Schmidt number (Sc) is defined using the effective diffusivity as

$$Sc = \frac{\mu}{\rho D_e} \tag{C-32}$$

Substituting Equation C-30 in the flux expression (Equation C-25), we get

$$\frac{J_i}{K} = \frac{D_i}{D_e} \left((1 - \frac{N_i}{P})(C_i^{*} - C_i^{O}) + N_i A_i (1 + \frac{1}{P})(C_T^{*} - C_T^{O}) \right) \tag{C-33}$$

This J_i/K is computed for each of the ions in the subroutines and returned to the main program, in the computer code developed for this model.

APPENDIX D

COLUMN MATERIAL BALANCES

Material balance equations around the column are required for determining the effluent concentration profiles. These material balances will use previously determined rate expressions for individual species. The overall column material balance for species i is given as:

$$\frac{u_s}{\in}\frac{\partial C_i}{\partial Z} + \frac{\partial C_i}{\partial t} + \frac{(1-\in)}{\in}\frac{\partial q_i}{\partial t} = 0 \qquad \text{(D-1)}$$

where :

u_s= superficial velocity, and = void fraction.

This expression can be simplified by using dimension-less variables in time and distance. The dimension-less expressions are expressed as:

$$\tau = \frac{K_i C_T^f}{d_p Q}\left(t - \frac{\in Z}{u_s}\right) \qquad \text{(D-2)}$$

and,

$$\xi = \frac{K_i(1-\in)}{u_s}\frac{Z}{d_p} \qquad \text{(D-3)}$$

K_i is the non-ionic mass transfer coefficient for species i, d_p is the particle diameter, Q is the resin capacity and C_T^f is the total cationic feed concentration. The above expressions are differentiated with respect to time and distance respectively to yield:

$$\frac{\partial\tau}{\partial t} = \frac{K_i C_T^f}{d_p Q}, \qquad \frac{\partial\tau}{\partial Z} = \frac{K_i C_T^f \in}{d_p Q u_s},$$

$$\frac{\partial\xi}{\partial t} = 0 \text{ and } \qquad \frac{\partial\xi}{\partial Z} = \frac{K_i C_f^T}{d_p Q u_s}$$

Now using the chain rule the original derivatives are expressed as:

$$\frac{\partial C_i}{\partial Z} = \frac{\partial C_i}{\partial\xi}\left(\frac{\partial\xi}{\partial Z}\right) + \frac{\partial C_i}{\partial\tau}\left(\frac{\partial\tau}{\partial Z}\right) = \frac{K_i(1-\in)}{u_s d_p}\left(\frac{\partial C_i}{\partial\xi}\right) - \frac{K_i C_T^f \in}{d_p u_s Q}\left(\frac{\partial C_i}{\partial\tau}\right) \qquad \text{(D-3)}$$

$$\frac{\partial q_i}{\partial t} = \frac{\partial q_i}{\partial\tau}\left(\frac{\partial\tau}{\partial t}\right) + \frac{\partial q_i}{\partial\xi}\left(\frac{\partial\xi}{\partial t}\right) = \frac{K_i C_T^f}{d_p Q}\frac{\partial q_i}{\partial\tau} + 0\,\frac{\partial q_i}{\partial\xi} \qquad \text{(D-4)}$$

Replacing these into the material balance yields:

$$\frac{\partial C_i}{\partial\xi} + \frac{C_T^f}{Q}\frac{\partial q_i}{\partial\tau} = 0 \qquad \text{(D-5)}$$

This expression is easier to handle. Introducing the fractions in liquid phase and resin phase as:

$x_i = C_i / C_T^f$, and $q_i = Qy_i$

This substitution into the material balance equation yields:

$$\frac{\partial x_i}{\partial\xi} + \frac{\partial y_i}{\partial\tau} = 0 \qquad \text{(D-6)}$$

In the current code, chloride is selected as the reference species. Since all the material balance is to be solved using same steps in τ and ξ, expressions for the base species result as:

$$\tau = \tau_c = \frac{K_c C_T^f}{d_{pa} Q_a}(t - \frac{\in Z}{u_s}) \qquad \text{(D-7)}$$

and

$$\xi = \xi_c = \frac{K_c(1 - \in)}{u_s d_{pa}} Z \qquad \text{(D-8)}$$

The partial derivatives of all the species can be written in terms of the reference ion as follows: Cations:

$$\frac{\partial x_i}{\partial \xi_c} = \frac{\partial x_i}{\partial \xi_i}(\frac{\partial \xi_i}{\partial \xi_c}) = \frac{K_i}{K_c}\frac{d_{pa}}{d_{pc}}\frac{\partial x_i}{\partial \xi_i} \qquad \text{(D-9)}$$

$$\frac{\partial y_i}{\partial \tau_c} = \frac{\partial y_i}{\partial \tau_i}(\frac{\partial \tau_i}{\partial \tau_c}) = \frac{K_i}{K_c}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c}\frac{\partial y_i}{\partial \tau_i} \qquad \text{(D-10)}$$

and anions:

$$\frac{\partial x_i}{\partial \xi_c} = \frac{\partial x_i}{\partial \xi_i}(\frac{\partial \xi_i}{\partial \xi_c}) = \frac{K_i}{K_c}\frac{\partial x_i}{\partial \xi_i} \qquad \text{(D-11)}$$

$$\frac{\partial y_i}{\partial \tau_c} = \frac{\partial y_i}{\partial \tau_i}(\frac{\partial \tau_i}{\partial \tau_c}) = \frac{K_i}{K_c}\frac{\partial y_i}{\partial \tau_i} \qquad \text{(D-12)}$$

Replacing these partial derivatives into the general material balance equation and introducing the cation and anion resin volume fractions (FCR, FAR) within the bed, we get

$$\frac{\partial x_i}{\partial \xi_c} + \mathrm{FCR}\frac{\partial y_i}{\partial y_c} = 0 \qquad \text{(cations)} \qquad \text{(D-13)}$$

$$\frac{\partial x_i}{\partial \xi_c} + \mathrm{FAR}\frac{\partial y_i}{\partial y_c} = 0 \qquad \text{(anions)} \qquad \text{(D-14)}$$

Now the rate expressions developed earlier have to be modified to incorporate the dimensionless variables that have been introduced. This involves changing t to τ_c as the basis for each of the individual ions.

$$\frac{dy_i}{dt} = \frac{-J_i a_s}{Q} \qquad \text{(D-15)}$$

Changing from t to τ_i results:

$$\frac{dy_i}{d\tau} = \left(\frac{-J_i a_s}{Q}\right)\left(\frac{d_p Q}{K_i C_f}\right) \qquad \text{(D-16)}$$

Now changing from τ to τ_c basis and noting that $a_s d_p = 6$, we get

$$\frac{\partial y_i}{\partial \tau_c} = \left(-\frac{6J_i}{K_i C_f}\right)\frac{K_i}{K_c}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c} \qquad \text{(cations)} \qquad \text{(D-17)}$$

$$\frac{\partial y_i}{\partial \tau_c} = \left(-\frac{6J_i}{K_i C_f}\right)\frac{K_i}{K_c} \qquad \text{(anions)} \qquad \text{(D-18)}$$

This is the final form of the dimensionless rate equations that describe the exchange process. These are combined with the material balances to predict the column effluent concentrations.

