MODELING OF BORON SORPTION EQUILIBRIUM AND KINETIC STUDIES OF ION EXCHANGE WITH BORON SOLUTION

By

JIDONG LOU

Bachelor of Engineering
Jiangsu Institute of Chemical Technology
Changzhou, Jiangsu, PRC
1982

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1993

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
December, 1997

MODELING OF BORON SORPTION EQUILIBRIUM AND KINETIC STUDIES OF ION EXCHANGE WITH BORON SOLUTION

Thesis Approved:

Gary L. Foutch
Thesis Adviser

Mark S. High

Arland H. Johannes

Jan Wagner

Wayne B Powell
Dean of the Graduate College

PREFACE

This work is directed primarily towards the applications of ion exchange processes in water-cooled nuclear power plants. The use of boron or boric acid and the specific features of boron sorption on ion exchange resin require a better understand of both theory and behavior of ion exchange applied to deal with boron solution. To meet the requirement, this work explores the mechanism of boron or boron forms sorption on strong base anion exchange resins and presents a correlation of the equilibrium capacity of anion exchange resins in boron aqueous solution. Emphasis has been placed on the illustration of the ion exchange kinetics to the applications of boron thermal regeneration and demineralization of coolant in primary circuit of a pressurized water reactor.

In fulfilling this work, I have had the benefit of precious help in a lot of ways. I wish to express my deepest appreciation to my major adviser, Dr. Gary L. Foutch. What I am today is largely due to his kind, guidance, inspiration, understanding, and invaluable helpfulness throughout my master and doctor programs. It is him to give me the chance to complete my education in this lovingly school and university. It is him to bring my dream into reality to be honored with the degree of Doctor of Philosophy. I am also grateful to Dr. Jan Wagner, Dr. Arland H. Johannes, Dr. Martin S. High, and Dr. Frank W. Chambers for serving on the advisory committee and very helpful suggestions.

Particular thanks go to Dr. Vikram Chowdiah for his help and suggestions throughout my study. Special gratitude and appreciation are expressed to my parents for their encouragement and sacrifice. I owe a deep debt of gratitude to my wife, Beilin Chen and my sons, Wenhao and Kevin for their encouragement, sacrifice, understanding, and patience throughout the course of this study.

Financial assistance from the School of Chemical Engineering at Oklahoma State University, and EPRI for the completion of this study, are gratefully appreciated. Helpfulness from faculty and staff of the School of Chemical Engineering during my study is also gratefully appreciated.

TABLE OF CONTENTS

LIST OF FIGURES

Figure Page

Chapter II

Chapter III

Chapter IV

Chapter V

NOMENCLATURE

a_s	interfacial surface area	$(\mathrm{cm}^2 / \mathrm{cm}^3)$
C	fluid phase concentration	$(\mathrm{meq/cm}^3)$
d_p	particle diameter	(cm)
D	self-diffusivity	$(\mathrm{cm}^2/\mathrm{sec})$
D_e	effective diffusivity	$(\mathrm{cm}^2/\mathrm{sec})$
F	Faraday's constant	(C/mol)
J_i	flux of *i*th species in the film	$(\mathrm{meq/cm}^2/\mathrm{sec})$
J_d	mass transfer factor	$\frac{k_L}{u}(Sc)^{2/3}$
k_i	liquid phase mass transfer coefficient	(cm/sec)
K	dissociation equilibrium constant	
K_A^B	resin selectivity coefficient for ion B in solution compared to A in resin	
K_W	water dissociation equilibrium constant	
q	resin phase concentration	(meq/ml)
Q	capacity of the resin	(meq/ml)
r	space coordinateal variable in normal of resin surface	(cm)
R	universal gas constant	
Re	particle Reynolds number	$\frac{d_p u_s \rho}{\mu}$
R_i	ratio of mass transfer coefficient	
Sc	Schmidt number	$\frac{\mu}{\rho D}$
T	temperature	(Kelvin)

t	time	(sec)
u_s	superficial velocity in axial flow packed-bed	(cm/sec)
V	volume of the packed resin	(cm^3)
z_i	valence of *i*th species	
z^*	equivalent valence	

Greek Letters

α	parameter	
β	dimensionless proportional coefficient of diffusion rate	
δ	the thickness of the film	(cm)
ε	bed void fraction	
η	parameter in Equation (3-28)	
τ	dimensionless time coordinate	
ξ	dimensionless distance coordinate	
ϕ	electric potential	(ergs/C)
μ	liquid solution viscosity	(g/cm/sec)
ρ	solution dencity	(g/cm^3)

Superscripts

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

Subscripts

a	acid molecule
A	ion exiting the resin phase
B	ion entering the resin phase, boric acid
B_{ij}	borates with boron atom ‘i’ and valence ‘j’
c	chloride ion
h	hydrogen ion
i	ionic species
n	sodium ion
o	hydroxide ion

CHAPTER I

INTRODUCTION

Development of modern society and lifestyle has largely been due to the discovery of electricity. We continue to explore ways of improving operation efficiency of power plants and minimizing the environment pollution from electrical power industries using fossil fuels and nuclear energy. The development of water processing technology by means of ion exchange is part of these efforts.

Ion exchange is a stoichiometric reaction process. Ions in the bulk solution are replaced by an equivalent amount of ions from the ion-exchange resins. Ion exchange units are usually operated as fixed beds. Beds containing either cation or anion exchange resins are called homogeneous beds. While beds containing both exchange resins at a certain ratio are referred to as mixed beds. The exchange process in the beds is both time and spatial dependent.

The application of ion exchange was found a century ago. Technology and theoretical studies of the process have been rapidly developed with industrial growth since the 1950s. Applications of ion exchange are associated with various industries – process, pharmaceutical, food, semiconductor, microelectronics and power, so that ion exchange has becomes an important separation method.

The application of ion exchange to water treatment in power industries includes softening, deionization for conventional and nuclear boilers, and dealkalation. The power industry is concerned with erosion-corrosion problems within the steam/water circuit of boilers. Ionic impurities in water corrode materials of construction within the circuit. In nuclear power plants, corrosion and radioactive impurities, such as sodium, transported by water cause more serious problems. These radioactive impurities can be deposited or absorbed on the surfaces of the core or become incorporated, in part, in the corrosion film (Cohen, 1969).

Although ion exchange processes were developed about one hundred years ago, improvements in products, techniques, economics and new applications are continuing. These improvements are driven by the special needs of applications such as boron thermal regeneration and the recovery or removal of boron from wastewater in nuclear power plants, which will be the main concern in this study.

Background of this Study

Boron, as boric acid, is used to absorb neutrons for chemical shim control of pressurized water reactors (PWR). Control is achieved through boron concentration changes in the reactor coolant to compensate for xenon transients and other reactivity changes from routine operation in the PWR. A special feature of boron sorption on strong base anion exchange resins is that the amount of boron adsorbed varies with temperature. This feature allows resin phase concentration changes by adjusting operation temperature of the strong base anion exchange resins. The process is referred to as the boron thermal regeneration system (BTRS).

In parallel with the usefulness of boron, some problems while using boron occur. Water containing boric acid can accelerate the corrosion of a steel drum in the reactor (Fletcher et al., 1960). Radioactive boron contamination leads to high disposal cost of the waste solution. In addition, boric acid in cement paste retards curing, leading to contamination of the coolant. Therefore, the treatment of boron and its waste from the primary circuit of PWR's is an important issue in nuclear power plants.

Many studies have been made on the issue. Technologies include ion exchange (Cohen, 1969; Tomizawa, 1979; Matsumoto et al., 1987b; Na, 1993), membrane separation (Kovalenko and Krasnov, 1984a, b; Matsumoto et al., 1987a; Bornemissza et al., 1987; Lee et al., 1991; Park, 1994), precipitation (Schroeder et al., 1981, 1984; Balint et al., 1986), solvent extraction (Narbutt et al., 1979; Hejda and Jedinakova, 1983). Cecille (1991) provided an extensive and detailed reference for the treatment of the radioactive waste. The advantages of ion exchange technology lead to boron thermal regeneration and demineralization for water purification of the steam/water circuit or primary liquid cleanup prior to disposal in the condense coolant discharge.

The ion exchange materials employed in nuclear applications are styrene-divinyl benzene copolymers, with 8 to 12 % cross-linking. Functional sulfonic acid and quaternary amine base groups are formed on the resin after polymerization by appropriate chemical treatment. The divinyl-benzene percentage is selected to achieve a balance between low solubility (low cross-linking) and hydrophilic character (high cross-linking) required to permit diffusion of ions through the resin structure. Since sodium is a radioactive element and chloride causes corrosion, resins primary in the Na^+ and Cl^- (free ions inside of resins) forms should be converted into other forms, such as H^+, Li^+,

NH_4^+, and OH^- forms, at the point of use. Limitations of such organic ion exchange resins, namely radiation damage, decomposition at high temperature, and oxidation, have prompted a search for materials not so limited. Inorganic ion exchange materials, hydrous oxides, and salts have been investigated for possible application in nuclear reactor systems.

Either homogeneous or mixed beds, or both types in combination, are applied to meet various requirements. In BTRS, the homogeneous bed with a strong base anion exchange resin is used. While in water demineralization, the mixed bed in H-OH form is preferred to produce high purity water since the hydrogen and hydroxyl ions released by the resins react to form water. Theory concerning the performance of the beds varies from homogeneous to mixed beds and should be treated separately.

Scope and Objective of the Study

The primary objective of this dissertation is to study the characteristics of boron sorption on ion exchange resins. The goals include:

1. To derive an equilibrium isotherms considering the effects of temperature and boron concentration on resin sorption capacity,
2. To develop a model to predict boron sorption on OH form anion exchange resins in BTRS, and,
3. To provide a predictive tool for mixed bed ion exchange operations with boron.

Boron sorption on OH form ion exchange resins is a focus of this study. The reversible process – desorption of boron from borate form anion exchange resin is not discussed in this work. However, the work presented here can be easily extended to deal with that application without obstacles.

The equilibrium isotherm is used to predict the resin capacity under various temperature and boron concentration conditions and to determine the equilibrium concentrations at the interface between the liquid film and the resin. The mathematical model is constructed to work with any OH form or borate-form anion exchanger resin. Values of the parameters in the model are generated by the regression of experimental data.

In order to fulfill these objectives, a better understand of aqueous boric acid solution is essential since boric acid is a weak electrolyte and the dissociation degree of boric acid in water and borate forms depend on temperature, boron concentration, and pH. A review of the aqueous boron chemistry is presented in Chapter II. The determination of borate forms and their concentrations in solution at various temperature, boron concentration, and pH will be developed in Chapter II. The characteristics of boron sorption on ion exchange resins are also discussed briefly.

A derivation of the equilibrium sorption isotherm is given in Chapter III. Model parameters for seven commercial anion resins are determined. Validation of the model with experimental data and the discussion of its applicable scope are also presented in Chapter III. A computer code used for data regression is given in the appendices.

In Chapter IV, based on BTRS conditions and the assumption of particle diffusion control, a model for boron sorption on OH form anion exchange resin is developed. A theory for boron sorption is postulated and discussed in details. Amberlite IRN 78LC resin is chosen for comparison with the model. Numerical approaches are discussed, and a computer code for boron thermal regeneration simulation by ion exchange is also developed in Chapter IV.

A model of mixed bed demineralization with boric acid in the influent will be presented in Chapter V. A kinetic model is developed based on the boron concentration range in the influent. Effects of feed concentrations and temperature on column dynamics are investigated in detail. Data from Nuclear Electric in England is to used to demonstrate the model.

Theoretical model developments should be verified experimentally. The shortage of data limits further discussion of these models. Discussion of possible model improvements is presented in Chapter VI. Limits and applicability of these models are also discussed.

REFERENCES

Balint, T., Drozda, T., Mozes, G., Kristof, M., Hanel, Eva, and Tilky, P. (1986), Combined Separating Process and Equipment for Decreasing the Nonradioactive Salt Content from Waste of Nuclear Power Stations, Patent No. 39687, Hungary.

Bornemissza, E., Kis Szilagyi, Eva, Kubo, S., Laszlo Nagyzsadanyi, K., Tilky, P. (1987). Recovery of Reusable Boric Acid Solutions from Radioactive Wastes and Solutions Produced in Atomic Power Plants, Patent No. 3634180, Germany.

Cecille, L. (1991). Radioactive Waste Management and Disposal. Elsevier Applied Science, London and New York.

Cohen, P. (1969). Water Coolant Technology of Power Reactors. Gordon and Breach Science Publishers, New York.

Fletcher, W. D., A. Krieg, and P. Cohen (1960). The behavior of austenitic stainless steel corrosion products in high temperature boric acid solutions, WCAP-1689 (rev), Westinghouse Electric Corporation, Atomic Power Department, December 1960; rev., May 1961.

Hejda, J. and Jedinakova, V. (1983). Separation of boric acid from radioactive wastes by liquid – liquid extraction, J Radioanaly. Chem., 80(1-2), 23-29.

Kovalenko, V. I. and Krasnov, B. P. (1984a). Membrane for Removing Boric Acid from Wastewater, Patent No. 1077901, U.S.S.R.

Kovalenko, V. I. and Krasnov, B. P. (1984b). Membrane for Removing Boric Acid from Wastewater, Patent No. 1085994, U.S.S.R.

Lee, K. W. (1991). Treatment of radioactive borated liquid wastes by reverse osmosis, Proceedings of The 1991 Joint International Waste Management Conference, 1, 265-269.

Matsumoto, H., Miyamoto, H., Nishihara, Y., Kizawa, H. (1987a). Treatment of Radioactive Wastewaters, Patent No. 87 32396, Japan.

Matsumoto, H., Miyamoto, H., Nishihara, Y., Kizawa, H. (1987b). Treatment of Radioactive Wastewaters from PWR, Patent No. 87 32397, Japan.Na, J. W. (1993).

Adsorption Characteristics of Boric Acid on Strong-Base Anion Exchange Resin, Ph.D. Thesis, Korea Advanced Institute of Science and Technology

Narbutt, J., Olza, J., Przybylowicz, Z., Siekierski, S. (1979). Separation of fission and corrosion products from boric acid solutions by solvent extraction, J. Radioanaly. Chem., 51(2), 185-190.

Park, J. K. (1994). A Study on the Separation of Boric Acid in Liquid Waste with Membrane Extractor, Ph.D. Thesis, Korea Advanced Institute of Science and Technology.

Schroeder, H. J., Ambros, R., Paffrath, G., Brenner, N. (1981). Recovery of Boric Acid from a Wasterwater Concentrate of a Nuclear Power Station, Patent No. 2950601, Germany.

Schroeder, H. J., Ambros, R., Paffrath, G., Brenner, N. (1984). Recovery of Boric Acid from Wasterwater Concentrates of Nuclear Plants, Patent No. 4435184, U.S.A.

Tomizawa, T. (1979). Studies on the absorption of boric acid on anion exchange resins. II. Effects of temperature on the adsorption characteristics of boric acid on strong base anion exchange resins. Denki Kagaku, 49(6), 339-342.

CHAPTER II

BORON SOLUTION CHEMISTRY AND SORPTION CHARACTERISTICS

Introduction

Boron is used in nuclear-related fields as a neutron absorbing material. There are two naturally occurring isotopes of boron, ^{10}B and ^{11}B. The ^{11}B isotope is predominant, about 80.39% (Muetterties, 1967). Between the two isotopes, a big difference is the thermal neutron absorption cross section. While ^{11}B has the cross section of 0.005 barns, ^{10}B has 3837 barns (Greenwood and Thomas, 1973). Therefore, the ^{10}B isotope is of considerable significance in nuclear chemistry because of its large cross section for thermal neutron capture. In nuclear power plants, ^{10}B has been as the chemical shim of a nuclear reactor since the early 1960s (Cohen, 1969). Recently, the use of ^{10}B has been extended to medical radiation treatment of malignant tissue and brain tumors for the capture of slow neutrons and α particle emission, which is subsequent to neutron capture (Fairchild and Myoha, 1985; Barth et al., 1990). However, in the most practical applications, natural boron, a mixture of ^{10}B and ^{11}B, is used instead of ^{10}B only because of the shortage of ^{10}B in nature and the high cost of the isotopic separation. With respect to design, performance and economics, boric acid has been demonstrated to be acceptable in the coolant as nuclear poison for reactor control, and does not adversely affect core fouling, system contamination, corrosion, etc.

Boron chemistry is a unique and complex discipline. It is impossible, nor intended, to describe all aspects of boron chemistry in this work. For the sorption or desorption of boric acid and borates from aqueous solution by ion exchange, it is necessary to understand the chemistry of aqueous borate and boric acid equilibrium in the system of interest. Moreover, the worthwhile and interesting aspects of boron chemistry reside in the characteristics of boric acid in aqueous solution. In this chapter, I will present some general information about the physical and chemical properties of boric acid in solution; the structure of borate ions, equilibrium, ionization mechanisms and applications of sorption on ion exchangers. A brief discussion of the ionization mechanisms of boric acid, reaction equilibrium and constants will also be presented.

Boron Solution Chemistry

The boron atom has the electron configuration: $1s^2$, $2s^2$, $2p^1$ and is placed in Group III of the Periodic Classification (Cotton and Wilkinson, 1980). With the chief oxidation state +3, boron may be considered a typical metalloid having properties intermediate between the metals and the electronegative non-metals. The tendency for boron is to form anionic rather than cationic complexes (Ross and Edwards, 1967).

The chemistry of a boron aqueous solution is characterized by the existence of a series of polyborate anionic species along with boric acid and monomeric borates, and by the fact that boric acid undergoes hydration before ionization. The formation of different borate groups and their structures depends on pH, temperature and boron concentration. At the acidic and basic extremes of pH, the primary species in solution are $B(OH)_3$ and the mononuclear borate ion. In a dilute boric acid solution (less than 0.025M), essentially only mononuclear species $B(OH)_3$ and $B(OH)_4^-$ are present (Cotton and Wilkinson, 1980). As boron concentration increases or temperature decreases, the possibility of forming polynuclear borates increases. Although there is no unanimous agreement about the structures and forms of polyborates, the evidence from data obtained by studies of freezing point depression, electrical conductance, hydrogen-ion concentration (emf or pH), X-ray diffraction, and Raman spectroscopy have indicated the formation of polynuclear species in solution.

Structures of Boric Acid and Borates

In commercial usage, the name, boric acid, is usually associated with orthoboric acid ($B(OH)_3$). Orthoboric acid crystallizes from aqueous solution as white, waxy plates. Its normal melting point is 170.9 °C. The dehydration of orthoboric acid (Kracek et al., 1938) below 130 °C, results in the formation of orthorhombic metaboric acid by the reaction

$$H_3BO_3 \longrightarrow HBO_2 + H_2O \qquad (2\text{-}1)$$

In aqueous solution, however, the only stable form of boric acid is orthoboric acid, while metaboric acid rapidly converts to orthoboric acid.

The crystal structure of boric acid is composed of discrete triangular $B(OH)_3$ molecules linked together by hydrogen bonds, $O—H \cdots O$, to form infinite layers of approximately hexagonal symmetry (Hibben, 1938). In solution, Hibben (1938) indicated that the structure of boric acid is almost identical to that of the crystalline phase based on Raman spectra.

The structure, however, in solution of the conjugate base of boric acid remains a mystery in spite of attempts to obtain a definitive answer to the problem. One can conceive of, at least, three possible structures for a monomeric borate ion of single negative charge; BO_2^-, $H_2BO_3^-$ (or $BO(OH)_2^-$), and $B(OH)_4^-$. The differences between these structures lie primarily in the coordination number of the boron atom (Edwards et al., 1954). The tetrahedral $B(OH)_4^-$ has been confirmed to be the only mononuclear borate present at the highest pH values. Unlike the tetrahedral $B(OH)_4^-$, there is no direct evidence for the existence of either a mononuclear trigonal borate ion, $BO(OH)_2^-$, or linear borate ion, BO_2^-, in solution (Ross and Edwards, 1967), though Carpeni and Souchay (1945) considered that the BO_2^- might be formed during the neutralization.

There is considerably less agreement as to the nature of the polyanions present. The problem is complicated by the facts that (a) the equilibrium formation constants are not large, (b) more than one polyanion is probably present, and (c) the polyanions present under one set of conditions are not necessarily the same as those under an alternative set (Ross and Edwards, 1967). In the 1950's, there did seem to be general agreement that the polyborate with three boron atoms and one negative charge is most important (Edwards, 1953; Antikainen, 1957; and Ingri et al., 1957). The equilibrium constant for formation according to the equation

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3^- \qquad (2\text{-}2)$$

where B_3^- represents a mononegative trimer, has been reported to be 110 by Edwards (1953), 145 by Ingri and co-workers (1957) and about 150 by Antikainen (1957). The divergence of the equilibrium constants might result from different temperatures. Since there is no evidence for an aqueous dimer, it is difficult to believe that such condensation would give a linear trimer. In general, when one particular polymer predominates, as in this case, it has a specific, nonlinear structure. The most probable structure for the trimer, with one negative charge, is a cyclic ring structure, which was confirmed by Maya (1976).

In addition, mononegative tetramers, pentamers, and hexamers have been postulated along with dinegative trimers, tetramers, and pentamers. In early studies of aqueous boric acid chemistry, several investigators (Kolthoff, 1926; Kolthoff and Bosch, 1927; and Menzel, 1927) concluded that, along with the monoborate ion $B(OH)_4^-$, tetraborate ions, $B_4O_7^{2-}$, and pentaborate ions, $B_5O_8^-$, were all presented in aqueous borate solutions with the pentaborate $B_5O_7^{2-}$ ions being extensively dissociated. Later, Carpeni and Souchay (1945) considered, from a study of neutralization curves of solutions of boric acid between 0.03 and 0.262M, that $B_5O_8^-$ and $HB_4O_7^-$ ions were formed successively during neutralization. They emphasized that condensation of boric acid was affected by the total boron concentration and pH of the solution, the importance of which had not been fully appreciated by previous workers. The data are not, however, conclusive for any one of these structures.

Summarizing the previous research about borate structures, Ross and Edwards (1967) listed these possible borates, their structures and classifications for detailed reference:

1. All borates, except of some gas species, have the structure of triangular-planar, tetrahedral, or triangular and tetrahedral.
2. There is no triangular and tetrahedral structure with monomers and dimers.

3. The major structure for trimers, tetramers, and pentamers is triangular and tetrahedral with rings or networks.
4. There exist some borates with more than one-dimension linkages.

Borates in Aqueous Solution

With the increasing applications of boron, it is not surprising that the equilibria in various boric acid and borate solutions, have been studied extensively. Ingri and his co-workers (1957,1962, 1963a,b, c) studied carefully the equilibria in concentrated boric acid and borate solutions at 25 °C, and demonstrated that boric acid attains a complex equilibrium with borate and polyborate ions. They used an emf (pH) measurement method with a hydrogen electrode to measure equilibrium of boric acid solution up to 3.0 M, which was considered to give the best information about the nuclearity of the dissolved polyborates over a large range of concentrations. They reached these conclusions: (a) the main species were $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$ in all media studied; (b) there were strong indications for the formation of $B_3O_3(OH)_5^{2-}$ and $B_5O_6(OH)_4^-$; (c) in dilute boric acid solutions having a total concentration of less than 0.01 M boron, the only important equilibrium is:

$$B(OH)_3 + OH^- \Leftrightarrow B(OH)_4^- \qquad (2\text{-}3)$$

This conclusion was confirmed by several researchers (Anderson et al., 1964; Momii and Nachtrieb, 1967). Furthermore, by direct determination of the volume of ionization, and from studies of the pressure coefficient of dissociation, the following reaction also exists in dilute solutions:

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+ \qquad (2\text{-}4)$$

The two processes are coupled to the water autoprotolytic equilibrium and cannot be distinguished thermodynamically (Corti et al., 1979).

Maya (1976) identified directly polyborate ions in solution at 25 °C by using Raman spectroscopy, which was known to be ideally suited for the derivation of structural information about ions in solution. His studies may be summarized as follows:

- The band at 613 cm^{-1} observable in the solutions from pH 6.1 to 9.0 is assigned to a triborate ion containing the boraxine ring.
- The tetraborate ion is identified in solution on the basis of a line at 567 cm^{-1}.
- The evidence of the presence of pentaborate ion in solution was found at pH 6.1, 7.0 and 8.0, and the corresponding bands were 527, 763 and 914 cm^{-1}. Observation of the spectra shows that the pentaborate line at 763 cm^{-1} gradually disappears with the increase of pH.
- The proportion of tetrahedral $B(OH)_4^-$ increases with the increase of pH.

Both pentaborate and triborate ions are univalent with one negative charge. Later, Toshiyuki and co-workers (1979) confirmed Maya's results independently with the Raman spectroscopy. In addition, they found more evidence of mononegative trimers and dinegative tetramers in solution from the spectra.

Physicochemical Properties

The physicochemical properties reviewed here will include boric acid solubility in water and organic solvents, the heat of solution, the osmotic and activity coefficients, and the equilibrium constants.

The solubility of boric acid in water increases rapidly with an increase in temperature. Table 2-1 lists the experimental solubility of boric acid in water at various temperatures (Perry and Chilton, 1984). The presence of inorganic salts may enhance or depress the solubility of boric acid in water. Adding potassium chloride, potassium sulfate, or sodium sulfate, increases the solubility, while the solubility is decreased by adding lithium chloride or sodium chloride. Boric acid is also quite soluble in many organic solvents. Some examples are tabulated in Table 2-2 (Kirk and Othmer, 1978).

The heat of solution is dependent upon concentration. For solution in the range of 0.03-0.9m, the molar heat of solution may be estimated by the empirical relation (Kirk and Othmer, 1978):

$$\Delta H = \left(22062 - 222 \cdot m + 979 \cdot e^{-123 \cdot m}\right) \quad (J/mol). \qquad (2\text{-}5)$$

The osmotic and activity coefficients of some simple borates in aqueous solution at 25 °C are determined by the following relationships (Platford, 1969):

The osmotic coefficient is given by

$$\phi = 2\frac{m_R \phi_R}{nm} \qquad (2\text{-}6)$$

and with the above estimation of the osmotic coefficient, the mean activity coefficient is calculated by Equation (2-7)

$$-\ln \gamma_{\pm} = 1 - \phi + 2\int_{0}^{m^{0.5}} \frac{(1-\phi)}{m^{0.5}} dm^{0.5} \qquad (2\text{-}7)$$

The term *nm* in Equation (2-3) should be replaced by a summation over all the solutes if there is more than one solute species in solution.

Table 2-1

Solubility of Boric Acid in Water
At Various Temperature

Temperature °C	Molality	Temperature °C	Molality
0	0.4304	60	2.3961
10	0.5776	70	2.7067
20	0.8154	80	3.8424
30	1.0678	90	4.9151
40	1.4108	100	6.5119
50	1.8670		

For an estimation of the dissociation constant of boric acid from 10 to 50 °C, Owen (1934) suggested the following expression

$$\mathrm{pKa} = 9.023 + 8.0 \times 10^{-5}\left[76.7 - (\mathrm{T} - 273.15)\right]^2 \qquad (2\text{-}8)$$

Later, Manov et al. (1944) proposed a semi-empirical relation:

$$\mathrm{pKa} = -\log \mathrm{Ka} = \frac{2237.94}{\mathrm{T}} - 3.305 + 0.016883\mathrm{T} \qquad (2\text{-}9)$$

Equation (2-9) made it possible to estimate the dissociation constant of boric acid for the overall temperature range. Equations (2-8) and (2-9) can be applied to boron concentrations as low as 0.01M.

Table 2-2

Solubility of Boric Acid in Organic Solvents

Solvent	Temperature (°C)	%H_3BO_3 by wt. of solution.	g-H_3BO_3
Glycerol, 98.5%	20	19.9	
86.5%	20	12.1	
Ethylene glycol	25	18.5	
Diethylene glycol	25	13.6	
Ethyl acetate	25	1.5	
Acetone	25	0.6	
Acetic acid, 100%	30	6.3	
Methanol	25		173.9
Ethanol	25		94.4
n-Propanol	25		59.4
2-Methylbutanol	25		35.3
Dioxane	25		ca 14.6
Pyridine	25		ca 70.0
Aniline	20	0.15	

Ionization Mechanisms and Ionic Equilibrium

Boric acid is a very weakly dissociated acid in aqueous solution. The behavior of boric acid in solution acts as a Lewis acid (adds an OH^-) rather than a Brönsted acid (loss of H^+). Bell et al. (1967) pointed out that there are at least four mechanisms, which are feasible pathways for the ionization reaction. Using the symbol N to denote any Brönsted base (this base will often be water), the four general mechanisms are as follows.

1. $B(OH)_3 + N \longleftrightarrow BO(OH)_2^- + HN^+$ (2-10)

$BO(OH)_2^- + H_2O \longleftrightarrow B(OH)_4^-$ (2-11)

2. $B(OH)_3 + H_2O \longleftrightarrow B(OH)_3(OH_2)$ (2-12)

$B(OH)_3(OH_2) + N \longleftrightarrow B(OH)_4^- + HN^+$ (2-13)

3. $B(OH)_3 + H_2O + N \longleftrightarrow B(OH)_4^- + HN^+$ (2-14)

4. $H_2O + N \longleftrightarrow OH^- + HN^+$ (2-15)

$B(OH)_3 + OH^- \Leftrightarrow B(OH)_4^-$ (2-16)

All of the known reactions involve simple boron-oxygen bond breaking and formation. These processes can be very rapid and spontaneous; for instance, the specific rate constant of reaction in Equation (2-16) is about 10^{10} mole liter^{-1} sec^{-1} (Anderson et al., 1964).

Edwards et al. (1955, 1959, and 1961) demonstrated that the simple borate ion and related monomeric ions such as phenylboronate and peroxyborate are tetrahedral. Therefore, the hypothetical hydration reaction to form the hydroxyborate ion

$H_2BO_3^- + H_2O \longleftrightarrow B(OH)_4^-$ (2-17)

must have a negative free energy and proceeds spontaneously to the right. It is possible to calculate the equilibrium constant for the hydration reaction above by using the known pKa values for boric acid. This estimated constant is about 2000, which indicates that the tetrahedral anion is about 5 kcal • mole^{-1} more stable in aqueous solution than the trigonal anion (Ross and Edwards, 1967).

When both the hydroxyborate ion and its conjugate acid are present in solution, the result is polymerization and the formation of water (Ross and Edwards, 1967). The reactions have been described as akin to neutralization (Edwards et al., 1961), and the equilibrium among boric acid, monoborate ions and polyborates in solution can be reversible rapidly depending on pH, temperature and concentration.

In the studies of boric acid equilibrium, Ingri and his co-workers (1963) suggested that the reactions of boric acid with water could generally be presented as:

$$\alpha B(OH)_3 + \beta OH^- \xleftrightarrow{K_{\alpha\beta}} (OH^-)_\beta[B(OH)_3]_\alpha \tag{2-18}$$

or

$$\alpha B(OH)_3 + \beta H_2O \xleftrightarrow{K^*_{\alpha\beta}} (OH^-)_\beta[B(OH)_3]_\alpha + \beta H^+ \tag{2-19}$$

where $K_{\alpha\beta}$ and $K^*_{\alpha\beta}$ are the formation constants, given as

$$K_{\alpha\beta} = \frac{\left[(OH^-)_\beta(B(OH)_3)_\alpha\right]}{\left[OH^-\right]^\beta\left[B(OH)_3\right]^\alpha} \tag{2-20}$$

$$K^*_{\alpha\beta} = \frac{\left[(OH^-)_\beta(B(OH)_3)_\alpha\right]}{\left[H^+\right]^{-\beta}\left[B(OH)_3\right]^\alpha} \tag{2-21}$$

and

$$K^*_{\alpha\beta}K_w^{-\beta} = K_{\alpha\beta} \tag{2-22}$$

Mesmer and co-workers (1972a, b) employed high-temperature potentiometric techniques to study boric acid equilibrium in KCl solution at a temperature range from 50 to 200 °C and concentrations below 0.6 M. They postulated that the significant polynuclear species of dimers, trimers, tetramers and pentamers were $B_2(OH)_7^-$, $B_3(OH)_{10}^-$, $B_4(OH)_{14}^{2-}$ and $B_5(OH)_{18}^{3-}$. According to this postulation, a hypothetical relation can be expressed as

$$\alpha B(OH)_3 + \beta OH^- \xleftrightarrow{K_{\beta\alpha}} B_\alpha (OH)_{\beta+3\alpha}^{\beta-} \tag{2-23}$$

where $K_{\beta\alpha}$ is the formation constant, which was also given in their studies and was corrected later for these possible formations of polynuclear species:

$$\log K_{11} = \frac{1573.21}{T} + 28.6059 + 0.012078 \cdot T - 13.2258 \cdot \log T \tag{2-24}$$

$$\log K_{12} = \frac{2756.1}{T} - 18.996 + 5.835 \cdot \log T \tag{2-25}$$

$$\log K_{13} = \frac{3339.5}{T} - 8.084 + 1.497 \cdot \log T \tag{2-26}$$

$$\log K_{24} = \frac{12820}{T} - 134.56 + 42.105 \cdot \log T \tag{2-27}$$

$$\log K_{35} = \frac{14099}{T} - 118.115 - 36.237 \cdot \log T \tag{2-28}$$

Constants given here are cited from Baes and Mesmer (1976). Equations (2-24) - (2-28) can be valid at temperatures up to 290 °C. Effect of solution boron concentration on constants of reaction equilibrium is less significant and can be neglected.

Mesmer's relation is frequently cited in the literature for the equilibrium calculation of boric acid in aqueous solution (Riddle, 1993, Na, 1993, McGarvey, 1995) and will be applied in this work.

Sorption Characteristics

Ion exchange is useful in procedures to determine or remove boron or boric acid from various sources. Korkisch (1989) outlined the general methods for the applications of determining or removing boron from industrial solutions. These methods include:

- passing a solution through strong acid cation exchanger resins to remove metals;
- the acidic solution generated by the cation exchange column passing through a bed of a weakly basic anion exchanger to remove strong acids;
- the boric acid then determined by colorimetrically; and
- using a strong anion exchange resin to remove boric acid from solution.

In this work, the removal of boron from solutions will be a focus.

Some complex reactions involve the sorption of boron or boric acid on ion exchangers. In solution, as mentioned above, boric acid dissociates to form monoborate and different polyborates depending on solution pH. The number and amount of polyborates in solution also depend on the boron concentration and temperature. In resins, boric acid is prone to ionization through the reaction with the free ion - hydroxide, escaping from the bonding force of the function group to form monoborate or polyborates, then bonding on these functional groups. The monoborate further tends to form polyborates.

The formation of polyborate inside resin results in the increase of the apparent sorption capacity of resin toward boron. This is a specific feature of boron sorption on ion exchangers. Consider that the degree of polyborates formation inside the resin is subject to boric acid concentration in the external solution and temperature as well.

Therefore, the control of feed concentration and operating temperature may lead to different boron diffusion directions in the sorption of boric acid or boron. Combining the equilibrium between both sides of the interface, between the boric acid and borates in the solution and inside of resins gives the unique sorption characteristics of boron on the ion exchanger. These characteristics must be understood in order to deal with the sorption process and to develop specific applications for related industries; for instance, the boron thermal regeneration system in nuclear power plants.

Concentration Distribution in Solution

The determination of concentration distribution of boric acid and borates is based on the postulation proposed by Mesmer and his co-workers (1972a, b), which was given in Equation (2-23). The corresponding reaction equilibrium constant relations were presented in Equations (2-24) to (2-30). The moles and mole fractions of boron in different boron species were calculated as a function of the total boron feed concentration, temperature, and pH. For the applications of interest in later Chapters, the temperature range was chosen from 10 to 60 ^{0}C, and the total boron concentration range was 100 to 6500 ppm (about 0.009 to 0.6 M in boron). Equations (2-24) to (2-30) are a set of algebraic equations, solved numerically by applying the Newton-Raphson method. A computer code developed to solve these equations is attached in the Appendix A. Results obtained are presented in Figures (II-1) to (II-9).

Figure (II-1) shows the dissociation degree of boric acid in its aqueous solution at a given temperature. It is obvious to see the predominant concentration of boric acid in the solution. Comparing the concentration ranges among these species, the concentrations of borates can be neglected in the boron-sorption point of view. Among borates, the monoborate $B(OH)_4^-$ is important in the low concentration range, while the concentration of polyborates increase with increasing total boron concentration and become more important species than the monoborate at higher concentrations.

For easy comparison, results presented through Figures (II-2) to (II-9) account for the boron mole fraction contained by each boron form. These results show that boron distribution in these forms is strongly dependent on the feed concentration, pH, and temperature. A summary of these phenomena is given as follows:

1. Boric acid is the dominant species in solution under the situations: a) without other cations except hydrogen ion existing in solution, which can be concluded from Figure (II-1), and b) pH less than 7. In these cases, the concentration of boron contained in boric acid is about 3 to 4 orders of magnitude above that of the total ionic species. Then, the contribution of these ionic species to the sorption of boron on ion exchanger can be neglected without serious error.
2. At low feed concentrations (below 100 ppm boron), the tetrahedral $B(OH)_4^-$ is the only significant ionic species existing in the solution. The tetrahedral $B(OH)_4^-$ becomes the dominant species for boron as pH increases to 10 for total boron concentration less than 3000 ppm, or pH above 11 for a total boron concentration above 5000 ppm at all temperatures. Consequently, it is not necessary to account the contribution of molecule and polyborate forms to sorption of boron on ion exchanger at that higher pH range, but it is not the case in nuclear electric power industry.

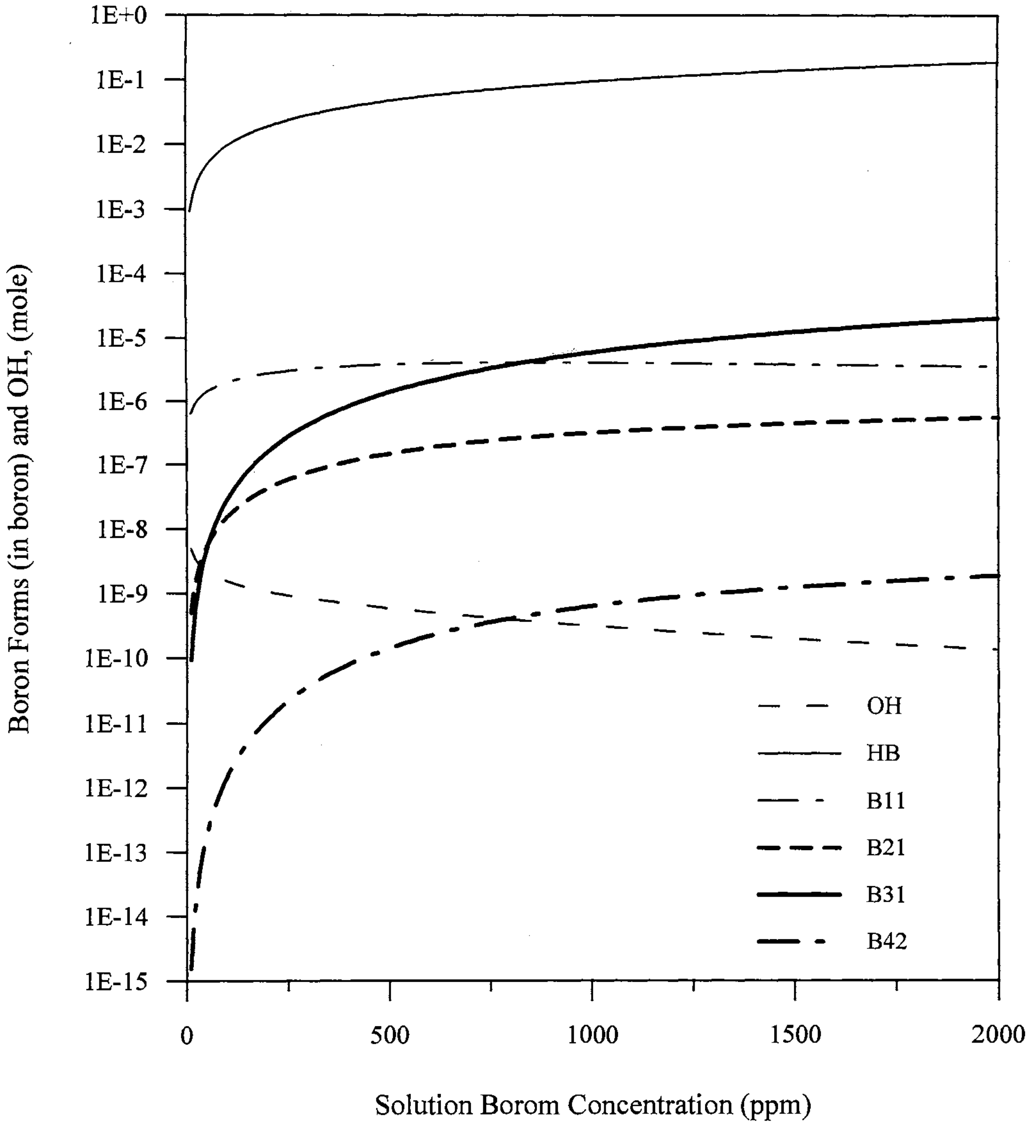

Figure II - 1 Concentration of anionic species in boric acid aqueous solution as function of boron concentration at the given temperature 10 C

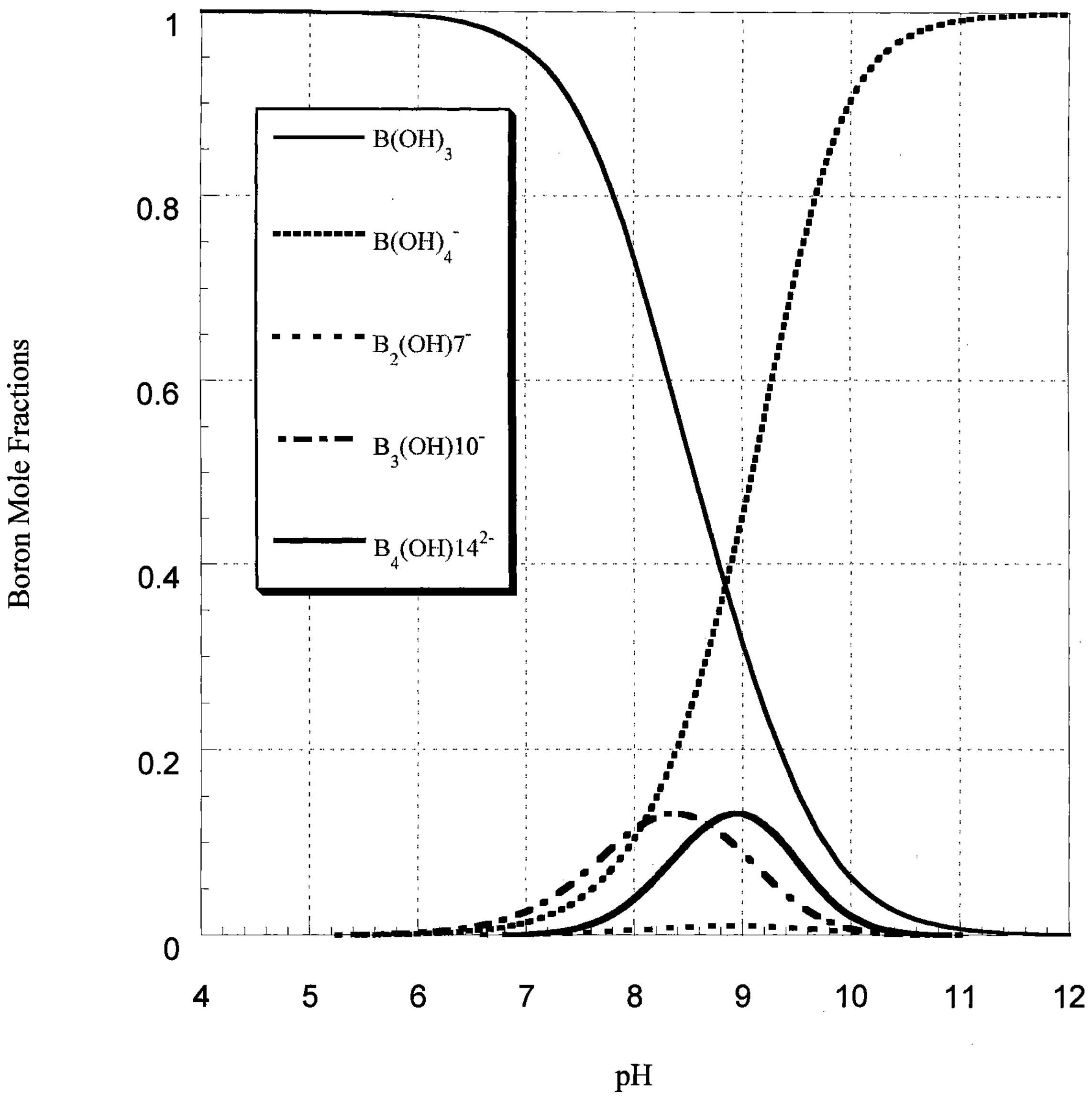

Figure II - 2 Distribution of Boron Forms in Solution as Function of Boron Concentration, Temperature, and pH with Boron = 1000 ppm, T = 10 °C

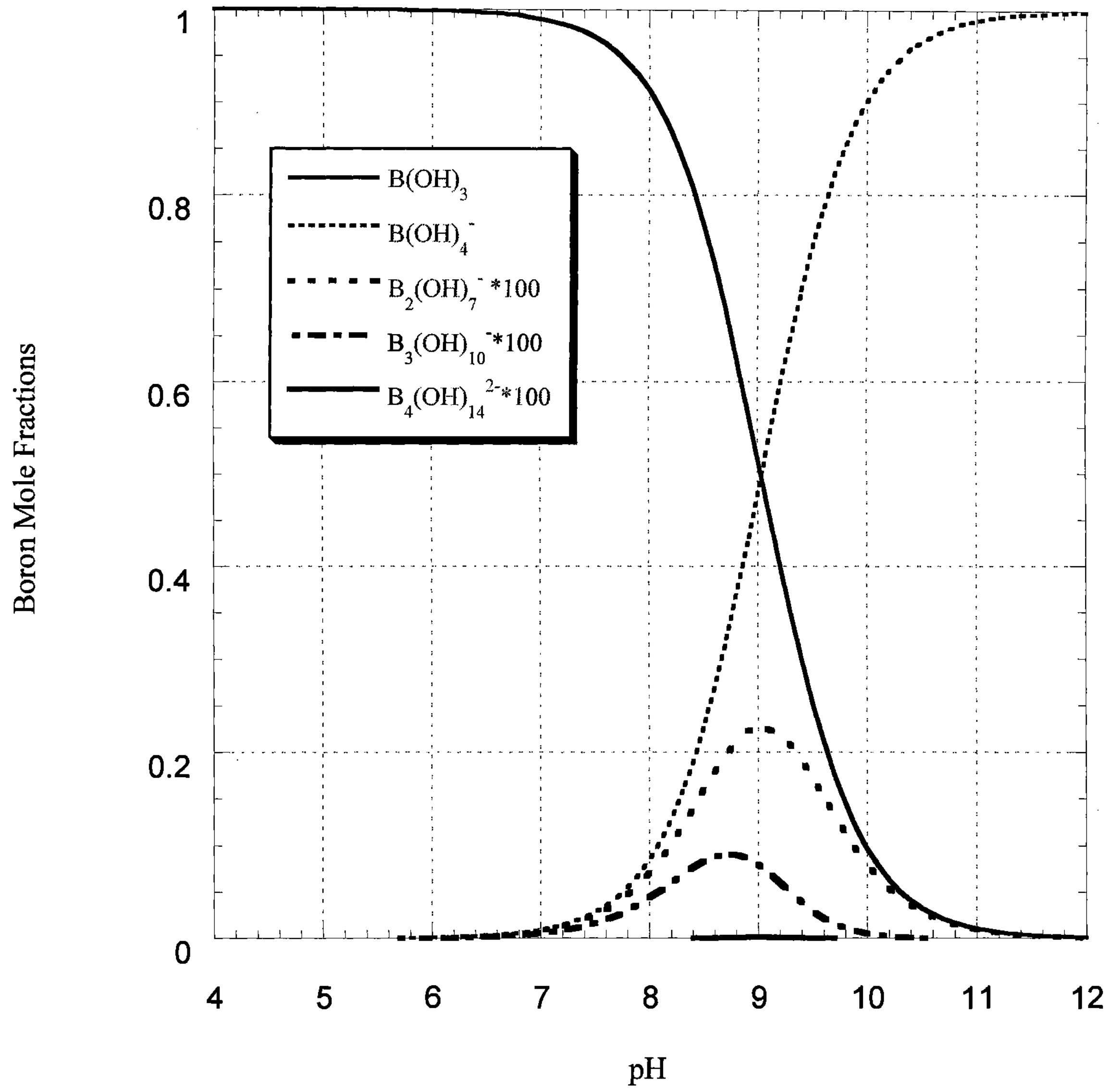

Figure II - 3 Distribution of Boron Forms in Solution as Function of Boron Concentration, Temperature, and pH with Boron = 100 ppm, T = 10 °C

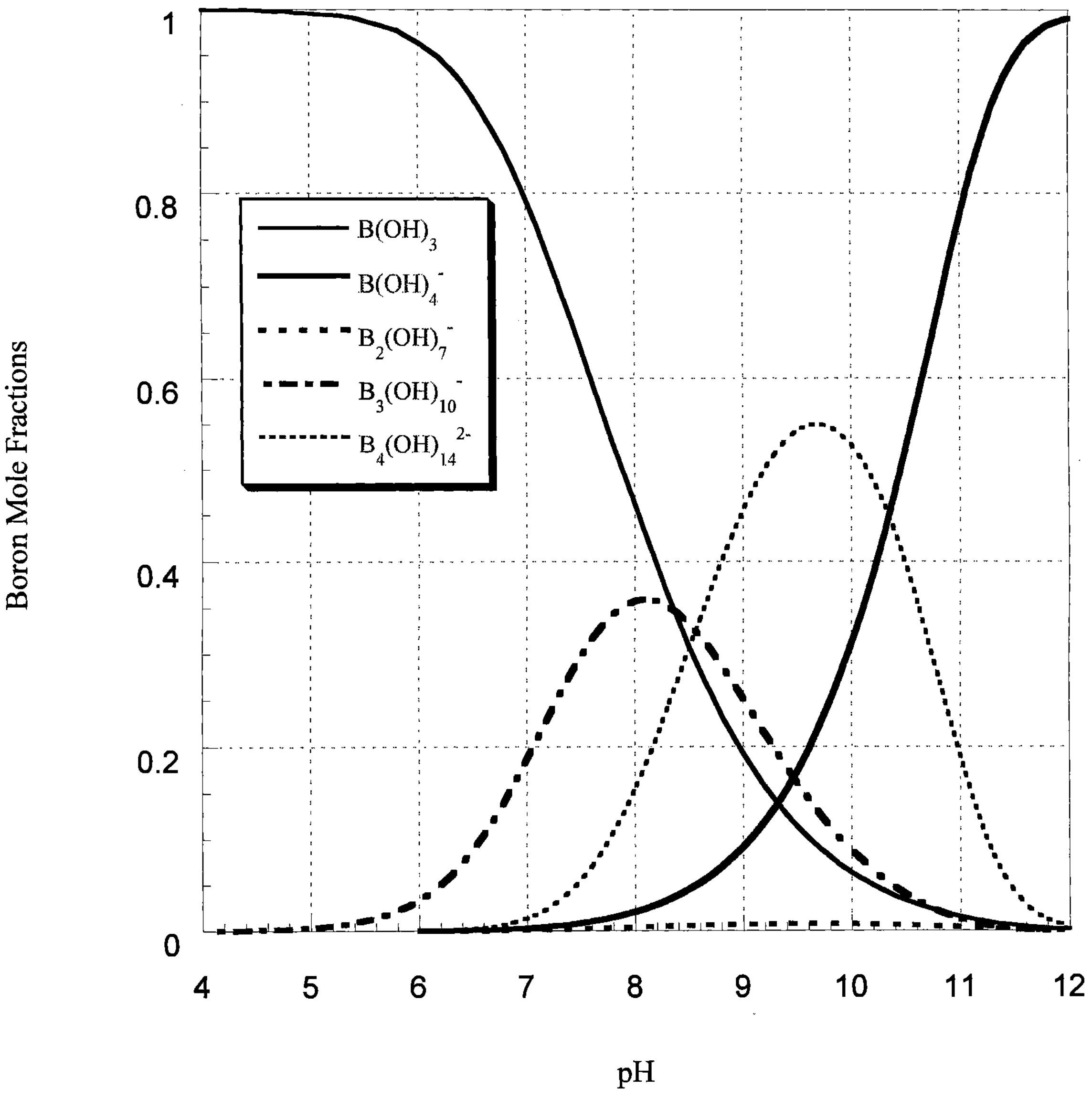

Figure II - 4 Distribution of Boron Forms in Solution as Function of Boron Concentration, Temperature, and pH with Boron = 6500 ppm, T = 10 °C

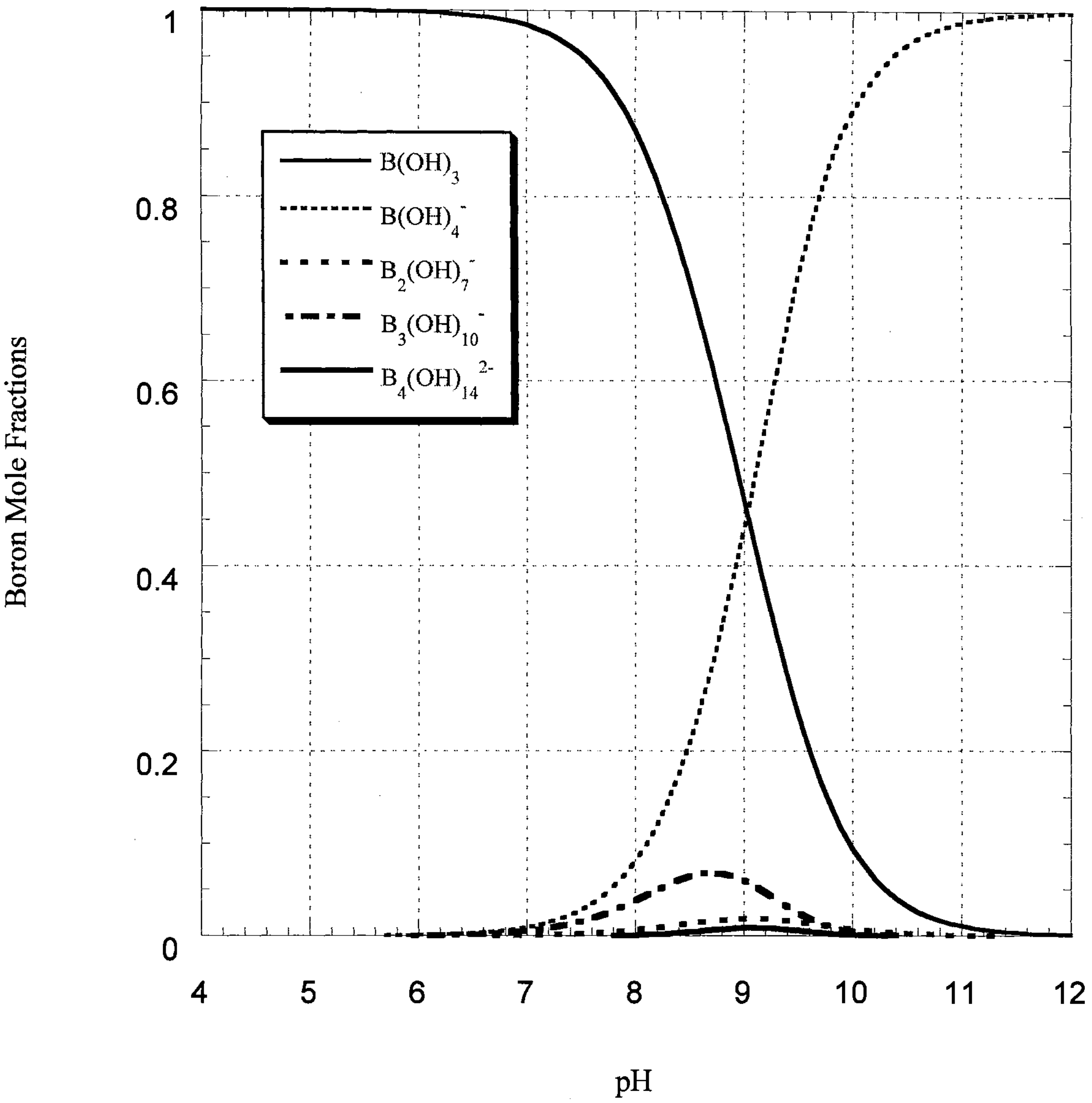

Figure II - 5 Distribution of Boron Forms in Solution as Function of Boron Concentration, Temperature, and pH with Boron = 1000 ppm, T = 60 °C