APPENDIX E

COMPUTER CODE FOR EQUILIBRIUM MODEL

```
******************************************************************************
*      PROGRAM TO CALCULATE EQUILIBRIUM AND KINETIC LEAKAGES                 *
*      (APPLICABLE TO BOTH HYDROGEN AND AMINE CYCLES)                        *
*                                                                            *
*      DISCLAIMER: THIS COMPUTER CODE IS THE INTELLECTUAL PROPERTY           *
*                  OF OSU AND CANNOT BE USED WITHOUT THE EXPLICIT            *
*                  PERMISSION OF OKLAHOMA STATE UNIVERSITY                   *
*                                                                            *
*      DEVELOPED BY VINAY SUNKAVALLI & Dr. FOUTCH                            *
*                                                                            *
*      CODE LAST EDITED: JUNE 15, 1995                                       *
******************************************************************************
*    NOMENCLATURE:                                                           *
*                                                                            *
*    INPUT  VARIABLES:                                                       *
*                                                                            *
*    CYCLE          Hydrogen or amine cycle                                  *
*    NOCAT          Number of cations                                        *
*    NOAN           Number of anions                                         *
*    VACAT(I)       Valency of cation i                                      *
*    VAAN(I)        Valency of anion i                                       *
*    YCINIT(I)      Initial loading fraction of cation i  in the resin phase *
*    YAINIT(I)      Initial loading fraction of anion i  in the resin phase  *
*    SELC(I)        Selectivity of cation  i                                 *
*    SELA(I)        Selectivity of anion  i                                  *
*    CATEW(I)       Equivalent weight  of cation i                           *
*    ANEW(I)        Equivalent weight of anion  i                            *
*    CAT_CAP        Capacity of the cationic resin (meq/ml)                  *
*    AN_CAP         Capacity of the anionic resin (meq/ml)                   *
*    FCR            Fraction of cationic resin                               *
*    FAR            Fraction of anionic resin                                *
*    CFCAT(I)       Feed concentration of cation  i  (meq/ml)                *
*    CFAN(I)        Feed concentration of  anion  i   (meq/ml)               *
*    DIFFCAT(I)     Diffusivity of cation i  ( cm2/s)                        *
*    DIFFAN(I)      Diffusivity of anion i  (cm2/s)                          *
*    CAT_DIA        Cationic bead diameter (cm)                              *
*    AN_DIA         Anionic bead diameter (cm)                               *
*    RES_HT         Resin bed depth (cm)                                     *
*    BED_DIA        Bed diameter (cm)                                        *
*    VOID_FRAC      Bed void fraction                                        *
*    TEMPC          Inlet water temperature in °C                            *
```

```
*   VOL_FLOW        Water flow rate (cm3/sec)                                          *
*   CTOT            Total concentration of amine (meq/ml)                              *
*   SELAM           Selectivity of  the amine relative to the hydrogen ion             *
*   PKA             Dissociation constant of the amine                                 *
*                                                                                      *
*   OTHER VARIABLES USED IN THE CODE:                                                  *
*                                                                                      *
*   TEMPK           Temperature in °K                                                  *
*   PKW             Dissociation constant of water                                     *
*   VAH             Valency of hydrogen ( Basis Cation )                               *
*   VAOH            Valency of hydroxide (Basis Anion )                                *
*   DEN             Water density                                                      *
*   CYCAT(I)        Concentration of cation  i  in resin phase                         *
*   CYAN(I)         Concentration of anion  i  in resin phase                          *
*   CYH             Concentration of  hydrogen /amine in the resin phase               *
*   CYOH            Concentration of hydroxide in the resin phase                      *
*   CXH             Equilibrium concentration of basis cation                          *
*   CXCAT(I)        Equilibrium concentration  of cation i                             *
*   CXAN(I)         Equilibrium concentration of anion  i                              *
*   VS              Superficial velocity                                               *
*   VISC            Viscosity                                                          *
*   REYCAT          Reynolds number for cations                                        *
*   REYAN           Reynolds number for anions                                         *
*   SCHCAT(I)       Schmidt number for cation i                                        *
*   SCHAN(I)        Schmidt number for anion  i                                        *
*   CATMTCT(I)      Mass transfer coefficient of cation i  calculated from correlation's *
*   ANMTCT(I)       Mass transfer coefficient of anion i  calculated from correlation's  *
*   CATMTCE(I)      Mass transfer coefficient of cation i  supplied by the user        *
*   ANMTCE(I)       Mass transfer coefficient of anion i  supplied by the user         *
*   CHTD            Dimensionless column height                                        *
*   NSLICES         Number of slices                                                   *
*   CXBCAT(I)       Concentration of cation i  in the  Bulk liquid  phase              *
*   CXBAN(I)        Concentration of anion i  in the Bulk liquid phase                 *
*   CTOTCAT         Sum of the cation concentrations ( excluding the basis cation) *
*   CTOTAN          Sum of the anion concentrations ( excluding the basis anion )      *
*   CHB             Hydrogen ion concentration in the bulk liquid phase                *
*   COHB            Hydroxyl ion concentration in the bulk liquid phase                *
*   COUTCAT(I)      Effluent concentration of cation i                                 *
*   COUTAN(I)       Effluent concentration of anion  i                                 *
*   POW             Power in the equation ( ratio of  the ionic valency to that of basis ions) *
*   XI              Dimensionless distance step                                        *
****************************************************************************************

      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1        SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2        VAH,VAOH,PKW,PKA,CTOT,SELAM
      DIMENSION   YCINIT(10),YAINIT(10),COUTAN(10),COUTCAT(10),
     1        CATEW(10),ANEW(10),CXBCAT(10),CXBAN(10),
     2        CFCAT(10),CFAN(10),ANMTC(10),CATMTC(10),
     3        CATFLUX(10),ANFLUX(10),DIFFCAT(10),DIFFAN(10),
     4        SCHCAT(10),SCHAN(10),ANMTCT(10),CATMTCT(10),
     5        ANMTCE(10),CATMTCE(10),KLEAKC(10),KLEAKA(10)
      CHARACTER*1  FLAG,FLAG1,FLAG2
      CHARACTER*20 INPFILE,OUTFILE
```

```
      INTEGER    CYCLE

C     ************************************************************
C     CORRELATIONS-KATAOKA & CARBERRY TO CALCULATE THE MASS TRANSFER
C     COEFFICIENTS BASED ON REYNOLDS & SCHMIDT  NUMBERS
C     ************************************************************
      F1(R,S) = 1.15*VS/(VOID_FRAC*(S**(2./3.))*(R**0.5))
      F2(R,S) = 1.85*VS*((VOID_FRAC/(1.-VOID_FRAC))**(1./3.))/
     1        (VOID_FRAC*(S**(2./3.))*(R**(2./3.)))

C     ************************************************************
C     INPUT DATA BLOCK
C     ************************************************************

      VAH=1.0  ! (VALENCY OF HYDROGEN ION)
      VAOH=-1.0 ! (VALENCY OF HYDROXYL ION)

      WRITE(*,*)'Do you want to input data from a file (Y/N)?'
      READ(*,201)FLAG
  201 FORMAT(1A)
      IF(FLAG.EQ.'Y'.OR.FLAG.EQ.'y')THEN
        WRITE(*,*)'Enter the input file name.'
        READ(*,202)INPFILE
  202   FORMAT(20A)
        OPEN(UNIT=9,FILE=INPFILE)
        READ(9,*)CYCLE

C     ************************************************************
C     READING THE INPUT DATA FOR CATIONS
C     ************************************************************

        READ(9,*)NOCAT
        READ(9,*)(VACAT(I),I=1,NOCAT)
        READ(9,*)(YCINIT(I),I=1,NOCAT)
        READ(9,*)(SELC(I),I=1,NOCAT)
        READ(9,*)(CATEW(I),I=1,NOCAT)
        READ(9,*)CAT_CAP
        READ(9,*)FCR
        READ(9,*)(CFCAT(I),I=1,NOCAT)
        READ(9,*)(DIFFCAT(I),I=1,NOCAT)

C     ************************************************************
C     READING THE INPUT DATA FOR ANIONS
C     ************************************************************

        READ(9,*)NOAN
        READ(9,*)(VAAN(I),I=1,NOAN)
        READ(9,*)(YAINIT(I),I=1,NOAN)
        READ(9,*)(SELA(I),I=1,NOAN)
        READ(9,*)(ANEW(I),I=1,NOAN)
        READ(9,*)AN_CAP
        READ(9,*)FAR
        READ(9,*)(CFAN(I),I=1,NOAN)
        READ(9,*)(DIFFAN(I),I=1,NOAN)
```

```
C     ***************************************************************
C     READING SOME GENERAL INPUT
C     ***************************************************************
       READ(9,*)AN_DIA,CAT_DIA
       READ(9,*)RES_HT,BED_DIA,VOID_FRAC
       READ(9,*)TEMPC,PH
       READ(9,*)VOL_FLOW

       IF(CYCLE.EQ.2) THEN
         READ(9,*)CTOT
         READ(9,*)SELAM
         READ(9,*)PKA
       ENDIF

      ELSE  !(i.e.,IF THE USER CHOOSES TO GIVE THE INPUT FROM SCREEN)

       WRITE(*,*) 'Input 1 for H-cycle or 2 for amine cycle'
       READ(*,*) CYCLE

C     ***************************************************************
C     READING THE INPUT DATA FOR CATIONS
C     ***************************************************************

       WRITE(*,*)'Input number of cations(excluding hydrogen for '
       write(*,*)'H-cycle and hydrogen & amine for amine cycle )'
       READ(*,*)  NOCAT
       WRITE(*,*)'Input their valences.'
       READ(*,*)  (VACAT(I),I=1,NOCAT)
       WRITE(*,*)'Input initial loading fractions, respectively.'
       READ(*,*)  (YCINIT(I),I=1,NOCAT)
       WRITE(*,*)'Input their selectivities relative to hydrogen.'
       READ(*,*)  (SELC(I),I=1,NOCAT)
       WRITE(*,*)'Input their equivalent weights.'
       READ(*,*)  (CATEW(I),I=1,NOCAT)
       WRITE(*,*)'Input the cationic resin capacity (meq/ml).'
       READ(*,*)  CAT_CAP
       WRITE(*,*)'Enter the cationic resin fraction by volume.'
       READ(*,*)  FCR
       WRITE(*,*)'Enter the cation inlet concentrations (meq/ml).'
       READ(*,*)  (CFCAT(I),I=1,NOCAT)
       WRITE(*,*)'Enter the ionic diffusivities (cm2/s).'
       READ(*,*)  (DIFFCAT(I),I=1,NOCAT)

C     ****************************************************************
C     READING THE INPUT DATA FOR ANIONS
C     ****************************************************************

       WRITE(*,*)'Input number of anions (excluding hydroxide).'
       READ(*,*)  NOAN
       WRITE(*,*)'Input their valences (negative).'
       READ(*,*)  (VAAN(I),I=1,NOAN)
       WRITE(*,*)'Input initial loading fractions, respectively.'
       READ(*,*)  (YAINIT(I),I=1,NOAN)
```

```
        WRITE(*,*)'Input their selectivities relative to hydroxide.'
        READ(*,*)  (SELA(I),I=1,NOAN)
        WRITE(*,*)'Input their equivalent weights.'
        READ(*,*)  (ANEW(I),I=1,NOAN)
        WRITE(*,*)'Input the anionic resin capacity (meq/ml).'
        READ(*,*)  AN_CAP
        WRITE(*,*)'Enter the anionic resin fraction by volume.'
        READ(*,*)  FAR
        WRITE(*,*)'Enter the anion inlet concentrations (meq/ml).'
        READ(*,*)  (CFAN(I),I=1,NOAN)
        WRITE(*,*)'Enter the ionic diffusivities (cm2/s).'
        READ(*,*)  (DIFFAN(I),I=1,NOAN)

C    *************************************************************
C    READING THE GENERAL INPUT
C    *************************************************************

        WRITE(*,*)'Enter the cation and anion particle diameters (cm).'
        READ(*,*)  CAT_DIA,AN_DIA
        WRITE(*,*)'Enter bed depth(cm), diameter(cm) and void fraction'
        READ(*,*)  RES_HT,BED_DIA,VOID_FRAC
        WRITE(*,*)'Input operating temperature (C) and pH.'
        READ(*,*)  TEMPC,PH
        WRITE(*,*)'Enter the inlet flow rate(cm3/s).'
        READ(*,*)  VOL_FLOW

        IF (CYCLE.EQ.2) THEN
          WRITE(*,*)'Input the total amine inlet conc. (meq/ml).'
          READ(*,*)  CTOT
          WRITE(*,*)'Input the selectivity of the amine relative'
          WRITE(*,*)'to the hydrogen ion'
          READ(*,*)  SELAM
          WRITE(*,*)'Enter the amine dissociation constant.'
          READ(*,*)  PKA
        ENDIF

      ENDIF


C    **************************************************************
C    Calculate water density and dissociation constant
C    **************************************************************

      S1=374.11-TEMPC
      S2=S1**0.33333
      DEN=sqrt((1+0.1342489*S2-3.946263 e-3*S1)/
     1   (3.1975-0.3151548*S2-1.203374e-3*S1+7.48908e-13*(S1**4)))

      TEMPK=TEMPC+273.15
      ALOGPKW = -6.0875+0.0176*TEMPK+4470.99/TEMPK
      PKW=10**(-ALOGPKW)

C    *************************************************************
C    CALCULATING THE  SELECTIVITIES OF THE CATIONS WITH RESPECT TO
```

```
C    THE AMINE FOR AMINE CYCLE
C    **************************************************************

     IF (CYCLE.EQ.2) THEN

      DO 11 I=1,NOCAT
      SELC(I)=SELC(I)*( (1./SELAM)**VACAT(I) )
   11  CONTINUE

     END IF

C    **************************************************************
C    CALCULATION OF THE IONIC RESIN PHASE CONCENTRATIONS FROM
C    THE INITIAL FRACTIONAL LOADINGS
C    **************************************************************

     DO 12 I=1,NOCAT
     CYCAT(I)=YCINIT(I)*CAT_CAP
   12 CONTINUE
     CYH=CAT_CAP-SUM(CYCAT,NOCAT)

     DO 13 I=1,NOAN
     CYAN(I)=YAINIT(I)*AN_CAP
   13 CONTINUE
     CYOH=AN_CAP-SUM(CYAN,NOAN)

C    **************************************************************
C    IMPLEMENT NEWTON-RAPHSON METHOD TO SOLVE CHARGE BALANCE
C    EQUATION FOR BASIS CATION CONCENTRATIONS:
C    [H+] ---> FOR HYDROGEN CYCLE,   [Amine+] ---> FOR AMINE CYCLE
C    **************************************************************

     IF(CYCLE.EQ.1)THEN
      CXH=10**(-PH)      !(INITIAL GUESS)
      ITER=0
    1  IF(ITER.GT.10000) GO TO 3
      ITER=ITER+1
      CXHOLD=CXH
      CXH=CXH-(FUNCH(CXH)/DFUNCH(CXH))
      IF(ABS(CXHOLD/CXH-1.0).GT.1E-4) GO TO 1

     ELSE

      CXOH=PKW/(10**(-PH))  !(INITIAL GUESS)
      ITER=0
    2  IF(ITER.GT.10000) GO TO 3
      ITER=ITER+1
      IF(CXOH.LT.1.0E-14)THEN
         CXOH=1.0E-04
      ENDIF
      CXOHOLD=CXOH
      CXOH=CXOH-(FUNCA(CXOH)/DFUNCA(CXOH))
      IF(ABS(CXOHOLD/CXOH-1.0).GT.1E-4) GO TO 2
```

```
      ENDIF

    3 CONTINUE

      IF(CYCLE.EQ.1)THEN
       CXOH=PKW/CXH
      ELSE
       CXH=PKA*CTOT/(PKA+CXOH)
      ENDIF

C     ************************************************************
C     CALCULATION OF EQUILIBRIUM CONCENTRATIONS OF REMAINING CATIONS
C     ************************************************************

      DO 14 I=1,NOCAT
      CXCAT(I)=CYCAT(I)*((CXH/CYH)**(VACAT(I)/VAH))/(SELC(I)
     1      **(1./VAH))
   14 CONTINUE

C     ************************************************************
C     CALCULATION OF EQUILIBRIUM CONCENTRATIONS OF REMAINING ANIONS
C     ************************************************************

      DO 15 I=1,NOAN
      CXAN(I)=CYAN(I)*((CXOH/CYOH)**(VAAN(I)/VAOH))/(SELA(I)
     1      **(1./ABS(VAOH)))
   15 CONTINUE

C     ************************************************************
C     CALCULATE THE SUPERFICIAL VELOCITY
C     ************************************************************

      AREA=3.1415927*(BED_DIA**2)/4
      VS = VOL_FLOW/AREA

C     ************************************************************
C     CALCULATE THE REYNOLDS & SCHMIDT NUMBERS AND MASS TRANSFER
C     COEFFICIENTS
C     ************************************************************

      VISC=1.43123+TEMPC*(0.000127065*TEMPC-0.0241537)
      REYCAT=CAT_DIA*100*VS*DEN/((1.-VOID_FRAC)*VISC)
      REYAN=AN_DIA*100*VS*DEN/((1.-VOID_FRAC)*VISC)

      DO 16 I=1,NOAN
      SCHAN(I)=(VISC/100.)/DEN/DIFFAN(I)
      IF(REYAN.LT.20)THEN
        ANMTCT(I)=F2(REYAN,SCHAN(I))
      ELSE
        ANMTCT(I)=F1(REYAN,SCHAN(I))
      ENDIF
   16 CONTINUE

      WRITE(*,*)
```

```
  WRITE(*,*)'The mass transfer coefficients of the anions'
  WRITE(*,*)'calculated using the correlations are :'
  WRITE(*,*)(ANMTCT(I),I=1,NOAN)
  WRITE(*,*)

  DO 17 I=1,NOCAT