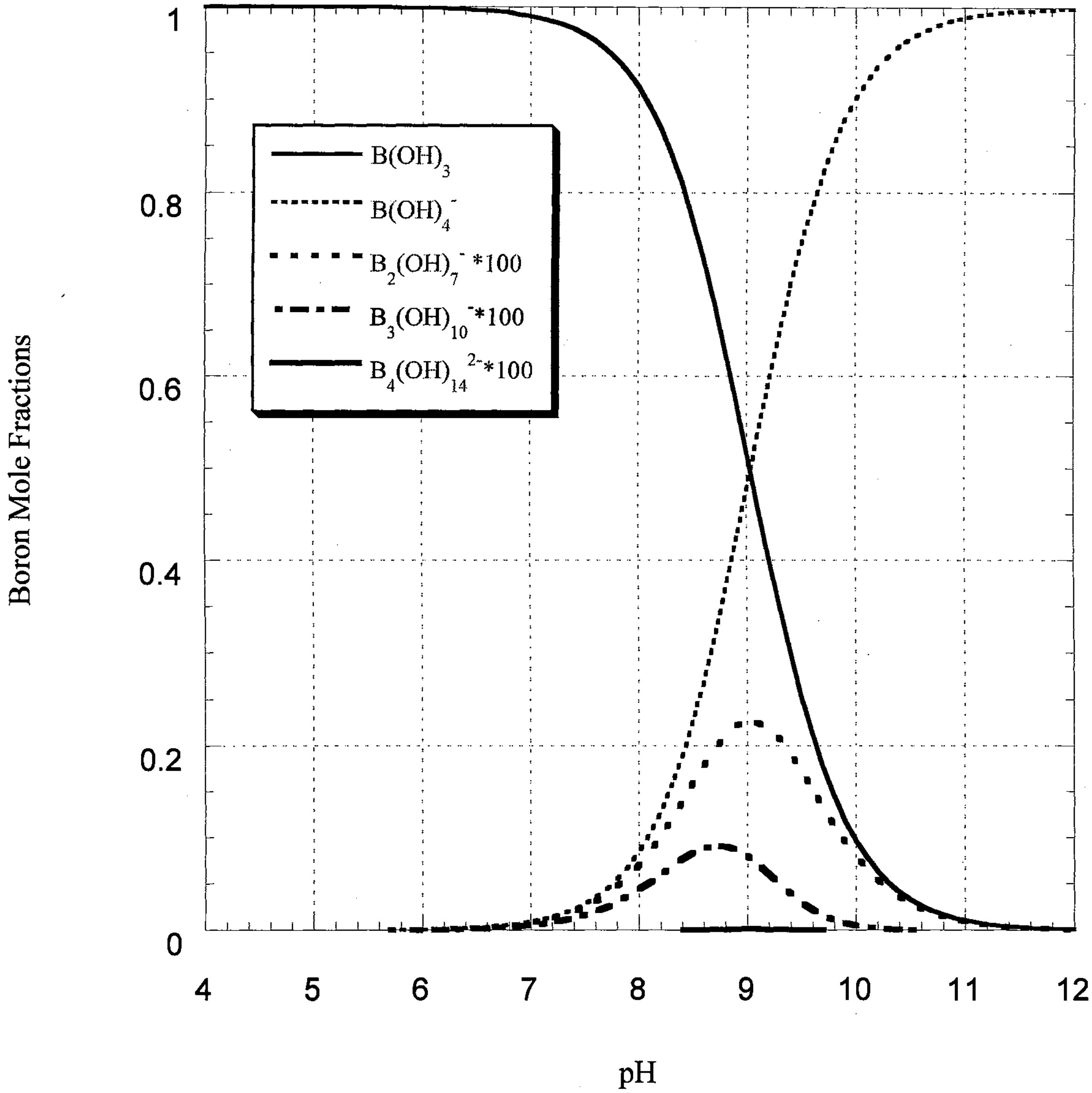

Figure II - 6 Distribution of boron forms in solution as a function of the total boron concentration, temperature, and pH with Boron = 100 ppm, T = 60 °C

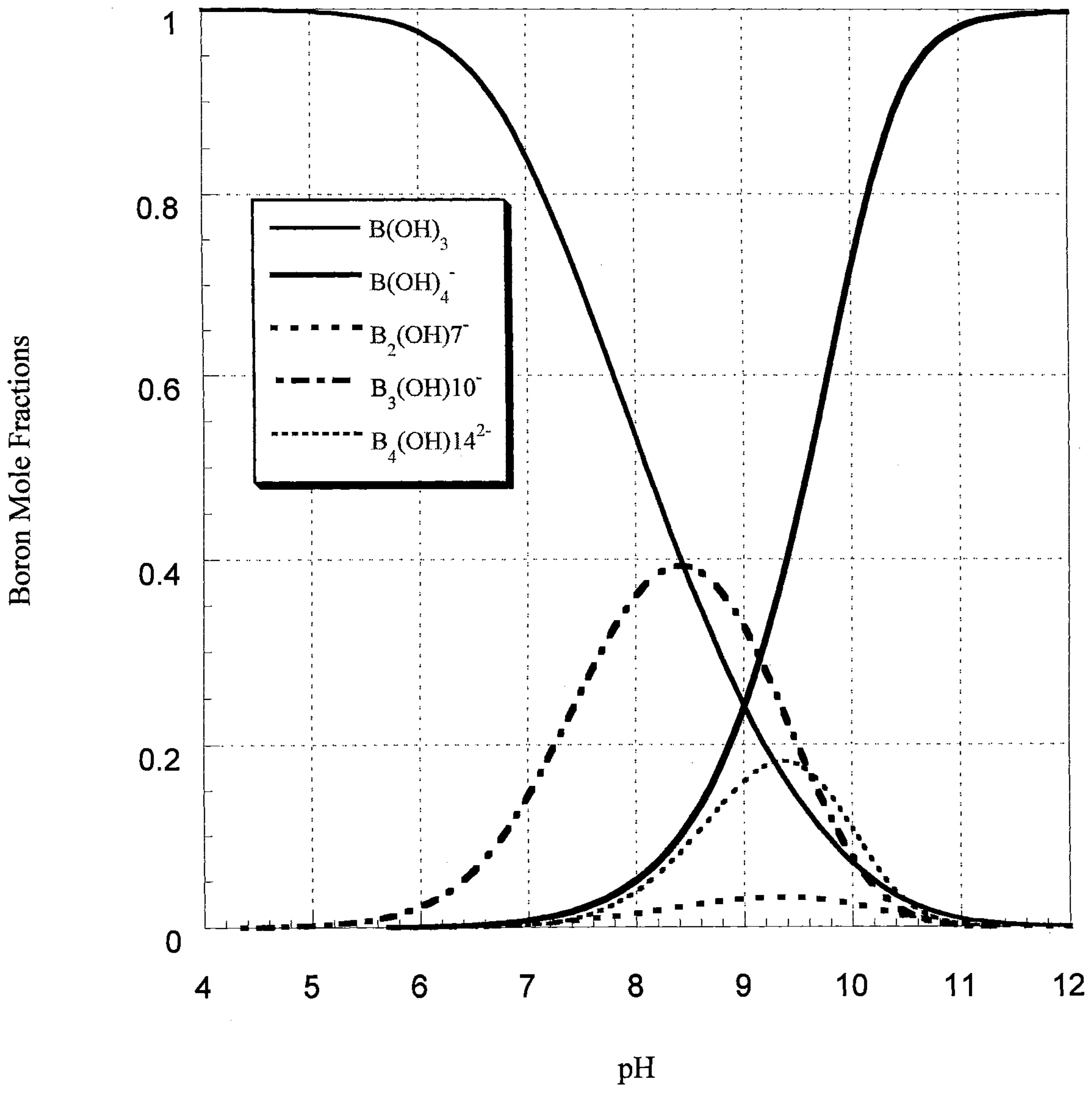

Figure II - 7 Distribution of boron forms in solution as a function of the total boron concentration, temperature, and pH with Boron = 6500 ppm, T = 60 °C

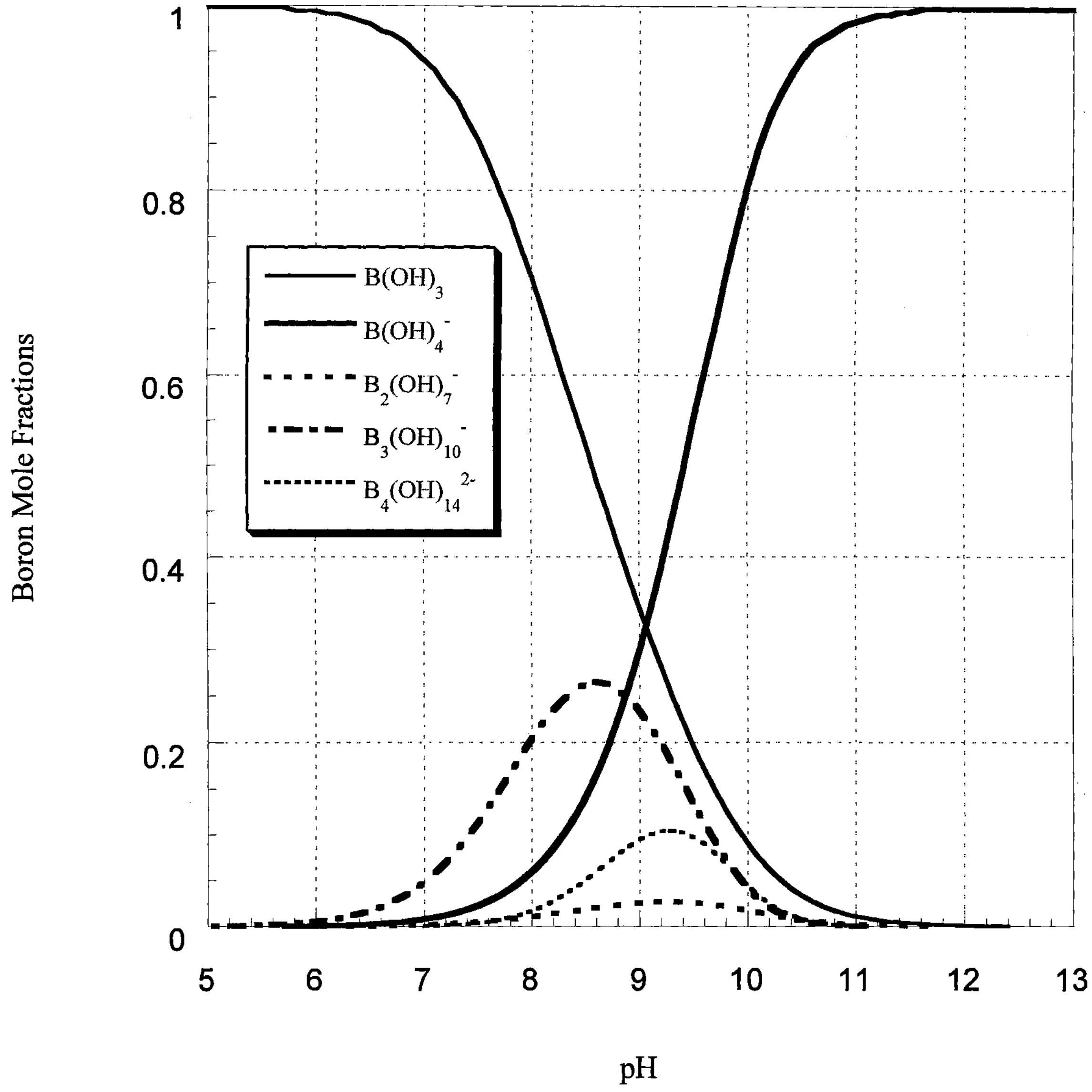

Figure II-8 Distribution of Boron Forms in Solution as Function of Boron Concentration, Temperature, and pH with Boron = 3000 ppm, T = 50 °C

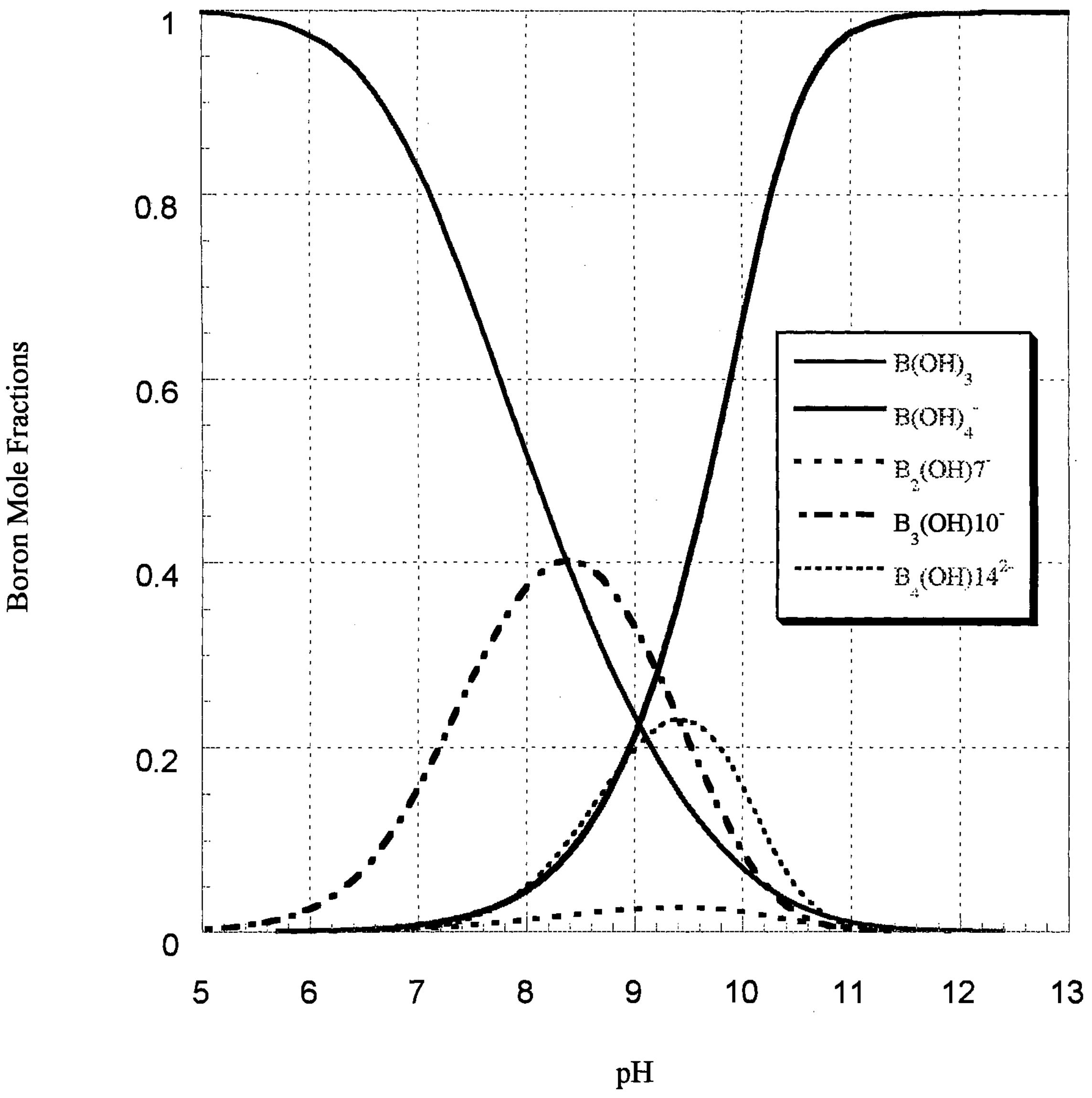

Figure II-9 Distribution of boron forms in solution as a function of boron concentration, temperature, and pH with Boron = 6500 ppm , T = 50 °C

3. At higher feed concentrations (above 0.1M or 1000 ppm boron), some polyborates, for instance, dimers, trimers, tetramers, and pentamers, along with boric acid and the tetrahedral $B(OH)_4^-$, may appear significantly in the solution within the pH range between 7 to 11. Among these polyborates, the trimer $B_3(OH)_{10}^-$ is dominant at lower pH and higher temperature, and the tetramer $B_4(OH)_{14}^{2-}$ is dominant at higher pH and lower temperature. It can be concluded here within the middle pH region: a) At lower boron concentration and higher temperature borates containing less boron atoms are the most significant ionic species of boron carrying forms than borates containing more boron atoms. b) At higher boron concentration and lower temperature, polyborates containing more boron atoms can be the dominant ionic species.
4. The amount of polyborates increases with decreasing temperature at a given feed concentration and pH. It is worthy to note that polyborates, for instance, $B_3(OH)_{10}^-$ and $B_4(OH)_{14}^{2-}$, can be the most significant boron containing species in solution at total boron concentrations as high as 6500 ppm and temperature as low as 10 °C within a certain pH region, as indicated in Figure (II-4). This tendency is of importance to the success of chemical separation of boron using ion exchange. The contribution of polyborates toward boron sorption is dominant in this situation.

These conclusions agree with previous work by Mesmer (1972), Na (1993), and McGarvey (1995). There may exist other borates in solution, especially at a higher concentration and low temperature as discussed above. Of interest is the tendency of boric solution under different conditions. One can extract a basic principle, in boron sorption on ion exchanger or by membrane,

1. At a low boron concentration or high temperature we only need to consider the contribution by boric acid and monoborate, otherwise
2. We must take polyborates into account in sorption process, although boric acid is a weakly dissociated acid.

Sorption Equilibrium

There are, in general, two categories of adsorption, physical adsorption and chemisorption. Physical sorption, or van der Waals adsorption, a readily reversible phenomenon, involves only relatively weak intermolecular forces between molecules of the solid and the substance adsorbed. Chemisorption, or activated adsorption, is a result of chemical interaction, essentially contains the formation of a chemical bond between the sorbate species and the sorbent surface. The sorption of boron, largely boric acid, on ion exchange resins is a mixed process of physical and chemical sorption. Both phenomena may occur simultaneously. In fact, ion exchange is close to chemical sorption.

There are some successful models to describe equilibrium adsorption. Of them, Langmuir or Langmuir-type and Freundlich isotherms are the most frequently applied in solution sorption. The former is limited to use in systems with weak interaction between molecules and a homogeneous, or nearly homogeneous, sorption surface. The later is an empirical equation. Through fitting of experimental data to obtain its parameters, it is more useful in heterogeneous systems. A brief review of these models for analyzing and understanding boron sorption on ion exchange resins is desirable.

The Langmuir model, based on the assumption of ideal localized sorption without interaction on a completely homogeneous surface, can be derived from a sophisticated thermodynamic perspective, though it is obtainable from a simple kinetic derivation. For a single solute or two component exchange, the Langmuir isotherm is

$$q = \frac{q^{\infty} K_L C}{1 + K_L C} \tag{2-31}$$

where q is the relative capacity of resin, q^{∞} is the fixed capacity of resin and should therefore be a temperature-independent constant, C is the solution concentration, and K_L is the equilibrium constant. The temperature dependence of K_L should follow a Gibbs energy change of reaction:

$$K_L = K_{L0} \exp\left(-\frac{\Delta G}{RT}\right) \tag{2-32}$$

Since adsorption is exothermic (negative ΔH), K_L should decrease with an increase of temperature.

For multicomponent systems with solutes individually following Langmuir isotherms, Langmuir equilibrium relation can be extended as given in Equation (2-33)

$$q_i = \frac{q_i^{\infty} K_i C_i}{1 + \sum_{j}^{n-1} K_j C_j} \tag{2-33}$$

where subscribes *i,* and *j* indicate each single solute in the system. This equation gives reasonable estimates when the single solute q^{∞}'s agree closely (Vermeulen et al., 1984).

The ideal Langmuir model gives an appropriate representation of the system behavior at low concentration but breaks down in the saturation region where the effects of molecular interaction become pronounced (Ruthven, 1984). The assumption of no interaction between adsorbed molecules is clearly unrealistic since the existence of some possible forces of attraction, at least, the Van der Waals force. Deviations from the ideal Langmuir model can occur due to either heterogeneity of sites or interaction between adsorbed molecules when one applies this model to a real system. A number of refinements to the Langmuir-type isotherms (Lacher, 1937, Fowler and Guggenhein, 1939) are also restricted to the systems with weak molecule interactions on neighboring sites, which are usually involved by nonpolar sorbate molecules and at low concentration.

Adsorption from solution or on a catalyst surface does not in general appear as ideal Langmuir behavior. For many cases the experimental results can be fairly well represented by Freundlich's exponential isotherm (Sips, 1948, Moore, 1962), which is given by

$$q = K_F C^{1/n} \tag{2-34}$$

where C is the concentration when equilibrium is reached, *n* is an empirical constant usually greater than unity (for favorable situations, less than unity for unfavorable situations, Vermeulen et al., 1984), and K_F is a constant. Both constants *n* and K_F are dependent on temperature. The Freundlich isotherm implies that if log q is plotted against log C, a straight line is obtained with slope 1/n and intercept K_F. The Freundlich isotherm is usually applied to dilute solutions, which can be both physical sorption and chemisorption. This empirical equation is also useful in cases where the actual identity of the solute is not known (Treybal, 1980).

The sorption equilibrium of boron on anion resins may be treated as multilayer sorption, besides the chemical bonding force and the chemical reaction involved. Following the first sorption of the tetrahedral $B(OH)_4^-$ on a site, sorption of subsequent boric acid on the active site can be consecutively carried out through chemical reaction to form polyborates. That tendency is dependent of concentration, pH and temperature, as emphasized in previous sections. To describe concentration equilibrium between resin and solution, one may chose a similar type of sorption equilibrium to Freundlich as indicated by Equation (2-34). It must be noted that K_F in Equation (2-34) is not only temperature dependent, but also resin properties dependent, for instance, cross-linking. To avoid unnecessary confusion, it is better to write the proposed equilibrium relation as follows:

$$q = \alpha K(T) C^{1/n} \tag{2-35}$$

The detail of developing the equilibrium model of boron sorption on the OH^- form resin will be given in Chapter III.

Sorption Kinetics

The reactions involved in boron sorption on ion exchange resin are spontaneous. Diffusion processes either though the liquid film or in the resin particle, therefore, will determine the boron sorption rate. A corresponding criterion of which diffusion is the controlling step may be adopted from Helfferich (1962). When the counterion A is in the exchange resin phase and B in the solution initially, the criterion can be expressed by Equations. (2-36) and (2-37):

Particle diffusion control:

$$\frac{q\overline{D}\delta}{CDR}\left(5+2\alpha_{B}^{A}\right) << 1, \qquad (2\text{-}36)$$

and Film diffusion control:

$$\frac{q\overline{D}\delta}{CDR}\left(5+2\alpha_{B}^{A}\right) >> 1, \qquad (2\text{-}37)$$

In the range between two limits, both resistances should be considered in a model development.

Consider both molecular and ionic boron forms diffusion involved in the process. If the solution concentration of boron is quite low, which is usual the case under film diffusion control, we know, from Fig. (II-1), that the boric acid molecule is the dominant species containing boron in the solution. Consequently, the diffusion of molecules through the film should be the rate-determining factor. The governing equation for this process, correspondingly, is described by Fick's law. That is:

$$J = -D\nabla C \qquad (2\text{-}38)$$

In the situation where the contribution of ionic species toward boron sorption cannot be neglected, it is better to use Fick's law for diffusion of the boric acid molecule and to apply the Nernst-Planck equation

$$J = -D\left[\nabla C + \frac{zFC}{RT}\nabla\Phi\right] \qquad (2\text{-}39)$$

for ionic species (Blickenstaff et al., 1967; Lou, 1993). Both situations involve the determination of the interface concentrations on both sides of the resin surface. A common way to implement this task is to apply the selectivity relationship, which relates the interface concentrations by the mass action law. With a binary system, this relationship is

$$K_A^B = \left(\frac{q_B^*}{C_B^*}\right)^{z_A}\left(\frac{C_A^*}{q_A^*}\right)^{z_B} \tag{2-40}$$

for the ion-exchange reaction

$$\overline{R} - A^{z_A} + B^{z_B} \longleftrightarrow \overline{R} - B^{z_B} + A^{z_A} \tag{2-41}$$

For particle diffusion control, which is valid in systems with high concentration of boron, the rate expression for both molecule and ionic species can be:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\overline{D}\cdot r^2\frac{\partial q}{\partial r}\right) \tag{2-42}$$

The diffusion coefficient inside the resin $\overline{D}$ is concentration dependent, which adds the complication of kinetic effects toward modeling such systems. Consider boron inside the resin largely as these ionic forms. The concentration dependency of these diffusion coefficients may be obtained by applying the Nernst-Planck equation.

With a moderate concentration, there can be no dominant controlling step of diffusion at both sides of the resin surface. The diffusion resistance on both sides is comparable in these situations and should be considered in model development. Taking account of resistance on both sides will be reflected in the determination of the interface concentrations. This situation will be discussed in some detail in the Chapter IV.

Sorption Mechanism of Boron on Resins

Boron sorption on anion exchange resins includes both the boric acid molecule and ionic borate. Ion exchange was discussed in detail by Helfferich (1962). The sorption of molecular boric acid on anion exchange resins will be discussed below.

During the process, boric acid is first polarized by the attraction of the electrical field near the surface of the ion exchange resin and diffuses to the interface. Then it forms the tetrahedral $B(OH)_4^-$ or polyborate by reaction with the free OH^- ion inside resin. Finally, sorption occurs as $B(OH)_4^-$ or polyborate on a site inside the resin.

When concentration is low, the liquid side gradient is quite small and the film resistance controls molecular diffusion of boric acid through the film. Consequently, the interface concentration of boric acid is very low. There are not enough boric acid molecules involved in the reaction to form polyborates. The tetrahedral $B(OH)_4^-$ formed on the resin side becomes the dominant borate species sorbed on resin sites, which results in a relatively low apparent resin capacity. This was shown experimentally by Tomizawa (1979; 1981).

As solution concentration increases, the gradient on the liquid side and the interface concentration also increases. There are more boric acid molecules reacting at the same time. The tendency to form polyborates increases, which results in an increase of the apparent resin capacity as solution concentration increases. The front of major reactions inside the resin will move toward the core as concentration increases.