  SCHCAT(I)=(VISC/100.)/DEN/DIFFCAT(I)
  IF(REYCAT.LT.20)THEN
   CATMTCT(I)=F2(REYCAT,SCHCAT(I))
  ELSE
   CATMTCT(I)=F1(REYCAT,SCHCAT(I))
  ENDIF
17 CONTINUE

  WRITE(*,*)'The mass transfer coefficients of the cations '
  WRITE(*,*)'calculated using the correlations are :'
  WRITE(*,*)(CATMTCT(I),I=1,NOCAT)
  WRITE(*,*)
  WRITE(*,*)'Do you wish to see the results based on your'
  WRITE(*,*)'Mass transfer coefficients also? (y/n)'
  READ(*,201)FLAG1
  IF(FLAG1.EQ.'Y'.OR.FLAG1.EQ.'y')THEN
   DO 40 I=1,NOAN
   WRITE(*,101)I
101  FORMAT(' Input the mass transfer coeff. of anion(cm/s):',I2)
   READ(*,*)  ANMTCE(I)
40  CONTINUE

   DO 41 I=1,NOCAT
   WRITE(*,102)I
102  FORMAT(' Input the mass transfer coeff. of cation(cm/s):',I2)
   READ(*,*)  CATMTCE(I)
41  CONTINUE

  NFLAGC=0
  II=0
  DO 42 I=1, NOCAT
  IF(CATMTCE(I).LE.0.5*CATMTCT(I))THEN
   NFLAGC=1
   II=II+1
   KLEAKC(II)=1
  ENDIF
42 CONTINUE

  NFLAGA=0
  JJ=0
  DO 43 I=1, NOAN
  IF(ANMTCE(I).LE.0.5*ANMTCT(I))THEN
   NFLAGA=1
   JJ=JJ+1
   KLEAKA(JJ)=1
  ENDIF
43 CONTINUE
```

```
      IF(NFLAGC.EQ.1.OR.NFLAGA.EQ.1)THEN
      WRITE(*,*)'*******************************************************'
      WRITE(*,*)'The mass transfer coefficients you have entered '
      WRITE(*,*)'indicates that kinetic leakage is a potential problem.'
      WRITE(*,*)'Your input values are less than half of the expected'
      WRITE(*,*)'mass transfer coefficients predicted by theory at the'
      WRITE(*,*)'operating conditions you have given for the following'
      WRITE(*,*)'ions :'
      WRITE(*,203)(KLEAKC(I),I=1,II)
  203 FORMAT(' cations:',2X,10(I2,2X))
      WRITE(*,204)(KLEAKA(I),I=1,JJ)
  204 FORMAT(' anions :',2X,10(I2,2X))

      WRITE(*,*)'This program will calculate effluent concentrations '
      WRITE(*,*)'based on both the theoretical (internally generated) '
      WRITE(*,*)'and experimental (your inputted) mass transfer '
      WRITE(*,*)'coefficients. Two results are possible :'
      WRITE(*,*)'1) The ionic concentrations from the bed may be higher'
      WRITE(*,*)'for your value indicating current kinetic leakage is '
      WRITE(*,*)'possible. 2) The ionic concentrations for both mass '
      WRITE(*,*)'transfer coefficients are essentially the same '
      WRITE(*,*)'indicating no kinetic leakage currently. '
      WRITE(*,*)'If case2 is observed you may wish to rerun this '
      WRITE(*,*)'program with potential condenser tube leak '
      WRITE(*,*)'concentrations in order to determine if kinetic '
      WRITE(*,*)'leakage will occur under these conditions.'
      WRITE(*,*)'*******************************************************'
      ENDIF

      ENDIF

C     **************************************************************
C     STARTING OF THE LOOP TO CALCULATE THE LEAKAGES BASED ON THE
C     THEORETICAL MASS TRANSFER COEFFICIENTS AND THE USER SUPPLIED
C     MASS TRANSFER COEFFICIENTS IN TWO SUCCESSIVE RUNS.
C     **************************************************************

      IF(FLAG1.EQ.'Y'.OR.FLAG1.EQ.'y')THEN
       NTIMES=2
      ELSE
       NTIMES=1
      ENDIF

      DO 33 K=1,NTIMES
      IF(K.EQ.1)THEN
       DO 331 KK = 1,NOAN
        ANMTC(KK)=ANMTCT(KK)
  331  CONTINUE

       DO 332 JJ = 1,NOCAT
        CATMTC(JJ)=CATMTCT(JJ)
  332  CONTINUE
      ELSE
       DO 333 KK = 1,NOAN
```

```
      ANMTC(KK)=ANMTCE(KK)
 333  CONTINUE

      DO 334 JJ = 1,NOCAT
       CATMTC(JJ)=CATMTCE(JJ)
 334  CONTINUE
      ENDIF

C     ***************************************************************
C     CALCULATION OF THE DIMENSIONLESS COLUMN HEIGHT AND THE
C     NUMBER OF SLICES DOWN THE COLUMN
C     ***************************************************************

      ANMTCB=AMAX(ANMTC,NOAN)
      CHTD1=ANMTCB*(1.-VOID_FRAC)*RES_HT/(VS*AN_DIA)
      CATMTCB=AMAX(CATMTC,NOCAT)
      CHTD2=CATMTCB*(1.-VOID_FRAC)*RES_HT/(VS*CAT_DIA)
      IF( CHTD1.GT.CHTD2 )THEN
       CHTD=CHTD1
      ELSE
       CHTD=CHTD2
      ENDIF

      XI=0.01
      NSLICES=CHTD/XI

C     ***************************************************************
C     INITIALIZING THE BULK PHASE CONCENTRATIONS TO THE FEED CONC.'S
C     ***************************************************************

      DO 18 I=1,NOAN
      CXBAN(I)=CFAN(I)
   18 CONTINUE

      DO 19 I=1,NOCAT
      CXBCAT(I)=CFCAT(I)
   19 CONTINUE

C     ***************************************************************
C     IMPLEMENTATION OF THE MATERIAL BALANCE DOWN THE COLUMN
C     ***************************************************************

      DO 26 J=1,NSLICES

      DO 20 I=1,NOAN
      ANFLUX(I)=ANMTC(I)*(CXAN(I)-CXBAN(I))
      CXBAN(I)=CXBAN(I)+XI*6*FAR*ANFLUX(I)/ANMTCB
   20 CONTINUE

      DO 21 I=1,NOCAT
      CATFLUX(I)=CATMTC(I)*(CXCAT(I)-CXBCAT(I))
      CXBCAT(I)=CXBCAT(I)+XI*6*FCR*AN_DIA*AN_CAP*CATFLUX(I)/(ANMTCB
     1      *CAT_DIA*CAT_CAP)
   21 CONTINUE
```

```
C    *************************************************************
C    CALCULATION OF [H+] OR [AMINE+] BY SOLVING CHARGE BALANCE
C    EQUATION IN THE BULK LIQUID
C    *************************************************************

      CTOTAN=0
      DO 22 I=1,NOAN
      CTOTAN=CTOTAN+VAAN(I)*CXBAN(I)
   22 CONTINUE

      CTOTCAT=0
      DO 23 I=1,NOCAT
      CTOTCAT=CTOTCAT+VACAT(I)*CXBCAT(I)
   23 CONTINUE

      B=-CTOTAN-CTOTCAT

      IF(CYCLE.EQ.1)THEN

       CHB=(B+SQRT(B**2+4*PKW))/2.
       PH=-LOG10(CHB)
       COHB=PKW/CHB

      ELSE

       COHB=CXOH
       ITER=0
    4  IF(ITER.GT.1000)GO TO 5
       ITER=ITER+1
       IF(COHB.LT.1.0E-14)THEN
          COHB=1.0E-04
       ENDIF
       COHBOLD=COHB
       COHB=COHB-FUNCAMN(COHB,B)/DFUNCAMN(COHB)
       IF(ABS(COHBOLD/COHB-1.0).GT.1E-4) GO TO 4

    5  CONTINUE
       CHB=PKA*CTOT/(PKA+COHB)
      ENDIF

C    *************************************************************
C    CALCULATION OF EQUILIBRIUM CONCENTRATIONS OF REMAINING CATIONS
C    FOR THE NEXT SLICE
C    *************************************************************

      DO 24 I=1,NOCAT
      CXCAT(I)=CYCAT(I)*((CHB/CYH)**(VACAT(I)/VAH))/(SELC(I)
     1       **(1./VAH))
   24 CONTINUE

C    *************************************************************
C    CALCULATION OF EQUILIBRIUM CONCENTRATIONS OF REMAINING ANIONS
C    FOR THE NEXT SLICE
```

```
C     ***************************************************************

      DO 25 I=1,NOAN
      CXAN(I)=CYAN(I)*((COHB/CYOH)**(VAAN(I)/VAOH))/(SELA(I)
     1        **(1./ABS(VAOH)))
   25 CONTINUE

   26 CONTINUE

C     ***************************************************************
C     CONVERTION OF CONCENTRATIONS FROM (meq/ml) TO ppb
C     ***************************************************************

      DO 27 I=1,NOCAT
      COUTCAT(I)=CXBCAT(I)*CATEW(I)/1.E-06
   27 CONTINUE

      DO 28 I=1,NOAN
      COUTAN(I)=CXBAN(I)*ANEW(I)/1.E-06
   28 CONTINUE

C     ***************************************************************
C     OUTPUT BLOCK
C     ***************************************************************

      IF(K.EQ.1)THEN
       WRITE(*,*)'Do you want to send the output to a file(Y/N)?'
       READ(*,205)FLAG2
  205  FORMAT(1A)

       IF(FLAG2.EQ.'Y'.OR.FLAG2.EQ.'y')THEN
        WRITE(*,*)'Enter the output filename.'
        READ(*,206)OUTFILE
  206    FORMAT(20A)
        OPEN(UNIT=10,FILE=OUTFILE)
        WRITE(10,*)'     *********************************'
        WRITE(10,207)
  207    FORMAT(8X, ' Equilibrium Leakage ')
        WRITE(10,*)'     *********************************'
        WRITE(10,*)

        IF(CYCLE.EQ.1)THEN
          WRITE(10,208)CHB
  208      FORMAT(6X,'[H+]=',E14.7,'meq/ml')
          WRITE(10,209)PH
  209      FORMAT(6X,'PH  =',F8.3)
        ELSE
          WRITE(10,210)CHB
  210      FORMAT(6X,'[Amine+]=',E14.7,1X,'meq/ml')
          WRITE(10,211)COHB
  211      FORMAT(6X,'[OH-]=',E14.7,1X,'meq/ml')
        ENDIF

        WRITE(10,*)
```

```
      WRITE(10,212)
212     FORMAT(5X,'S.No.',5X,'Cation Concentrations(in PPB).')

      DO 29 I=1,NOCAT
      WRITE(10,213)I,COUTCAT(I)
213     FORMAT(6X,I2,6X,E14.7)
 29    CONTINUE

      WRITE(10,*)
      WRITE(10,214)
214     FORMAT(5X,'S.No.',5X,'Anion Concentrations(in PPB)')

      DO 30 I=1,NOAN
      WRITE(10,215)I,COUTAN(I)
215     FORMAT(6X,I2,6X,E14.7)
 30    CONTINUE

     ELSE
       WRITE(*,*)'     **********************************'
       WRITE(*,216)
216      FORMAT(8X, 'Equilibrium Leakages')
       WRITE(*,*)'     **********************************'
       WRITE(*,*)

       IF(CYCLE.EQ.1)THEN
         WRITE(*,217)CHB
217        FORMAT(6X,'[H+]=',E14.7,'meq/ml')
         WRITE(*,218)PH
218        FORMAT(6X,'PH  =',F8.3)
       ELSE
         WRITE(*,219)CHB
219        FORMAT(6X,'[Amine+]=',E14.7,1X,'meq/ml')
         WRITE(*,220)COHB
220        FORMAT(6X,'[OH-]   =',E14.7,1X,'meq/ml')
       ENDIF

       WRITE(*,*)
       WRITE(*,221)
221      FORMAT(5X,'S.No.',5X,'Cation concentrations(in PPB)')

       DO 31 I=1,NOCAT
       WRITE(*,222)I,COUTCAT(I)
222      FORMAT(6X,I2,6X,E14.7)
 31      CONTINUE

       WRITE(*,*)
       WRITE(*,223)
223      FORMAT(5X,'S.No.',5X,'Anion Concentrations(in PPB)')
       DO 32 I=1,NOAN
       WRITE(*,224)I,COUTAN(I)
224      FORMAT(6X,I2,6X,E14.7)
 32      CONTINUE
     ENDIF
   ENDIF
```

```
       IF(K.EQ.2)THEN
      IF(FLAG2.EQ.'Y'.OR.FLAG2.EQ.'y')THEN
       WRITE(10,*)'     *********************************'
       WRITE(10,225)
225     FORMAT(8X,'*Leakages Based on user supplied MTC s*')
       WRITE(10,*)'     *********************************'
       WRITE(10,*)

       IF(CYCLE.EQ.1)THEN
          WRITE(10,226)CHB
226         FORMAT(6X,'[H+]=',E14.7,'meq/ml')
          WRITE(10,227)PH
227         FORMAT(6X,'PH  =',F8.3)
       ELSE
          WRITE(10,228)CHB
228         FORMAT(6X,'[Amine+]=',E14.7,1X,'meq/ml')
          WRITE(10,229)COHB
229         FORMAT(6X,'[OH-]  =',E14.7,1X,'meq/ml')
       ENDIF

       WRITE(10,*)
       WRITE(10,230)
230     FORMAT(5X,'S.No.',5X,'Cation Concentrations(in PPB).')

       DO 36 I=1,NOCAT
       WRITE(10,231)I,COUTCAT(I)
231     FORMAT(6X,I2,6X,E14.7)
 36     CONTINUE

       WRITE(10,*)
       WRITE(10,232)
232     FORMAT(5X,'S.No.',5X,'Anion Concentrations(in PPB)')

       DO 37 I=1,NOAN
       WRITE(10,233)I,COUTAN(I)
233     FORMAT(6X,I2,6X,E14.7)
 37     CONTINUE

      ELSE
        WRITE(*,*)'     *********************************'
        WRITE(*,234)
234       FORMAT(8X.'*Leakages Based on user supplied MTC s*')
        WRITE(*,*)'     *********************************'
        WRITE(*,*)

        IF(CYCLE.EQ.1)THEN
          WRITE(*,235)CHB
235         FORMAT(6X,'[H+]=',E14.7,'meq/ml')
          WRITE(*,236)PH
236         FORMAT(6X,'PH  =',F8.3)
        ELSE
          WRITE(*,237)CHB
237         FORMAT(6X,'[Amine+]=',E14.7,1X,'meq/ml')
          WRITE(*,238)COHB
```

```
 238        FORMAT(6X,'[OH-]=',E14.7,1X,'meq/ml')
        ENDIF

        WRITE(*,*)
        WRITE(*,239)
 239     FORMAT(5X,'S.No.',5X,'Cation concentrations(in PPB)')

        DO 38 I=1,NOCAT
        WRITE(*,240)I,COUTCAT(I)
 240     FORMAT(6X,I2,6X,E14.7)
  38     CONTINUE

        WRITE(*,*)
        WRITE(*,241)
 241     FORMAT(5X,'S.No.',5X,'Anion Concentrations(in PPB)')

        DO 39 I=1,NOAN
        WRITE(*,242)I,COUTAN(I)
 242     FORMAT(6X,I2,6X,E14.7)
  39     CONTINUE
       ENDIF
      ENDIF

  33 CONTINUE

      CLOSE(9)
      CLOSE(10)
      STOP
      END

C    ****************************************************************
C    FUNCTION TO CALCULATE THE CHARGE BALANCE FOR HYDROGEN CYCLE
C    ****************************************************************

      FUNCTION FUNCH(CXH)
      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1        SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2        VAH,VAOH,PKW,PKA,CTOT,SELAM

      SUMC=0
      DO 33 I=1,NOCAT
      SUMC=SUMC+CYCAT(I)*((CXH/CYH)**(VACAT(I)/VAH))
     1  /(SELC(I)**(1./VAH))
  33 CONTINUE

      SUMA=0
      DO 34 I=1,NOAN
      SUMA=SUMA+CYAN(I)*((PKW/(CXH*CYOH))**(VAAN(I)/VAOH))
     1  /(SELA(I)**(1./ABS(VAOH)))
  34 CONTINUE

C     ************************************************************
C     CHARGE BALANCE EQUATION FOR HYDROGEN CYCLE
C     ************************************************************
```

```
      FUNCH=CXH+SUMC-(PKW/CXH)-SUMA
      RETURN
      END

C     ****************************************************************
C     FUNCTION TO CALCULATE THE DERIVATIVE OF THE CHARGE BALANCE FOR
C     HYDROGEN CYCLE
C     ****************************************************************

      FUNCTION DFUNCH(CXH)
      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1        SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2        VAH,VAOH,PKW,PKA,CTOT,SELAM

      SUMC=0.0
      DO 35 I=1,NOCAT
      POW=VACAT(I)/VAH
      TEM=CYCAT(I)*POW*(CXH**(POW-1.))/((CYH**POW)
     1  *(SELC(I)**(1./VAH)))
      SUMC=SUMC+TEM
   35 CONTINUE

      SUMA=0.0
      DO 36 I=1,NOAN
      POW=VAAN(I)/VAOH
      TEM=CYAN(I)*((PKW/CYOH)**POW)*(-POW)*(CXH**(-POW-1))
     1  /(SELA(I)**(1./ABS(VAOH)))
      SUMA=SUMA+TEM
   36 CONTINUE

C       ***********************************************************
C       FIRST ORDER DERIVATIVE OF CHARGE BALANCE FOR H-CYCLE
C       ***********************************************************

      DFUNCH=1+SUMC+PKW*(1./(CXH**2.))-SUMA
      RETURN
      END

C     ****************************************************************
C     FUNCTION TO CALCULATE THE CHARGE BALANCE FOR AMINE CYCLE
C     ****************************************************************

      FUNCTION FUNCA(CXOH)
      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1        SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2        VAH,VAOH,PKW,PKA,CTOT,SELAM

      SUMC=0
      DO 37 I=1,NOCAT
      SUMC=SUMC+CYCAT(I)*((PKA*CTOT/((PKA+CXOH)*CYH))**
     1  (VACAT(I)/VAH))/(SELC(I)**(1./VAH))
   37 CONTINUE
```

```
      SUMA=0
      DO 38 I=1,NOAN
      SUMA=SUMA+CYAN(I)*((CXOH/CYOH)**(VAAN(I)/VAOH))
     1   /(SELA(I)**(1./ABS(VAOH)))
   38 CONTINUE

C     ***********************************************************
C     CHARGE BALANCE EQUATION FOR AMINE CYCLE
C     ***********************************************************

      FUNCA=PKA*CTOT/(PKA+CXOH)+SUMC-CXOH-SUMA+PKW/CXOH
      RETURN
      END

C   ***************************************************************
C   FUNCTION TO CALCULATE THE DERIVATIVE OF THE CHARGE BALANCE FOR
C   AMINE CYCLE
C   ***************************************************************

      FUNCTION DFUNCA(CXOH)
      COMMON      NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1        SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2        VAH,VAOH,PKW,PKA,CTOT,SELAM,VAAM

      SUMC=0.0
      DO 39 I=1,NOCAT
      POW=VACAT(I)/VAH
      TEM=CYCAT(I)*(-POW)*((PKA+CXOH)**(-POW-1.))*((PKA*CTOT
     1   /CYH)**POW)/(SELC(I)**(1./VAH))
      SUMC=SUMC+TEM
   39 CONTINUE

      SUMA=0.0
      DO 40 I=1,NOAN
      POW=VAAN(I)/VAOH
      TEM=CYAN(I)*(CYOH**(-POW))*POW*(CXOH**(POW-1))
     1   /(SELA(I)**(1./ABS(VAOH)))
      SUMA=SUMA+TEM
   40  CONTINUE

C     ***********************************************************
C     FIRST ORDER DERITIVE OF CHARGE BALANCE FOR AMINE CYCLE
C     ***********************************************************

      DFUNCA=SUMC+PKA*CTOT*(-1./((PKA+CXOH)**2.))+SUMA-1
     1    -PKW/(CXOH**2)
      RETURN
      END

C   ***************************************************************
C   FUNCTION TO CALCULATE CHARGE BALANCE FOR AMINE NEUTRALIZATION
C   ***************************************************************

      FUNCTION FUNCAMN(CXOH.B)
```

```
      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1       SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2       VAH,VAOH,PKW,PKA,CTOT,SELAM

      FUNCAMN=PKA*CTOT/(PKA+CXOH)-CXOH+PKW/CXOH-B
      RETURN
      END

C   ****************************************************************
C   FUNCTION TO CALCULATE THE DERIVATIVE OF THE CHARGE BALANCE FOR
C   NEUTRALIZATION IN AMINE CYCLE
C   ****************************************************************

      FUNCTION DFUNCAMN(CXOH)
      COMMON     NOCAT,NOAN,VACAT(10),VAAN(10),CYCAT(10),CYAN(10),
     1       SELC(10),SELA(10),CXCAT(10),CXAN(10),CYH,CYOH,
     2       VAH,VAOH,PKW,PKA,CTOT,SELAM

      DFUNCAMN=PKA*CTOT*(-1./((PKA+CXOH)**2.))-1-PKW/(CXOH**2)

      RETURN
      END

C   ****************************************************************
C   FUNCTION TO FIND THE SUM OF THE ELEMENTS OF AN ARRAY
C   ****************************************************************

      FUNCTION SUM(X,N)
      DIMENSION X(10)
      SUM=0.0
      DO 41 I=1,N
      SUM=SUM+X(I)
   41 CONTINUE
      RETURN
      END

C   ****************************************************************
C   FUNCTION TO FIND THE MAXIMUM NUMBER OF AN ARRAY
C   ****************************************************************

      FUNCTION AMAX(X,N)
      DIMENSION X(10)
      AMAX=X(1)
      DO 42 I=2,N
       IF( X(I).GT.AMAX)THEN
           AMAX=X(I)
        ENDIF
   42 CONTINUE
      RETURN
      END
```