Possible higher order reactions at the active site to form polyborates are suggested by de Miera (1985). Replacement of the tetrahedral $B(OH)_4^-$ by polyborates at the exchange site can occur according to selectivity coefficient data (Riddle, 1993).

This postulation is based on the results of boric acid distribution behavior in solution (Figures II-2 to II-9). Inside the resin, pH is quite high, with a range from 9 to 14 (Tomizawa, 1979; 1981). A strong tendency exists for the formation of $B(OH)_4^-$ through first order reaction on the OH^- form strong base anion resin, indicated by Equation (2-3) rather than by Equation (2-4). The $B(OH)_4^-$ will further react with boric acid inside the resin, including the active site to form polyborates. The tendency of reactions to form polyborates increases with increased solution concentration and with decreasing temperature, and it can be reversible. Relevant sorption equilibrium, generally an essential requirement for the analysis and design of this sorption process, is thus non-ideal and complicated.

Conclusions

1. The forms and quantities of borates vary with the conditions of the boric acid solution, which includes boron concentration, temperature, and pH. More work is needed to determine different boron forms within the resin structure, and either quantifying or ruling out any ionization mechanisms in solution under different conditions, especially at high concentrations and in buffer solution.
2. In solutions without other cations at low concentration, molecular boric acid is the only significant species containing boron. Consequently, the contribution of ionic species toward boron sorption on anion exchange resins can be neglected without significant error. This result can be used to minimize the effort toward modeling such processes, for instance, the boron thermal regeneration system.

3. At low concentrations (below 100 ppm boron), only a trace of polyborates can be found. The tetrahedral $B(OH)_4^-$ can be treated, from the sorption point of view, as the only ionic species containing boron.
4. Chemical reactions, such as ionization and neutralization, etc., can occur during the sorption process. These reactions are spontaneous and sorption is controlled by diffusion of boron species.
5. Boron sorption on ion exchange resins from solution proceeds akin to 'multilayer' adsorption. The layers are determined by the order of reaction taking place at the sites inside of resin. This process varies with concentration and temperature.
6. Use Fick's law to describe molecular boric acid diffusion and the Nernst – Planck equation for ionic species diffusion.

REFERENCES

Anderson, J. L., Eyring, E. M., and Whittaker, M. P. (1964). Temperature jump rate studies of polyborate formation in aqueous boric acid. J. Phys. Chem., 68, 1128-1132.

Antikainen, P. J. (1957). Thermodynamics of anionic chelate formation: I. Effect of temperature on the formation of mannitoboric acids, Suomen Kemistilehti, 30B, 185-188.

Baes, C. F. and Mesmer, R. E. (1976). The Hydrolysis of Cations, John Wiley and Sons, New York, NY.

Barth, R. F., A. H. Soloway, and R. G. Fairchild (1990). Boron neutron capture therapy of cancer, Cancer Research, 50, 1061-1070.

Bell, R. P., J. O. Edwards, and R. B. Jones (1967). The structure and acidity of boric acid, and their relation to reaction mechanisms, in The Chemistry of Boron and Its Compounds, by Muetterties, E. L., New York, John Wiley & Sons, Inc.

Blickenstaff, R. A., Wagner, J. D. and Dranoff, J. S. (1967). The Kinetics of Ion Exchange Accompanied by Irreversible Reaction. I. Film Diffusion Controlled Neutralization of a Strong Acid Exchanger by Strong Bases, J. Phys. Chem., 71, 1665-1669.

Bray P. J., J. O. Edwards, J. G. O'keefe, V. Ross, and I. Tatsuzaki (1961). Nuclear magnetic resonance studies of B^{11} in crystalline borates, J. Chem. Phys., 35, 435-442.

Carpeni, G. and Souchay, P. (1945). The Experimental laws of the variation of pH with dilution. J. Chim. Phys., 42, 149-167.

Cohen, P. (1969), Water Coolant Technology of Power Reactors, Gordon and Breach Science Publishers, New York.

Corti, H., Crovetto, R., and Roberto, F. P. (1980). Mobilities and ion-pairing in $LiB(OH)_4$ and $NaB(OH)_4$ aqueous solutions. A conductivity study. J. Solution Chem., 9(8), 617-625.

Cotton, F. A. and G. Wilkinson (1980). Advanced Inorganic Chemistry, New York, John Wiley & Sons, Inc.

de Miera, R. S., M. M. Urgell Comas and J. L. Iglesias (1985). Junta de Energia Nuclear, J.E.N. 580, Madrid.

Doonan, D. J. and L. D. Lower (1978). Boron oxides, boric acid, and borates, in Kirk Othmer Encyclopedia of Chemical Technology, 3rd ed., 4, 67-110, John Wiley and Sons. New York.

Edwards, J. O. (1953). Detection of anionic complexes by pH measurements: I. Polymeric borates, J. Am. Chem. Soc., 75, 6151-6154.

Edwards, J. O. (1954). Rates of substitution reactions in oxyanions. J. Chem. Edu., 31, 270-275.

Edwards, J. O., G. C. Morrison, V. F. Ross, and J. W. Schultz (1955). The structure of the aqueous borate ion, J. Am. Chem. Soc., 77, 266-268.

Edwards, J. O., H. R. Ellison, C. G. Lauro, and J. P. Lorand (1961), Advances in the Chemistry of Coordination Compounds, The Macmillan Co., New York.

Fairchild, R. G. and U. J. Myoha (1985), Neutron dosimetry in boron neutron capture therapy, Comm. Eng. Communities, EUR-7448, 2, 447.

Fowler, R. H. and E. A. Guggenhiem (1939), Statistical Thermodynamics, Cambridge University Press, Cambridge.

Greenwood, N. N. and Thomas, B. S. (1973), The Chemistry of Boron, London, Ann Arbor-Humphrey Science Publishers.

Helfferich, F. G. (1962). Ion Exchange. New York: McGraw Hill Book Company.

Hibben, J. H. (1938), The constitution of some boric oxide compounds, Am. J. Sci., 35A, 113-125.

Ingri, N, G. Lagerstrom, M. Frydman, and L. G. Sillen (1957), Equilibrium Studies of Polyanions II Polyboratesin $NaClO_4$, Acta Chem.Scand., 11, 1034-1058.

Ingri, N. (1963a). Equilibrium studies of polyanions. X. The first equilibrium steps in the acidification of $B(OH)_4^-$, an application of the self-medium method. Acta Chem. Scand., 17, 573-580.

Ingri, N. (1963b). Equilibrium studies of polyanions. XI. Polyborates in 3.0M NaBr, 3.0M LiBr, and 3.0M KBr, a comparison with data obtained in 3.0M $NaClO_4$. Acta Chem. Scand., 17, 581-589.

Ingri, N. (1963c), Equilibrium studies of polyanions containing B^{III}, Si^{IV}, Ge^{IV} and V^{V}, Svensk Kemisk Tidskrift, 199-230.

Johnston, H. L., H. N. Hersh and E. C. Kerr (1951). Low temperature heat capacities of inorganic solids: V. The heat capacity of pure elementary boron in both amorphous and crystalline conditions between 13 and 305 °K. Some free energies of formation J.Am. Chem. Soc., 73, 1112-1117.

Kolthoff, I. M. (1926). The change of the dissociation constant of boric acid with the concentration of this acid. Rec. Trav. Chim., 45, 501-507.

Kolthoff, I. M. and Bosch, W (1927). The abnormal change in pH in boric acid-sodium hydroxide mixtures at different concentrations and temperatures. Rec. Trav. Chim., 46, 180-188.

Korkisch, J. (1989). Their application to inorganic analytical chemistry, in Handbook of ion exchange resins, VI, CRC Press, Boca Raton, FL.

Lacher, J. R. (1937). A theoretical formula for the solubility of hydrogen in palladium, Proc. Roy. Soc., A161, 525.

Lorand, J. P. and J. O. Edwards (1959). Polyol complexes and structure of the benzeneboronate ion, J. Org. Chem., 24, 769.

Lou, J. (1993). Simulations of Borate Ion Exchange and Radial Flow for Reactor Water Clean Up System, M.S. Thesis, Oklahoma State University, Stillwater, Oklahoma.

Manov, G. G., N. J. Delollis and S. F. Acree (1944). Ionization constant of boric acid and the pH of certain borax-chloride buffer solutions from 0 to 60 °C, J. Res. Nat. Bur. Stand., 33, 287-306.

Maya, L. (1976). Identification of polyborate and fluoropolybarate ions in solution by Raman spectroscopy, Inorg. Chem., 15(9), 2179-2184.

McGarvey, F. X. (1995). Use of boric acid in nuclear reactors from an ion-exchange standpoint, Ultrapure Water, Oct. 47-52.

Menzel, J. (1927). Boric acids and alkali borates. I. The free boric acids. II. The alkali borates in H_2O solution. Z. Anorg. Chem., 164, 22.

Mesmer, R. E., C. F. Baes Jr., and F. H. Sweeton (1972a) Acidity Measurement at Elevated Temperatures. VI. Boric Acid Equilibria, Inorg. Chem., 11(3), 537-543.

Mesmer, R. E., C. F. Baes Jr., and F. H. Sweeton (1972b). Boric acid equilibria and pH in PWR coolants, Proceedings of the 32nd International Water Conference, Pittsburgh, PA, 55-62.

Momii, R. K. and Nachtrieb, N. H. (1967). Nuclear magnetic resonance study of borate-polyborate equilibria in aqueous solution. Inorg. Chem., 6, 1189-1192.

Moore, W. J. (1962). Physical Chemistry, 3rd, ed. Prentice Hall, Inc., Englewood Cliffs, NJ.

Muetterties, E. L. (1967), The Chemistry of Boron and Its Compounds, New York, John Wiley & Sons, Inc.

Na, J. W. (1993), Adsorption Characteristics of Boric Acid on Strong-Base Anion Exchange Resin, Ph.D. Dissertation, Korea Advanced Institute of Science and Technology.

Owen, B. B. (1934). The dissociation constant of boric acid from 10 to 50°. J. Phys. Chem., 56, 1695-1697.

Perry, R. H. and Chilton, C. H. (1984). Chem. Engineer's Handbook, 6th ed., New York: McGraw-Hill.

Platford, R. F. (1969). Osmotic and activity coefficients of some simple borates in aqueous solution at 25 °C, Canadian Journal of Chemistry, 47, 2271-2273.

Riddle, J. M. (1993). Temperature effects on equilibrium leakage from ion exchange resins, Presented to EPRI Condensate Polishing Workshop, New Orleans, LA.

Ross, V. F. and J. O. Edwards (1967), The structural chemistry of the borates, in The Chemistry of Boron and Its Compounds, by Muetterties, E. L., New York, John Wiley & Sons, Inc.

Ruthven, D. M. (1984). Principles of Adsorption and Adsorption Processes, John-Wiley & Sons, New York.

Sips, R. (1948). On the structure of a catalyst surface, J. Chem. Phys., 16 (5), 490.

Toshiyuki, H, (1979). Raman spectra of polyborate ions in aqueous solution, J. Inorg. Nucl. Chem., 41, 1217-1220.

Treybal, R. E. (1980). Mass Transfer Operations, McGraw-Hill, New York.

Vermeulen, T., M. D. LeVan, N. K. Hiester, and G. Klein (1984). Adsorption and ion exchange, in Chem. Engineer's Handbook, 6th ed., Perry, R. H. and C. H. Chilton (ed.), New York: McGraw-Hill.

CHAPTER III

A MODEL ON EFFECTS OF CONCENTRATION AND TEMPERATURE ON BORON SORPTION CAPACITY OF ION EXCHANGERS

Introduction

The sorption capacities of strong base anion exchange resins vary with temperature and the external boric acid concentration. This has been verified by experimental works and industrial practice (Peterka, 1980, Tomizawa, 1979, 1981, Dobrevsky and Konova, 1988). This temperature effect has been exploited to develop the boron thermal regeneration system (BTRS) in nuclear power plants. The mechanisms, however, have not yet been studied in detail due to the complicated polyborate formations, both in solution and inside the resin, under different situations. There is no literature that successfully describes the temperature dependence relationship of the sorption isotherm. The difficulty is a rigorous interpretation of the boron sorption rate that would allow a prediction of the boron sorption behavior on ion exchange resins. The need for such a relationship, therefore, becomes critical in predicting the sorption behavior of boron on ion exchange resins. In this Chapter, based on discussions in the last Chapter and through the examination of literature data, a semi-empirical model will be presented for this purpose.

An extensive study of the selection of anion exchange resins for boron thermal regeneration was given by Paterka (1980). Paterka examined Diaion resins of different crosslinkage and found, in addition to the dependence of temperature and solution concentration, the equilibrium capacity depends strongly on the degree of resin cross-linking. He showed that a maximum sorption capacity for boron could be obtained at about 7% crosslinkage. Beyond this point, the increase in loading at low crosslinkage related to swelling variations, while high crosslinkage resins demonstrated reduced capacity due to kinetic difficulty in converting the resins from one form to another. The typical effects of solution concentration and temperature on the boron sorption capacity of anion resins are indicated in Figures (III-1) and (III-2).

Tomizawa (1979, 1981) carried out studies, by using Diaion SAN-1 (strong base anion resin) in the OH^- form, of the solution concentration and temperature dependencies of apparent resin capacity, toward boron, in the sorption of boric acid. The results observed from his experiments are summarized as follows:

- At 25 °C, as solution concentration increases from 0.00925 to 0.647 mol/*l*, the average sorption capacity of the resin toward boron increases from 1.46 to 4.22 equiv./*l*-resin.
- For temperature at 5 and 70 °C, the capacity drops from 3.78 to 2.94, or from 1.58 to 1.15, at constant solution concentrations of 0.00925 and 0.278 mol/*l*, respectively.
- The pH within borate-form resin increased with rising temperature at constant solution concentration and the range of pH inside the resins is from 9 - 14.
- The presence of orthoborate ion, tetraborate (mono and divalent) ion and pentaborate (mono and divalent) were verified from the resin phase by chemical analysis.

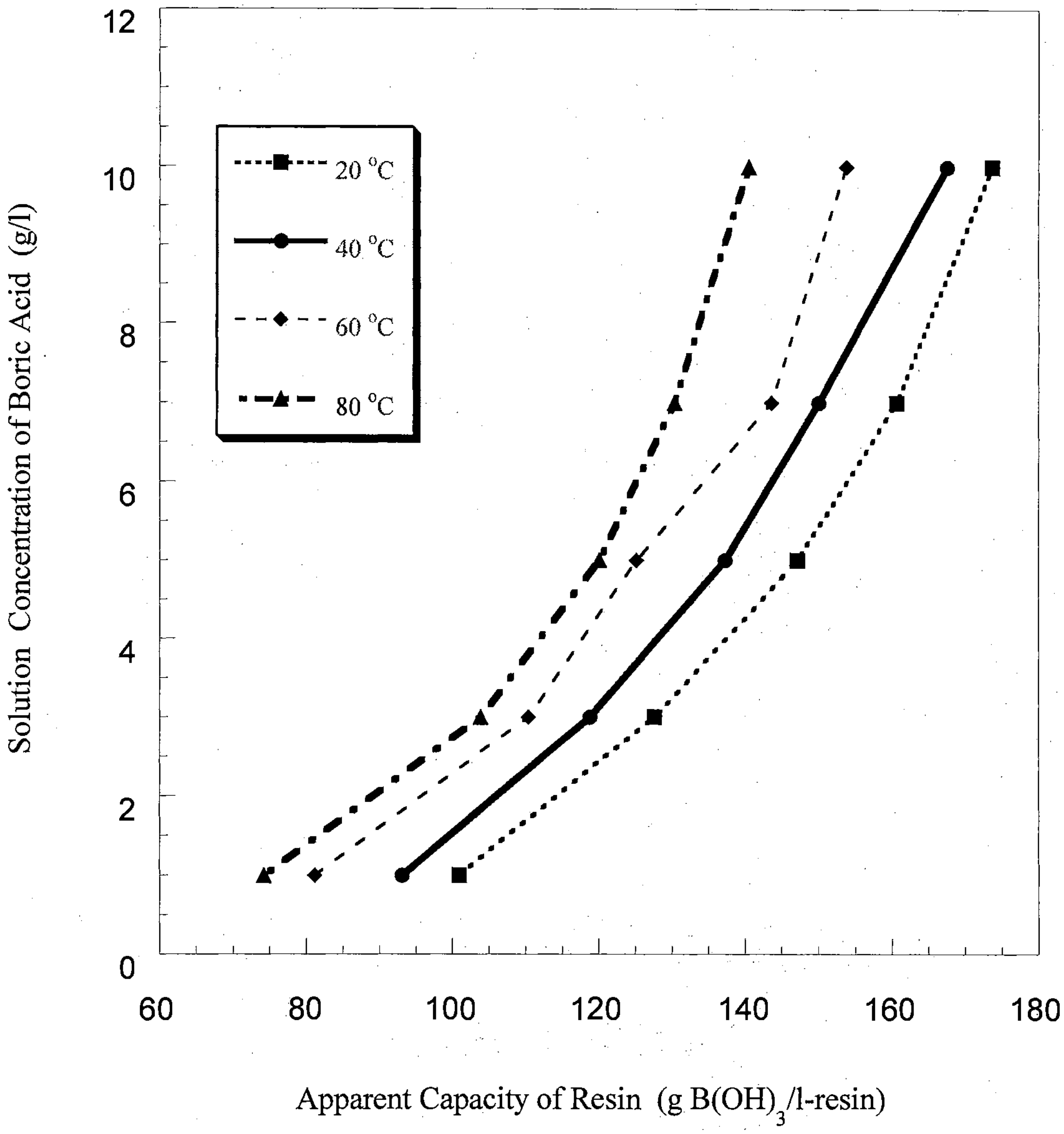

Figure III-1 Equilibrium Isotherm for Diaion PA312 Resin [Experimental Data from Peterka, 1980].

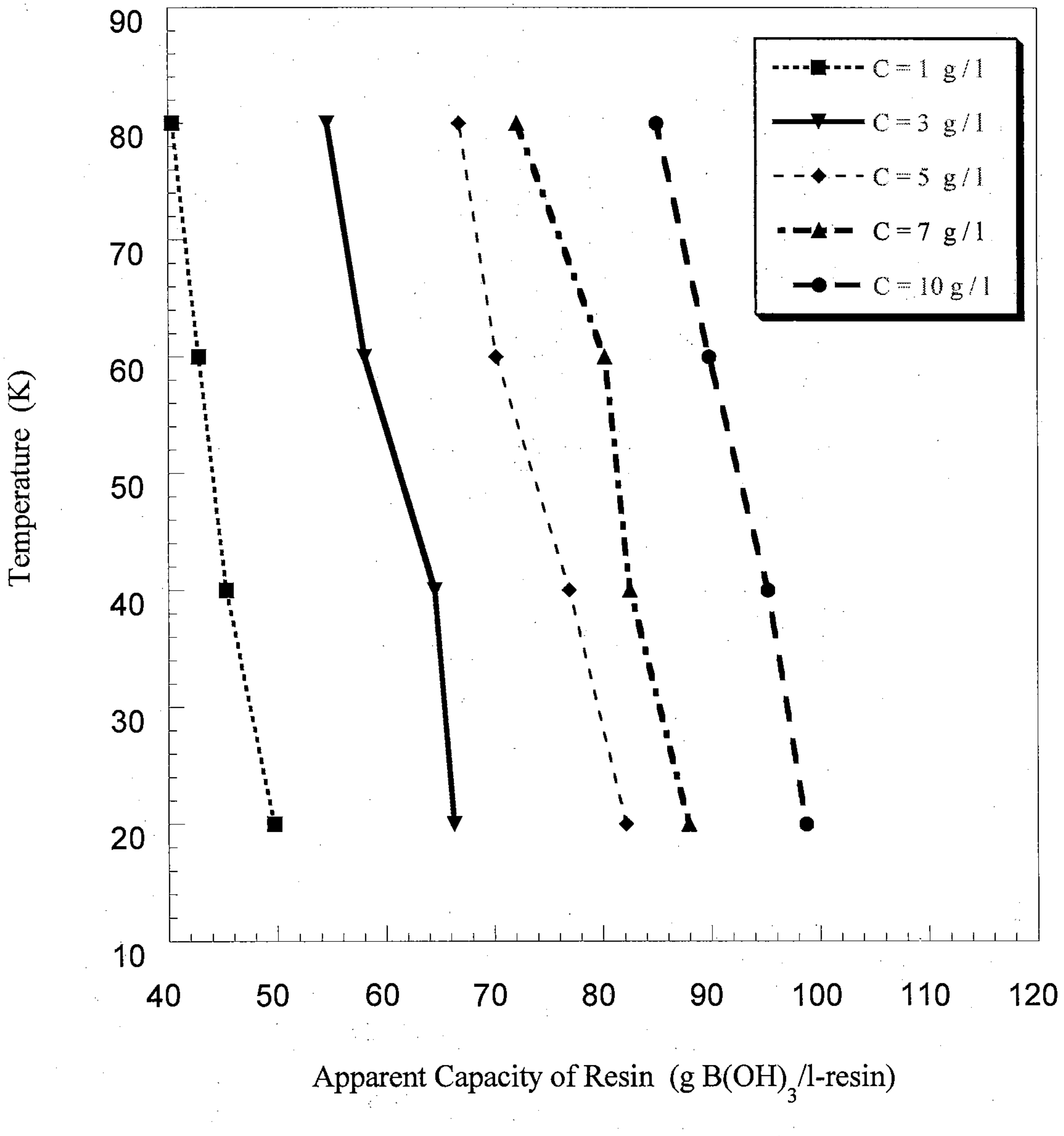

Figure III-2 Relations of Apparent Capacity and Temperature for Diaion PA306 [Experimental Data from Peterka, 1980]

Based on his observation, Tomizawa assumed that from 5 to 70 °C, orthoborate ion $B(OH)_4^-$, tetraborate ions (monovalent and divalent, B_4^- and B_4^{2-}), and pentaborate ions (monovalent and divalent, B_5^- and B_5^{2-}) were present in the resin and suggested that nominal equilibrium constants could be estimated for these five borate ion species. His results agree with Paterka's work, but his postulation, according to the previous studies of boron chemistry, seems to be questionable.

Na (1993) studied the equilibrium of boron sorption on strong base anion resin by using Amberlite IRN 78L. With this resin, he obtained a similar tendency of boron sorption. In his work, Na assumed that the monoborate ions adsorbed on sites tend to be replaced by polyborate ions as the external solution concentration of boric acid increases. By modifying the ideal Langmuir isotherm, Na proposed the following equilibrium isotherm relation.

$$q = q^{\infty}\left(\frac{K_L C}{1 + K_L C} + K_C C + K_O\right) \tag{3-1}$$

The first term in parentheses suggests that the sorption equilibrium obeys the ideal Langmuir isotherm at low solution concentration, the second term reflects the degree of replacement, and the third term was used to account for the rapid sorption feature of boric acid on the strong base anion exchangers. These coefficients, corresponding to each temperature chosen, were obtained from the regression of his experimental data.

Obviously, their work showed the behaviors of the boron sorption on strong base anion resins. The experimental data from Paterka and Na will be used in this work. Through the examination of boron solution chemistry, then from the change of Gibbs energy and the characteristics of diffusion, the development of an equilibrium isotherm for the sorption of boron on anion resins will be given in the following sections.

Distribution of Boron in Aqueous Solution and in Resin

There is no general literature agreement about all of the boron forms in aqueous solution. In this work, however, there is no necessity to account for every species containing boron. The contribution of boric acid molecules on the sorption of boron on ion exchange resin is dominant (recalled previously). Some borates considered to be significant as boron carriers are accounted for in the model for accuracy improvement. Reviewing the distributions of major boron carriers in solution and corresponding possible reactions is to give better understanding of possible reaction mechanisms inside the resins.

Distributions of Boron in Aqueous Solution

Generally speaking, there are two types of boric acid existing in the free state, metaboric acid (HBO_2) and orthoboric acid ($B(OH)_3$). The two types may be converted to each other by hydration or dehydration at certain conditions. In solution, metaboric acid rapidly converts to orthoboric acid because of the favorable situation of hydration.

As discussed in the last Chapter, the boric acid in aqueous solution weakly dissociates to form monoborate and some polyborates depending on temperature, concentration, and pH. The primary species in borate solution at the acidic and basic extremes of pH are $B(OH)_3$ and $B(OH)_4^-$, respectively. At low concentration (<0.025M in boron), $B(OH)_4^-$ is the only ionic species significant in solution, while at higher concentration it was postulated that some polyborates – triborates, tetraborates, and pentaborates – along with $B(OH)_4^-$, may exist. Among these polyborates postulated, the polyborate with three boron atoms and one negative charge is the most important (Edward, 1953; Ingri et al., 1957; Ross and Edwards, 1967; Mesmer et al., 1972).

There are two major postulations about the trimer borate. Edwards (1953) suggested, due to the ring type structure of trimeric hydroxyborate $B_3O_3(OH)_4^-$ and highly stable in solution, the following reaction to form $B_3O_3(OH)_4^-$,

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3O_3(OH)_4^- + 3H_2O \qquad (3\text{-}2)$$

while Mesmer et al (1972) assumed the reaction

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3(OH)_{10}^- \qquad (3\text{-}3)$$

leads to the formation of $B_3(OH)_{10}^-$. The equilibrium constant K, according to these authors, agrees within about two orders of magnitude.

In addition, the traces of polyborates, like tetraborates, and pentaborates, can be found in solutions with high boron concentration. Cotton and Wilkinson (1980) postulated the following equilibrium reaction.

$$2B(OH)_3 + 2B(OH)_4^- \longleftrightarrow B_4O_5(OH)_4^{2-} + 5H_2O \qquad (3\text{-}4)$$

And the formation of pentaborate

$$4B(OH)_3 + B(OH)_4^- \longleftrightarrow B_5O_6(OH)_4^- + 6H_2O \qquad (3\text{-}5)$$

was reported by Ross and Edwards (1967).

Under Mesmer et al.'s postulation (1972), the distributions of boron forms in boric acid solution quantitatively determined under various conditions were given in the Chapter II.

Distributions of Boron inside Resins

The reactions taking place in the resin phase to form polyborates may obey similar restrictions to those taking place in solution. The nature of the polyborate species in the resin has been discussed successively by Barbier et al. (1966), Kakihana et al. (1974), Tomizawa (1979, 1981, and 1983), and Miera et al. (1985). Within the resin phase, pH and the strength of electrical field are relative high, which are in favor of the ionization of boric acid. As boron concentration increases in the resin phase, pH decreases from its peak value and conditions inside the resin more favorably to form hydroxy polyborates with uni- or multi-valence (See Figures II-2 to II-9). Thus, there is more evidence of other polyborates found in their studies.

Tomizawa (1979), studying the adsorption characteristics of boric acid on strong base anion exchange resins, mentioned both tetraborate and pentaborate ions with divalence existing in the resin phase. He assumed that, along with orthoborate ion $B(OH)_4^-$, tetraborate ions (both monovalent and divalent), and pentaborate ion (both monovalent and divalent), are anticipated in the resin phase. Distributions of polyborate ions inside the resin at 25 °C, with an increase of boric acid concentration in solution, are:

- divalent tetraborate and pentaborate concentrations reach their peaks at boron concentration near 0.1 M, with a sharp decrease of orthoborate ion $B(OH)_4^-$;
- Then monovalent tetraborate and pentaborate concentrations increase to their maximum at boron solution concentration above 0.5 M, while the concentration of orthoborate ion $B(OH)_4^-$ goes to zero;

- At boron solution concentrations greater than 1 M, only tetraborate and pentaborate with monovalent exist inside the resins.

Later, Tomizawa (1981) showed that, in the same solution concentration region, the concentrations of polyborates in the resin phase decreased with increasing temperature, which was similar to results reported by Peterka (1980) and verified by Dobrevsky and Konova (1988).

Miera and his co-workers suggested the following reaction steps to indicate the possible polyborate species inside the resin and to account for the fixation of borate ions on an active site:

Dissociation of boric acid inside the resin, and exchange on the active site:

$$B(OH)_3 + OH^- \rightarrow B(OH)_4^- \tag{3-6}$$

With an increase of the solution concentrations, at the same site there are

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3O_3(OH)_4^- + 3H_2O \tag{3-7}$$

and

$$2B(OH)_3 + B_3O_3(OH)_4^- \Leftrightarrow B_5O_6(OH)_4^- + 3H_2O \tag{3-8}$$

They considered that the formation of polyborates with divalence (as $B_3O_3(OH)_5^{2-}$, and $B_3O_5(OH)_4^{2-}$) would be less possible since these reactions require an excess of OH^- ion.

The studies of equilibrium reactions at high solution concentrations (Fig. II-4, Fig. II-7, and Fig. II-9) in Chapter II indicate that with a decrease of temperature, the concentrations of polyborates containing more boron atoms increases, and that their peak concentrations appear at higher pH. Consider the effects of both solution concentration and temperature on distribution of boron inside of resin. The distributions, varying with temperature and solution concentration, of boron inside of resin may be suggested as follows:

- At a given temperature, the orthoborate ion $B(OH)_4^-$ is the major species containing boron atoms inside the resin at the beginning of sorption. With the increase of boron solution concentration, the concentration of orthoborate ion $B(OH)_4^-$ decreases. The higher solution concentration of boron, the faster the decrease of the concentration of the orthoborate ion $B(OH)_4^-$.
- Multivalent polyborates would be less possible to form inside the resin, but may appear at the early stage of sorption due to high hydroxide OH^- concentration.
- Ring type polyborates are more possible inside the resin due to their highly stable structure. This postulation indicates that $B_3O_3(OH)_4^-$, and $B_3O_3(OH)_5^{2-}$ are favorable species anticipated in the resin phase.
- As temperature increases, polyborates can be rapidly reversed to $B(OH)_4^-$ depending on solution concentration and pH inside the resin.

Derivation of the Model

Assuming that all of these possible reactions take place inside the resin, each reaction may be represented by:

$$a_i B + OH^- \xleftrightarrow{K_i} B_{a_i}^- \quad (3\text{-}9)$$

The total resin capacity may then be given by

$$Q = \sum \overline{C}_{B_{ai}} = \overline{C}_{B_{r,n}} \tag{3-10}$$

in which a_i is the number of boron atom for the *i*th polyborate; B represents $B(OH)_3$; B_{ai} is the borate with a_i number of boron atoms; and $B_{r,n}$ is the representative polyborate with the average boron atom *n* and the total fraction. According to the stoichiometric relations of the above reactions:

$$\overline{C}_{r,n} \propto K_r \overline{C}^{n}_{B(OH)_3} \tag{3-11}$$

then

$$Q = \alpha K_r \overline{C}^{n}_{B(OH)_3} \tag{3-12}$$

where K_r is the overall equilibrium constant of reactions; α is a proportional coefficient. Because K_r is a function of temperature and $\overline{C}^{n}_{B(OH)_3}$ can be related to the concentration of boric acid in solution in some way, now the problem is to find the relationships between the equilibrium constant K_r and temperature T, and between $\overline{C}^{n}_{B(OH)_3}$ and $C_{B(OH)_3}$ the concentration of boric acid in solution.

Effects of Temperature

The effects of temperature on the reaction equilibrium constant can be described by the change of Gibbs' energy. An approximate equation may be given as follows

$$K_r = A_0 \cdot \exp\left(-\frac{\Delta G}{RT}\right) \tag{3-13}$$

Suppose there are *m* reactions taking place inside resin to form polyborates. Apply Eq. (6) to each reaction

$$K_i = A_i \cdot \exp\left(-\frac{\Delta G_i}{RT}\right) \tag{3-14}$$

and summarize to give

$$K_r = \prod_{i=1}^{m} K_i = \prod_{i=1}^{m} A_i \cdot \exp\left(-\frac{\sum_{i=1}^{m} \Delta G_i}{RT}\right) = A_0 \cdot \exp\left(-\frac{\Delta G}{RT}\right) \tag{3-15}$$

or may be written approximately as

$$K_r = A \cdot \exp\left(-\frac{\Delta H}{RT}\right) \tag{3-16}$$

Integration of the following expression to give the relationship between heat and temperature:

$$\Delta H = \int C_p dT = \int (a_0 + b_0 T + c_0 T^2) dT = a_1 T + b_1 T^2 + c_1 T^3 \tag{3-17}$$

Substitute this relation into Eq. (9) and rearrange to give the resulting expression:

$$K_r = A^* \cdot \exp[-(bT + cT^2)] \tag{3-18}$$

in which A* is a proportionality constant at the given concentration, b and c are the coefficients reflecting the characteristics of these reactions and the effects of the bonding force of adsorption for a given resin. Therefore, one can rewrite Eq. (3-12) as

$$Q = \alpha' \overline{C}_B^n \cdot \exp[-(bT + cT^2)] \tag{3-19}$$

Effect of Concentrations

Because the reactions involved in both solution and resin phases take place very rapidly, diffusion processes should be the controlling steps for the rate of boron sorption on ion exchange resin. Under a constant temperature, the increase of boron concentration inside the resin can be described by the particle rate:

$$\frac{d\overline{C}_{B_{r,n}}}{dt} = -a_s \sum D_i \frac{dC_{B_i}}{dr} \tag{3-22}$$

From related reactions in solution, one can find, based on the stoichiometry

$$C_{B_i} = \Phi(C^{i}_{B(OH)_3}) \tag{3-23}$$

As a similar way of dealing with the boron concentration inside the resin, it should be possible to define a pseudo species for which its concentration, $C_{B_{r,m}}$, is equivalent, in terms of boron, to that of all these species containing boron in Equation (3-22). And by referencing Equation (3-23),

$$\frac{d\overline{C}_{B_{r,n}}}{dt} = -\lambda a_s D_{er} \frac{dC_{B_{r,m}}}{dr} = -\lambda' D_{er} \frac{dC^{m}_{B(OH)_3}}{dr} \tag{3-24}$$

where D_{er} is the effective diffusivity of the pseudo species, λ' is a proportionality constant at a certain temperature. With the assumptions of a linear driving force and negligible interfacial concentration, Equation (3-24) can be expressed approximately by

$$\frac{d\overline{C}_{B_{r,n}}}{dt} = \lambda^{*} k_{er} C^{m}_{B(OH)_3} \tag{3-25}$$

Integrating Equation (3-25) and ignoring the equilibrium concentration in solution at the end of sorption gives

$$\overline{C}_{B_{r,n}} = \beta C^{\eta}_{B(OH)_3,f} \tag{3-26}$$

or

$$\overline{C}^{n}_{B(OH)_3} = \beta' C^{\eta}_{B(OH)_3,f} \tag{3-27}$$

Where $C_{B(OH)_3,f}$ is the feed concentration of boric acid, β' is a proportional constant at a given temperature, η is the exponent of the concentration of boric acid in feed after taking account of the interactions among these species existing in the given solution.

Substitute Equation (3-27) into Equation (3-19) to obtain the model in which the variation of the sorption capacity of resin toward boron can be related to the feed concentration of boric acid in solution and temperature. That is:

$$Q = a \cdot C^{\eta}_{B(OH)_3,f} \cdot \exp[-(bT + cT^2)] \tag{3-28}$$

where the parameters a, b, c, and η are able to be determined by experiment data.

Determination of Parameters

Equation (3-28) is a nonlinear algebraic equation both in independent variables and in parameters. One may use the method of nonlinear least squares to determine these parameters. In this way, it is inevitable to require a guess value for each parameter to begin. It usually requires several tries to find a suitable starting value in some cases, especially in the problems with more than one parameter, like Equation (3-28). Fortunately, it is possible to transform the nonlinear equation into an alternative form that is linear in the parameters by taking the logarithm of both sides in the equation.

$$\ln Q = \ln a + \eta \ln C_{B(OH)_3,f} - (bT + cT^2) \tag{3-29}$$

or

$$y = A_1 + A_2 \ln C_{B(OH)_3,f} - (A_3 T + A_4 T^2) \tag{3-30}$$

in which

$$y = \ln Q; \qquad A_1 = \ln a; \qquad A_2 = \eta;$$

$A_3 = b;$ $A_4 = c$

By making the conversion, Equation (3-28) turns into Equation (3-30) that is a linear function of parameters A_1, A_2, A_3, and A_4 in logarithm. In this way it gives the great advantage of leading to a straightforward calculation which can usually be solved routinely on computer. However, the parameter values calculated by least squares from different forms of the same original equation will not be exactly the same, though often close. The solution obtained from linearized version, therefore, is used to provide the best starting estimates for the nonlinear calculation of Equation (3-28). Results both from the linearized version Equation (3-30) and from the original nonlinear form Equation (3-28) will be given in Tables III-1 and III-2 for comparison.

In addition, because the dependent variables y or Q depends on two independent variables - the feed concentration $C_{B(OH)_3,f}$ and temperature T, this model is a two-dimension problem. Each data point corresponds to a value of y, T, and $C_{B(OH)_3,f}$. In order to use the same minimization of error as in a one-dimension problem the algebraic equation for the unknown parameters in Equations (3-28) and (3-30), a method of multiple regression should be applied in this problem.

Results and Discussion

Results

Tables III-1 and III-2 list some commercial anion resins and the corresponding values of the parameters in Equations (3-30) and (3-28), respectively. The experimental data used for obtaining the values of these parameters were reported by Peterka (1980), and

Na (1993). The solution concentration range in terms of boric acid is about 1 to 10 g/liter (175 ppm to 1750 ppm in terms of boron), and the temperature range used in their experiment is 10 - 80 °C. If the units of the resin capacity Q, or lnQ, temperature T, and the feed concentration of boric acid $C_{B(OH)_3,f}$ in Eq. (3-28) are g boric acid /liter resin; K; and g boric acid/liter; respectively, the corresponding parameter values are listed in Tables III-1 and III-2,

Errors of Q predicted by the multiply nonlinear regression method are acceptable. The minimized errors by the sum of squared residuals for Eq. (3-30), defined in Eq. (3-31), are in the 10^{-4} order of magnitude.

$$\text{error} = \frac{\sum_{i=1}^{N}[y_i - (A_1 + A_2 \ln C_i - A_3 T_i - A_4 T_i^2)]^2}{N - P} \tag{3-31}$$

Table III – 1

Parameter Values in Equation (3-30)

Resin Types	A_1	A_2	A_3	A_4
Amberlite IRN78LC	5.06	0.286	-3.04×10^{-3}	1.45×10^{-5}
Diaion PA306	4.28	0.316	-1.79×10^{-4}	5.28×10^{-6}
Diaion PA308	7.85	0.308	0.0202	-2.59×10^{-5}
Diaion PA312	5.02	0.264	-4.15×10^{-4}	6.60×10^{-6}
Diaion PA316	8.33	0.263	0.0203	-2.56×10^{-5}
Diaion PA318	5.72	0.246	0.0481	-1.51×10^{-6}
Diaion SA10A	7.88	0.278	0.0180	-2.18×10^{-5}

Table III - 2

Parameter Values in Equation (3-28)

Resin Types	η	A (1/l-resin)	b (1/K)	c (K^{-2})
Amberlite IRN78LC	0.291	6.30×10^{2}	5.99×10^{-3}	-4.55×10^{-8}
Diaion PA306	0.321	4.34×10	-3.16×10^{-3}	9.68×10^{-6}
Diaion PA308	0.302	1.08×10^{3}	0.0149	-1.78×10^{-5}
Diaion PA312	0.262	9.10×10	-3.39×10^{-3}	1.09×10^{-5}
Diaion PA316	0.259	2.27×10^{3}	0.0167	-2.03×10^{-5}
Diaion PA318	0.249	3.31×10^{2}	0.0545	-2.65×10^{-6}
Diaion SA10A	0.282	4.80×10^{3}	0.0219	-2.80×10^{-5}

The standard deviation for Equation (3-28), which is defined as

$$\text{std.dev.} = \left\{ \frac{\sum_{i=1}^{N} [Q_{exp} - Q_{pred}]^2}{N-P} \right\}^{1/2} \tag{3-32}$$

are about 10^0 order of magnitude. The average and maximum relative errors, which are defined in Equations (3-33) and (3-34),

$$\text{Average Error of Q} = \frac{1}{N} \cdot \left| \sum_{i=1}^{N} \frac{Q_{i,exp} - Q_{i,pred}}{Q_{i,exp}} \right| \times 100\,\% \tag{3-33}$$

$$\text{Maximum Error of Q} = \text{Max} \left| \frac{Q_{i,exp} - Q_{i,pred}}{Q_{i,exp}} \right| \times 100 \tag{3-34}$$

are in about 1.0×10^{-2} and 5.0×10^{-2} %, respectively. These values of errors for different resin type are given in Tables III-3 and III-4.

Predicted results are plotted in Fig. III-3 through Fig. III-11 for the following anionic resins: Diaion SA10A, Diaion PA308, Diaion PA316, and Amberlite IRN78LC. Experiment data are also given in these figures for comparison.

Discussions

Equation (3-28), derived from the change of Gibbs' energy, gives the familiar exponential (Arrhenius) dependence of apparent capacity on absolute temperature. The exponential term indicates that only a part of the reaction leads to an increase of apparent capacity. In other wards, there must be some reversible reactions reflecting local unfavorable conditions to form polyborates. The other exponential concentration term is Freundlich type adsorption. In this isotherm, the exponential η is less than 1. The proportionality constant a accounts for the minimum total capacity of resin and the effects of the boron concentration gradient, diffusion resistance, and resin properties on the apparent capacity.

Results presented in Table III-2 and Figs. III-3 – III-11 show that the proposed model fits experiment data quite well. The parameter values in the model vary from resin to resin because of differences in many factors. These differences may include:

- their minimum total capacities;
- functional groups, which result in various bond forces with borates so that there are different effects on possible reactions and the replacement of borates, and;

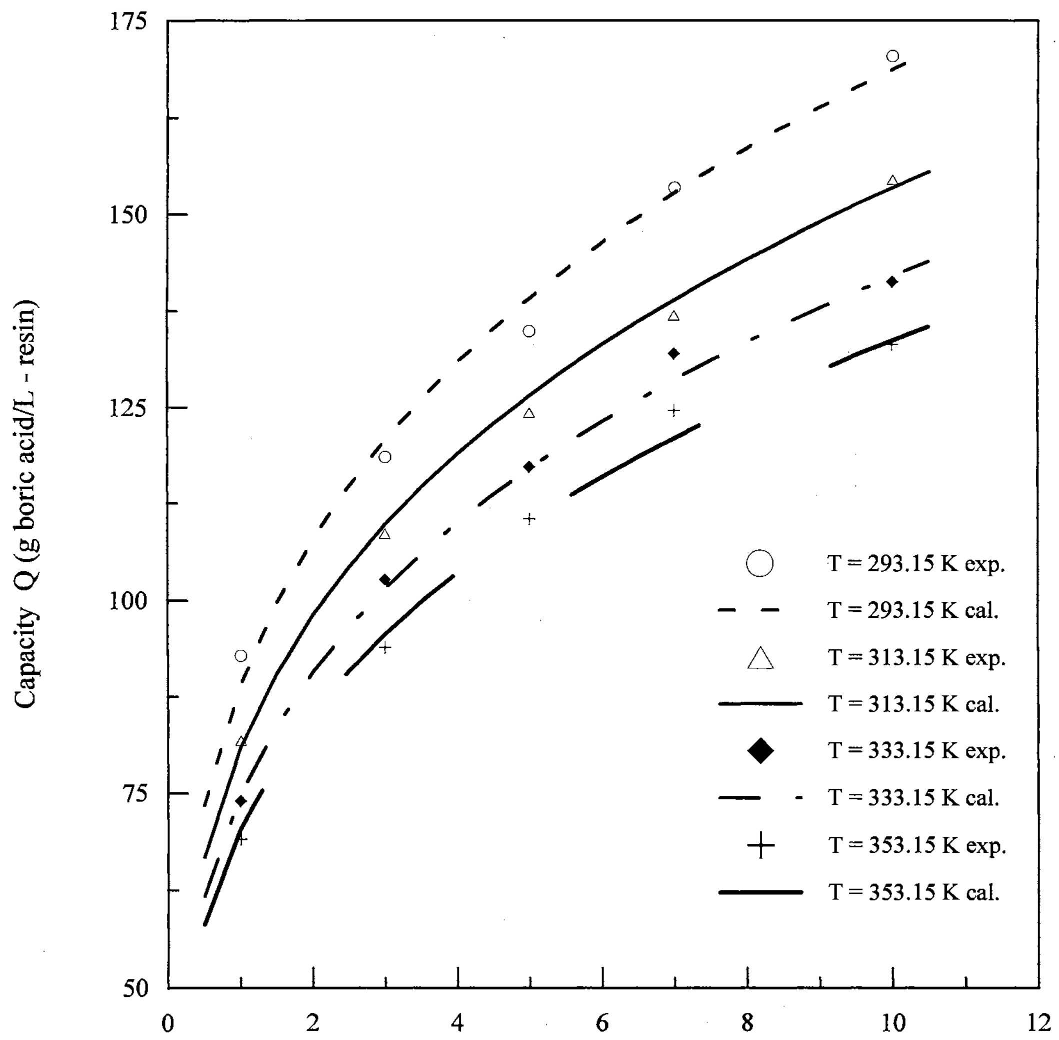

Figure III-3 Comparison of the experimental data and the model fitting for the effects of the solution concentration of boron on the boron sorption capacity of Diaion SA10A resin.

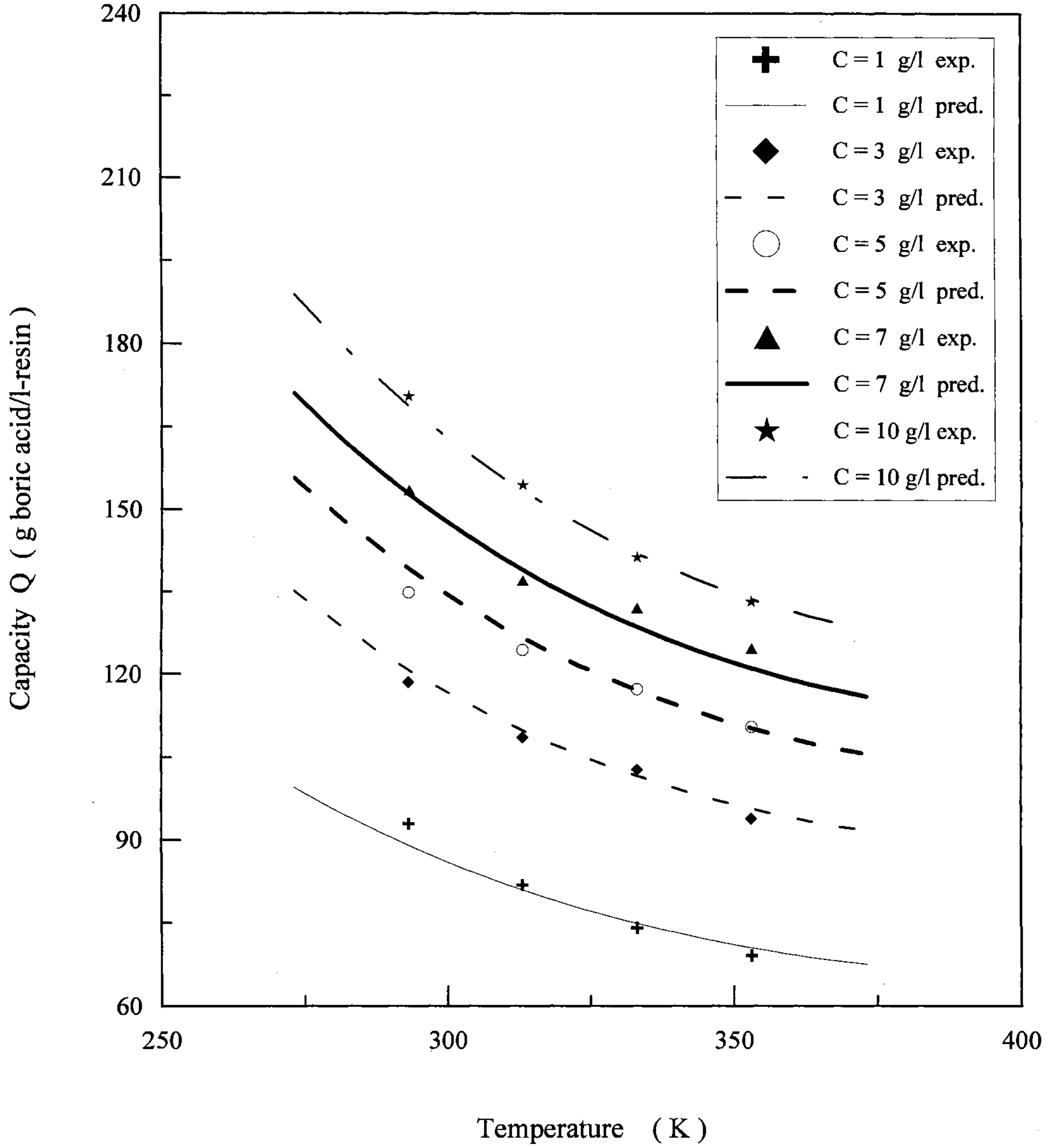

Figure III-4 Comparison of the experimental data and the model fitting for effects of temperature on the boron sorption capacity of Diaion SA10A resin.

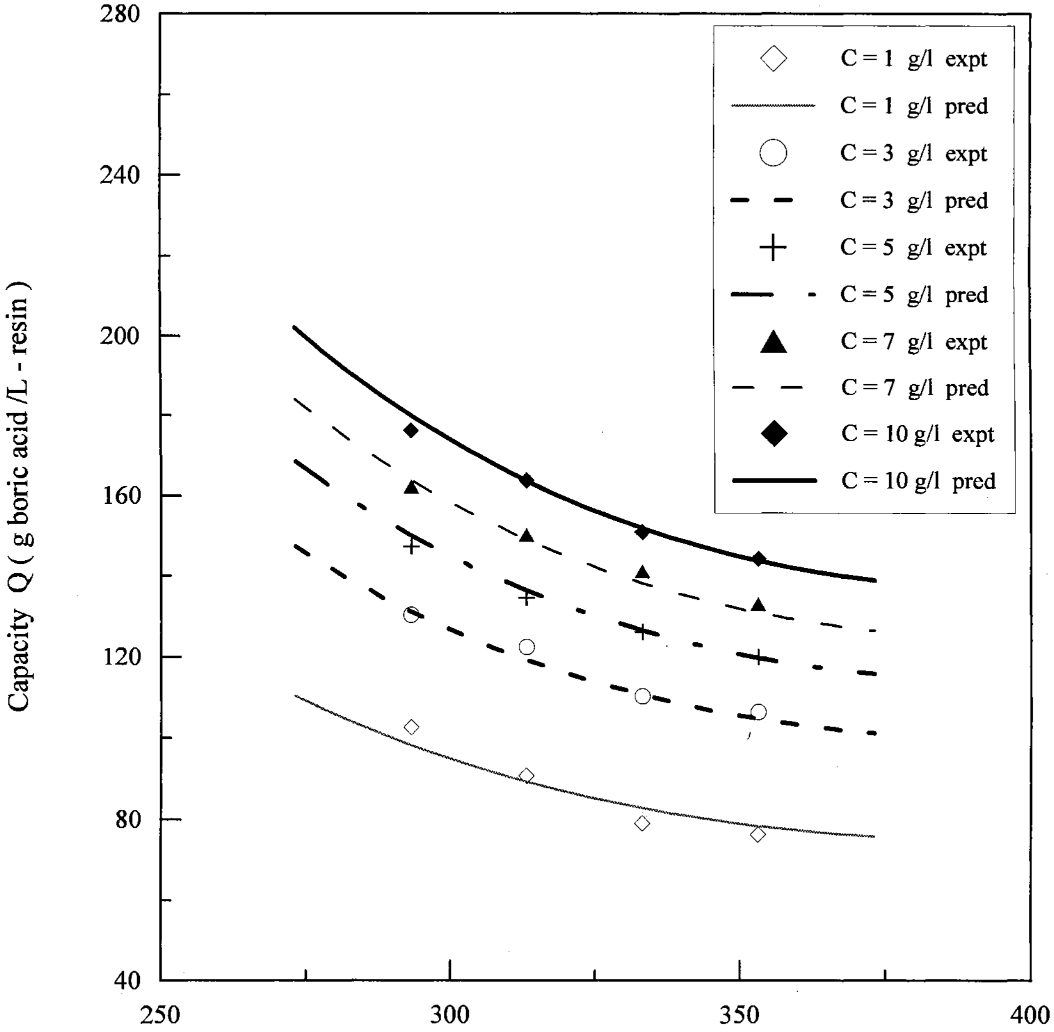

Figure III-5 Comparison of the experimental data and the model fitting for the effects of temperature on the boron sorption capacity of Diaion PA316 resin.

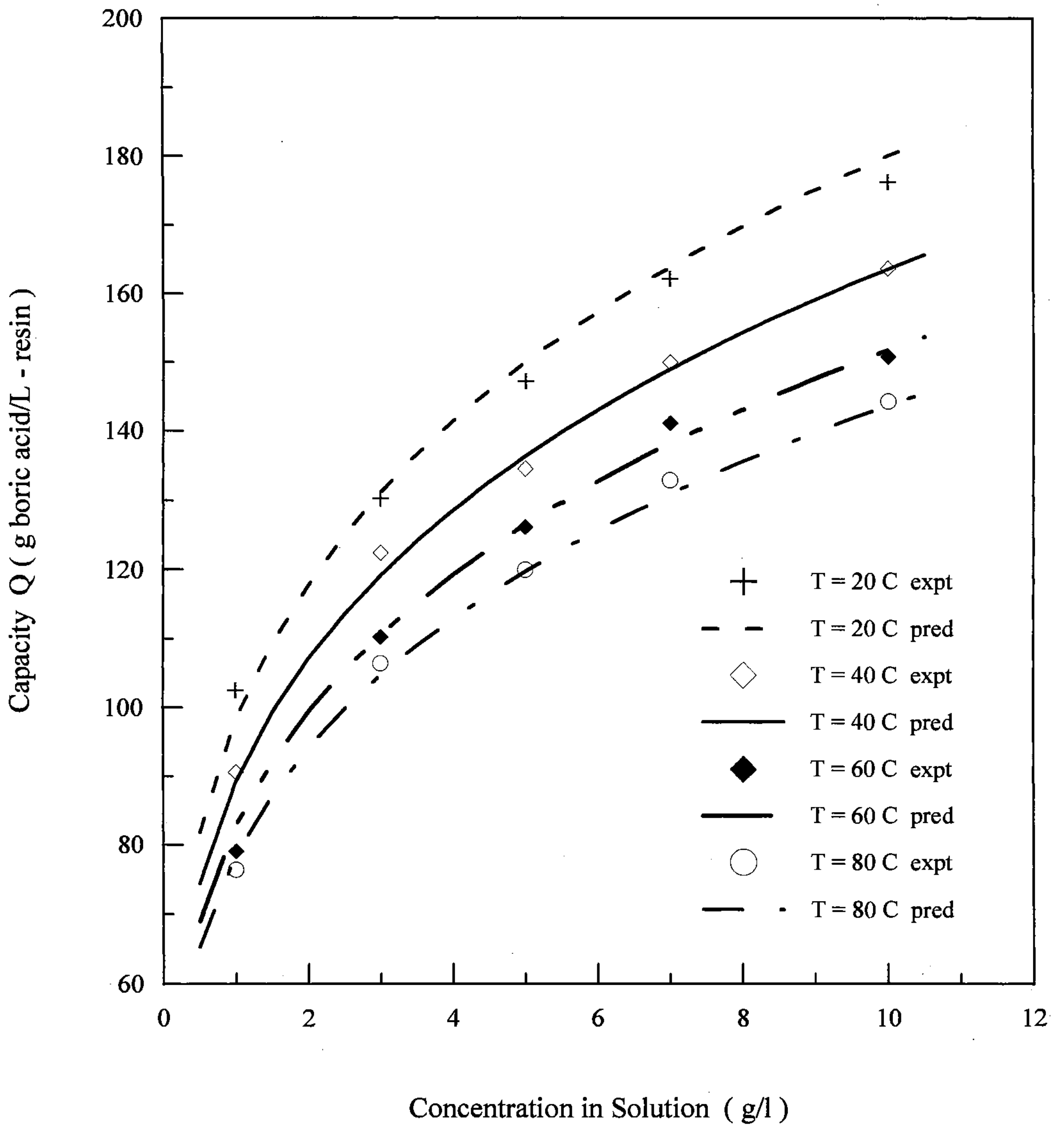

Figure III-6 Comparison of the experimental data and the model fitting for effects of the solution concentration of boron on the boron sorption capacity of Diaion PA316 resin.