APPENDIX F

COMPUTER CODE FOR RATE MODEL

```
***********************************************************************
*                                                                     *
*   MULTICOMPONENT MIXED-BED ION-EXCHANGE CODE FOR "EPRI"             *
*                                                                     *
*                                                                     *
*   DISCLAIMER: THIS COMPUTER CODE IS THE INTELLECTUAL                *
*               PROPERTY OF OSU AND CANNOT BE USED WITHOUT            *
*               THE EXPLICIT PERMISSION OF OKLAHOMA STATE             *
*               UNIVERSITY                                            *
*                                                                     *
*   This program predicts the effluent concentrations of a multicomponent system  *
*    in which there could be some cationic and anionic dissociative species       *
*                                                                     *
*   In this system,                                                   *
*   The number of non-dissociative cations may be:  8                 *
*   The number of non-dissociative anions may be:   8                 *
*   The number of dissociative species may be                         *
*                          monovalent amines:       5                 *
*                          Carbonates:              2                 *
*                                                                     *
*                                                                     *
*       Coded by:   Liu, Vinay, Hussey & Dr. Foutch                   *
*                   Oklahoma State University                         *
*                                                                     *
*       Last updated:  June 28, 1996                                  *
*---------------------------------------------------------------------*
*   NOTATION:                                                         *
*                                                                     *
*   CAT       - Suffix for cations                                    *
*   AMIN      - Suffix for amines                                     *
*   ANI       - Suffix for anions                                     *
*   CARB      - Suffix for carbonates                                 *
*   AMSTA     - Suffix for molecular amine                            *
*   CARBSTA   - Suffix for molecular carbonate                        *
*                                                                     *
*   INDICES:                                                          *
*                                                                     *
*   II        - CATIONS                                               *
*   JJ        - ANIONS                                                *
*   KK        - AMINES                                                *
*   LL        - CARBONATES                                            *
*                                                                     *
*==================================================================   *
```

```
*    NOMENCLATURE OF VARIABLES                                              *
*                                                                           *
*    ANI_DIA          Anion diameter (cm)                                   *
*    ANI_CAP          Anion capacity (meq/ml)                               *
*    BED_DIA          Bed diameter (cm)                                     *
*    CAT_DIA          Cation diameter (cm)                                  *
*    CAT_CAP          Cation capacity (meq/ml)                              *
*    CFCAT (I)        Feed concentration of cation i                        *
*    CFANI (I)        Feed concentration of anion i                         *
*    CFA              Total feed concentration of anions                    *
*    CFC              Total feed concentration of cations                   *
*    CF               Total feed concentration                              *
*    CBCAT (I)        Bulk phase concentration of cation i                  *
*    CBANI (I)        Bulk phase concentration of anion i                   *
*    CBAMIN (I)       Bulk phase concentration of amine i                   *
*    CBAMSTA (I)      Bulk phase concentration of molecular amine           *
*    CBCARB (I)       Bulk phase concentration of carbonate i               *
*    CBC (I)          Combined array of CBCAT (I) and CBAMIN (I)            *
*    CBA (I)          Combined array of CBANI (I) and CBCARB (I)            *
*    CFEED_AMIN(I)    Feed concentration of amine i                         *
*    CFEED_CARB       Feed concentration of carbonate                       *
*    CTO_AMIN(I)      Total concentration of amine i                        *
*    CTO_CARB         Total concentraton of carbonate                       *
*    CHTD             Dimensionless column height                           *
*    DEC              Effective diffusivity of cations                      *
*    DEA              Effective diffusivity of anions                       *
*    DEN              Density of water (g/cm3)                              *
*    DISSW            Dissociation constant of water                        *
*    DIFU_CAT (I)     Diffusivity of cation i (cm2/s)                       *
*    DIFU_ANI (I)     Diffusivity of anion i (cm2/s)                        *
*    DIFU_AMIN (I)    Diffusivity of amine i (cm2/s)                        *
*    DIFU_AMSTA(I)    Diffusivity of molecular amine (cm2/s)                *
*    DIFU_CARB (I)    Diffusivity of carbonates (cm2/s)                     *
*    DIFU_CARBSTA     Diffusivity of molecular carbonate(cm2/s)             *
*    DIFUCOMC (I)     Combined array of cationic diffusivities              *
*    DIFUCOMA (I)     Combined array of anionic diffusivities               *
*    DISSAMIN (I)     Dissociation constant of amines                       *
*    DISSCARB (I)     Dissociation constant of carbonates                   *
*    EWANI(I)         Equivalent weight of cation i                         *
*    EWCAT(I)         Equivalent weight of anion i                          *
*    EWAMIN(I)        Equivalent weight of amine i                          *
*    EWAMSTA(I)       Equivalent weight of molecular amine                  *
*    EWCARB(I)        Equivalent weight of carbonate i                      *
*    EWCARBSTA        Equivalent weight of molecular carbonate              *
*    FCR              Volume fraction of cationic resin                     *
*    FAR              Volume fraction of anionic resin                      *
*    INDEXC(I)        Index of cation i                                     *
*    INDEXA(I)        Index of anion i                                      *
*    MTC_ANI (I)      Mass transfer coefficient of anion i (cm/s)           *
*    MTC_CAT (I)      Mass transfer coefficient of cation i                 *
*    MTC_AMIN (I)     Mass transfer coefficient of amine i                  *
*    MTC_AMSTA (I)    Mass transfer coefficient of molecular amine          *
*    MTC_CARB (I)     Mass transfer coefficient of carbonate  i             *
*    MTC_CARBSTA      Mass transfer coefficient of molecular carbonate      *
```

```
*   MTC_REF           Mass transfer coefficient of reference ion              *
*   NOCAT             Number of non-dissociative cations                      *
*   NOANI             Number of non-dissociative anions                       *
*   NOAMIN            Number of amines                                        *
*   NOCARB            Number of carbonates                                    *
*   NC                Number of all cations (NOCAT + NOAMIN)                  *
*   NA                Number of all anions (NOANI + NOCARB)                   *
*   NOSLICE           Number of slices                                        *
*   NEXC(I)           Number of exchanging cations in slice i                 *
*   NEXA(I)           Number of exchanging anions in slice i                  *
*   OUT_CAT (I)       Outlet concentration of cation i   (ppb)                *
*   OUT_ANI (I)       Outlet concentration of anion i    (ppb)                *
*   OUT_AMIN (I)      Outlet concentration of amine i    (ppb)                *
*   OUT_AMSTA (I)     Outlet concentration of molecular amine                 *
*   OUT_CARB (I)      Outlet concentration of carbonate i (ppb)               *
*   OUT_CARBSTA       Outlet concentration of molecular carbonate             *
*   PRIORITY_C(I)     Priority of cation i                                    *
*   PRIORITY_A(I)     Priority of anion i                                     *
*   RATE_COMC (I)     Mass transfer rate of cation i                          *
*   RATE_COMA (I)     Mass transfer rate of anion i                           *
*   RATE_AMSTA (I)    Mass transfer rate of molecular amine                   *
*   RATE_CARBSTA      Mass transfer rate of molecular carbonate i             *
*   RE_ANI            Reynolds number of anions                               *
*   RE_CAT            Reynolds number of cations                              *
*   RES_HT            Resin (column) height (cm)                              *
*   SCH_ANI (I)       Schmidt number of anion i                               *
*   SCH_AMSTA         Schmidt number of molecular amine                       *
*   SCH_CAT (I)       Schmidt number of cation  i                             *
*   SCH_CARBSTA       Schmidt number of molecular carbonate                   *
*   SEL_CAT (I)       Selectivity of cation i                                 *
*   SELH              Selectivity of hydrogen                                 *
*   SELCOMC (I)       Combined array of SEL_CAT (I) and SEL_AMIN (I)          *
*   SELCOMA (I)       Combined array of SEL_ANI (I) and SEL_CARB (I)          *
*   TAU               Step size for the time                                  *
*   XI                Step size for the distance                              *
*   XI1               Distance step for the first few slices                  *
*   VAANI (I)         Valency of cation i                                     *
*   VACAT (I)         Valency of anion i                                      *
*   VAAMIN (I)        Valency of amine i                                      *
*   VACARB (I)        Valency of carbonate i                                  *
*   VACOMC (I)        Combined array of VACAT (I) and VAAMIN (I)              *
*   VACOMA (I)        Combined array of VAANI (I) and VACARB (I)              *
*   VAH               Valency of hydrogen                                     *
*   VAOH              Valency of hydroxide                                    *
*   VOID_FRAC         Void fraction of the bed                                *
*   VOL_FLOW          Volume flow rate (cm3/s)                                *
*   VS                Superficial velocity (cm/s)                             *
*   VISCO             Viscosity of water  (centipoise)                        *
*   TMPC              Inlet water temperature  (deg. celsius)                 *
*   XBC(I,K)          Fraction of cation i in bulk phase                      *
*   XBA(I,K)          Fraction of anion i in bulk phase                       *
*   XBAMINSTA(I,K)    Fraction of molecular amine i in bulk phase             *
*   XBCARBSTA(K)      Fraction of molecular carbonate in bulk phase           *
*   XANICUR(I)        Current fraction of anion i in bulk phase               *
```

```
*    XCATCUR(I)        Current fraction of cation i in bulk phase             *
*    YANICUR(I)        Current fraction of anion i in resin phase             *
*    YCATCUR(I)        Current fraction of cation i in resin phase            *
*    YAINIT (I)        Initial loading of anion i in resin phase              *
*    YCINIT (I)        Initial loading of cation i in resin phase             *
*    YAMIN_INIT        Initial loading of amine i in resin phase              *
*    YCRAB_INIT        Initial loading of carbonate i                         *
*    YRC(I,J,K )       Fraction of cation i in resin phase                    *
*    YRA(I,J,K)        Fraction of anion i in resin phase                     *
*                                                                             *
*******************************************************************************

      IMPLICIT  REAL*8 (A-H,O-Z)
      COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
     1       SELCOMC(15),SELCOMA(15)
      COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
     1       DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
     1       DIFU_CARBSTA
      COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
     1       VACOMC(15),VACOMA(15)
      COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
     1       EWCARBSTA
      COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
     1       CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
     1       CFC,CFA,CF,CBCARBSTA
      COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
      COMMON /F/XBH,XBOH,SUMYC,SUMYA
      COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
     1       FLUXC(15),FLUXA(15),DEC,DEA
      COMMON /I/INDEXC(15),INDEXA(15)

      REAL*8 RATE_COMC(15,5000),RATE_COMA(15,5000),RATE_AMSTA(5,5000),
     1 RATE_CARBSTA(5000),
     1 CFCAT(8),CFANI(8),CFAMIN(5),CFCARB(2),CFEED_AMIN(5),CFAMSTA(5),
     1 CFEED_CARB,CFCARBSTA,
     1 YCINIT(8),YAINIT(8),YAMIN_INIT(5),YCARB_INIT(2),
     1 COEC(15),COEA(15),COEAMSTA(5),COECARBSTA,
     1 OUT_CAT(8), OUT_ANI(8),OUT_AMIN(5),OUT_AMSTA(5),
     1 OUT_AMINT(5),OUT_CARB(2),OUT_CARBT,
     1 YCATCUR(15),YANICUR(15),XCATCUR(15),XANICUR(15),
     1 YRC(15,4,5000),YRA(15,4,5000),XBC(15,5000),
     1 XBA(15,5000),XBCAT(10,5000),XBANI(10,5000),XBAMIN(5,5000),
     1 XBAMSTA(5,5000),XBCARB(2,5000),XBCARBSTA(5000),DISSW,
     1 SCH_CAT(8),SCH_ANI(8),SCH_AMIN(5),SCH_AMSTA(5),SCH_CARB(2),
     1 SCH_CARBSTA,
     1 MTC_CAT(8),MTC_ANI(8),MTC_AMIN(5),MTC_AMSTA(5),MTC_CARB(2),
     1 MTC_C,MTC_A,MTC_COMC(15),MTC_COMA(15),MTC_REF,MTC_FUNC,
     1 MTC_CARBSTA

      DIMENSION NEXC(5000),NEXA(5000),PRIORITY_C(15),PRIORITY_A(15)


      CHARACTER*1 FLAG,TFLAG
      CHARACTER*20 INPFILE
```

```
*   ---------------------------------------------------------------
*   Dwivedi & Upadhyay's correlation for calculating mass
*   transfer coefficients
*   ---------------------------------------------------------------

      MTC_FUNC(R,S,DIFU,DIA) = DIFU/DIA *(S**(1./3.))*R*
     1 (0.765/((VOID_FRAC*R)**0.82) + 0.365/((VOID_FRAC*R)**0.386))


*   ------------------
*   Reading the data
*   ------------------

      WRITE(*,*)"Enter the input file name"
      READ(*,500)INPFILE
 500  FORMAT(20A)

      OPEN(UNIT = 9, FILE = INPFILE, STATUS = 'UNKNOWN')
*   -----------------------------------------------------------------------
*   Flag to account for desulphonation effects if SO4-2 is present in
*   the system.If this flag is "Y/y" the desulphonation effects will
*   be included for SO4-2. If it is "N/n" it will not be included.
*   -----------------------------------------------------------------------

      READ(9,501) FLAG
 501  FORMAT(1A)

*   -----------------------------------------------------------------------
*   Reading the time and distance steps.The second distance step is
*   for the first few steps of the numerical integration. Usually
*   XI1 is set 1/10th of XI.
*   -----------------------------------------------------------------------

          READ(9,*) TAU, XI, XI1
*   -----------------------------------------------------------------------
*   Reading the number of non-dissociative cations,non-dissociative
*   anions,amines and the carbonates respectively.A maximum of five
*   monovalent amines can be handled.If carbonate is present "NOCARB"
*   should be "2" to account for both HCO3- and CO3-2, otherwise it
*   should be zero.
*   -----------------------------------------------------------------------

          READ(9,*) NOCAT,NOANI,NOAMIN,NOCARB

      IF(NOCAT.GT.8.OR.NOCAT.LT.0)THEN
        WRITE(*,*)"Number of cations should be between 0 and 8"
      ENDIF

      IF(NOANI.GT.8.OR.NOANI.LT.0)THEN
        WRITE(*,*)"Number of anions should be between 0 and 8"
      ENDIF

      IF(NOAMIN.GT.5.OR.NOAMIN.LT.0)THEN
        WRITE(*,*)"Number of amines should be between 0 and 5"
```

```
      ENDIF

      IF(NOCARB.LT.0.OR.NOCARB.GT.2.OR.NOCARB.EQ.1)THEN
        WRITE(*,*)"Number of carbonates must be 0 or 2"
      ENDIF
*
*     -----------------------------------------------------------
*      Reading the resin diameters and capacities.
*     -----------------------------------------------------------

            READ(9,*) CAT_DIA, ANI_DIA, CAT_CAP, ANI_CAP
*     -----------------------------------------------------------
*      Reading the bed diameter, resin height, void fraction, flowrate
*     -----------------------------------------------------------

            READ(9,*) BED_DIA, RES_HT,VOID_FRAC,VOL_FLOW
*     -----------------------------------------------------------
*      Reading the cationic and anionic resin fractions,feed temperature
*      and pH.
*     -----------------------------------------------------------

            READ(9,*) FCR,FAR,TMPC,PH
*     -----------------------------------------------------------
*      Reading the data for cations(Initial loading, feed concentration,
*      valency, selectivity, equivalent weight, diffusivity)
*     -----------------------------------------------------------

      DO 2 II = 1,NOCAT
        READ(9,*)YCINIT(II),CFCAT(II),VACAT(II),SEL_CAT(II),EWCAT(II),
     1        DIFU_CAT(II)
    2 CONTINUE
*     -----------------------------------------------------------
*      Reading the data for anions(Initial loading, feed concentration,
*      valency, selectivity, equivalent weight, diffusivity)
*     -----------------------------------------------------------

      DO 4 JJ = 1,NOANI
        READ(9,*)YAINIT(JJ),CFANI(JJ),VAANI(JJ),SEL_ANI(JJ),EWANI(JJ),
     1        DIFU_ANI(JJ)
    4 CONTINUE

*     -----------------------------------------------------------
*     Reading the data for amines. Input for each amine is read in two
*     lines. First line consists of Initial loading,valency,selectivity
*     equivalent weight,dissociation constant and diffusivity of the
*     ionic form amine and total feed concentration. Second line consists
*     of equivalent weight and diffusivity of the amine in molecular form.
*     -----------------------------------------------------------

      IF (NOAMIN.GE.1) THEN
        DO 6 KK=1,NOAMIN
          READ(9,*)YAMIN_INIT(KK),VAAMIN(KK),SELAMIN(KK),EWAMIN(KK),
     1          DISSAMIN(KK),DIFU_AMIN(KK),CFEED_AMIN(KK)
             READ(9,*)EWAMSTA(KK),DIFU_AMSTA(KK)
    6   CONTINUE
```

```
      ENDIF
*     _____________________________________________________________
*     Reading the data for carbonate.The data is read in four lines.
*     First line consists of the total feed concentration. Second and