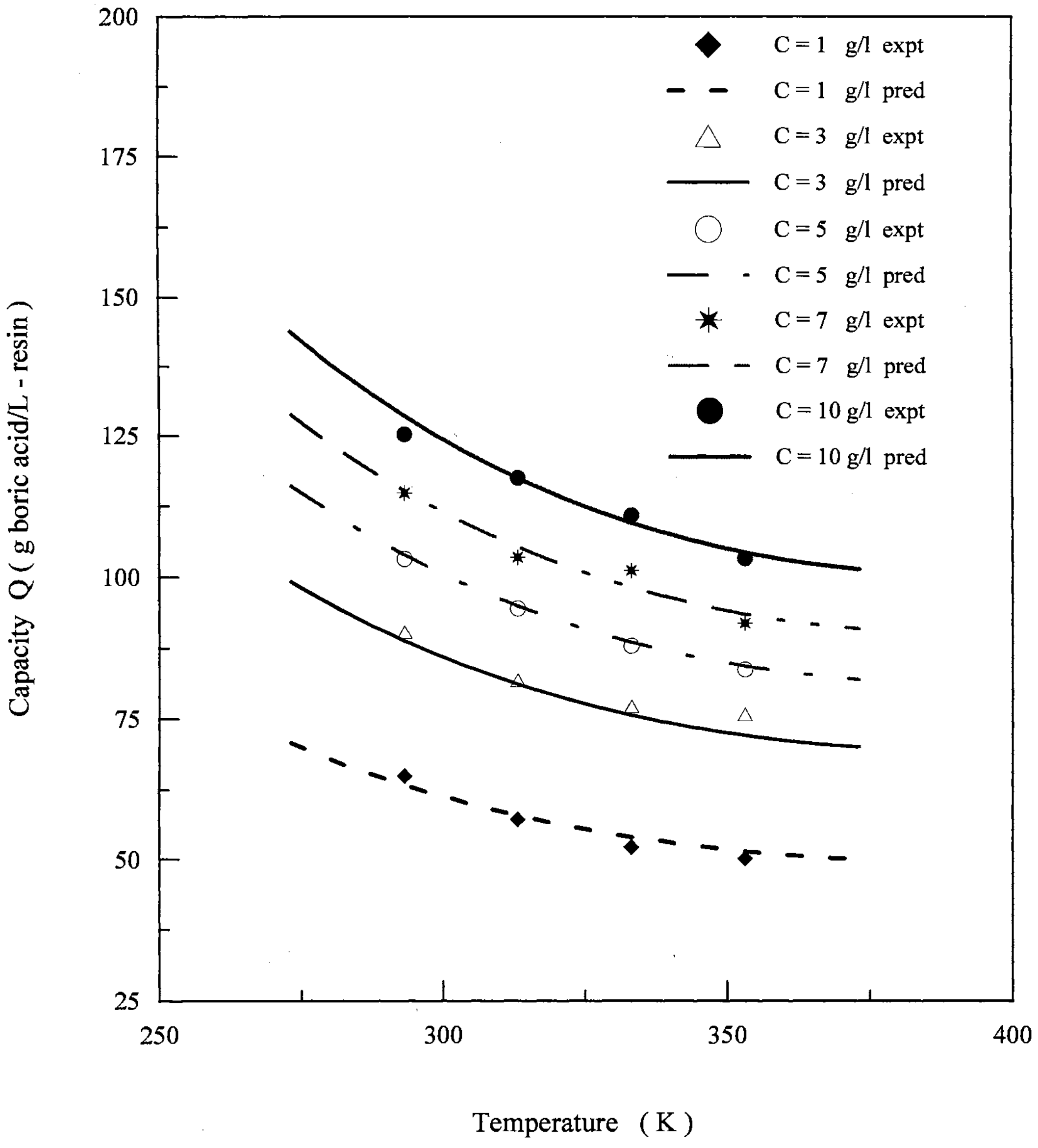

Figure III-7 Comparison of the experimental data and the model fitting for the effects of temperature on the boron sorption capacity of Diaion PA308 resin.

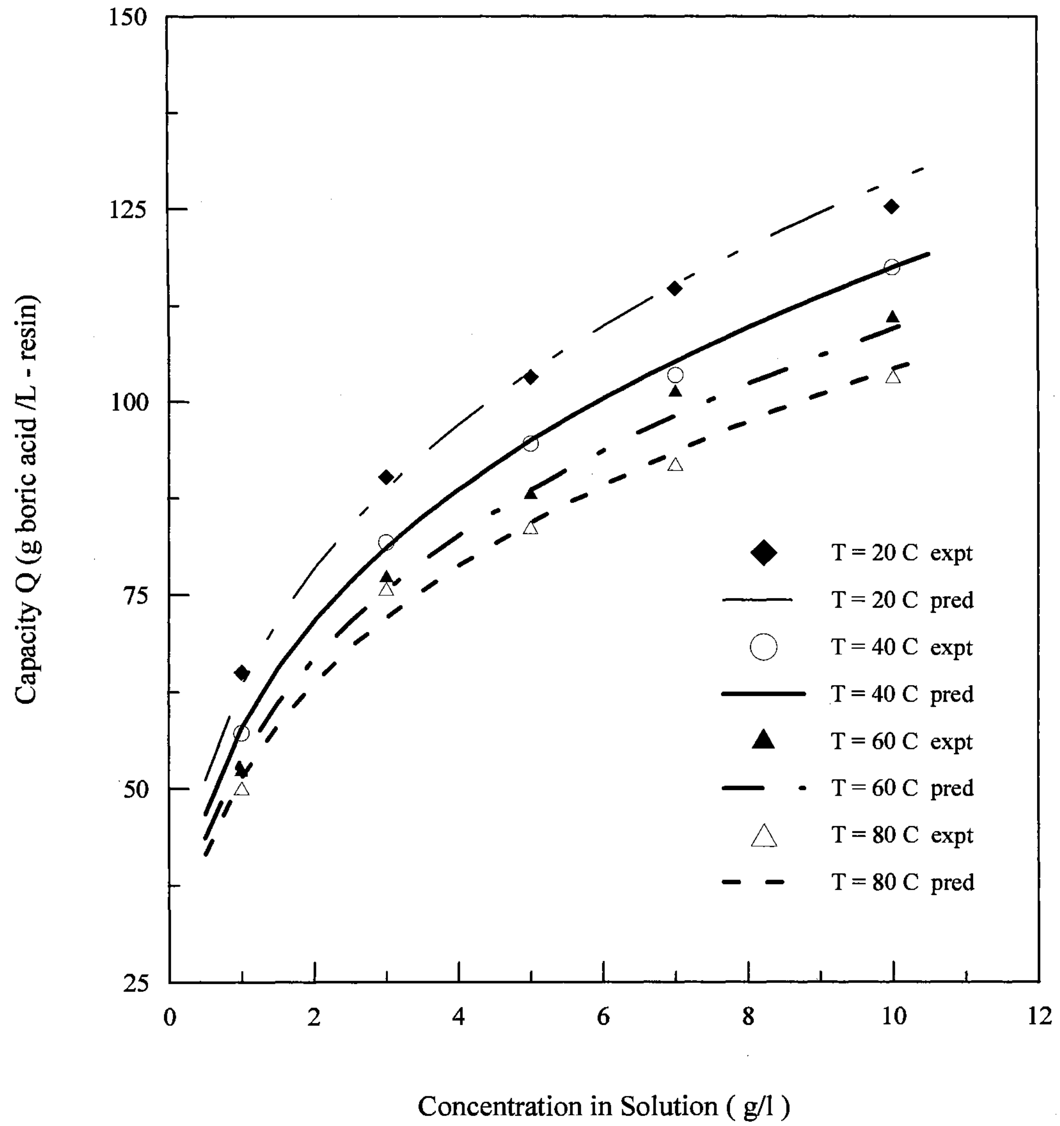

Figure III-8 Comparison of the experimental data and the model fitting for the effects of the solution concentration of boron on the boron sorption sapacity of Diaion PA308 resin.

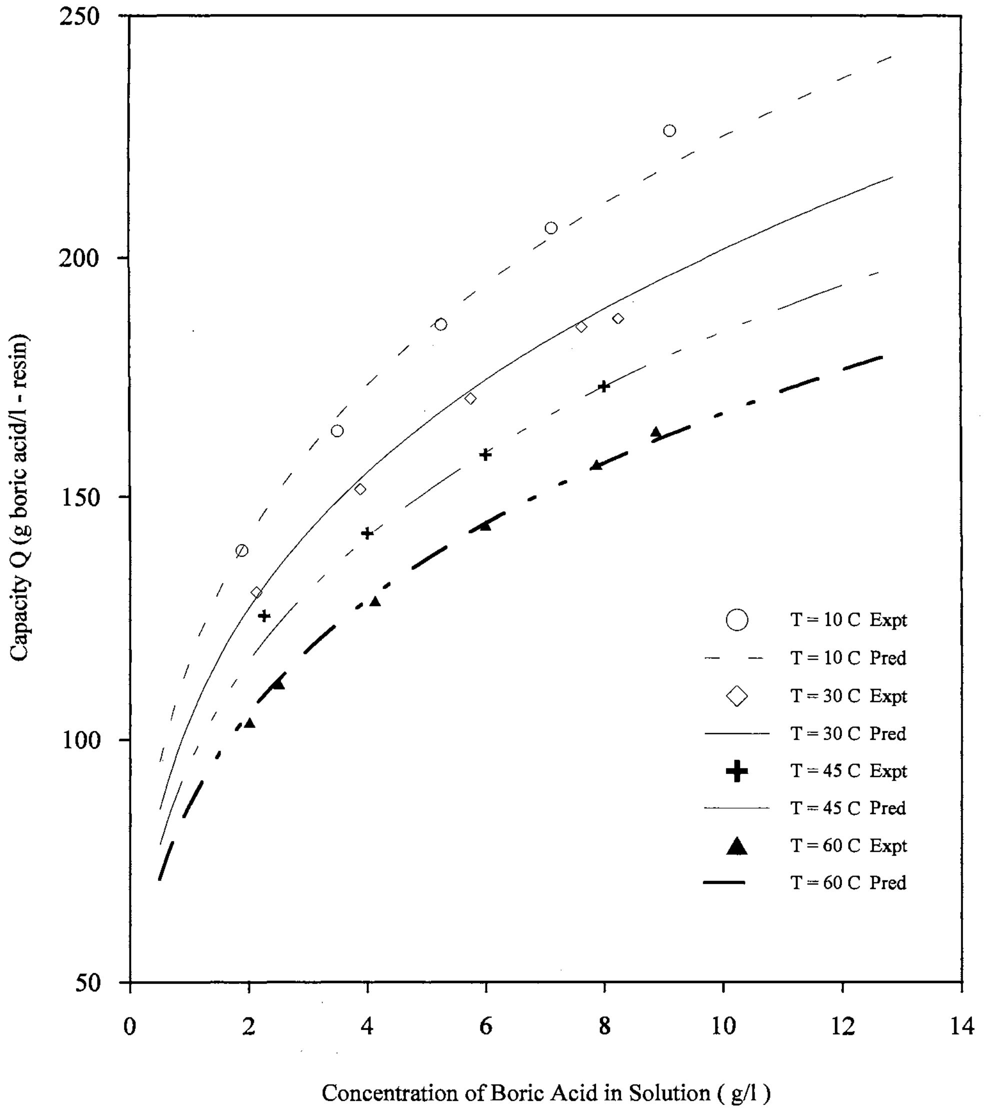

Figure III-9 Comparison of experimental data and Eq. (3-28) prediction for the effects of temperature on the sorption capacity of Amberlite IRN78LC resin

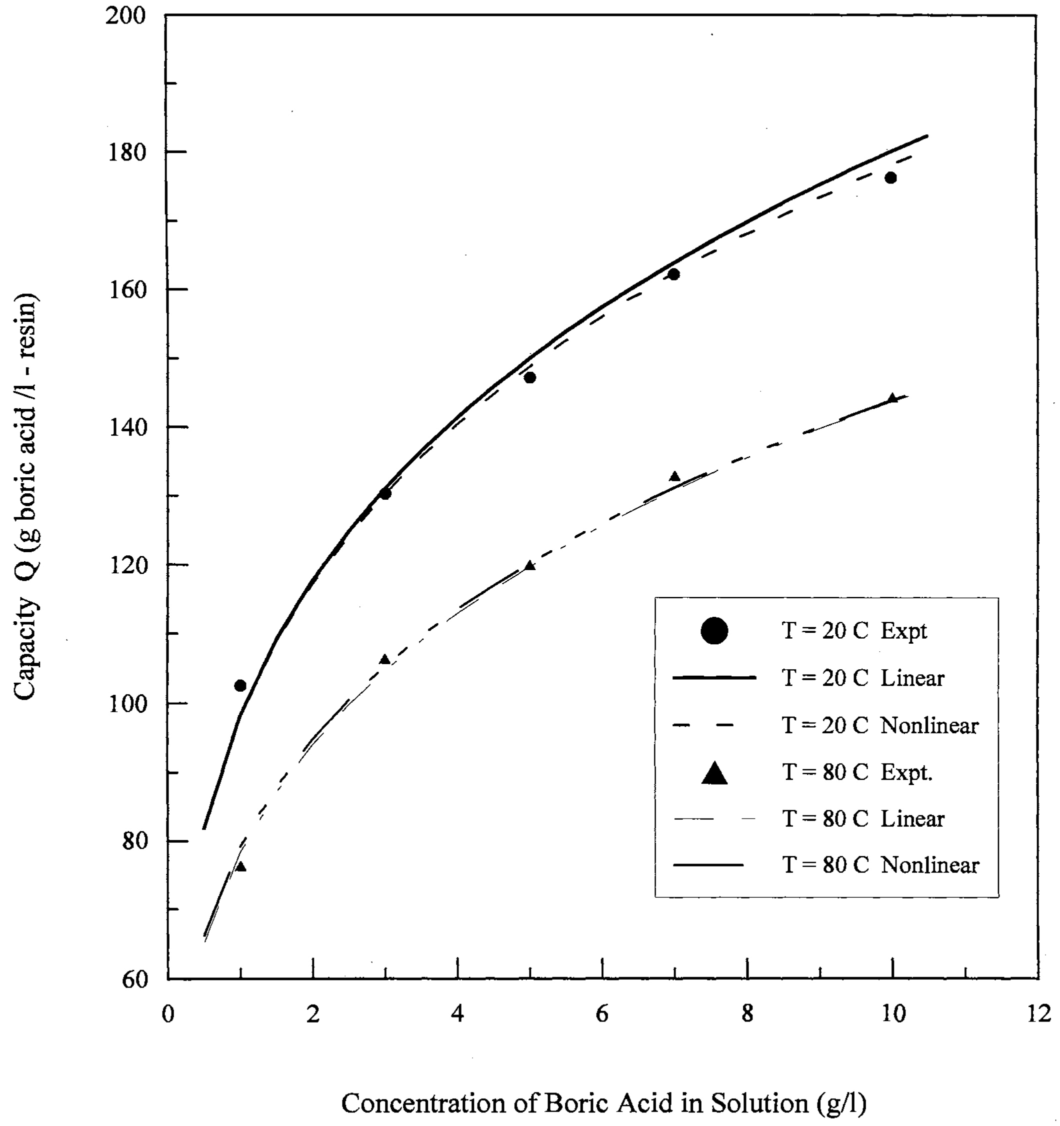

Figure III-10 Comparison of results by linear and nonlinear regressions with the experiment Data for Diaion PA316 resin at T = 20, 80 C

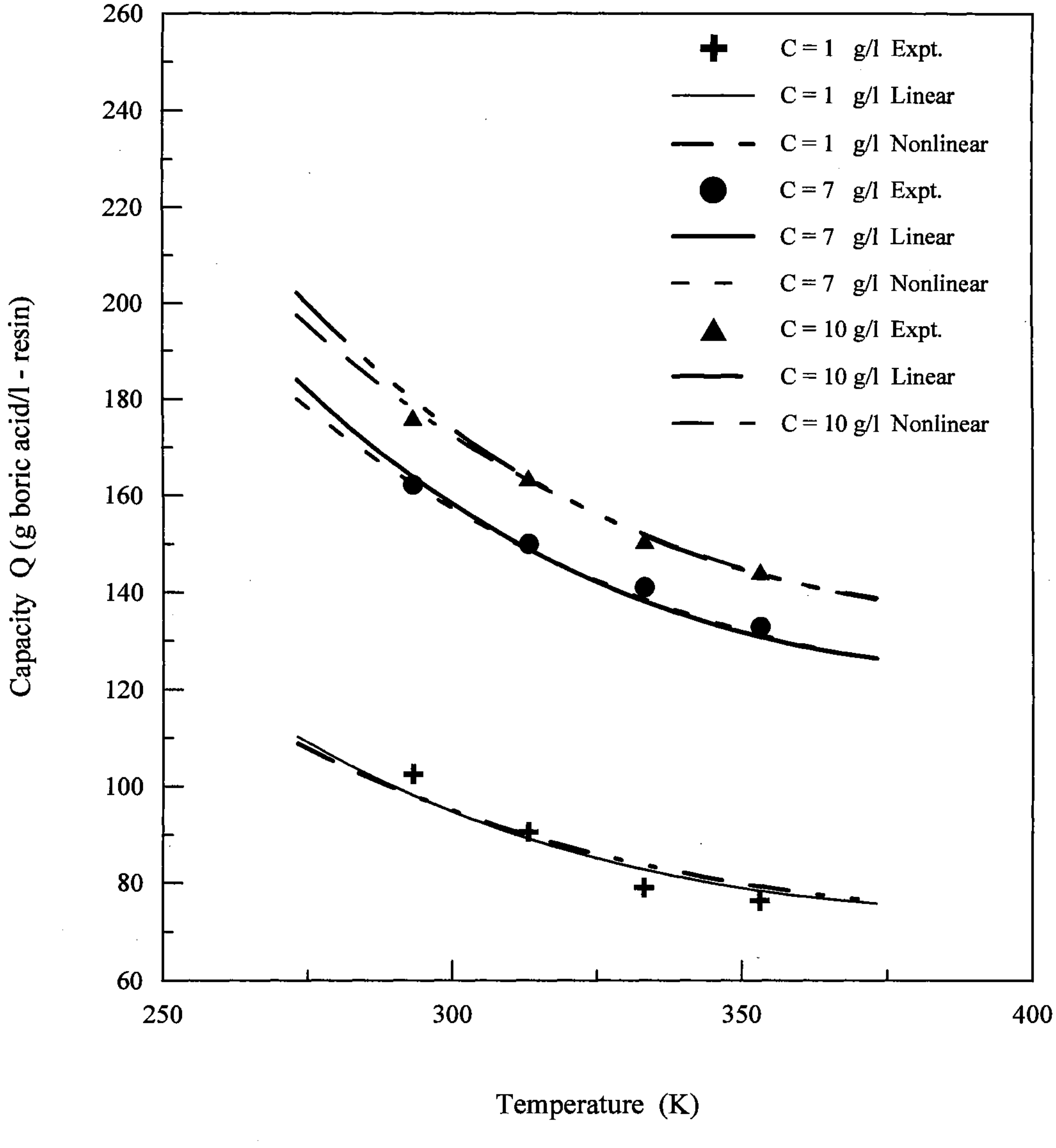

Figure III-11 Comparison of results by linear and nonlinear regression with the experiment data for Diaion PA316 resin under C = 1.0, 7.0, and 10.0 g / l, respectively.

Table III - 3

Minimized Errors and Maximum Errors by Eq. (3-30)

Resin Types	Number of Date Points N	Minimized Errors of y	Maximum Errors of y	Maximum Errors % of Q
Amberlite IRN78LC	20	3.65×10^{-4}	4.74×10^{-2}	4.63
Diaion PA306	20	5.20×10^{-4}	3.91×10^{-2}	3.84
Diaion PA308	20	5.31×10^{-4}	5.11×10^{-2}	4.98
Diaion PA312	20	5.10×10^{-4}	4.16×10^{-2}	4.07
Diaion PA316	20	4.96×10^{-4}	4.64×10^{-2}	4.53
Diaion PA318	20	5.09×10^{-4}	3.42×10^{-2}	3.36
Diaion SA10A	20	4.18×10^{-4}	4.34×10^{-2}	4.25

Table III - 4

Standard Deviation and Relative Errors by Eq. (3-28)

Resin Types	Number of Date Points N	Standard Deviates	Average Errors %	Maximum Errors %
Amberlite IRN78LC	20	9.08	1.29	5.38
Diaion PA306	20	2.42	1.78	4.11
Diaion PA308	20	3.20	1.70	4.83
Diaion PA312	20	5.97	1.59	4.51
Diaion PA316	20	5.31	1.46	5.91
Diaion PA318	20	5.83	1.74	3.91
Diaion SA10A	20	7.20	1.74	5.29

- the degrees of swelling and structures which result in the overall resistance to boric acid and borates transfer, etc.

Both forms Eqs. (3-28) and (3-30) work well. The original form Eq. (3-28), however, works better at higher concentration and lower temperature ranges, which is more an accurate reflection of the conditions used to derive the model. Comparison of these two forms with experiment data is given in Figs. III-10 and III-11.

Conclusion

A satisfactory relationship among sorption capacities of strong base anion resins with temperature and concentration was derived in this work. The values of parameters in this model were given for some commercial resins in Table 2. Predictions by the model are quite good compared with experiment data from different sources. The model can be applied

- To predict limitation of resin capacity, based on various operation conditions, for both boric acid sorption and desorption on strong base anion resins in the boron thermal regeneration system and other applications of boron sorption on ion exchange resins, for instance, demineralization containing boron
- As a basic relation for development of equilibrium model of boron sorption or desorption on OH form strong anion ion exchange resins
- As the equilibrium condition between the resin and the bulk liquid phases to determine the interfacial boron concentration, at the resin surface, for rate models.

However, the recommended operating conditions are in the regions of temperatures from 10 - 80 °C and boron concentrations from 100 ppm to 2000 ppm.

REFERENCES

Barbier, Y., R. Rosset and B. Tremillon (1966). N° 572. – Etude des ions condenses du bore au moyen des resines echangeuses d'anions, Bull. Soc. Chim. Fr., 10, 3352.

Cotton, F. A. and G. Wilkinson (1980). Advanced Inorganic Chemistry, New York, John Wiley & Sons, Inc.

de Miera, R. S., M. M. Urgell Comas and J. L. Iglesias (1985). Junta de Energia Nuclear, J.E.N. 580, Madrid.

Dobrevsky, I. D. and G. Konova (1988). Ion-Exchange System for Control of Boric Acid Concentration in Reactor Water Operated at 20 °C and 80 °C, Reactive Polymers, 7, 273-276.

Edwards, J. O. (1953). Detection of anionic complexes by pH measurements: I. Polymeric borates, J. Am. Chem. Soc., 75, 6151-6154.

Ingri, N, G. Lagerstrom, M. Frydman, and L. G. Sillen (1957). Equilibrium Studies of Polyanions II Polyborates in $NaClO_4$, Acta Chem.Scand., 11, 1034-1058.

Kakihana, H., M. Kotaka, S. Sato and M. Nomura (1977). Fundamental studies on the ion-exchange separation of boron isotopes, Bull. Chem. Soc. Jpn., 50 (1), 158-163.

Mesmer, R. E., C. F. Baes Jr., and F. H. Sweeton (1972). Acidity Measurement at Elevated Temperatures. VI. Boric Acid Equilibria, Inorg. Chem., 11(3), 537-543.

Na, J. W. (1993). Adsorption Characteristics of Boric Acid on Strong-Base Anion Exchange Resin, PhD. Dissertation, Korea Advanced Institute of Science and Technology.

Peterka, F. (1980). Selection of Anion-Exchange Resins for Boron Thermal-Regeneration Systems, Journal of Chromatography, 201, 359-370.

Ross, V. F. and J. O. Edwards (1967). The structural chemistry of the borates, in The Chemistry of Boron and Its Compounds, by Muetterties, E. L., New York, John Wiley & Sons, Inc.

Tomizawa, T. (1979). Studies on the Absorption of Boric Acid on Anion Exchange Resin I. Absorption Characteristics of Boric Acid on Strong Base Anion Exchange Resins, Denki Kagaku, 47 (10), 602-607.

Tomizawa, T. (1981). Studies on the Absorption of Boric Acid on Anion Exchange Resin II. Effects of temperature on the absorption characteristics of boric acid on strong base anion exchange resins, Denki Kagaku, 49 (6), 339-342.

Tomizawa, T. (1983). Studies on the Absorption of Boric Acid on Anion Exchange Resin VII. Adsorption kinetics of boric acid on borate-form anion Exchange Resins, Denki Kagaku, 51 (8), 686-690.

CHAPTER IV

KINETICS OF BORON SORPTION ON STRONG BASE ANION EXCHANGE RESINS

Introduction

Boric acid is used for chemical shim control in pressurized water reactors (PWR). Boron concentration changes in the reactor coolant compensate for xenon transient and other reactivity changes. The boron thermal regeneration system (BTRS) was designed to implement these changes by taking advantage of the fact that the amount of boron adsorbed on ion exchange resins varies with temperature. In BTRS, boron is adsorbed on ion exchange resin at low temperature and released at higher temperature. This operation is based on the variation of the boron apparent capacity on the resin with temperature. By applying BTRS, the amount of reactor coolant to be reprocessed is minimized, reducing the BRS load at the end of the cycle and maintaining better control of reactor coolant chemistry.

The selection of suitable resins and the sorption or desorption behavior of boron in BTRS have been the subject of both theoretical and experimental investigations. Suitable resins are the keys in BTRS technology. In large-scale cooling water treatment, the most widely used anion exchangers are strong base resins with 8-12% divinylbenzene (DVB) cross-linking (Lin, 1973). The general BTRS resin requirements may include: higher equilibrium capacity with temperature dependency, good thermal stability, and good resistance to radiation damage. Peterka (1980), concentrating on the most suitable resins for BTRS applications, elucidated the effects of anion exchange resin structure on sorption capacity. He showed that the equilibrium capacity varied with the degree of crosslinkage and a maximum boron capacity could be obtained at about 7%. By comparing different anion exchange resin types, he concluded that only strongly basic resins are suitable for BTRS and Amberlite IRN 78 was economical in commercial use.