*     the third lines consist of bicarbonate(HCO3-) and carbonate(CO3-2)
*     data respectively.Each of these lines have initial loading,valency
*     selectivity,equivalent weight,dissociation constant & diffusivity
*     of the respective ions. The fourth line consists of the equivalent
*     weight and the diffusivity of the carbonate in molecular form.
*     _____________________________________________________________

      IF (NOCARB.GE.1) THEN
        READ(9,*) CFEED_CARB
        DO 8 LL=1,NOCARB
          READ(9,*)YCARB_INIT(LL),VACARB(LL),SELCARB(LL),EWCARB(LL),
     1         DISSCARB(LL),DIFU_CARB(LL)
 8      CONTINUE
        READ(9,*) EWCARBSTA,DIFU_CARBSTA
      ENDIF
*     _____________________________________________________________
*     Initializing the indices
*     _____________________________________________________________

      DO 10 II=1,NOCAT
        INDEXC(II) = II
 10   CONTINUE

      IF(NOAMIN.GE.1)THEN
        DO 12 KK=1,NOAMIN
          INDEXC(NOCAT+KK) = NOCAT+KK
 12     CONTINUE
      ENDIF

      DO 14 JJ=1,NOANI
        INDEXA(JJ) = JJ
 14   CONTINUE

      IF(NOCARB.GE.1)THEN
        DO 16 LL=1,NOCARB
          INDEXA(NOANI+LL) = NOANI+LL
 16     CONTINUE
      ENDIF
*     _____________________________________________________________
*     Setting the valences and selectivities of hydrogen and hydroxide.
*     _____________________________________________________________

      VAH = 1.0
      VAOH = -1.0
      SELH = 1.0
      SELOH = 1.0

*     _____________________________________________________________
*     Calculating the diffusivities of hydrogen & hydroxide.
*     _____________________________________________________________
```

```
      RTF = (8.931D-10)*(TMPC+273.16)
      DIFUH=RTF*(221.7134+5.5294*TMPC-0.014445*TMPC*TMPC)
      DIFUOH=RTF*(104.74113+3.807544*TMPC)

*     ____________________________________________________________
*     Calculating the viscosity and dissociation constant of water.
*     ____________________________________________________________

      VISCO = 1.43123+TMPC*(0.000127065*TMPC-0.0241537)
      ALOGDISSW = 4470.99/(TMPC+273.15)-6.0875+0.01706*(TMPC+273.15)
      DISSW = 10**(-ALOGDISSW)
*     ____________________________________________
*     Calculating the density of water.
*     ____________________________________________

      SS1 = 374.11 - TMPC
      SS2 = SS1**0.33333
      DEN = SQRT((1+0.1342489*SS2-3.946263E-3*SS1)/
     1     (3.1975-0.3151548*SS2-1.203374E-3*SS1+7.48908E-13
     1      *(SS1**4)))

*     ___________________________________________________
*     Calculating the column area and superficial velocity.
*     ___________________________________________________

      AREA = 3.1415927*(BED_DIA**2.)/4.
      VS = VOL_FLOW/AREA

*     ____________________________________________________________
*     Assume the bulk concentrations in the first slice to be equal
*     to the inlet concentrations, and then call the equilibrium
*     subroutine 'DISSOEQ' to calculate the concentrations of
*     dissociation species in this slice.
*     ____________________________________________________________

      DO 18 II=1,NOCAT
        CBCAT(II)=CFCAT(II)
 18   CONTINUE

      DO 20 JJ=1,NOANI
        CBANI(JJ)=CFANI(JJ)
 20   CONTINUE

          IF(NOAMIN.GE.1)THEN
        DO 22 KK = 1,NOAMIN
             CTO_AMIN(KK) = CFEED_AMIN(KK)
 22     CONTINUE
          ENDIF

          IF(NOCARB.GE.1)THEN
        CTO_CARB = CFEED_CARB
          ENDIF
```

```
      PH_OLD=PH
      CALL DISSOEQ(PH_OLD,PH_NEW,IFLAG)
      IF(IFLAG.EQ.1) THEN
        WRITE(*,*)"Abnormal exit from 'dissoeq' subroutine"
              WRITE(*,*)"(outside the loop)"
        GO TO 538
      ENDIF
*
*      Storing the feed concentrations of H+ and OH-.
*      ------------------------------------------------------------
            CFH = CBH
            CFOH = CBOH
      PH_FEED = PH_NEW

*     ------------------------------------------------------------
*     Setting the feed concentrations of the ionic and molecular forms
*     of the amines equal to the bulk concentrations in the first slice
*     which are calculated in the equilibrium subroutine.
*     ------------------------------------------------------------

      IF(NOAMIN.GE.1)THEN
        DO 24 KK = 1,NOAMIN
          CFAMIN(KK) = CBAMIN(KK)
          CFAMSTA(KK) = CBAMSTA(KK)
 24     CONTINUE
      ENDIF
*     ------------------------------------------------------------
*     Setting the feed concentrations of the ionic and molecular forms
*     of the carbonate equal to the bulk concentrations in the first slice
*     which are calculated in the equilibrium subroutine.
*     ------------------------------------------------------------

      IF(NOCARB.GE.1)THEN
        CFCARB(1) = CBCARB(1)
        CFCARB(2) = CBCARB(2)
        CFCARBSTA = CBCARBSTA
      ENDIF
*     ------------------------------------------------------------
*     Printing the concentrations after the equilibrium calculation
*     ------------------------------------------------------------
      WRITE(*,*)"**********************************************"
      WRITE(*,502)PH
      WRITE(*,503)PH_NEW
 502  FORMAT('Input value of the feed pH      = ',F5.2)
 503  FORMAT('Calculated value of the feed pH = ',F5.2)
      WRITE(*,*)
      WRITE(*,*)"Feed concentrations at equilibrium:"
      WRITE(*,*)"cations:"
      WRITE(*,504)(CBCAT(I),I=1,NOCAT)
      WRITE(*,*)

           IF(NOAMIN.GE.1)THEN
       WRITE(*,*)"Amines(CTotal,Amine+,Amine*):"
```

```
      DO 26 I=1,NOAMIN
        WRITE(*,504)CTO_AMIN(I),CBAMIN(I),CBAMSTA(I)
26     CONTINUE
      WRITE(*,*)
         ENDIF

   WRITE(*,*)"Anions:"
   WRITE(*,504)(CBANI(J),J=1,NOANI)
   WRITE(*,*)

         IF(NOCARB.GE.1)THEN
     WRITE(*,*)"Carbonate(Total,HCO3-,CO3-2,H2CO3*):"
     WRITE(*,504)CTO_CARB,(CBCARB(I),I=1,NOCARB),CBCARBSTA
     WRITE(*,*)
         ENDIF

504  FORMAT(8(E12.4,4X))
   WRITE(*,*)"************************************************"

*   ------------------------------------------------------------------
*   Calculating the total feed concentrations of the cationic and anionic
*   species.
*   ------------------------------------------------------------------

   CFC = 0.0
   DO 28 II = 1,NOCAT
     CFC = CFC + CFCAT(II)
28  CONTINUE

   IF (NOAMIN.GE.1) THEN
     DO 30 KK=1,NOAMIN
       CFC = CFC + CBAMIN(KK)
30     CONTINUE
   END IF
   CFC = CFC + CBH

   CFA = 0.0
   DO 32 JJ = 1, NOANI
         CFA = CFA + CFANI(JJ)
32  CONTINUE

   IF (NOCARB.GE.1) THEN
      DO 34 LL = 1, NOCARB
        CFA = CFA + CBCARB(LL)
34      CONTINUE
   END IF
        CFA = CFA + CBOH
*   ------------------------------------------------------------------
*   Setting the total feed concentration equal to the total conc.
*   of cations which is also equal to the total concentration of
*   anions because of charge balance.
*   ------------------------------------------------------------------
        CF = CFC
```

```
*
*    Calculating Reynolds Numbers.
*
      IF (VOID_FRAC.GE.1.0) THEN
        WRITE (*,*) " VOID_FRAC = 1, Abnormal exit"
        GOTO 538
      END IF

      RE_CAT = CAT_DIA*100.*VS*DEN/((1.-VOID_FRAC)*VISCO)
      RE_ANI = ANI_DIA*100.*VS*DEN/((1.-VOID_FRAC)*VISCO)
*
*    Calculating Schmidt Numbers.
*
      DO 36 II=1, NOCAT
        SCH_CAT(II) = (VISCO/100.)/DEN/DIFU_CAT(II)
 36   CONTINUE

      IF (NOAMIN.GE.1) THEN
        DO 38 KK =1,NOAMIN
              SCH_AMIN(KK) = (VISCO/100.)/DEN/DIFU_AMIN(KK)
              SCH_AMSTA(KK) = (VISCO/100.)/DEN/DIFU_AMSTA(KK)
 38     CONTINUE
      END IF

      DO 40 JJ=1,NOANI
        SCH_ANI(JJ) = (VISCO/100.)/DEN/DIFU_ANI(JJ)
 40   CONTINUE

      IF (NOCARB.GE.1) THEN
        DO 42 LL=1,NOCARB
          SCH_CARB(LL) = (VISCO/100.)/DEN/DIFU_CARB(LL)
 42     CONTINUE
        SCH_CARBSTA = (VISCO/100.)/DEN/DIFU_CARBSTA
      END IF
*
*    Calculating the mass transfer coefficients.
*

      DO 44 II=1,NOCAT
        MTC_CAT(II) = MTC_FUNC(RE_CAT,SCH_CAT(II),DIFU_CAT(II)
     1               ,CAT_DIA)
 44   CONTINUE

      IF (NOAMIN.GE.1) THEN
        DO 46 KK=1,NOAMIN
              MTC_AMIN(KK) = MTC_FUNC(RE_CAT,SCH_AMIN(KK),DIFU_AMIN(KK)
     1               ,CAT_DIA)
              MTC_AMSTA(KK) = MTC_FUNC(RE_CAT,SCH_AMSTA(KK),DIFU_AMSTA(KK)
     1               ,CAT_DIA)
 46     CONTINUE
      END IF

      DO 48 JJ=1,NOANI
          MTC_ANI(JJ) = MTC_FUNC(RE_ANI,SCH_ANI(JJ),DIFU_ANI(JJ)
```

```
     1                ,ANI_DIA)
 48   CONTINUE

      IF (NOCARB.GE.1) THEN
        DO 50 LL=1,NOCARB
              MTC_CARB(LL) = MTC_FUNC(RE_ANI,SCH_CARB(LL),DIFU_CARB(LL)
     1                ,ANI_DIA)
 50     CONTINUE
        MTC_CARBSTA = MTC_FUNC(RE_ANI,SCH_CARBSTA,DIFU_CARBSTA,ANI_DIA)
      END IF

*     ------------------------------------------------------------
*     Combining the selectivities, valences, diffusivities and mass
*     transfer coefficients for the interfacial and flux calculations.
*     ------------------------------------------------------------

      NC = NOCAT + NOAMIN
      NA = NOANI + NOCARB

      DO 52 II = 1, NOCAT
        SELCOMC(II) = SEL_CAT(II)
        VACOMC(II) = VACAT(II)
        DIFUCOMC(II) = DIFU_CAT(II)
             MTC_COMC(II) = MTC_CAT(II)
 52   CONTINUE

      IF (NOAMIN.GE.1) THEN
        DO 54 KK = 1, NOAMIN
          SELCOMC(NOCAT+KK) = SELAMIN(KK)
          VACOMC(NOCAT+KK) = VAAMIN(KK)
          DIFUCOMC(NOCAT+KK) = DIFU_AMIN(KK)
               MTC_COMC(NOCAT+KK) = MTC_AMIN(KK)
 54     CONTINUE
      END IF

      SELCOMC(NC+1) = SELH
      VACOMC(NC+1) = VAH
      DIFUCOMC(NC+1) = DIFUH

      DO 56 JJ = 1, NOANI
        SELCOMA(JJ) = SEL_ANI(JJ)
        VACOMA(JJ) = VAANI(JJ)
        DIFUCOMA(JJ) = DIFU_ANI(JJ)
             MTC_COMA(JJ) = MTC_ANI(JJ)
 56   CONTINUE

      IF (NOCARB.GE.1) THEN
        DO 58 LL = 1, NOCARB
          SELCOMA(NOANI+LL) = SELCARB(LL)
          VACOMA(NOANI+LL) = VACARB(LL)
          DIFUCOMA(NOANI+LL) = DIFU_CARB(LL)
               MTC_COMA(NOANI+LL) = MTC_CARB(LL)
 58     CONTINUE
      END IF
```

```
      SELCOMA(NA+1) = SELOH
      VACOMA(NA+1) = VAOH
      DIFUCOMA(NA+1) = DIFUOH
*
*     ------------------------------------------------------------------
*      Calling the subroutine to sort the valences,selectivities,
*      diffusivities and indices.
*
*     ------------------------------------------------------------------

       CALL SORT_IONS()
*
*     ------------------------------------------------------------------
*     Setting the priorities of the ions.
*
*     ------------------------------------------------------------------
      DO 60 II = 1,NC
        PRIORITY_C(INDEXC(II)) = II
 60   CONTINUE

      DO 62 JJ = 1,NA
        PRIORITY_A(INDEXA(JJ)) = JJ
 62   CONTINUE

*
*     ------------------------------------------------------------------
*     Choosing the reference ion for calculations. The anion with
*     largest mass transfer coefficient is chosen as reference
*
*     ------------------------------------------------------------------
      NN = 1
      DO 64 JJ = 2, NA
        IF (MTC_COMA(NN).LT.MTC_COMA(JJ)) THEN
          NN = JJ
        END IF
 64   CONTINUE
      MTC_REF = MTC_COMA(NN)

*
*     ------------------------------------------------------------------
*      Pick hydroxide as the reference, if no other anion is present.
*
*     ------------------------------------------------------------------
      IF(NA.EQ.0)THEN
        SCH_OH = (VISCO/100.)/DEN/DIFUOH
        MTC_REF = MTC_FUNC(RE_ANI,SCH_OH,DIFUOH,ANI_DIA)
      ENDIF

*
*     ------------------------------------------------------------------
*     Calculating the dimensionless column height(CHTD) and the total
*     number of distance steps (NOSLICE) down the column.
*
*     ------------------------------------------------------------------

      IF (VS.LE.0.0 .OR. ANI_DIA .LE. 0.0) THEN
        WRITE(*,*)"ERROR: VS <= 0.0 and/or ANI_DIA <= 0.0"
        GOTO 538
      ENDIF

      CHTD = MTC_REF*(1.-VOID_FRAC)*RES_HT/(VS*ANI_DIA)
      NOSLICE = CHTD/XI-3+3*XI/XI1
      WRITE(*,*)
```

```
      WRITE(*,*)"Number of slices =",NOSLICE
      WRITE(*,*)

      IF(NOSLICE.GE.5000)THEN
        WRITE(*,*)"ERROR: Insufficient array sizes"
        GO TO 538
      ENDIF

*
*     ------------------------------------------------------------
*     Set the initial resin loadings throughout the column. Resin loadings
*     are assumed to be uniform throughout the column.
*     ------------------------------------------------------------

      MT = NOSLICE + 1
      DO 74 M = 1, MT
        DO 66 II = 1,NOCAT
          YRC( PRIORITY_C(II),1,M ) = YCINIT(II)
 66     CONTINUE

        IF (NOAMIN.GE.1) THEN
          DO 68 KK = 1, NOAMIN
            YRC( PRIORITY_C(NOCAT+KK),1,M) = YAMIN_INIT(KK)
 68       CONTINUE
        END IF

        DO 70 JJ = 1, NOANI
          YRA( PRIORITY_A(JJ),1,M) = YAINIT(JJ)
 70     CONTINUE

        IF (NOCARB.GE.1) THEN
          DO 72 LL = 1,NOCARB
            YRA( PRIORITY_A(NOANI+LL),1,M) = YCARB_INIT(LL)
 72       CONTINUE
        END IF

 74   CONTINUE
*
*     ------------------------------------------------------------
*     Calculating dimensionless program time limit based on inlet
*     conditions (at Z = 0)
*     ------------------------------------------------------------

      IF (VOL_FLOW .LE.0.0 .OR. CF.LE.0.0) THEN
        WRITE(*,*) "ERROR: VOL_FLOW <= 0.0 and/or CF <= 0.0"
        GOTO 538
      ENDIF

      TMAXC = CAT_CAP*3.142*(BED_DIA/2.)**2.*RES_HT*FCR
     1       /(VOL_FLOW*CF*60.)
      TMAXA = ANI_CAP*3.142*(BED_DIA/2.)**2.*RES_HT*FAR
     1       /(VOL_FLOW*CF*60.)

      IF(TMAXC.GE.TMAXA) THEN
        TMAX = TMAXC
      ELSE
```

```
        TMAX = TMAXA
      ENDIF

      IF (ANI_DIA .LE.0.0 .OR. ANI_CAP .LE.0.0) THEN
        WRITE(*,*)"ERROR: ANI_DIA <= 0.0 OR ANI_CAP <= 0.0"
        GOTO 538
      END IF

      TAUMAX = MTC_REF*CF*(TMAX*60.)/(ANI_DIA*ANI_CAP)

      DMAX=TMAX/1440.

      WRITE(*,505)
      WRITE(*,506) DMAX
      WRITE(*,507)
 505  FORMAT('Program run time is based on total resin capacity and')
 506  FORMAT('flow conditions. The program will show results for',F12.1)
 507  FORMAT('days of column operation for the current conditions.')

      WRITE(*,*)
      WRITE(*,*)"Do you wish to see the results for a different"
      WRITE(*,*)"number of days? (y/n)"
      READ(*,501)TFLAG

      IF(TFLAG.EQ.'Y'.OR.TFLAG.EQ.'y')THEN
        WRITE(*,*)"Enter the number of days"
        READ(*,*)DMAX_USER

        TMAX_USER = DMAX_USER*1440.
        TAUMAX = MTC_REF*CF*(TMAX_USER*60.)/(ANI_DIA*ANI_CAP)
      ENDIF
*     ------------------------------------------------------------
*     Printing the headings for concentration profiles
*     ------------------------------------------------------------
      WRITE(*,*)"*********************************************************"
      WRITE(*,*)"Printing breakthrough curves."
      WRITE(*,*)"The output columns are in the following order:"
      IF(NOAMIN.EQ.0.AND.NOCARB.EQ.0)THEN
        WRITE(*,*)" Time - pH - Cations - Anions"
        WRITE(*,*)"(Days)      (ppb)    (ppb)"
      ELSE IF(NOAMIN.GT.0.AND.NOCARB.EQ.0)THEN
        WRITE(*,*)" Time - pH - Cations - Amines - Anions"
        WRITE(*,*)"(Days)      (ppb)   (ppb)    (ppb)"
      ELSE IF(NOAMIN.EQ.0.AND.NOCARB.GT.0)THEN
        WRITE(*,*)" Time - pH - Cations - Anions - Carbonate"
        WRITE(*,*)"(Days)      (ppb)   (ppb)    (ppb)"
        WRITE(*,*)"                    (as H2CO3)"
      ELSE IF(NOAMIN.GT.0.AND.NOCARB.GT.0)THEN
        WRITE(*,*)" Time - pH - Cations - Amines - Anions - Carbonate"
        WRITE(*,*)"(Days)      (ppb)   (ppb)    (ppb)    (ppb) "
        WRITE(*,*)"                             (as H2CO3)"
      ENDIF
      WRITE(*,*)"*********************************************************"
*     ----------------------------------------
```

```
*  Initialize values prior to iterative loops
*
         J = 1
         JK = 1
         TAUTOT = 0.
         JFLAG = 0
         KPRINT = 10

      DO 76 K = 1, NOSLICE
        NEXC(K) =  (NC+1)  ! Initially all the ions exchange in all
        NEXA(K) =  (NA+1)  ! the slices
 76     CONTINUE

*
*  Defining the desulphonation term (Fisher's data)
*

      IF (FLAG.EQ.'Y'.OR.FLAG.EQ.'y') THEN
         S1 = (7.5E+6*EXP(-10278.6/(TMPC+273.16))*CHTD
     1   *3.1415927*(BED_DIA**2.)*CAT_CAP)*(VS*ANI_DIA)*FCR
     1   /(NOSLICE*3600.*4.0*VOL_FLOW*MTC_REF*(1.-VOID_FRAC))

                 DD = S1/CF
      ELSEIF (FLAG.EQ.'N'.OR.FLAG.EQ.'n') THEN
         DD = 0.0
      END IF

*
*  Calculating the constants outside the loops to avoid repititive
*  calculations inside the loops. These constants are used inside
*  the loops during rate calculations.
*
      IF (MTC_REF .LE. 0.0) THEN
         WRITE(*,*) "ERROR: MTC_REF <= 0.0"
        GOTO 538
      END IF

      CONP = -6.*ANI_DIA/(MTC_REF*CAT_DIA*CF)
      CONS = -6./(MTC_REF*CF)
      CONY = ANI_CAP/CAT_CAP

*****************************************************************************
*  Beginning of time step loop within which all column calculations are
*  implemented, time is incremented and outlet concentrations checked.
*****************************************************************************
 111  CONTINUE
           IF (TAUTOT.GT.TAUMAX) GOTO 538

       IF (J.EQ.4) THEN
                  JD = 1
           ELSE
                  JD = J + 1
           ENDIF
*
```

```
*   Setting liquid phase fractional concentrations for each species
*   in the first slice of the matrix.
*   ________________________________________________________________

    IF (CF .LE. 0.0) THEN
      WRITE(*,*) "ERROR: CF <= 0.0"
      GOTO 538
    ENDIF

    DO 78 II = 1,NOCAT
      XBCAT(II,1) = CFCAT(II)/CF
 78 CONTINUE

    IF (NOAMIN.GE.1) THEN
     DO 80 KK = 1,NOAMIN
       XBAMIN(KK,1) = CFAMIN(KK)/CF
       XBAMSTA(KK,1) = CFAMSTA(KK)/CF
       CBAMSTA(KK) = CFAMSTA(KK)
 80   CONTINUE
    END IF

    DO 82 JJ = 1,NOANI
           XBANI(JJ,1) = CFANI(JJ)/CF
 82 CONTINUE

    IF (NOCARB.GE.1) THEN
      DO 84 LL = 1, NOCARB
       XBCARB(LL,1) = CFCARB(LL)/CF
 84    CONTINUE
      XBCARBSTA(1) = CFCARBSTA/CF
      CBCARBSTA = CFCARBSTA
    END IF

*   ________________________________________________________________
*   Setting the total amine and carbonate concentrations in the first
*   slice equal to the feed concentrations.
*   ________________________________________________________________

    IF(NOAMIN.GE.1)THEN
      DO 86 II = 1,NOAMIN
        CTO_AMIN(II) = CFEED_AMIN(II)
 86    CONTINUE
    ENDIF

    IF(NOCARB.GE.1)THEN
      CTO_CARB = CFEED_CARB
    ENDIF

*   ________________________________________
*   Combining of the arrays
*   ________________________________________

    DO 88 II = 1, NOCAT
      XBC( PRIORITY_C(II),1) = XBCAT(II,1)
```

```
88  CONTINUE

    IF (NOAMIN.GE.1) THEN
      DO 90 KK = 1, NOAMIN
        XBC( PRIORITY_C(NOCAT+KK),1) = XBAMIN(KK,1)
90     CONTINUE
    END IF

    DO 92 JJ = 1, NOANI
      XBA( PRIORITY_A(JJ),1) = XBANI(JJ,1)
92  CONTINUE

    IF (NOCARB.GE.1) THEN
      DO 94 LL = 1, NOCARB
        XBA( PRIORITY_A(NOANI+LL),1) = XBCARB(LL,1)
94     CONTINUE
    ENDIF