BTRS kinetic studies include both boron sorption on strong base resins and the desorption of boron from borate form resin. Tomizawa (1981 and 1982) performed kinetic experiments: an OH^- form resin (Diaion SAN-1) was used for boron sorption at low temperature, and reversibly, as the borate formed, for the desorption of boron at higher temperature. Kinetic data were analyzed using the shrinking core model. From the boron concentration measurement within resin C_R and solution C_S, the amount of water in the resin ω, and the average number of boron atoms n on each site, and the total sorption time t_0, the reaction rate constant k_d could be determined by the following relations:

$$k_d = \frac{1}{\alpha(C_R - C_S)} \frac{R^2}{2t_0} \tag{4-1}$$

$$C_R = \frac{10.82(n_i - n_f)C_p^B}{W_R \omega} \tag{4-2}$$

and

$$\alpha = \frac{W_R}{10.82(n_i - n_f)C_p^B} \tag{4-3}$$

Where the subscripts i and f indicate the initial and final conditions, respectively, W_R is the amount of resin used in experiment, and R is the resin radius.

His results, at boric acid concentration of 0.0925 mol dm^{-1}, indicated that the sorption and desorption process are quite complicated. The particle diffusion would be the rate-determining step of the boron sorption process at that concentration range, while the rate-determining step might shift from particle diffusion in the early stage to chemical reaction limitation at the later stage of desorption process.

Kononova and his co-workers (1987) investigated the kinetics of the sorption of boric acid by the ANB-11G resin from solutions containing 1 g/liter of boric acid (about 0.0162 M in terms of boron). Information from the experimental results also suggested that the chemical reaction limitation is not kinetically rate limiting within the concentration range of their experiments. The boron sorption rate can be influenced strongly by the resin size. Rising temperature can accelerate the sorption rate. In addition, the average observed activation energy is about 6 kcal mol^{-1}. All of these phenomena suggest that the diffusion processes govern boron sorption on strong base anion exchange resin.

However, Meichik et al. (1989) reached their conclusion, from their kinetic study of the boron sorption on ANBG and ANBT anion resins with the boric acid solution of boron concentration 0.0028 M, that the chemical reaction played a role as important as the intraparticle diffusion process for the rate-determining step.

The exchange rate of boron desorption from the borate form resin is essentially controlled by intraparticle diffusion of borates. The desorption rate increases with increasing temperature since higher temperature is favorable to decomposition of polyborates on the exchange sites. Experimentation (Tomizawa, 1982) could not clarify the chemical reaction limitation because the average activation energy obtained, approximately 7 kcal mol^{-1}, indicates the process is under diffusion control.

Many efforts toward understanding ion exchange kinetics accompanied by chemical reaction have been made in the past three decades. Helfferich (1965) presented a theoretical analysis of ion exchange kinetics in detail. He assumed that the reaction front could exist in the liquid film and at the surface of the resin particle. Theoretical approaches for such systems, through the fraction to equilibrium, include cases of both liquid-phase and intraparticle diffusion control. His postulation has been tested successfully by experimentation (Blickenstaff et al., 1967a, b; Wagner and Dranoff, 1967; Graham and Dranoff, 1972). Later, Kotaoka et al. (1976, 1977) studied the kinetics of the systems with irreversible chemical reactions in the liquid film. Reaction types involved contain the formations of acid, base, and the salt with the same counter-ions as the acid or base. The Nernst-Planck model was used in his study. Haub and Foutch (1986a,b) presented a theoretical model of binary systems with concentration approaching the dissociation of water to show the effects of neutralization reactions in the bulk solution for mixed bed ion exchange operations. Most of these solutions are restricted either for binary systems or equal-valence ions. A general description of the systems with irreversible chemical reactions in the film was recently given by Franzreb and his co-workers (1995). Their approach accounts for systems with arbitrary valences and arbitrary components. Although an approximate solution, restricted to the liquid diffusion-controlling systems, their approach provides a general and convenient method for ion exchange kinetic studies of practical systems. Though much progress has been made, ion exchange kinetic theories have so far not well defined the boron sorption systems, in which fast, reversible, chemical reactions accompany the diffusion of both ionic and molecule species from the bulk liquid to sites inside the resin.

Recently, in the investigation of kinetics of Na^+-H^+ ion exchange in concentrated buffer solutions of sodium tetraborate and boric acid, Koloini and his co-workers (1990) applied the Nernst-Planck equation for the determination of the variation of diffusion coefficient with the composition in the solid and liquid phases. Both the intraparticle and the film diffusion resistance were considered in their work for the prediction of breakthrough curves. A very favorable equilibrium condition was obtained from that system.

Even if the Nernst-Planck model is theoretically advanced to Fick's law for the kinetic study of ion exchange systems (Schlögl and Helfferich, 1957, Helfferich, 1962, 1983), it seems questionable to use the Nernst-Planck approach for systems with weakly dissociated molecules, for instance, aqueous boric acid solution. In such systems molecular diffusion plays a predominant role in the rate process. Consequently, the Nernst-Planck equation, which was developed for fully dissociated electrolytes, is no longer theoretically valid toward the approach of the rate in these systems (Périé et al., 1991). The use of Fick's law for molecule diffusion and the Nernst-Planck model incorporating all interactions among diffusing ion species was suggested in the works of Wagner and Dranoff (1967), and Lou (1993).

As emphasized in Chapters II and III, boron adheres on sites through chemical reactions to form polyborates that characters the boron sorption process on strong base anion exchange resin. Theoretical interpretation of rate data could be difficult due to the different simultaneous processes involved in boron sorption on OH^- form resin, or desorption from borate-form resin, even if the useful information can be derived from the simplified models available in Chapter III.

The aim of this work is to investigate boron sorption kinetics on strong base anion resins and to provide a practical model for the prediction of BTRS sorption behavior. Study of the desorption process will not be included in this work. Conditions focused on in this work are:

- Concentration range about 0.1 to 0.2 mol dm^{-1} in boron.
- Operation temperature range from 10 - 60 °C.
- Amberlite IRN 78L - OH^- form anion resin.

These conditions are applied commonly in BTRS. As discussed above, mass transfer resistance, the external stagnant fluid film resistance and the intraparticle diffusion resistance control the process exchange rate. With the concentration range, according to Equations (2-36) and (2-37), each of the two limiting models, film and particle resistance, are not well suited to this work. Contributions of both the film and intraparticle diffusion resistance to describe the process rate will be considered in this model.

Theoretical Approach

The theoretical study of BTRS includes boron sorption equilibrium isotherm, kinetic behavior, and column dynamics. The equilibrium isotherm has been addressed in Chapter III. The nature of the equilibrium relationship shown is typically non-linear and favorable over the concentration and operation temperature range.

The kinetic behavior of boron sorption is more complicated than ordinary ion exchange. As discussed in the previous Chapters, the temperature and concentration dependency of apparent boron resin capacity, and the migration of various boron forms accompanied by reversible reaction characterize boron sorption on ion exchanger resins. In addition, different diffusion patterns for both ionic and molecular species through the film and particle, are involved in the boron sorption in BTRS. Obviously, the complexity of the process results in the difficulty of kinetic interpretation of sorption behavior.

The overall column dynamics are characterized by the flow pattern and mass transfer front that propagates with a defined velocity determined by the equilibrium isotherm. The boron material balance throughout the bed and around the resin particles describes the dynamic response of the column, and determines the location and form of the concentration front subject to the initial and boundary conditions.

The theory of kinetics and dynamic behavior of the BTRS system will be developed in this section. The complexity of the mathematical model depends on the system concentration range, the choice of rate expression and the column flow pattern.

For fixed bed ion exchange, axial dispersion is usually negligible. The linear driving force for film and particle diffusion control, as demonstrated by Glueckauf (1955), have been used extensively in previous studies. Owing to its simplicity and theoretical basis, incorporating an equilibrium isotherm, derived in the last Chapter, a plug flow model and a linear rate expression should be adequate in this study. A diffusion model is also given for comparison.

Assumptions

Reasonable assumptions are based on system process conditions. For this system the boric acid dissociation equilibrium is assumed to obey the rule indicated in Eq. (2-23).

Traces of other borates possibly in solution are neglected. The local equilibrium can be obtained at the solid-film interface, and the selectivity relationship resulting from a binary system can be extended to describe such local equilibria. Although the complex formation varies with different conditions (boron concentration, functional groups of the resin, structure, temperature, and pH), as discussed above, the rates of reaction may be considered to have no influence on the diffusion process. Diffusion resistance, both in the liquid side and the resin phase, is important to the boron sorption rate but at different stages. The former will govern early sorption, while the latter is dominant in later stages. This possibility, and its mechanism, will be addressed in the section on Kinetics of Boron Sorption.

In addition, the assumptions applied commonly in ion exchange kinetics are:

- linear driving force
- quasi-stationary or pseudo steady state film diffusion
- unity activity coefficients
- constant individual diffusion coefficients of the ions and the neutral molecule
- complete Donnan exclusion, no net co-ion flux within the film
- electrical neutrality
- homogeneous ion exchanger particles
- negligible swelling changes of the ion exchanger
- plug flow, no dispersion in both radial and axial directions
- isothermal, isobaric operation

Of course, some assumptions may not reflect accurately the practical sorption process in BTRS. Particularly, the assumptions of isothermal behavior and absence of swelling changes, are less justified here than in ordinary ion exchange due to considerable heat produced from the reactions. The concentration may not be uniform since the gradients exist near each ion exchanger particle and non-ideal flow situation. Moreover, mass transfer obviously varies with time and space. However, for a practical ion exchange process, the variations of concentration with space in the film are much more important than with time. It is thus reasonable to assume pseudo steady state exchange. Models derived on these assumptions can merely represent an approximate rate law.

Determination of the Bulk Concentrations

As discussed in Chapter II, there are many types of ionic borate species, along with the boric acid molecule, involved in the migration of boron from the liquid to the resin. Some borate types are uncertain in aqueous boric acid at the given conditions. However, the concentrations of borates are quite low in the solution phase of BTRS. The fact that most borates do not contribute to the migration of boron toward resins leads to the simplification of this problem. The clarification of the species containing significant numbers of boron and the determination of their concentrations are then necessary.

By applying the equilibrium relationship presented by Mesmer et al. (1972a,b),

$$\alpha B(OH)_3 + \beta OH^- \xleftrightarrow{K_{\beta\alpha}} B_\alpha (OH)_{\beta+3\alpha}^{\beta-} \tag{4-4}$$

the concentration of every borates postulated for a given concentration of total boron can be determined by combining the charge balance relations, mass conservation, and water dissociation.

With the aid of the water formation relation,

$$K_W = C_{OH} \cdot C_H \tag{4-5}$$

ionization for borates and their corresponding equilibrium constants are given by Eq. (4-6) through Eq. (4-13)

$$B(OH)_3 + OH^- \xleftrightarrow{k_{11}} B(OH)_4^- \qquad (4\text{-}6)$$

$$k_{11} = \frac{[B_{11}^-]}{[B]\cdot[OH^-]} \quad \text{or} \quad K_{11} = K_W k_{11} = \frac{[B_{11}^-]\cdot[H^+]}{[B]} \qquad (4\text{-}7)$$

$$2B(OH)_3 + OH^- \xleftrightarrow{k_{21}} B_2(OH)_7^- \qquad (4\text{-}8)$$

$$k_{21} = \frac{[B_{21}^-]}{[B]^2\cdot[OH^-]} \quad \text{or} \quad K_{21} = K_W k_{21} = \frac{[B_{21}^-]\cdot[H^+]}{[B]^2} \qquad (4\text{-}9)$$

$$3B(OH)_3 + OH^- \xleftrightarrow{k_{31}} B_3(OH)_{10}^- \qquad (4\text{-}10)$$

$$k_{31} = \frac{[B_{31}^-]}{[B]^3\cdot[OH^-]} \quad \text{or} \quad K_{31} = K_W k_{31} = \frac{[B_{31}^-]\cdot[H^+]}{[B]^3} \qquad (4\text{-}11)$$

$$4B(OH)_3 + 2OH^- \xleftrightarrow{k_{42}} B_4(OH)_{14}^= \qquad (4\text{-}12)$$

$$k_{42} = \frac{[B_{42}^=]}{[B]^4\cdot[OH^-]^2} \quad \text{or} \quad K_{42} = K_W^2 k_{42} = \frac{[B_{42}^=]\cdot[H^+]^2}{[B]^4} \qquad (4\text{-}13)$$

The charge balance and the mass conservation are given in Eqs. (4-14) and (4-15), respectively.

$$C_H = C_{B_{11}} + C_{B_{21}} + C_{B_{31}} + 2C_{B_{42}} + C_{OH} \qquad (4\text{-}14)$$

$$C_{BT} = C_B + C_{B_{11}} + 2C_{B_{21}} + 3C_{B_{31}} + 4C_{B_{42}} \qquad (4\text{-}15)$$

Substitute Eqs. (4-7), (4-9), (4-11), and (4-13) into Eq. (4-14) and solve for C_H to give:

$$C_H = \frac{1}{3}(DK_{11}C_B + DK_{21}{C_B}^2 + DK_{31}{C_B}^3 + K_W) \qquad (4\text{-}16)$$

Then the concentration of hydroxide can be obtained from Eq. (4-5) with the result of Eq. (4-16), which is:

$$C_{OH} = K_W / C_H \tag{4-17}$$

The solution will be by trail and error. With appropriate initial guess for the concentration of boric acid C_B, Eq. (4-16) can be solved by Newton-Raphson. The concentrations of other species are then obtained from Eqs. (4-7), (4-9), (4-11), and (4-13). The detailed work is given in Appendix A. The results were presented in Figure II-1, Chapter II.

With the concentration of boron of 1500 ppm and without salt in solution, the pH is around 4.5. Under these conditions, Figure II-1 showed that the boric acid concentration is 3 to 4 orders of magnitude higher than the total ionic species. The molecule of boric acid can thus be the only species concerned as the boron carrier in the solution.

Kinetics of Boron Sorption

The sorption of boron on strong base resin seems to be governed by a different mechanism. If A denotes the counter-ion initially contained in the resin (here OH^-), B indicates the boric acid molecule, AB is the tetrahedral $B(OH)_4^-$, and C represents polyborates, the following ion exchange processes may occur simultaneously in the system.

Process I: Consumption of the counterion released by the ion exchanger.

$$\overline{RA} + B \longleftrightarrow \overline{RAB} \tag{4-18}$$

$$\overline{RA} + C + B \longleftrightarrow \overline{RC} + AB \tag{4-19}$$

Process II: Ion exchange with the initial counterion and replacement of the tetrahedral ion by polyborates according to selectivity.

$$\overline{\mathrm{RA}} + \mathrm{AB} \longleftrightarrow \overline{\mathrm{RAB}} + \mathrm{A} \tag{4-20}$$

$$\overline{\mathrm{RAB}} + \mathrm{C} \longleftrightarrow \overline{\mathrm{RC}} + \mathrm{AB} \tag{4-21}$$

Process III: Complex formation at sites

$$\overline{\mathrm{RAB}} + (\mathrm{n}-1)\mathrm{B} \longleftrightarrow \overline{\mathrm{RAB}_{\mathrm{n}}} \tag{4-22}$$

These reactions may take place at the interface and at sites inside the resin. OH^- ions will be eliminated as soon as they reach the interface. The co-ion H^+ has much less opportunity to participate in the reaction, at the interface, with the counter-ion OH^- released by the resin because of Donnan exclusion and the maintenance of the charge balance in the liquid.

At the early stage, boric acid molecules intrude into the resin. At the resin surface, the reaction consuming OH^- ions occurs mainly to form the tetrahedral $B(OH)_4^-$ due to high pH. The processes indicated in Equations (4-18) to (4-20) are dominant as long as the resin still contains enough OH^- ion for consumption of these reactions. The migration of boric acid molecule across the liquid film to the resin surface characters the rate limitation rather than inter-diffusion of the counter-ions, as in ordinary ion exchange. Later, replacement of polyborates and complex formations at sites, represented in Equations (4-21) and (4-22), become the major processes. A sharp boundary may be formed due to slow mobility of boric acid molecules and polyborates inside the resin. Film diffusion control is no longer valid and the rate-controlling step becomes particle diffusion. The moment that the minimum equilibrium capacity of the resin exhausts is a good reference point to divide the two stages.

With film diffusion control, the resistance to diffusion of molecular boric acid toward the interface will be under chief consideration for the sorption rate of boron. The flux of the molecule can be described by Fick's first law of diffusion in Equation (4-23).

$$J_B = -D_B \nabla C_B \tag{4-23}$$

If the linear driving force assumption at the liquid side is applied, Equation (4-23) can be expressed as:

$$J_B = -k_L (C_B^o - C_B^*) \tag{4-24}$$

and the particle rate is given, by applying the assumption of a linear driving force.

$$\frac{dq_B}{dt} = a_s k_L (C_B^o - C_B^*) \tag{4-25}$$

Where k_L is the mass transfer coefficient of molecular boric acid on the liquid side, and can be determined by the Dwivedi-Upadhyay correlation (Dwivedi and Upadhyay, 1977), which is given by:

$$J_d = \frac{1}{\varepsilon}\left(\frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}\right) \tag{4-26}$$

For these ionic species, by using the Nernst-Planck equation, their fluxes can be given as:

$$J_i = -D_i\left[\frac{\partial C_i}{\partial r} + z_i \frac{FC_i}{RT}\frac{\partial \Phi}{\partial r}\right] \tag{4-27}$$

Through the equilibrium relations in Eq. (4-4), the relation of concentration of *i*th borate to boric acid is given by:

$$C_B^i = \frac{1}{k_i K_W^{|z_i|}} C_i C_H^{|z_i|} = \frac{1}{K_i} C_i C_H^{|z_i|} \tag{4-28}$$

The electrical potential term in Equation (4-27) can be replaced by the concentration gradient of co-ions under the assumptions of no co-ions flux and no net electrical current. In this system, the only co-ion is hydrogen. Thus Equation (4-27) can be rewritten as

$$J_i = -D_i \left[\frac{\partial C_i}{\partial r} - z_i \frac{C_i}{C_H} \frac{\partial C_H}{\partial r} \right] \tag{4-29}$$

Differentiation of Eq. (4-28) leads to the concentration gradient relationship among borate, boric acid and hydrogen. This is

$$\frac{\partial C_i}{\partial r} = K_i \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \frac{\partial C_B}{\partial r} - \frac{|z_i| C_i}{C_H} \frac{\partial C_H}{\partial r} \tag{4-30}$$

Substituting Equations (4-30) and (4-28) into Equation (4-29) to eliminate borate concentration and its gradient and hydrogen concentration gradient, one is able to express the borate flux in terms of the concentrations of boric acid and hydrogen in the bulk:

$$J_i = -D_i K_i \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \frac{\partial C_B}{\partial r} \tag{4-31}$$

Then the total boron flux in the film is

$$J_{BT} = J_B + \sum J_i = -De \frac{\partial C_B}{\partial r} \tag{4-32}$$

Where the apparent diffusivity is:

$$De = -\left(D_B + \sum D_i K_i \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \right) \tag{4-33}$$

See Appendix B for details of the derivation. Eq. (4-25) can be then rewritten, by adding the corrector of *De* for the mass transfer coefficient, as:

$$\frac{dq}{dt} = a_s k_L De \cdot (C^o_{BT} - C^*_{BT}) \qquad (4\text{-}34)$$

Therefore, the particle rate is ready to be determined in the film diffusion control as soon as its boundary, the interfacial concentration of the total boron, is specified.

With the particle diffusion control, pH inside the resin decreases from the peak value due to the sharp decrease of OH^- ions, which are consumed in the reactions. Some molecular boric acid converts to borates by ionization that produces more polyborates (See Figures II-4, 6, and 8). The rest of the boric acid is continuing to ionization along the way of diffusion to the sites and finally sorption on the exchange sites through complex formation. Mixed diffusion patterns of boric acid molecules and borates characterize diffusion inside the resin. If Fick's law and the Nernst-Planck equation are adopted for the fluxes of the molecule and borates, respectively, there are:

for boric acid molecules:

$$a_s J_B = -D_B \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q_B}{\partial r}\right) \qquad (4\text{-}35)$$

for the other ionic species:

$$a_s J_i = -D_i \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_i}{\partial r}\right) + z_i \frac{F q_i}{RT} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \Phi}{\partial r}\right)\right] \qquad (4\text{-}36)$$

The solution for the concentration history for such a mathematical model will obviously be cumbersome as the different expressions for species are introduced. Consider the dominant concentration gradient in the resin phase as the particle diffusion control. It is reasonable to omit the electric potential term in Eq. (4-36). This simplification leads to the flux of the total boron as

$$a_s J_{BT} = -\sum D_i \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_i}{\partial r}\right) \tag{4-37}$$

And the particle rate of the total boron is

$$\frac{\partial q}{\partial t} = -a_s J_{BT} = \sum D_i \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_i}{\partial r}\right) \tag{4-38}$$

At a given temperature, the number and type of borates in the resin phase depend on the concentration of total boron and pH inside the resin. To determine the variation accurately with the change of time during the sorption process is difficult. A further simplification is necessary in order to obtain the concentration distribution within the resin and to predict the breakthrough curve effectively. The introduction of a pseudo species with the average boron atoms and the total fraction is a possible way to proceed. The particle rate can be expressed simply by relating the diffusion of the pseudo species instead of the summation of the total boron forms in Eq. (4-38). That is:

$$\frac{\partial q}{\partial t} = \overline{De}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \tag{4-39}$$

The diffusion coefficient of the pseudo species $\overline{De}$ is the apparent self-diffusion coefficient for the total boron forms, an empirical parameter, and can be determined experimentally. The corresponding physical meaning is that the resulting equilibrium concentration in the resin phase reflects the apparent capacity of the resin.

The initial and boundary conditions of Equation (4-39) are:

I. C. $q = 0,$ at $0 \le r \le R,$ $t = 0$ (4-40)

B. C. 1 $\frac{\partial q}{\partial r} = 0,$ at $r = 0,$ $t \ge 0$ (4-41)

B. C. 2 $q = q^*,$ at $r = R;$ $t > 0$ (4-42)

And the average concentration in resin is given by:

$$\bar{q} = \frac{8}{R^3}\int_0^R q \cdot r^2 \cdot dr \qquad (4\text{-}43)$$

If resistance, both at the liquid side and at the resin side, needs to be considered, the second boundary condition becomes the Robin boundary condition:

$$\text{B. C. 2} \qquad \left.\frac{\partial q}{\partial r}\right|_{r=R} = \frac{k'_L}{\overline{De}}(C^o_{BT} - C^*_{BT}), \quad \text{at} \quad r = R; \qquad t > 0 \qquad (4\text{-}44)$$

Eq. (4-44) was obtained by the balance of flux to the solid phase and through the film surrounding the exterior surface. With the assumption of the linear driving force: the flux in the liquid side is

$$J_L = -k'_L(C^o_{BT} - C^*_{BT}) \qquad (4\text{-}45)$$

and the flux in the resin side

$$J_P = -\overline{De}\frac{\partial q}{\partial r} \qquad \text{at} \qquad r = R \qquad (4\text{-}46)$$

No accumulation at the interface leads to,

$$J_L = J_P \qquad (4\text{-}47)$$

which gives the second boundary condition at the resin surface in Eq. (4-44).

Solutions of Eqs. (4-39) to (4-44) can be obtained numerically once the interface concentration has been determined. Obviously, the solution of this diffusion model is complicated. Though there are several numerical methods available to solve this set of equations, common practice is to use the simple linear driving force model with the equivalent mass transfer coefficient estimated as chosen in Equation (4-34). For particle diffusion control, the rate can be expressed analogous to Eq. (4-34):

$$\frac{d\bar{q}}{dt} = \bar{k}_e(q^* - \bar{q}) \tag{4-48}$$

which is subject to the initial condition:

$$\bar{q} = \bar{q}_o, \qquad \text{at} \qquad t = t_o \tag{4-49}$$

Errors resulted from this approach are smaller than might be expected (Ruthven, 1984) and can be minimized by using an appropriate correlation to evaluate the equivalent mass transfer coefficient. Glueckauf (1955) first pointed out the equivalence between a linear rate model and the diffusion model and derived, in a linear system, the expression of the equivalent mass transfer coefficient:

$$\bar{k}_e = 15\frac{\overline{De}}{R^2} \tag{4-50}$$

He demonstrated the validity of the expression under various boundary conditions. By comparison of theoretical breakthrough curves calculated from the Rosen solution of the diffusion model (Rosen, 1952 and 1954) and linearized rate model, Ruthven (1984) shows good agreement with the approach of Eq. (4-50). Therefore, the approximate approach will be adopted in this work to avoid the complexity of the diffusion model. The specifications of the concentrations at the interface for both film and particle diffusion control will be addressed in the next section.

Interfacial Concentrations

The interface concentrations are the boundaries of these particle rates, and their relationships must reflect the equilibrium isotherm defined in this model. Consider first the two limitations of diffusion control. If the process is under liquid side diffusion control, the distribution of concentration in the resin phase can be treated as uniform.

Correspondingly, the interface concentration at the resin side q* equals the average concentration $\bar{q}$ in the resin. On the other limitation, the resistance of diffusion in the liquid side is negligible. The interface concentration C* at the liquid side can be set as the bulk concentration. The left interface concentration at the other side for the two limitations can be estimated, under the assumption of local equilibrium reached at the interface, by Eq. (3-28) in Chapter III.

For film diffusion control, if using the average boron concentration in the resin q replaces the total apparent capacity Q, the interface concentration at the liquid side in Eq. (4-34) is given as:

$$C_{BT}^{*} = \left[\frac{q}{a}\exp(bT + cT^2)\right]^{1/\eta} \tag{4-51}$$

In a similar way the interface concentration at the resin side in Eq. (4-43) enables to be expressed as, for particle diffusion control:

$$q^{*} = a \cdot (C_{BT}^{o})^{\eta} \exp[-(bT + cT^2)] \tag{4-52}$$

If diffusion resistance at both sides needs to be accounted for in the calculation of the particle rate or the boron flux, Eq. (3-28) can still be applied to determine the interface concentration at the liquid side by using the initial state conditions of the resin. For the cases without the parameters in Eq. (3-28) available, the interface concentrations may be determined by using the selectivity coefficient expression- a Langmuir type equation. The procedures to use the selectivity relation for the determination of the interface concentrations are given in Appendix C.

Dynamics of Column

In an ion exchange column, the equilibrium isotherm determines the nature of the concentration front, and the shape of the concentration profile is linked largely with the kinetic influence. The movement of the concentration front or mass transfer zone and its response to a perturbation in the feed conditions are described by the overall material balance through the column with the combination of the particle rate.

In a fixed bed column with ideal plug flow there is no axial dispersion suggested. The differential material balance of boron for an element of the column in the fluid phase is given

$$\frac{\partial C_{BT}}{\partial t}+\frac{u}{\varepsilon}\frac{\partial C_{BT}}{\partial z}+\frac{1-\varepsilon}{\varepsilon}\frac{\partial \overline{q}}{\partial t}=0 \qquad (4\text{-}53)$$

Eq. (4-54) is subject to the initial and boundary conditions:

I. C. $C_{BT}=0,$ at $t=0,$ $z=z$ (4-54)

I. C. $\overline{q}=0,$ at $t=0,$ $z=z$ (4-55)

B. C. $C_{BT}=C_{BT}^{f},$ at $t=t,$ $z=0$ (4-56)

The term $\frac{\partial \overline{q}}{\partial t}$ is determined by the particle rate that is expressed, in general, as:

$$\frac{\partial \overline{q}}{\partial t}=F(q,C_{BT}) \qquad (4\text{-}57)$$

In order to obtain the solution for the location of the concentration front of the total boron in the column or the history of effluent boron concentration it is necessary to solve Equation (4-53), subject to the initial and boundary conditions specified in Equations (4-54) to (4-56), and an appropriate rate equation simultaneously. Under the diffusion control process specified, Equation (4-57) can be replaced by either Equation (4-34) or Equation (4-48).