*************************************************************************
*    Beginning of distance loop
*************************************************************************
*   ____________________________________________________________________
*   Loop to increment distance (bed length) at a fixed time.
*   ____________________________________________________________________

    DO 400 K = 1, NOSLICE

     IF (K .EQ. 1) THEN

       DO 96 II = 1, NC
         CBC(II) = XBC(II,K)*CF
96      CONTINUE

       DO 98 JJ = 1, NA
         CBA (JJ) = XBA(JJ,K)*CF
98      CONTINUE

*        ______________________________________________________________
*        Call subroutines to calculate interfacial concentrations
*        and fluxes for cations and anions
*        ______________________________________________________________

*        ______________________________________________________________
*        Calculating the sum of loading fractions.
*        ______________________________________________________________
       SUMYC = 0.0
       DO 100 II = 1,NEXC(K)-1
         SUMYC = SUMYC + YRC(II,J,K)
100      CONTINUE
       YRC(NEXC(K),J,K) = 1.0 - SUMYC

       SUMYA = 0.0
       DO 102 JJ = 1,NEXA(K)-1
         SUMYA = SUMYA + YRA(JJ,J,K)
102      CONTINUE
```

```
      YRA(NEXA(K),J,K) = 1.0-SUMYA

*
*     ------------------------------------------------------------
*     Calculating the number of exchanging ions.
*     ------------------------------------------------------------

      IF(SUMYC.GE.0.9999 .AND. NEXC(K).GE.2) THEN
         NEXC(K) = NEXC(K)-1
      END IF

      IF (SUMYA.GE.0.9999 .AND. NEXA(K).GE.2) THEN
         NEXA(K) = NEXA(K)-1
      END IF

      IF(NEXC(K).EQ.NC+1)THEN
        CBC(NC+1) = CFH
      ENDIF

      IF(NEXA(K).EQ.NA+1)THEN
        CBA(NA+1) = CFOH
      ENDIF

*
*     ------------------------------------------------------------
*     Copying the current resin and liquid phase fractions to
*     single dimension arrays to pass to the "CATION" subroutine
*     ------------------------------------------------------------
      DO 104 II = 1,NEXC(K)-1
        YCATCUR(II) = YRC(II,J,K)
        XCATCUR(II) = XBC(II,K)
 104    CONTINUE
      YCATCUR(NEXC(K)) = YRC(NEXC(K),J,K)

       DO 106 JJ = 1,NEXA(K)-1
        YANICUR(JJ) = YRA(JJ,J,K)
        XANICUR(JJ) = XBA(JJ,K)
 106    CONTINUE
      YANICUR(NEXA(K)) = YRA(NEXA(K),J,K)

      IF (NEXC(K).GE.2)THEN
        NTEMPC = NEXC(K)
        NTEMPA = NEXA(K)
        CALL CATION(YCATCUR,XCATCUR,NTEMPC,NTEMPA,IFLAG)
        IF(IFLAG.EQ.1)THEN
         WRITE(*,*)"ERROR:Abnormal exit from 'cation' subroutine"
         GO TO 538
        ENDIF

        IF (DEC.EQ.0.) THEN
         WRITE(*,*) "ERROR: DEC = 0 "
         GOTO 538
        END IF

*
*       ----------------------------------------------------------
*       Calculating the effective mass transfer coefficient
```

```
*         ______________________________________________________________________
          SCH_C = (VISCO/100.0)/DEN/DEC
          MTC_C = MTC_FUNC(RE_CAT,SCH_C,DEC,CAT_DIA)

*
*         ______________________________________________________________________
*         Setting the fluxes of non-exchanging ions to zero
*         ______________________________________________________________________
          IF(NEXC(K).LT.NC)THEN
            DO 108 II = NEXC(K)+1,NC
              FLUXC(II) = 0.0
 108          CONTINUE
          ENDIF
        ELSE

          DO 110 II = 1, NC
            FLUXC(II) = 0.0
 110        CONTINUE
        ENDIF

        IF(NEXA(K).GE.2)THEN
          NTEMPC = NEXC(K)
          NTEMPA = NEXA(K)
          CALL ANION(YANICUR,XANICUR,NTEMPC,NTEMPA,IFLAG)
          IF(IFLAG.EQ.1)THEN
           WRITE(*,*)"ERROR:Abnormal exit from 'anion' subroutine"
           GO TO 538
          ENDIF

          IF (DEA.EQ.0.) THEN
            WRITE(*,*) "ERROR: DEA = 0 "
            GOTO 538
          END IF
*         ______________________________________________________________________
*         Calculating the effective mass transfer coefficient
*         ______________________________________________________________________

          SCH_A = (VISCO/100.0)/DEN/DEA
          MTC_A = MTC_FUNC(RE_ANI,SCH_A,DEA,ANI_DIA)
*         ______________________________________________________________________
*         Setting the fluxes of non-exchanging ions to zero
*         ______________________________________________________________________

          IF( NEXA(K).LT.NA)THEN
            DO 112 JJ = NEXA(K)+1,NA
              FLUXA(JJ) = 0.0
 112          CONTINUE
          ENDIF

        ELSE
           DO 114 JJ = 1, NA
             FLUXA(JJ) = 0.0
 114         CONTINUE
        END IF
```

```
*     ------------------------------------------------------------
*     Calculating the rates
*     ------------------------------------------------------------

      DO 116 II = 1,NC
        RATE_COMC(II,1) = FLUXC(II)*MTC_C*CONP*CONY
116     CONTINUE

      IF(NOAMIN.GE.1)THEN
       DO 118 KK = 1,NOAMIN
        ITEMP = PRIORITY_C(NOCAT+KK)
        IF( NEXC(K).GE.ITEMP.AND.YRC(ITEMP,J,1).LT.0.99)THEN
         RATE_AMSTA(KK,1) = MTC_AMSTA(KK)*CBAMSTA(KK)*(-CONP)*CONY
        ELSE
             RATE_AMSTA(KK,1) = 0.0
        ENDIF
118      CONTINUE
      ENDIF

      DO 120 JJ = 1,NA
        RATE_COMA(JJ,1) = FLUXA(JJ)*MTC_A*CONS
120     CONTINUE

      IF(NOCARB.GE.1)THEN
        ITEMP = PRIORITY_A(NOANI+1)
        IF(NEXA(K).GE.ITEMP.AND.YRA(ITEMP,J,1).LT.0.99)THEN
          RATE_CARBSTA(1) = MTC_CARBSTA*CBCARBSTA*(-CONS)
        ELSE
          RATE_CARBSTA(1) = 0.0
        ENDIF
      ENDIF

*     ------------------------------------------------------------
*     Calculating the resin loadings for the next time step.
*     ------------------------------------------------------------
      DO 122 II = 1,NC
        YRC(II,JD,1) = YRC(II,J,1)+TAU*RATE_COMC(II,1)
        IF (YRC(II,JD,1).LE.0.0)THEN
          YRC(II,JD,1) = 0.0
        ENDIF
122     CONTINUE

      DO 124 JJ = 1,NA
        YRA(JJ,JD,1) = YRA(JJ,J,1)+TAU*RATE_COMA(JJ,1)
        IF(YRA(JJ,JD,1).LE.0.0)THEN
          YRA(JJ,JD,1) = 0.0
        ENDIF
124     CONTINUE


*     ------------------------------------------------------------
*     Adding the protonation term for the amines.
*     ------------------------------------------------------------
```

```
        IF(NOAMIN.GE.1)THEN
          DO 126 II = NOCAT+1,NC
            YRC(II,JD,1) = YRC(II,JD,1)+TAU*RATE_AMSTA(II-NOCAT,1)
 126        CONTINUE
              ENDIF

*       ----------------------------------------------------------------
*       Adding the effect of molecular form of carbonate diffusing
*       into the resin to the bicarbonate loading.
*       ----------------------------------------------------------------

        IF(NOCARB.GE.1)THEN
          YRA(NOANI+1,JD,1)=YRA(NOANI+1,JD,1)+TAU*RATE_CARBSTA(1)
        ENDIF

      END IF
*     ------------------------------------------------------------------
*     Implement implicit portion of the "gears backward method" to
*     calculate bulk phase fraction for the next distance step based
*     on the previous values, for the first three steps Euler's
*     first-order method is used.
*     ------------------------------------------------------------------

      ISTEPS = 3*XI/XI1 !no. of steps to be taken with a small step size

      IF(K.LE.3)THEN

        DO 128 II = 1, NC
          XBC(II,K+1)=XBC(II,K)-XI1*FCR*RATE_COMC(II,K)
 128    CONTINUE

*       ------------------------------------------------------------
*       Calculate fraction of undissociated amine
*       ------------------------------------------------------------
        IF(NOAMIN.GE.1)THEN
          DO 130 II = 1, NOAMIN
            XBAMSTA(II,K+1)=XBAMSTA(II,K)-XI1*FCR*RATE_AMSTA(II,K)
 130        CONTINUE
        ENDIF

        DO 132 JJ = 1, NA
          XBA(JJ,K+1)=XBA(JJ,K)-XI1*FAR*RATE_COMA(JJ,K)
*         ------------------------------------------------------------
*         Adding the desulphonation term to the sulfate. Sulfate
*         identified by its equivalent weight.
*         ------------------------------------------------------------
          IF (EWANI(JJ).EQ.48.0)  THEN
            XBA(JJ,K+1) = XBA(JJ,K+1) + DD
          END IF
 132    CONTINUE

        IF(NOCARB.GE.1)THEN
          XBCARBSTA(K+1)=XBCARBSTA(K)-XI1*FCR*RATE_CARBSTA(K)
        ENDIF
```

```
  ELSE IF(K.GT.3.AND.K.LE.ISTEPS)THEN

    DO 134 II = 1,NC
      COEC(II) = 3.*XBC(II,K-3)-16.*XBC(II,K-2)+ 36.*
 1          XBC(II,K-1) - 48.*XBC(II,K)
134   CONTINUE

    DO 136 II = 1, NC
      XBC(II,K+1) = -XI1*12.*FCR*RATE_COMC(II,K)/25.-COEC(II)/25.
136   CONTINUE

        IF(NOAMIN.GE.1)THEN
      DO 138 II = 1,NOAMIN
        COEAMSTA(II) = 3.*XBAMSTA(II,K-3)-16.*XBAMSTA(II,K-2)+
 1             36.*XBAMSTA(II,K-1) - 48.*XBAMSTA(II,K)
138     CONTINUE

      DO 140 II = 1, NOAMIN
        XBAMSTA(II,K+1) = -XI1*12.*FCR*RATE_AMSTA(II,K)/25.
 1                         -COEAMSTA(II)/25.
140     CONTINUE
         ENDIF

    DO 142 JJ  = 1,NA
       COEA(JJ) =3.*XBA(JJ,K-3)-16.*XBA(JJ,K-2)+36.*
 1          XBA(JJ,K-1)-48.*XBA(JJ,K)
142   CONTINUE

    DO 144 JJ = 1,NA
       XBA(JJ,K+1) =-XI1*12.*FAR*RATE_COMA(JJ,K)/25.-COEA(JJ)/25.
*       ______________________________________________________________
*       Adding the desulphonation term to the sulfate. Sulfate is
*       identified by its equivalent weight.
*       ______________________________________________________________
       IF (EWANI(JJ).EQ.48.0)  THEN
         XBA(JJ,K+1) = XBA(JJ,K+1) + DD
       END IF
144   CONTINUE

    IF(NOCARB.GE.1)THEN
      COECARBSTA = 3.*XBCARBSTA(K-3)-16.*XBCARBSTA(K-2)+
 1            36.*XBCARBSTA(K-1)-48.*XBCARBSTA(K)
      XBCARBSTA(K+1) =  -XI1*12.*FAR*RATE_CARBSTA(K)/25.
 1             -COECARBSTA/25.
    ENDIF

  ELSE IF(K.GE.(ISTEPS+1).AND.K.LE.(ISTEPS+3))THEN


     IF(K.EQ.ISTEPS+1) THEN
       K1 = 1
       K2 = ISTEPS/3+1
       K3 = ISTEPS*2/3+1
```

```
          K4 = K
        ELSE IF(K.EQ.ISTEPS+2)THEN
           K1 = ISTEPS/3+1
           K2 = ISTEPS*2/3+1
           K3 = ISTEPS+1
           K4 = K
        ELSE IF(K.EQ.ISTEPS+3)THEN
            K1 = ISTEPS*2/3+1
            K2 = ISTEPS+1
            K3 = K-1
            K4 = K
        ENDIF

        DO 146 II = 1,NC
          COEC(II) = 3.*XBC(II,K1)-16.*XBC(II,K2)+ 36.*
     1          XBC(II,K3) - 48.*XBC(II,K4)
 146     CONTINUE

        DO 148 II = 1, NC
          XBC(II,K+1) = -XI*12.*FCR*RATE_COMC(II,K)/25
     1              -COEC(II)/25.
 148     CONTINUE

            IF(NOAMIN.GE.1)THEN
          DO 150 II = 1,NOAMIN
           COEAMSTA(II) = 3.*XBAMSTA(II,K1)-16.*XBAMSTA(II,K2)+
     1            36.*XBAMSTA(II,K3)-48.*XBAMSTA(II,K4)
 150       CONTINUE

          DO 152 II = 1, NOAMIN
           XBAMSTA(II,K+1) = -XI*12.*FCR*RATE_AMSTA(II,K)/25
     1                  -COEAMSTA(II)/25.
 152       CONTINUE
            ENDIF

        DO 154 JJ  = 1,NA
          COEA(JJ) =3.*XBA(JJ,K1)-16.*XBA(JJ,K2)+36.*
     1          XBA(JJ,K3)-48.*XBA(JJ,K4)
 154     CONTINUE

        DO 156 JJ = 1, NA
          XBA(JJ,K+1) =-XI*12.*FAR*RATE_COMA(JJ,K)/25.
     1            -COEA(JJ)/25.
*        ______________________________________________
*        Adding the desulphonation term to the sulfate. Sulfate
*        is identified by its equivalent weight.
*        ______________________________________________
          IF (EWANI(JJ).EQ.48.0)  THEN
            XBA(JJ,K+1) = XBA(JJ,K+1) + DD
          END IF
 156     CONTINUE

       IF(NOCARB.GE.1)THEN
        COECARBSTA = 3.*XBCARBSTA(K1)-16.*XBCARBSTA(K2)+
```

```
     1            36.*XBCARBSTA(K3)-48.*XBCARBSTA(K4)
         XBCARBSTA(K+1) =  -XI1*12.*FAR*RATE_CARBSTA(K)/25.
     1              -COECARBSTA/25.
        ENDIF

      ELSE IF(K.GT.ISTEPS+3)THEN
         DO 158 II = 1,NC
           COEC(II) = 3.*XBC(II,K-3)-16.*XBC(II,K-2)+ 36.*
     1           XBC(II,K-1) - 48.*XBC(II,K)
 158      CONTINUE

         DO 160 II = 1, NC
          XBC(II,K+1) = -XI*12.*FCR*RATE_COMC(II,K)/25.-COEC(II)/25.
 160      CONTINUE

         DO 162 II = 1,NOAMIN
          COEAMSTA(II) = 3.*XBAMSTA(II,K-3)-16.*XBAMSTA(II,K-2)+
     1             36.*XBAMSTA(II,K-1) - 48.*XBAMSTA(II,K)
 162      CONTINUE

         DO 164 II = 1, NOAMIN
          XBAMSTA(II,K+1) = -XI*12.*FCR*RATE_AMSTA(II,K)/25.
     1                -COEAMSTA(II)/25.
 164      CONTINUE

         DO 166 JJ  = 1,NA
          COEA(JJ) =3.*XBA(JJ,K-3)-16.*XBA(JJ,K-2)+36.*
     1          XBA(JJ,K-1)-48.*XBA(JJ,K)
 166      CONTINUE

         DO 168 JJ = 1,NA
          XBA(JJ,K+1) =-XI*12.*FAR*RATE_COMA(JJ,K)/25.-COEA(JJ)/25.

*          ______________________________________________________
*           Adding the desulphonation term to the sulfate. Sulfate is
*           identified by its equivalent weight.
*          ______________________________________________________
          IF (EWANI(JJ).EQ.48.0)  THEN
            XBA(JJ,K+1) = XBA(JJ,K+1) + DD
          END IF
 168     CONTINUE

        IF(NOCARB.GE.1)THEN
         COECARBSTA = 3.*XBCARBSTA(K-3)-16.*XBCARBSTA(K-2)+
     1            36.*XBCARBSTA(K-1)-48.*XBCARBSTA(K)
         XBCARBSTA(K+1) =  -XI1*12.*FAR*RATE_CARBSTA(K)/25.
     1              -COECARBSTA/25.
        ENDIF

      END IF

*     ____________________________________________________________
```

```
*   Determine concentrations for this distance step and recalculate
*   bulk phase equilibria.
*   ______________________________________________________________

    DO 170 II = 1,NC
      CBC(II)=XBC(II,K+1)*CF
 170  CONTINUE

    DO 172 JJ = 1,NA
      CBA(JJ)=XBA(JJ,K+1)*CF
 172  CONTINUE

C------ Splitting of the arrays -----------

    DO 174 II = 1, NOCAT
      CBCAT(II) = CBC(PRIORITY_C(II))
 174  CONTINUE

    DO 176 JJ = 1, NOANI
      CBANI(JJ) = CBA(PRIORITY_A(JJ))
 176  CONTINUE

    IF (NOAMIN.GE.1) THEN
      DO 178 KK = 1, NOAMIN
        CBAMIN(KK) = CBC(PRIORITY_C(NOCAT+KK))
 178    CONTINUE
    END IF

    IF (NOCARB.GE.1) THEN
      DO 180 LL = 1, NOCARB
        CBCARB(LL) = CBA(PRIORITY_A(NOANI+LL))
 180    CONTINUE
    END IF
C------------------------------------------

*   ______________________________________________________
*   Calculate the concentrations of the molecular amines and
*   carbonate in the next slice
*   ______________________________________________________

    IF(NOAMIN.GE.1)THEN
      DO 182 II = 1,NOAMIN
       IF( XBAMSTA(II,K+1).LE.0.0)THEN
          XBAMSTA(II,K+1) = 0.0
       ENDIF
       CBAMSTA(II) = XBAMSTA(II,K+1)*CF
 182   CONTINUE
    ENDIF

    IF(NOCARB.GE.1)THEN
      IF( XBCARBSTA(K+1).LE.0.0)THEN
         XBCARBSTA(K+1) = 0.0
      ENDIF
       CBCARBSTA = XBCARBSTA(K+1)*CF
```

```
      ENDIF

*     ________________________________________________
*      Calculating the new total amine concentration
*     ________________________________________________
      IF(NOAMIN.GE.1)THEN
        DO 184 II = 1,NOAMIN
          CTO_AMIN(II) = CBAMIN(II)+CBAMSTA(II)
 184      CONTINUE
            ENDIF
*     ___________________________________________________
*      Calculating the new total carbonate concentration
*     ___________________________________________________
      IF(NOCARB.GE.1)THEN
        CTO_CARB = CBCARB(1)+CBCARB(2)+CBCARBSTA
      ENDIF

      IF(K.EQ.1)THEN
        PH_OLD = PH_FEED
      ELSE
        PH_OLD = PH_NEW
      ENDIF
      CALL DISSOEQ(PH_OLD,PH_NEW,IFLAG)
      IF(IFLAG.EQ.1)THEN
          WRITE(*,*)"ERROR: Abnormal exit from 'dissoeq' subroutine"
                   WRITE(*,*)"(inside loop)"
                   GO TO 538
      ENDIF
*     ____________________________________________________________
*     Determine rates at constant XI for solutions of the TAU
*     material balance
*     ____________________________________________________________

*     __________________________________________________________
*      Calculating the sum of initial loadings
*     __________________________________________________________
      SUMYC = 0.0
      DO 186 II = 1,NEXC(K+1)-1
        SUMYC = SUMYC + YRC(II,J,K+1)
 186  CONTINUE
      YRC(NEXC(K+1),J,K+1) = 1.0 - SUMYC


      SUMYA = 0.0
      DO 188 JJ = 1,NEXA(K+1)-1
        SUMYA = SUMYA + YRA(JJ,J,K+1)
 188  CONTINUE
      YRA(NEXA(K+1),J,K+1) = 1.0 - SUMYA
*     __________________________________________________________
*      Calculating the number of exchanging ions.
*     __________________________________________________________

      IF(SUMYC.GE.0.9999 .AND. NEXC(K+1).GE.2) THEN
```

```
        NEXC(K+1) = NEXC(K+1)-1
      END IF

      IF (SUMYA.GE.0.9999 .AND. NEXA(K+1).GE.2) THEN
        NEXA(K+1) = NEXA(K+1)-1
      END IF

      IF(NEXC(K+1).EQ.NC+1)THEN
        CBC(NC+1) = CBH
      ENDIF

      IF(NEXA(K+1).EQ.NA+1)THEN
        CBA(NA+1) = CBOH
      ENDIF

*     ------------------------------------------------------------
*     Copying the current resin and liquid phase fractions to
*     single dimension arrays to pass to the "CATION" subroutine
*     ------------------------------------------------------------

      DO 190 II = 1,NEXC(K+1)-1
        YCATCUR(II) = YRC(II,J,K+1)
        XCATCUR(II) = XBC(II,K+1)
 190  CONTINUE
      YCATCUR(NEXC(K+1)) = YRC(NEXC(K+1),J,K+1)

      DO 192 JJ = 1,NEXA(K+1)-1
        YANICUR(JJ) = YRA(JJ,J,K+1)
        XANICUR(JJ) = XBA(JJ,K+1)
 192  CONTINUE
      YANICUR(NEXA(K+1)) = YRA(NEXA(K+1),J,K+1)

      IF(NEXC(K+1).GE.2)THEN
        NTEMPC = NEXC(K+1)
        NTEMPA = NEXA(K+1)
        CALL CATION(YCATCUR,XCATCUR,NTEMPC,NTEMPA,IFLAG)
        IF(IFLAG.EQ.1)THEN
         WRITE(*,*)"ERROR: Abnormal exit from 'cation' subroutine"
         GO TO 538
        ENDIF

*       ----------------------------------------------------------
*       Recalculate the mass transfer coefficients based on the
*       effective diffusivities.
*       ----------------------------------------------------------

        IF (DEC.EQ.0.) THEN
         WRITE(*,*) "ERROR: DEC = 0 "
         GOTO 538
        END IF

        SCH_C = (VISCO/100)/DEN/DEC
        MTC_C = MTC_FUNC(RE_CAT,SCH_C,DEC,CAT_DIA)
*       ------------------------------------------------------------
```

```
*      Setting the fluxes of non-exchanging ions to zero
*

       IF(NEXC(K+1).LT.NC)THEN
         DO 194 II = NEXC(K+1)+1,NC
           FLUXC(II) = 0.0
 194      CONTINUE
       ENDIF

     ELSE
       DO 196 II = 1,NC
         FLUXC(II) = 0.0
 196   CONTINUE
     ENDIF



     IF(NEXA(K+1).GE.2)THEN
       NTEMPC = NEXC(K+1)
       NTEMPA = NEXA(K+1)
       CALL ANION(YANICUR,XANICUR,NTEMPC,NTEMPA,IFLAG)
       IF(IFLAG.EQ.1)THEN
        WRITE(*,*)"ERROR: Abnormal exit from 'anion' subroutine"
        GO TO 538
       ENDIF
*
*      Recalculate the mass transfer coefficients based on the
*      effective diffusivities.
*

       IF (DEA.EQ.0.) THEN
         WRITE(*,*) "ERROR: DEA = 0 "
         GOTO 538
       END IF

       SCH_A = (VISCO/100)/DEN/DEA
       MTC_A = MTC_FUNC(RE_ANI,SCH_A,DEA,ANI_DIA)
*
*      Setting the fluxes of non-exchanging ions to zero
*

       IF(NEXA(K+1).LT.NA)THEN
         DO 198 JJ = NEXA(K+1)+1,NA
           FLUXA(JJ) = 0.0
 198      CONTINUE
       ENDIF
     ELSE
       DO 200 JJ = 1, NA
         FLUXA(JJ) = 0.0
 200   CONTINUE

     ENDIF

*
```

```
*   Calculating the rates and the loadings for the next time step
*   ----------------------------------------------------------------
    DO 202 II = 1,NC
      RATE_COMC(II,K+1) = FLUXC(II)*MTC_C*CONP*CONY
      YRC(II,JD,K+1) = YRC(II,J,K+1)+TAU*RATE_COMC(II,K+1)
      IF (YRC(II,JD,K+1).LE.0.0)THEN
        YRC(II,JD,K+1) = 0.0
      ENDIF
202 CONTINUE

    IF(NOAMIN.GE.1)THEN
     DO 204 KK = 1,NOAMIN
      ITEMP = PRIORITY_C(NOCAT+KK)
      IF(NEXC(K+1).GE.ITEMP.AND.YRC(ITEMP,J,1).LT.0.99)THEN
       RATE_AMSTA(KK,K+1) = MTC_AMSTA(KK)*CBAMSTA(KK)*(-CONP)*CONY
      ELSE
       RATE_AMSTA(KK,K+1) = 0.0
      ENDIF
204  CONTINUE
*
*    ----------------------------------------------
*    Add the protonation term for the amines
*
*    ----------------------------------------------
     DO 206 II=NOCAT+1,NC
      YRC(II,JD,K+1) = YRC(II,JD,K+1)+TAU*RATE_AMSTA(II-NOCAT,K+1)
206  CONTINUE
       ENDIF

    DO 208 JJ = 1,NA
     RATE_COMA(JJ,K+1) = FLUXA(JJ)*MTC_A*CONS
     YRA(JJ,JD,K+1) = YRA(JJ,J,K+1)+TAU*RATE_COMA(JJ,K+1)
     IF (YRA(JJ,JD,K+1).LE.0.0)THEN
       YRA(JJ,JD,K+1) = 0.0
     ENDIF
208 CONTINUE

    IF(NOCARB.GE.1)THEN
     ITEMP = PRIORITY_A(NOANI+1)
     IF(NEXA(K+1).GE.ITEMP.AND.YRA(ITEMP,J,1).LT.0.99)THEN
       RATE_CARBSTA(K+1) = MTC_CARBSTA*CBCARBSTA*(-CONS)
     ELSE
       RATE_CARBSTA(K+1) = 0.0
     END IF
     YRA(NOANI+1,JD,K+1) = YRA(NOANI+1,JD,K+1)+TAU*RATE_CARBSTA(K+1)
    ENDIF


400 CONTINUE
*************************************************************************
*   End of distance loop
*************************************************************************

*
*   -------------------------------
*   Print breakthrough curves
*   -------------------------------
```

```
*------- Converting outlet concentrations into " ppb"

      DO 210 II = 1,NOCAT
        OUT_CAT(II) = CBCAT(II)*EWCAT(II)/1.E-6
 210  CONTINUE

           IF (NOAMIN.GE.1) THEN
         DO 212 KK =1, NOAMIN
           OUT_AMIN(KK) = CBAMIN(KK)*EWAMIN(KK)/1.E-6
           OUT_AMSTA(KK) = CBAMSTA(KK)*EWAMSTA(KK)/1.E-6
           OUT_AMINT(KK) = CTO_AMIN(KK)*EWAMSTA(KK)/1.E-6
 212       CONTINUE
      END IF

      DO 214 JJ = 1,NOANI
        OUT_ANI(JJ) = CBANI(JJ)*EWANI(JJ)/1.E-6
 214  CONTINUE

      IF (NOCARB.GE.1) THEN
        DO 216 LL = 1, NOCARB
               OUT_CARB(LL) = CBCARB(LL)*EWCARB(LL)/1.E-6
 216      CONTINUE
        OUT_CARBT = CTO_CARB*EWCARBSTA/1.E-06
      END IF

*-------

      TAUTIM = TAUTOT*ANI_DIA*ANI_CAP/(MTC_REF*CF*60.)/1440.
      PH = ALOGDISSW + LOG10(CBOH)
*     _______________________________________________
*     Store every tenth iteration to the print file
*     _______________________________________________

      IF (KPRINT.NE.10) GOTO 218
       IF(NOCARB.GE.1)THEN
         WRITE(*,508)TAUTIM,PH,(OUT_CAT(II),II=1,NOCAT),
     1                (OUT_AMINT(JJ),JJ = 1,NOAMIN),
     1                (OUT_ANI(KK),KK=1,NOANI),
     1                OUT_CARBT
       ELSE
        WRITE(*,508)TAUTIM,PH,(OUT_CAT(II),II=1,NOCAT),
     1                (OUT_AMINT(JJ),JJ = 1,NOAMIN),
     1                (OUT_ANI(KK),KK=1,NOANI)
       ENDIF
 508  FORMAT(1X,F10.4,4X,F8.4,16(4X,E12.4))

          KPRINT = 0

 218 CONTINUE

          KPRINT = KPRINT+1
          JK = J
          IF (J.EQ.4) THEN
```

```
      J = 1
        ELSE
          J = J+1
        ENDIF
*   ____________________________________
*   End of time loop
*   ____________________________________

        IF (JFLAG.EQ.1) STOP
        TAUTOT = TAUTOT + TAU

   GOTO 111
*************************************************************************
*   End of time loop
*************************************************************************
 538  STOP
   CLOSE(9)
   END

*  ______________________________
*  End of main program  !
*  ______________________________



*************************************************************************
*   Subroutine "DISSOEQ" to calculate the pH to satisfy the charge
*   balance. It also calculates the new concentrations of the disso-
*   ciative species. It calls the function "SOLVER" and "FUNC"
*   during the calculations. It finds the root for the charge balance
*   equation using bisection method. If more than one root are found
*   it selects the root nearest to the value in the previous slice.
*   PHOLD - pH in the previous slice.
*   PHNEW - pH in the current slice, this is calculated here.
*************************************************************************

      SUBROUTINE DISSOEQ(PHOLD,PHNEW,IFLAG)
      IMPLICIT  REAL*8 (A-H,O-Z)
      COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
     1        SELCOMC(15),SELCOMA(15)
      COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
     1        DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
     1        DIFU_CARBSTA
      COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
     1        VACOMC(15),VACOMA(15)
      COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
     1        EWCARBSTA
      COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
     1        CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
     1        CFC,CFA,CF,CBCARBSTA
      COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
      COMMON /F/XBH,XBOH,SUMYC,SUMYA
      COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
     1        FLUXC(15),FLUXA(15),DEC,DEA
```

```
      COMMON /I/INDEXC(15),INDEXA(15)

      REAL*8 LEFT, RIGHT, LEFTVAL,RIGHTVAL,ROOTS(10)
      REAL*8 DIFF, NEWDIFF,OLDROOT,NEWROOT,DISSW

*     ------------------------------------------------------------
*      This section of the code tries to identify the sections of the
*      pH scale from 1-14 which has the roots and finds the roots.
*     ------------------------------------------------------------
      I = 1
      LEFT = 1.0E-14    !Start from pH = 14(left end of the section)
      RIGHT = 1.0E-13       !Right end of the section
      DO WHILE( RIGHT.LE.1.0E-01 )
                LEFTVAL = FUNC( LEFT, IFLAG )
                IF(IFLAG.EQ.1)THEN
                        WRITE(*,*)"Abnormal exit from 'func'"
                        GO TO 999
                ENDIF

                RIGHTVAL = FUNC( RIGHT, IFLAG )
                IF(IFLAG.EQ.1)THEN
                        WRITE(*,*)"Abnormal exit from 'func'"
                        GO TO 999
                ENDIF

                IF(LEFTVAL*RIGHTVAL.LT.0.0)THEN   !Check if there is a root
                        ROOTS(I) = SOLVER( LEFT, RIGHT, IFLAG )
                        IF(IFLAG.EQ.1)THEN
                                WRITE(*,*)"Abnormal exit from 'solver'"
                                GO TO 999
                        ENDIF

                        I = I+1
                        LEFT = RIGHT
                        RIGHT = RIGHT*10
                ELSE    !if there is no root increase the section length
                        RIGHT = RIGHT*10
                ENDIF
      END DO

*--------------- End of finding the roots ----------------------

*     ------------------------------------------------------------
*     Selecting an appropriate root in case of more than one root
*     ------------------------------------------------------------
      IF(I.EQ.1)THEN
                WRITE(*,*)"No roots between pH 0-14"
                IFLAG = 1
      ELSE
                OLDROOT = 10**(-PHOLD)
                NEWROOT = ROOTS(1)
                DIFF = ABS( OLDROOT - NEWROOT )

                K=2
```

```
              DO WHILE( K.LE.I-1 )
                     NEWDIFF = ABS( OLDROOT - ROOTS(K) )
                     IF( NEWDIFF.LT.DIFF )THEN
                            DIFF = NEWDIFF
                            NEWROOT = ROOTS(K)
                     ENDIF
                     K=K+1
              END DO

              CBH = NEWROOT
              IF(NEWROOT.LE.0)THEN
                     IFLAG = 1
                     GO TO 999
              ENDIF

*
 ________________________________________________________________
*   Calculating the concentrations based on the new pH.
*
 ________________________________________________________________

              CBOH = DISSW/NEWROOT
              PHNEW = -LOG10( NEWROOT )

              IF(NOAMIN.GE.1)THEN
                     DO 11 I=1,NOAMIN
                            IF((CBH*DISSAMIN(I)+DISSW).EQ.0
   1                        .OR. DISSAMIN(I).LE.0)THEN
                                   IFLAG = 1
                                   GO TO 999
                            ENDIF
            CBAMIN(I) = DISSAMIN(I)*CTO_AMIN(I)*CBH
   1          /(CBH*DISSAMIN(I)+DISSW)
                CBAMSTA(I) = CBAMIN(I)*CBOH/DISSAMIN(I)
 11                  CONTINUE
              ENDIF

              IF(NOCARB.GE.1)THEN
         IF(DISSCARB(1).LE.0 .OR. DISSCARB(2).LE.0) THEN
              IFLAG = 1
              GO TO 999
         ENDIF
           CBCARB(1) = CTO_CARB/(CBH/DISSCARB(1)+
   1            DISSCARB(2)/CBH+1)
           CBCARB(2) = DISSCARB(2)*CBCARB(1)/CBH !--CO3-2--
           CBCARBSTA = CBH*CBCARB(1)/DISSCARB(1)
              ENDIF
    ENDIF

999   RETURN
    END


*********************************************************************
*  Function which solves for a root bounded between two values.
*  Uses bisection method to find the root.
```

```
*******************************************************************
   FUNCTION SOLVER(LEFT,RIGHT,IFLAG)
   IMPLICIT REAL*8(A-H,O-Z)
   REAL*8 LEFT, MID, RIGHT, LEFTVAL, RIGHTVAL, MIDVAL

   DO WHILE( ABS(1.0 - LEFT/RIGHT).GT.1E-04 )
            LEFTVAL = FUNC( LEFT,IFLAG)
            IF(IFLAG.EQ.1)THEN
                  WRITE(*,*)"Abnormal exit from 'func'"
                  GO TO 999
            ENDIF

            RIGHTVAL = FUNC( RIGHT, IFLAG)
            IF(IFLAG.EQ.1)THEN
                  WRITE(*,*)"Abnormal exit from 'func'"
                  GO TO 999
            ENDIF

            MID = (LEFT + RIGHT)/2.0
            MIDVAL = FUNC( MID, IFLAG)
            IF(IFLAG.EQ.1)THEN
                  WRITE(*,*)"Abnormal exit from 'func'"
                  GO TO 999
            ENDIF

            IF( LEFTVAL*MIDVAL.LT.0.0 )THEN
                  RIGHT = MID
            ELSE
                  LEFT = MID
            ENDIF
   END DO

   SOLVER = (LEFT+RIGHT)/2
999 RETURN
   END

**************************************************************
*   Function to evaluate the charge balance function
**************************************************************

    FUNCTION FUNC( HPLUS, IFLAG )
    IMPLICIT  REAL*8 (A-H,O-Z)
    COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
   1      SELCOMC(15),SELCOMA(15)
    COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
   1      DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
   1      DIFU_CARBSTA
    COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
   1      VACOMC(15),VACOMA(15)
    COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
   1      EWCARBSTA
    COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
   1      CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
   1      CFC,CFA,CF,CBCARBSTA
```

```
   COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
   COMMON /F/XBH,XBOH,SUMYC,SUMYA
   COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
  1       FLUXC(15),FLUXA(15),DEC,DEA
   COMMON /I/INDEXC(15),INDEXA(15)

  REAL*8 FUNC,CTOTANI,CTOTCAT,DISSW


  CTOTCAT = 0
  CTOTANI = 0

  DO 11 I=1,NOCAT
   IF(CBCAT(I).LT.0.0)THEN
    WRITE(*,*)"Negative bulk concentrations encounted in func."
    IFLAG = 1
    GO TO 999
   ENDIF

   CTOTCAT = CTOTCAT + CBCAT(I)
11 CONTINUE

  IF(NOAMIN.GE.1)THEN
   DO 12 I=1,NOAMIN
    IF((HPLUS*DISSAMIN(I)+DISSW).LE.0 .OR. DISSW.LE.0
  1    .OR. HPLUS.LE.0 .OR.DISSAMIN(I).LE.0)THEN
      WRITE(*,*)"DIVIDE BY ZERO ENCOUNTERED"
          IFLAG = 1
          GO TO 999
    ENDIF

    IF(CTO_AMIN(I).LT.0.0)THEN
      WRITE(*,*)"Negative total amin conc. encountered in func"
      IFLAG = 1
      GO TO 999
    ENDIF

    CBAMIN(I) = DISSAMIN(I)*CTO_AMIN(I)*HPLUS
  1         /(HPLUS*DISSAMIN(I)+DISSW)
    CTOTCAT = CTOTCAT + CBAMIN(I)
12  CONTINUE
  ENDIF

  CTOTCAT = CTOTCAT + HPLUS

  DO 13 I=1,NOANI
   IF(CBANI(I).LT.0.0)THEN
    WRITE(*,*)"Negative bulk concentrations encounted in func."
    IFLAG = 1
    GO TO 999
   ENDIF

               CTOTANI = CTOTANI +  CBANI(I)
13 CONTINUE
```

```
      IF(NOCARB.GE.1)THEN
                  IF( (HPLUS/DISSCARB(1)+DISSCARB(2)/HPLUS+1).LE.0
     1             .OR. HPLUS.LE.0 .OR.DISSCARB(1).LE.0
     1             .OR. DISSCARB(2).LE.0 )THEN
           WRITE(*,*)"DIVIDE BY ZERO ENCOUNTERED"
           IFLAG = 1
                  GO TO 999
         ENDIF
                  CBCARB(1) = CTO_CARB/(HPLUS/DISSCARB(1)
     1          +DISSCARB(2)/HPLUS+1)       !** HCO3- **
         CBCARB(2) = DISSCARB(2)*CBCARB(1)/HPLUS !** CO3-2 **
                  CTOTANI = CTOTANI+CBCARB(1)+CBCARB(2)
      ENDIF

      CTOTANI = CTOTANI+ DISSW/HPLUS

      FUNC = CTOTCAT - CTOTANI
  999 RETURN
      END


************************************************************************
*   Subroutine "CATION" to calculate the interfacial concentrations
*   and fluxes of cations using Franzreb's flux expressions
************************************************************************

      SUBROUTINE CATION(YYC,XXC,NCATION,NANION,IFLAG)
       IMPLICIT  REAL*8 (A-H,O-Z)
       COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
     1        SELCOMC(15),SELCOMA(15)
       COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
     1        DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
     1        DIFU_CARBSTA
       COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
     1        VACOMC(15),VACOMA(15)
       COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
     1        EWCARBSTA
       COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
     1        CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
     1        CFC,CFA,CF,CBCARBSTA
       COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
       COMMON /F/XBH,XBOH,SUMYC,SUMYA
       COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
     1        FLUXC(15),FLUXA(15),DEC,DEA
       COMMON /I/INDEXC(15),INDEXA(15)

       REAL*8 YYC(15),XXC(15),XXN(15),CCO(15),N(15),
     1    BB(15),AA(15),CBN(15),CI(15),R1(15),XXI(15)

*--------------------------------------------------------------
*   Finding the total concentration of cations in bulk phase
*--------------------------------------------------------------
```

```
    CTO = 0.0
    DO 5 I = 1, NCATION   !(Total number of cations)
      CTO = CTO + CBC(I)
 5   CONTINUE
*--------------------------------------------------------------
*  Finding bulk equivalent fraction relative to feed concentration
*--------------------------------------------------------------

    DO 7 II = 1, NCATION-1
      IF (CTO.EQ.0.) THEN
        WRITE(*,*) "CTO = 0, Divided by zero, exit"
        IFLAG = 1
        GOTO 65
      END IF
      XXN(II) = XXC(II)*CFC/CTO
 7   CONTINUE

    SUMXB = 0.0
    DO 8 II = 1,NCATION-1
      SUMXB = SUMXB + XXN(II)
 8   CONTINUE
    XXN(NCATION) = 1. - SUMXB
*
*  Converting the equivalent concentration to molar concentration
*

    DO 9 JJ = 1, NANION
      CCO(JJ) = CBA(JJ)/ABS(VACOMA(JJ))
 9   CONTINUE

*--------------------------------------------------------
*  Calculate the summation of (Zj**2)*Cj or (Zj*Cj)
*--------------------------------------------------------

    SUMZN = 0.0
    DO 10 JJ = 1, NANION
      SUMZN = SUMZN + (VACOMA(JJ)**2.)*CCO(JJ)
 10  CONTINUE

    SUMZD = 0.0
    DO 11 JJ = 1, NANION
      SUMZD = SUMZD + (VACOMA(JJ)*CCO(JJ))
 11  CONTINUE

    IF (SUMZD.EQ.0.) THEN
      WRITE(*,*) "SUMZD = 0 (in 'cation' subroutine), exit"
      IFLAG = 1
      GOTO 65
    ENDIF
*-----------

    ZY = SUMZN/SUMZD    ! Mean valency of coions

    DO 12 II = 1, NCATION
```

```
      IF (ZY .EQ. 0.) THEN
        WRITE(*,*) "ZY = 0 (in 'cation' subroutine), exit"
        GOTO 65
      END IF
      N(II) = - VACOMC(II)/ZY    ! relative valency to pseudo ion
 12   CONTINUE

*----------------------------------------------------------
*  Start the iteration to find the total interfacial conc
*----------------------------------------------------------

     CTI = CTO
     EPS = 1.0E-15
     ITER = 0
 15  CONTINUE
     ITER = ITER+1

*----- Call subroutine to calcualte the interfacial conc for each species----

      CALL INTERCOM(YYC,SELCOMC,VACOMC,CTI,CAT_CAP,NCATION,XXI,IFLAG)
      IF (IFLAG.EQ.1) THEN
       WRITE(*,*)"Abnormal exit from 'intercom' subroutine"
       GO TO 65
      ENDIF

*
*   Calculation of the total interfacial concentration CTI
*

      SUMPN = 0.0
      DO 20 II = 1, NCATION
       SUMPN = SUMPN + ABS(N(II)*DIFUCOMC(II)*(XXI(II)-XXN(II)))
 20   CONTINUE

      SUMPD = 0.0
      DO 25 II = 1, NCATION
       SUMPD = SUMPD + ABS(DIFUCOMC(II)*(XXI(II) - XXN(II)))
 25   CONTINUE

      P = SUMPN/SUMPD        ! The P value in Franzreb's expression

      SUMTN = 0.0
      DO 35 II = 1, NCATION
        SUMTN = SUMTN + (1.+ N(II))*DIFUCOMC(II)*XXN(II)
 35   CONTINUE

      SUMTD = 0.0
      DO 45 II = 1, NCATION
        SUMTD = SUMTD + (1.+ N(II))*DIFUCOMC(II)*XXI(II)
 45   CONTINUE

      IF ((P+1.) .EQ. 0. .OR. SUMTD .EQ. 0.) THEN
        IFLAG = 1
        WRITE(*.*) " P = -1, OR SUMTD = 0, Divided by zero"
```

```
        GOTO 65
      ENDIF

*------ The CTI expression based on Franzreb's algorithm -----

      CTIN = (SUMTN/SUMTD)**(1./(P+1.))*CTO

      IF(ITER.GE.10000)THEN
        WRITE(*,*)"Abnormal exit from 'cation' subroutine"
        IFLAG =1
        GO TO 65
      ENDIF

* ----- The CTI expression based on Franzreb's algorithm -----

          IF ((ABS(CTIN - CTI)/CTIN) .GT. EPS) THEN
          CTI = CTIN
          GO TO 15
        ELSE
          CTI = CTIN
        END IF

*________________________________________________________________
*  Calculation of flux and effective diffusivities using
*  Franzreb's flux expressions
*________________________________________________________________

*__________________________________________________________________
*  If total interfacial concentration is equal to the total bulk
*  concentration, then individual interfacial concentrations will
*  be equal to their bulk concentrations according to the relation
*  between CTI and CTO in franzreb's expressions
*___________________________________________________________________

     IF( CTI.EQ.CTO ) THEN
       DO 46  II = 1,NCATION
         FLUXC(II) = 0.0
 46     CONTINUE
       GO TO 65
     ENDIF

     W = 1.0        ! The charge coefficient,for cations w = 1

*----- Calculate the Bi value in Franzreb's algorithm ------

     DO 50 II = 1,NCATION
       IF ((CTI**(-P-1.)-CTO**(-P-1.)) .EQ. 0) THEN
         IFLAG = 1
         WRITE(*,*)"Divide by 0 in calculating BB(II), cation"
         GOTO 65
       ENDIF
       BB(II) = W*(XXI(II)-XXN(II))/(CTI**(-P-1.)-CTO**(-P-1.))
 50  CONTINUE
```

```
*------ Converting concentrations from equivalents to molar -----

      DO 51 II = 1,NCATION
        CBN(II) = W*CBC(II)/VACOMC(II)
 51   CONTINUE

*------ Calculate the Ai value in Franzreb's algorithm -----*

      DO 53 II = 1,NCATION
        IF (CTO.EQ.0) THEN
         IFLAG = 1
         WRITE(*,*) "CTO = 0, Divided by zero"
         GOTO 65
        ENDIF
        AA(II) = (VACOMC(II)*CBN(II)-BB(II)*CTO**(-P))/CTO
 53   CONTINUE

*-----------------------------------------------------------------
*   Calculate the interfacial concentration for each species from
*   equivalent fractions at the interface
*-----------------------------------------------------------------

      DO 55 II = 1,NCATION
        CI(II) = W*XXI(II)*CTI/VACOMC(II)
 55   CONTINUE

*-----------------------------------------------------------------
*  Calculating the flux Ji for cations using Franzreb's expression
*-----------------------------------------------------------------

      DO 57 II = 1,NCATION
        IF (P.EQ.0) THEN
         WRITE(*,*) " P = 0, Divided by 0 in 'cation' subroutine"
         IFLAG = 0
         GOTO 65
        END IF
        R1(II) = DIFUCOMC(II)*((1.-N(II)/P)*(CI(II)-CBN(II))
     1        +N(II)*(AA(II)/VACOMC(II))*(1.+1./P)*(CTI-CTO))
 57   CONTINUE

      SIGR = 0.0
      DO 59 II = 1,NCATION
       SIGR = SIGR + ABS(R1(II))
 59   CONTINUE

      SIGD = 0.0
      DO 61 II = 1,NCATION
       SIGD = SIGD + ABS(CI(II)-CBN(II))
 61   CONTINUE

      IF (SIGD .EQ.0) THEN
       IFLAG = 1
       WRITE(*.*) " SIGD = 0, Divided by zero in 'cation' subrou."
       GOTO 65
```

```
   END IF
   DEC = SIGR/SIGD   !Calculate the effective diffusivity for cations

   DO 63 II = 1,NCATION
     FLUXC(II) = W*VACOMC(II)*R1(II)/DEC   ! The ratio of Ji/K
63  CONTINUE

65  RETURN
   END




**********************************************************************
*  Subroutine "ANION" to calculate the anionic interfacial concen-
*  trations and fluxes.
**********************************************************************

   SUBROUTINE ANION(YYA,XXA,NCATION,NANION,IFLAG)
    IMPLICIT  REAL*8 (A-H,O-Z)
    COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
  1        SELCOMC(15),SELCOMA(15)
    COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
  1        DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
  1        DIFU_CARBSTA
    COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
  1        VACOMC(15),VACOMA(15)
    COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
  1        EWCARBSTA
    COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
  1        CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
  1        CFC,CFA,CF,CBCARBSTA
    COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
    COMMON /F/XBH,XBOH,SUMYC,SUMYA
    COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
  1        FLUXC(15),FLUXA(15),DEC,DEA
    COMMON /I/INDEXC(15),INDEXA(15)

    REAL*8 YYA(15),XXA(15),XXN(15),CCO(15),N(15),
  1     BB(15),AA(15),CBN(15),CI(15),R1(15),XXI(15)

*------------------------------------------------------------
*  Finding the total concentration for cations at bulk phase
*------------------------------------------------------------

    CTO = 0.0
    DO 5 JJ = 1, NANION !(Total number of anions)
      CTO = CTO + CBA(JJ)
 5  CONTINUE
*-----------------------------------------------------------------
*  Finding bulk equivalent fractions relative to feed concentration
*-----------------------------------------------------------------

    DO 7 JJ = 1, NANION-1
```

```
      IF (CTO .EQ.0) THEN
       WRITE(*,*) "CTO = 0, Divided by zero in 'anion' subroutine"
       IFLAG = 1
       GOTO 65
      ENDIF
      XXN(JJ) = XXA(JJ)*CFA/CTO
 7   CONTINUE

    SUMXB = 0.0
    DO 8 JJ = 1,NANION-1
      SUMXB = SUMXB + XXN(JJ)
 8   CONTINUE
    XXN(NANION) = 1. - SUMXB
*
*----------------------------------------------------------------------
* Converting the equivalent concentrations into molar concentrations
*----------------------------------------------------------------------

    DO 9 II = 1, NCATION
      CCO(II) = CBC(II)/ABS(VACOMC(II))
 9   CONTINUE

*-----------------------------------------------------
*  Calculate the summation of (Zi**2)*Ci or (Zi*Ci)
*-----------------------------------------------------

    SUMZN = 0.0
    DO 10 II = 1, NCATION
      SUMZN = SUMZN + (VACOMC(II)**2.)*CCO(II)
 10  CONTINUE

    SUMZD = 0.0
    DO 11 II = 1, NCATION
      SUMZD = SUMZD + (VACOMC(II)*CCO(II))  ! The summation of Zi*Ci
 11  CONTINUE

    IF (SUMZD .EQ. 0.0) THEN
      WRITE(*,*) "SUMZD = 0, Divided by zero, exit"
      IFLAG = 1
      GOTO 65
    ENDIF
*----------------

    ZY = SUMZN/SUMZD      ! Mean valency of coions

    DO 12 JJ = 1, NANION
      IF (ZY .EQ. 0.0) THEN
        WRITE(*,*) "ZY =0, Divided by zero (in anion subroutine)"
        GOTO 65
      ENDIF

      N(JJ) = - VACOMA(JJ)/ZY   ! Relative valency of anions to pseudoion
 12  CONTINUE

*----------------------------------------------------------------
```

```
* Start the iteration to find the total interfacial concentration
*--------------------------------------------------------------

    CTI = CTO         ! Initial guess of CTI
    EPS = 1.0E-15      ! Set the iteration tolerance
    ITER = 0
 15  CONTINUE
    ITER = ITER+1

*----------------------------------------------------------------
*  Call subroutine to calculate the interfacial concentration
*  for each species
*----------------------------------------------------------------

    CALL INTERCOM(YYA,SELCOMA,VACOMA,CTI,ANI_CAP,NANION,XXI,IFLAG)
    IF(IFLAG.EQ.1)THEN
      WRITE(*,*)"Abnormal exit from 'intercom' subroutine"
      GO TO 65
    ENDIF
*
*  _____________________________________________________________
*   Calculation of the total interfacial concentration CTI
*  _____________________________________________________________

    SUMPN = 0.0
    DO 20 JJ = 1, NANION
      SUMPN = SUMPN + ABS(N(JJ)*DIFUCOMA(JJ)*(XXI(JJ)-XXN(JJ)))
 20  CONTINUE

    SUMPD = 0.0
    DO 25 JJ = 1, NANION
      SUMPD = SUMPD + ABS(DIFUCOMA(JJ)*(XXI(JJ) - XXN(JJ)))
 25  CONTINUE

    P = SUMPN/SUMPD     ! The P value in Franzreb's expression

    SUMTN = 0.0
    DO 35 JJ = 1, NANION
      SUMTN = SUMTN + (1.+ N(JJ))*DIFUCOMA(JJ)*XXN(JJ)
 35  CONTINUE

    SUMTD = 0.0
    DO 45 JJ = 1, NANION
      SUMTD = SUMTD + (1.+ N(JJ))*DIFUCOMA(JJ)*XXI(JJ)
 45  CONTINUE

    IF ((P+1.) .EQ. 0. .OR. SUMTD .EQ. 0.) THEN
      IFLAG = 1
      WRITE(*,*) " P = -1, or SUMTD = 0, Divided by zero"
      GOTO 65
    ENDIF

*------Calculate the CTI based on Franzreb's algorithm -----

    CTIN = (SUMTN/SUMTD)**(1./(P+1.))*CTO
```

```
      IF(ITER.GE.10000)THEN
        WRITE(*,*)"NUMBER OF ITERATIONS EXCEEDED",ITER
        WRITE(*,*)"CTIN,CTI:",CTIN,CTI
        WRITE(*,*)"Abnormal exit from 'anion' subroutine"
        IFLAG =1
        GO TO 65
      ENDIF

      IF ((ABS(CTIN - CTI)/CTIN) .GT. EPS) THEN
         CTI = CTIN
         GO TO 15
      ELSE
         CTI = CTIN
      END IF

*    ____________________________________________________________
*    Calculation of flux and effective diffusivities using
*    Franzreb's expressions
*    ____________________________________________________________

*    ________________________________________________________________
*    If total interfacial concentration is equal to the total bulk
*    concentration, then individual interfacial concentrations will
*    be equal to their bulk concentrations according to the relation
*    between CTI and CTO in franzreb's expressions
*    ________________________________________________________________

      IF( CTI.EQ.CTO ) THEN
        DO 46  JJ = 1,NANION
          FLUXA(JJ) = 0.0
 46     CONTINUE
        GO TO 65
      ENDIF
      W = -1.0  !The charge coefficient, w = -1.0 for anions

*------Calculate the coefficient of Bj in Franzreb's method ---------

      DO 50 JJ = 1,NANION
        IF ((CTI**(-P-1.)-CTO**(-P-1.)) .EQ. 0) THEN
         IFLAG = 1
         WRITE(*,*)"Divide by 0 while calculating BB(JJ) in 'anion'"
         GOTO 65
        ENDIF
        BB(JJ) = W*(XXI(JJ)-XXN(JJ))/(CTI**(-P-1.)-CTO**(-P-1.))
 50   CONTINUE

*------- Converting the equivalent concentrations into molar ----

      DO 51 JJ = 1,NANION
        CBN(JJ) = W*CBA(JJ)/VACOMA(JJ)
 51   CONTINUE

*--------
```

```
      IF (CTO.EQ.0) THEN
        IFLAG = 1
        WRITE(*,*) "CTO = 0, while calculating AA(JJ) in 'anion'"
        GOTO 65
      ENDIF

*----- Calculate the coefficient of Bj in Franzreb's method ---------

      DO 53 JJ = 1,NANION
        AA(JJ) = (VACOMA(JJ)*CBN(JJ)-BB(JJ)*CTO**(-P))/CTO
 53   CONTINUE

*-----------------------------------------------------------------
*     Calculate the interfacial concentration for each species from
*     equivalent fractions at the interface
*-----------------------------------------------------------------

      DO 55 JJ = 1,NANION
        CI(JJ) = W*XXI(JJ)*CTI/VACOMA(JJ)
 55   CONTINUE

*-----------------------------------------------------------------
*    Calculating the flux Ji for anions using Franzreb's expression
*-----------------------------------------------------------------

      DO 57 JJ = 1,NANION
       IF (P.EQ.0) THEN
         WRITE(*,*) " P = 0 in 'anion' subroutine"
         IFLAG = 0
         GOTO 65
       END IF
             ! The flux expression in Franzreb's method

       R1(JJ) = DIFUCOMA(JJ)*((1.-N(JJ)/P)*(CI(JJ)-CBN(JJ))
     1         +N(JJ)*(AA(JJ)/VACOMA(JJ))*(1.+1./P)*(CTI-CTO))

 57   CONTINUE

      SIGR = 0.0
      DO 59 JJ = 1,NANION
       SIGR = SIGR + ABS(R1(JJ))
 59   CONTINUE

          SIGD = 0.0
      DO 61 JJ = 1,NANION
       SIGD = SIGD + ABS(CI(JJ)-CBN(JJ))
 61   CONTINUE

      IF (SIGD .EQ.0) THEN
       IFLAG = 1
       WRITE(*,*) " SIGD = 0, in 'anion' subroutine "
       GOTO 65
      END IF
```

```
      DEA = SIGR/SIGD   ! The effective diffusivity for anions

      DO 63 JJ = 1,NANION
        FLUXA(JJ) = W*VACOMA(JJ)*R1(JJ)/DEA   ! The ratio of Ji/K for anions
63    CONTINUE

65    RETURN
         END


*************************************************************************
* Subroutine "INTERCOM" to calculate the interfacial concentrations
*************************************************************************

      SUBROUTINE INTERCOM(Y,K,ZT,CTOT,Q,N,X,IFLAG)
      IMPLICIT REAL*8(A-H,O-Z)
      EXTERNAL POL
      REAL*8 Y(15),X(15),KT(15),K(15),Z(15),CTOT,Q,ORD(15),KREF,LAM(15)
      REAL*8 XSUM,ZT(15)
      INTEGER N,IFLAG

      DO 2 I = 1, N
        Z(I) = ABS(ZT(I))
2     CONTINUE



*  ______________________________________________________________________
*    Calculate the values of LAM for each component, and calculate
*    the order of the concentration as determined by the ratio of
*    the ion valence to the reference ion valence.
*  ______________________________________________________________________
      YTEST = 0.0
      IFLAG = 0

      DO 5 I=1,N
       IF(Y(I).LT.0.0) THEN
          WRITE(*,*)"Negative loadings encounted in 'intercom'"
          IFLAG = 1
          RETURN
       ENDIF
       YTEST = YTEST + Y(I)
5     CONTINUE


       IF (ABS(YTEST-1.0).GT. 1.0e-1) THEN
         WRITE(*,*) 'INITIAL LOADINGS MUST SUM TO 1.0'
         IFLAG = 1
         go to 26
       ELSEIF (CTOT.eq.0.0) THEN
         WRITE(*,*) 'Total interfacial concentration equals zero'
         IFLAG = 1
         RETURN
```

```
        ELSE
        ENDIF


      CALL SELMEAN(K,KREF,Y,YREF,N,IFLAG)
      CALL CHARGEMEAN(Z,ZREF,Y,Q,N,IFLAG)
      CALL SELREF(K,KT,Z,N,KREF,ZREF,IFLAG)
      DO 10 I = 1,N
        LAM(I) = Y(I)*(KT(I)**(-1/ZREF))*(YREF**(-Z(I)/ZREF))*(Q/CTOT)
     1        **(1-(Z(I)/ZREF))
        ORD(I) = Z(I)/ZREF
 10    CONTINUE
*
*----------------------------------------------------------------------
*     Construct the polynomial and solve for the root using the
*     regula falsi (false position) search algorithm.
*
*----------------------------------------------------------------------
      X1=0.0
      XACC=1e-10
      X2=1.0
      XROOT = REGFALS(POL,X1,X2,XACC,LAM,ORD,N,IFLAG)

      IF(IFLAG.eq.1)THEN
        WRITE(*,*)"LOADINGS:",(Y(I),I=1,N)
        WRITE(*,*)"SELECTIVITIES:",(k(I),I=1,N)
        WRITE(*,*)"VALENCIES:",(Z(I),I=1,N)
        WRITE(*,*) CTOT,Q,N
        RETURN
      ENDIF

      DO 22 I = 1,N
      X(I)=LAM(I)*XROOT**(ORD(I))
 22    CONTINUE
      XSUM = 0.0
      DO 23 I = 1,N
        XSUM = XSUM + X(I)
 23    CONTINUE
      DO 24 I=1,N
        X(I) = X(I)/XSUM

 24    CONTINUE
 26    RETURN
      END

*********************************************************************
*     Function which calculates the value of the molar fraction
*     polynomial expression.
*********************************************************************

      FUNCTION POL(X,LAM,ORD,n)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 X,LAM(15),ORD(15)
      INTEGER N
      POL = -1.
```

```
   DO 25 I = 1,N
     POL = POL + LAM(I)*X**(ORD(I))
25  CONTINUE

26  RETURN
   END

*******************************************************************
*  Subroutine SELMEAN
*  This subroutine calculates the mean selectivity coefficient
*  given the current resin loading.  See the documentation
*  enclosed with this code for the derivation of the mean sel-
*  ectivity coefficient
*
*    K(I)= Selectivity array with respect to refer
*    K(I)= Selectivity array with respect to reference ion
*    Y(I)= Current resin loading (meq/ml)
*    YREF = Equivalent ionic fraction of new reference ion,
*           by definition it has a value of 1.0
*    N = number of cations or anions (includes dissociative
*         species)
*    KREF = the selectivity of the new reference ion with
*         respect to the old one.
*******************************************************************

   SUBROUTINE SELMEAN(K,KREF,Y,YREF,n,IFLAG)
   IMPLICIT REAL*8(A-H,O-Z)
   REAL*8 K(15),KREF,Y(15),YREF
   INTEGER N,IFLAG
   KREF = 1.
   YREF = 1.
   DO 10 I = 1,N
   IF (K(I).LT.0.0) THEN
      WRITE(*,*) 'Negative selectivity, abnormal exit'
      IFLAG = 1
      RETURN
     ENDIF
     KREF = KREF*(K(I)**Y(I))
10  CONTINUE
   RETURN
   END

*******************************************************************
*  Subroutine CHARGEMEAN
*  This subroutine calculates the mean ionic valence as
*  described by equation 6 in Franzreb's flux expressions
*  The variables used are:
*     Q = the total capacity of the resin (meq/ml)
*     Z(I) = the charge array of either cations or anions
*     ZN = the summation term in the numerator of Franzreb's
*        expression
*     ZD = the summation term in the denominator of Franzreb's
*        expression
*     ZREF = the mean ionic valence
```

```
*     Y(I) = the equivalent fraction array of  cations or
*         anions (meq/ml)
*     YT(I) = mole fraction resin loading array (mol/l)
*     N = the number of either cations or anions
*******************************************************************

      SUBROUTINE CHARGEMEAN(Z,ZREF,Y,Q,n,IFLAG)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 Z(15),Y(15),Qt(15),Q,zn,zd,ZREF
      INTEGER N,IFLAG
      ZN = 0.
      ZD = 0.
      ZREF = 0.

*----- Convert equivalent ionic capacities to molar capacities

      DO 5 I = 1,N
       Qt(I) = Q*Y(I)/ABS(Z(I))
 5    CONTINUE

*----- Apply mean valence relationship to calculate the mean valence

      DO 10 I = 1,N
        ZN = ZN + (Z(I)**2)*Qt(I)
        ZD = ZD + Z(I)*Qt(I)
 10     CONTINUE
        IF (ZD.EQ.0.0) THEN
         IFLAG = 1
         WRITE(*,*) 'Mean valency denominator equals zero'
         RETURN
        ELSE
        ENDIF

      ZREF = ZN/ZD
      RETURN
      END

*******************************************************************
*  Subroutine SELREF
*  This subroutine changes the reference ion in the selectivity
*  coefficient array for either cations or anions of arbitrary
*  valence
*  The variables used are:
*     K = Selectivity array with common reference ion
*     KREF = Selectivity of new reference with respect to the
*        old reference
*     N = number of cations or anions in system, also size of
*        arrays
*     Z = ion charge array
*     ZREF = reference ion charge
*******************************************************************

      SUBROUTINE SELREF(K,KT,Z,N,KREF,ZREF,IFLAG)
      IMPLICIT REAL*8(A-H,O-Z)
```

```
      REAL*8 K(15),KT(15),KREF,Z(15),ZREF
      INTEGER N,IFLAG
      DO 10 I = 1,N
        IF (KREF.EQ.0.0) THEN
          WRITE (*,*) 'Refefence selectivity equals zero'
          IFLAG = 1
          RETURN
         ENDIF
         KT(I)=(K(I)**ZREF)/(KREF**Z(I))
 10   CONTINUE
      RETURN
      END

************************************************************************
*     Function to solve the polynomial using regula-falsi method.
************************************************************************
      FUNCTION REGFALS(POL,X1,X2,XACC,LAM,ORD,N,IFLAG)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER MAXIT
      REAL*8 REGFALS,X1,X2,XACC,POL,LAM(15),ORD(15)
      INTEGER N,IFLAG
      EXTERNAL POL
      PARAMETER (MAXIT=50)
      INTEGER J
      REAL*8 DEL,DX,F,FH,FL,SWAP,XH,XL

      FL=POL(X1,LAM,ORD,N)
      FH=POL(X2,LAM,ORD,N)

      IF(FL*FH.GT.0.) THEN
        WRITE(*,*) 'Root must be bracked in regfls'
        IFLAG=1
        RETURN
      ENDIF

      IF(FL.LT.0.)THEN
        XL=X1
        XH=X2
      ELSE
        XL=X2
        XH=X1
        SWAP=FL
        FL=FH
        FH=SWAP
      ENDIF
      DX=XH-XL
      DO 11 J=1,MAXIT
        REGFALS=XL+DX*FL/(FL-FH)
        F=POL(REGFALS,LAM,ORD,N)
        IF(F.LT.0.) THEN
         DEL=XL-REGFALS
         XL=REGFALS
         FL=F
        ELSE
```

```
         DEL=XH-REGFALS
         XH=REGFALS
         FH=f
        ENDIF
        DX=XH-XL
       IF(ABS(DEL).LT.XACC.OR.F.EQ.0.) RETURN
 11    CONTINUE

      IF(J.GE.MAXIT)THEN
       IFLAG = 1
       WRITE(*,*)'Regfals exceeds maximun iterations'
       RETURN

      ENDIF
      END


************************************************************************
*     Subroutine to sort the selectivities, diffusivities and the
*     valences. They are sorted in the decreasing order of their
*     valences. The ions of same valency are sorted in the descending
*     order of their selectivities. Bubble sort algorithm is used to
*     sort the arrays.
************************************************************************

      SUBROUTINE SORT_IONS()
       IMPLICIT  REAL*8 (A-H,O-Z)
       COMMON /S/SEL_CAT(8),SEL_ANI(8),SELAMIN(5),SELCARB(2),
     1        SELCOMC(15),SELCOMA(15)
       COMMON /D/DIFU_CAT(8),DIFU_ANI(8),DIFU_AMIN(5),DIFU_AMSTA(5),
     1        DIFU_CARB(2),DIFUH,DIFUOH,DIFUCOMC(15),DIFUCOMA(15),
     1        DIFU_CARBSTA
       COMMON /V/VACAT(8),VAANI(8),VAAMIN(5),VACARB(2),VAH,VAOH,
     1        VACOMC(15),VACOMA(15)
       COMMON /E/EWCAT(8),EWANI(8),EWAMIN(5),EWAMSTA(5),EWCARB(2),
     1        EWCARBSTA
       COMMON /C/CBCAT(8),CBANI(8),CBAMIN(5),CBAMSTA(5),CBCARB(2),
     1        CTO_CARB,CTO_AMIN(5),CBH,CBOH,CBC(15),CBA(15),
     1        CFC,CFA,CF,CBCARBSTA
       COMMON /N/NOCAT,NOANI,NOAMIN,NOCARB,NC,NA
       COMMON /F/XBH,XBOH,SUMYC,SUMYA
       COMMON /P/TMPC,DISSW,DISSAMIN(5),DISSCARB(2),CAT_CAP,ANI_CAP,
     1        FLUXC(15),FLUXA(15),DEC,DEA
       COMMON /I/INDEXC(15),INDEXA(15)


*
*      ----------------------------------------------------------
*      Sorting the cation data
*      ----------------------------------------------------------
       DO 44 II = 1,NC-1
         DO 33 JJ = II+1,NC

          IF(VACOMC(II).LT.VACOMC(JJ))THEN
*              ------------------------------
```

```
*           Interchange valences
*           ________________________________
          TEMP = VACOMC(II)
          VACOMC(II) = VACOMC(JJ)
          VACOMC(JJ) = TEMP
*
*           ________________________________
*           Interchange selectivities
*           ________________________________
          TEMP = SELCOMC(II)
          SELCOMC(II) = SELCOMC(JJ)
          SELCOMC(JJ) = TEMP
*
*           ________________________________
*           Interchange diffusivities
*           ________________________________
          TEMP = DIFUCOMC(II)
          DIFUCOMC(II) = DIFUCOMC(JJ)
          DIFUCOMC(JJ) = TEMP
*
*           _______________________________
*           Interchange indices
*           _______________________________
          TEMP = INDEXC(II)
          INDEXC(II) = INDEXC(JJ)
          INDEXC(JJ) = TEMP

       ELSE IF(VACOMC(II).EQ.VACOMC(JJ).AND.
     1        SELCOMC(II).LT.SELCOMC(JJ)) THEN
*
*           ________________________________
*           Interchange valences
*           ________________________________
          TEMP = VACOMC(II)
          VACOMC(II) = VACOMC(JJ)
          VACOMC(JJ) = TEMP
*
*           ________________________________
*           Interchange selectivities
*           ________________________________
          TEMP = SELCOMC(II)
          SELCOMC(II) = SELCOMC(JJ)
          SELCOMC(JJ) = TEMP
*
*           ________________________________
*           Interchange diffusivities
*           ________________________________
          TEMP = DIFUCOMC(II)
          DIFUCOMC(II) = DIFUCOMC(JJ)
          DIFUCOMC(JJ) = TEMP
*
*           _______________________________
*           Interchange indices
*           _______________________________
          TEMP = INDEXC(II)
          INDEXC(II) = INDEXC(JJ)
          INDEXC(JJ) = TEMP

       ENDIF

  33   CONTINUE
```

```
 44  CONTINUE
*
*    ______________________________________________________
*    Sorting the anion data
*    ______________________________________________________
     DO 66 II = 1,NA-1
       DO 55 JJ = II+1,NA

         IF(VACOMA(II).GT.VACOMA(JJ))THEN
*
*           ______________________________
*           Interchange valences
*           ______________________________
           TEMP = VACOMA(II)
           VACOMA(II) = VACOMA(JJ)
           VACOMA(JJ) = TEMP
*
*           ______________________________
*           Interchange selectivities
*           ______________________________
           TEMP = SELCOMA(II)
           SELCOMA(II) = SELCOMA(JJ)
           SELCOMA(JJ) = TEMP
*
*           ______________________________
*           Interchange diffusivities
*           ______________________________
           TEMP = DIFUCOMA(II)
           DIFUCOMA(II) = DIFUCOMA(JJ)
           DIFUCOMA(JJ) = TEMP
*
*           _____________________________
*           Interchange indices
*           _____________________________
           TEMP = INDEXA(II)
           INDEXA(II) = INDEXA(JJ)
           INDEXA(JJ) = TEMP

         ELSE IF(VACOMA(II).EQ.VACOMA(JJ).AND.
    1           SELCOMA(II).LT.SELCOMA(JJ)) THEN
*
*           ______________________________
*           Interchange valences
*           ______________________________
           TEMP = VACOMA(II)
           VACOMA(II) = VACOMA(JJ)
           VACOMA(JJ) = TEMP
*
*           ______________________________
*           Interchange selectivities
*           ______________________________
           TEMP = SELCOMA(II)
           SELCOMA(II) = SELCOMA(JJ)
           SELCOMA(JJ) = TEMP
*
*           ______________________________
*           Interchange diffusivities
*           ______________________________
           TEMP = DIFUCOMA(II)
           DIFUCOMA(II) = DIFUCOMA(JJ)
           DIFUCOMA(JJ) = TEMP
```

```
*
*             Interchange indices
*
              TEMP = INDEXA(II)
              INDEXA(II) = INDEXA(JJ)
              INDEXA(JJ) = TEMP

           ENDIF

 55        CONTINUE
 66     CONTINUE

       RETURN
       END
```

VITA

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