Since all boron forms are interrelated by reaction equilibrium at the given temperature, it is not necessary to write mass balance equations for each species. The concentrations of these species in the solution can be readily determined by Equations (4-5) through (4-17) as soon as the total boron concentration has been found.

With a dimensionless transform in distance and time coordinates, the set of Equations (4-50) and (4-53) can be rewritten as:

$$\frac{\partial X}{\partial \xi} + \frac{\partial Y}{\partial \tau} = 0 \qquad (4\text{-}58)$$

$$\frac{\partial Y}{\partial \tau} = f(Y,X) \qquad (4\text{-}59)$$

with the initial and boundary conditions:

I. C. $X = 0,$ at $\tau = 0,$ $\xi = \xi$ (4-60)

I. C. $Y = 0,$ at $\tau = 0,$ $\xi = \xi$ (4-61)

B. C. $X = X^f,$ at $\tau = \tau,$ $\xi = 0$ (4-62)

where the dimensionless parameters are defined as following:

$$\xi = \frac{k_i(1-\varepsilon)}{u}\frac{z}{d_p} \qquad (4\text{-}63)$$

$$\tau = \frac{k_i C_i^f}{d_p Q}\left(t - \frac{z\varepsilon}{u}\right) \qquad (4\text{-}64)$$

$$Y = \frac{\bar{q}}{Q} \qquad (4\text{-}65)$$

and

$$X = \frac{C_{BT}}{C_{BT}^{f}} \tag{4-66}$$

The explicit forms of Equation (4-59) are given in dimensionless form, for film diffusion control:

$$\frac{\partial Y}{\partial \tau} = 6Ri(X^{o} - X^{*}) \tag{4-67}$$

for the particle diffusion control, by applying Eq. (3-28):

$$\frac{\partial Y}{\partial \tau} = 60\gamma(Y^{*} - Y) \tag{4-68}$$

where

$$Ri = \left(\frac{De}{D_B}\right)^{2/3} \tag{4-69}$$

$$\gamma = \frac{\overline{De}}{k_L d_p} \cdot a \cdot \exp\left[-\left(bT + cT^2\right)\right] \cdot (C_{BT}^{f})^{\eta-1} \tag{4-70}$$

Y^* in Equation (4-68) is not a function of the average concentration fraction Y in the resin, but is strongly dependent of the solution concentration. Therefore, integration of Equation (4-68) gives.

$$Y^{*} - Y = C_1 \exp(-60\gamma\tau) \tag{4-71}$$

where the integration constant

$$C_1 = Y^{*} \tag{4-72}$$

is subject to the initial condition

$$Y = 0, \qquad \text{at} \qquad \tau = 0, \tag{4-73}$$

Substitution of Equation (4-72) into Equation (4-71) leads to the relation between Y^* and Y

$$Y = Y^{*}\left[1 - \exp(-60\gamma\tau)\right] \tag{4-74}$$

The dimensionless forms of the model are analogous to those used to describe heat transfer in a packed bed, and many of the solutions (Furnas, 1930; Walter, 1945; and Klinkenberg, 1954) were derived for an analogous heat transfer problem. Unfortunately, infinite series or error functions were involved in these solution expressions, even if in some approximate forms, so that the numerical effort is inevitably to be paid for the solutions for the breakthrough curve. Therefore, direct numerical solution of the model equations is applied in this work.

Numerical Approach

For an optimal design of an industrial ion exchange process, accurate modeling and simulation of the dynamic behavior of the column is important. Numerical methods are an alternative to analytical solutions when complex rate equations, equilibrium relations, and irregular boundary conditions are encountered in multicomponent ion exchange column performance. The solution of convective diffusion equations, and modeling of the coupling among different individual components, is a major difficulty in the simulation of ion exchange dynamics.

The method of characteristics reduces first order hyperbolic partial differential equations to an equal sized system of ordinary differential equations (Costa et al., 1986). Many investigators have applied the method to adsorption packed columns (Acrivos, 1956) to solve material balance equations in binary and multicomponent ion exchange columns (Dranoff and Lapidus, 1958 and 1961; Helfferich, 1962; and Omatete et al., 1980), and for cation and anion resins in mixed beds (Haub and Foutch, 1986b). This technique was also used in this work.

Equations (4-58) and (4-59), which describe, in a dimensionless form, the material balance of boron in an element of column and the exchange rate around a particle within the element, are coupled first order ODE's. As soon as the bulk concentrations, interface concentrations, and effective diffusivity or equivalent mass transfer coefficients are obtained, these equations are easily solved numerically with the restrictions specified in Equations (4-60) to (4-62).

The reaction equilibrium of boric acid dissociation leads to a set of algebraic equations. Solving the set of equations by the Newton-Raphson method gives the boric acid concentration for the determination of the effective diffusivity defined in Eq. (4-33). Euler and Adam's-Bashforth explicit methods were applied in this work for solving the ODE's. Runge-Kutta fourth order was combined for the initial starting values of Adam's-Bashforth method to improve the accuracy to the third order in the dimensionless distance increment. A computer code applying these methods to solve this model is given in Appendix F.

The orthogonal collocation method of solving partial differential equations – an implicit method – is particularly useful for the solution of boundary value problems (Raghavan and Ruthven, 1983). This method was applied previously to the simulation of fixed-bed reactors (Hansen, 1971, Karanth and Hughes, 1974) and later to the simulation of adsorption columns (Liapis and Rippin, 1978, Raghavan and Ruthven, 1983). It is relatively fast to obtain solutions of comparable accuracy by various other standard numerical methods leads to the wide use of the orthogonal collocation method in solving ion exchange and adsorption column problems.

Incorporating the Lagrangian polynomials as a trial function and the Gauss-Jacobi quadrature for improving accuracy, the orthogonal collocation approach was used to solve the diffusion model in Equations (4-39) to (4-44) for comparison with the linear rate approach. The corresponding procedures of this approach and its computer code are given in Appendix G.

Results and Discussion

In the calculation of the predicted response curves, the interface concentrations were estimated from the correlation of Chapter III and the effective diffusivity in the resin phase was from Périé's experimental measurements (Périé et al., 1991). By this model, a typical breakthrough curve of the boron sorption on OH^- form anion resin in BTRS is plotted in Figure IV-1 and the distribution profiles varying with time are given in Figure IV-2.

The sharp front of these curves indicates that a very favorable sorption isotherm and high exchange rate can be expected by using strong base anion resins in BTRS. The sorption behavior can be largely contributed to the following reasons:

1. dominant boric acid molecular diffusion in the liquid film has less interactions with other diffusing species
2. instantaneous ionization of boric acid molecules at the interface
3. fast polyborate formations inside the resin

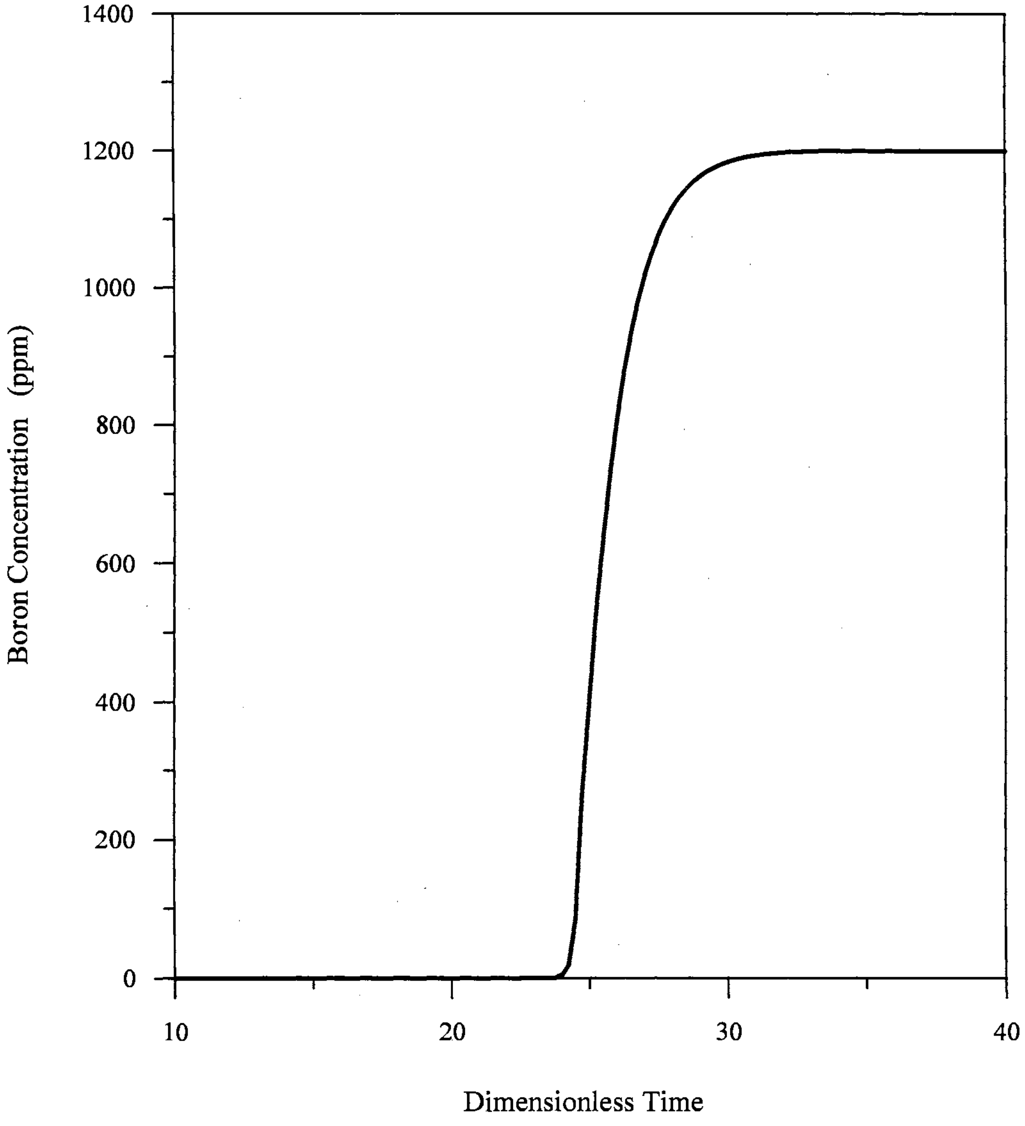

Figure IV-1 A typical breakthrough curve of boron sorption in Boron Thermal Regeneration with total feed concentration of boron 1200 ppm.

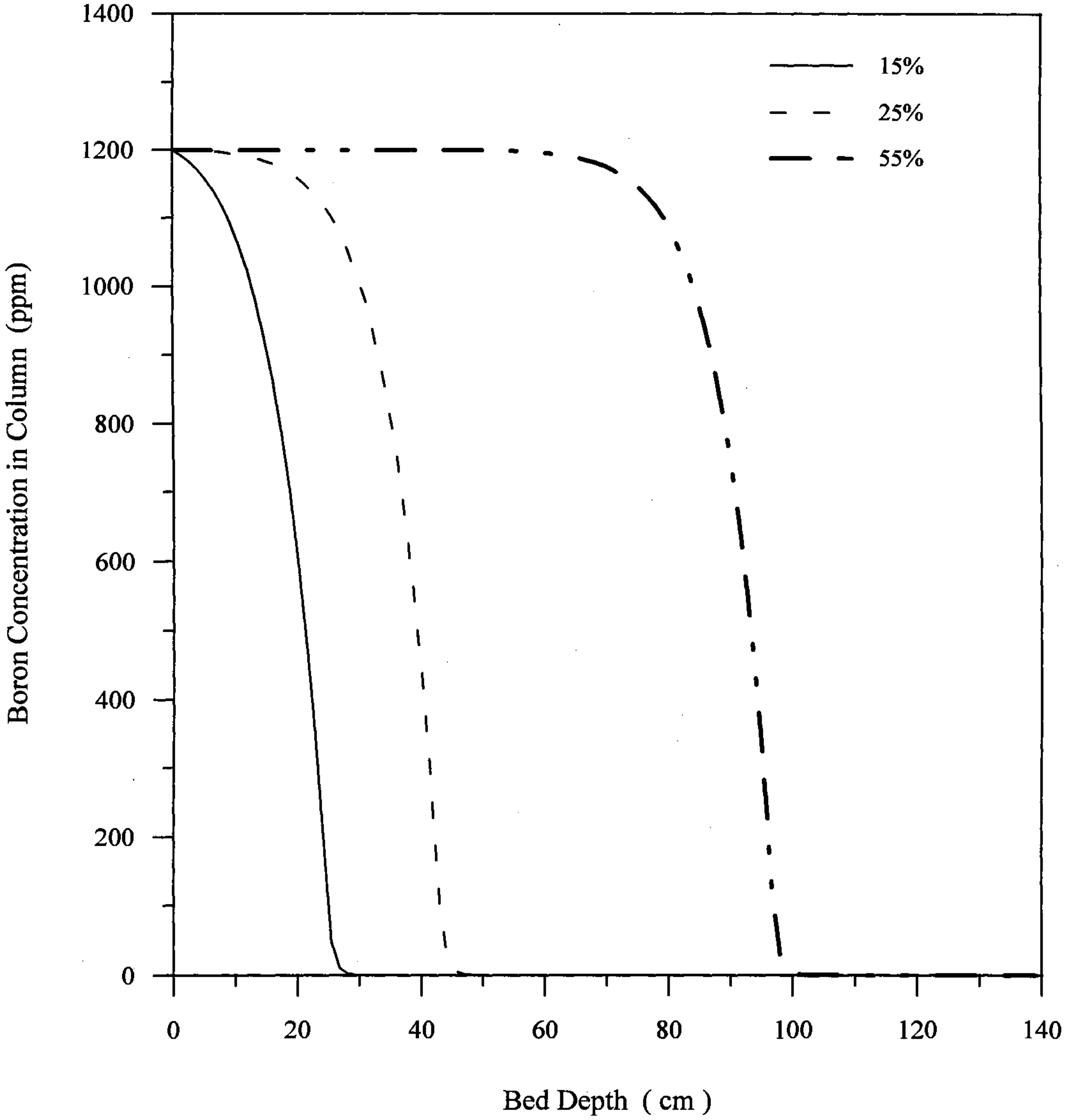

Figure IV-2 Simulated motions of boron concentration profiles through the bed with the feed concentration of boron 1200 ppm, at the theoretical operation time allowed of 15 %, 25 %, and 55 %, respectively.

Donnan exclusion leads to no net co-ion flux within the film, which means that the concentration gradient of hydrogen ions in this case is constant. In other words, the concentration gradients of boric acid molecules and borates are constant due to the equilibrium relations between the these boron carriers and hydrogen ions. Fast reversible chemical reactions balance the concentrations between boric acid and various borates in the film. This largely reduces possible interactions among diffusion species that may produce the resistance to boron carrier transport from the bulk liquid to the interface. The immediate consumption of hydroxide ions releasing from the resin at the interface partly reduces the interactions of co-sign ions.

The instantaneous ionization of boric acid molecules at the interface results in an extremely low concentration of boric acid molecules at the interface, which gives the largest possible driving force for the diffusion of boric acid molecules. This can be considered to be valid, at least before much of the minimum capacity of the resin has been consumed.

The rapid polyborate formation at sites inside the resin dramatically increases the apparent capacity of the resin for boron, and is in favor of the formation of a sharp boundary between the interface and the interior of the resin in the later stage of boron sorption. They are therefore in favor of fast exchange rate and the postulation of the linear driving force.

Effects of temperature on the boron sorption were summarized in Figures IV-3 and IV-5. The exchange rate depends weakly on temperature for the condition studied. The reasons are due to the weak temperature dependency for mass transfer coefficient and

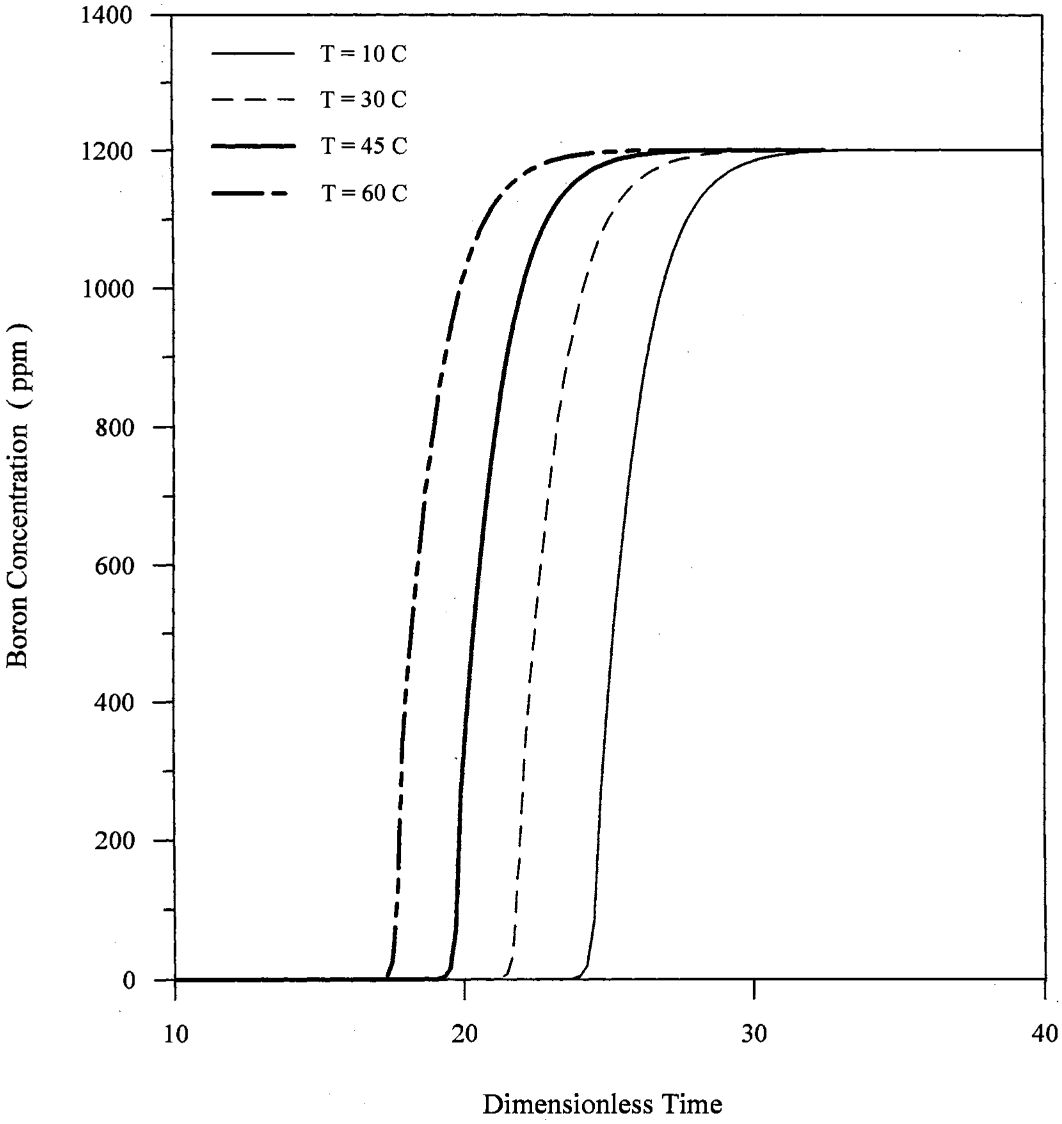

Figure IV-3 Effects of temperature on breakthrough curves of the boron sorption in BTRS with the total feed concentration of boron 1200 ppm and OH form anion resins.

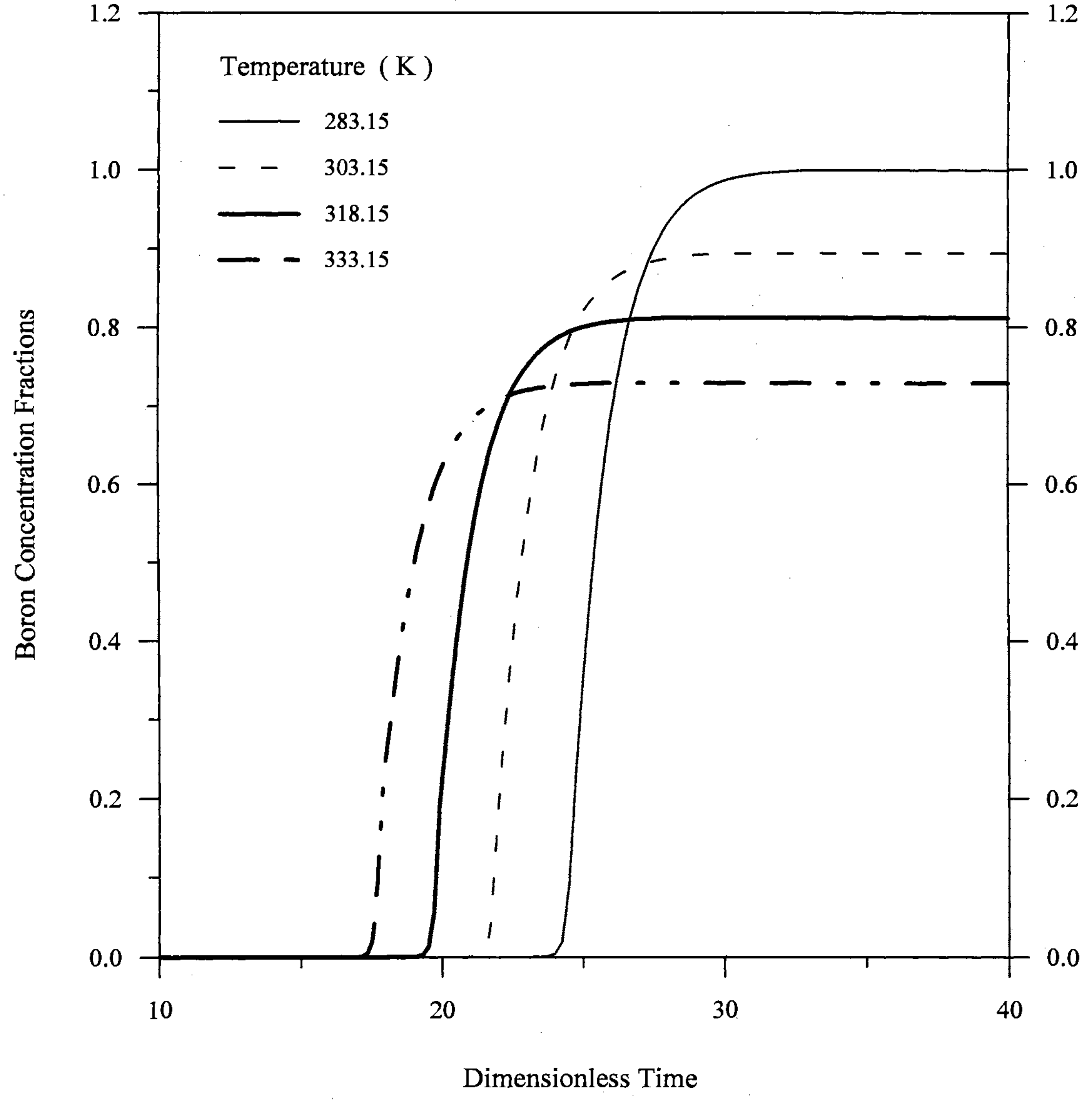

Figure IV-4 Comparison of the apparent sorption capacity toward boron under various temperatures with the feed boron concentration 1200 ppm.

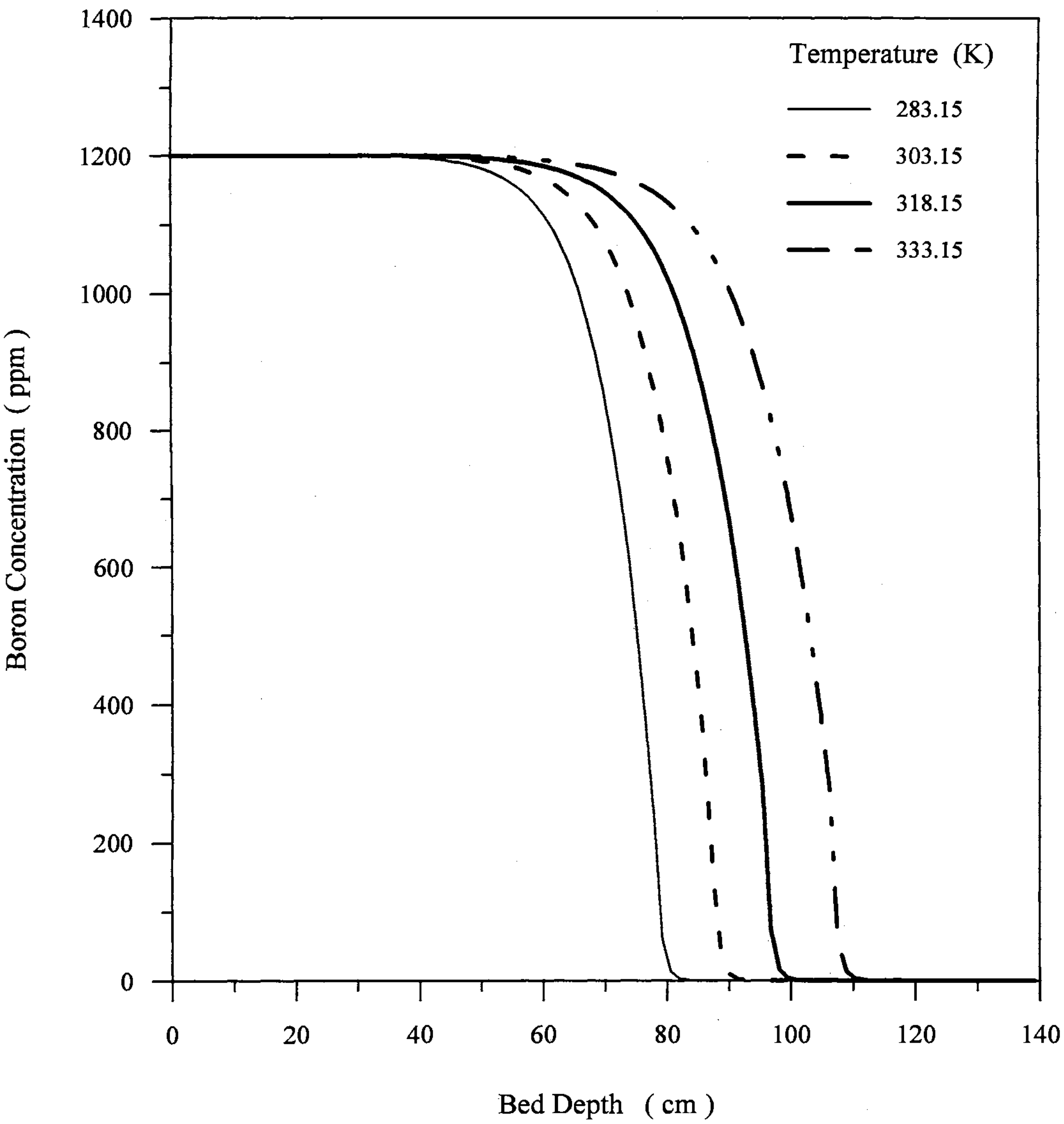

Figure IV-5 Comparison of concentration distribution profiles under various temperatures at a given time with the feed boron concentration 1200 ppm.

the negligible concentration of ionic species dissociated from boric acid at the applicable range of temperature.

The apparent capacity of the resin, however, varies with the change of temperature. It is about 25% higher at 10 °C than at 60 °C. Correspondingly, the concentration front at higher temperature is deeper toward the column bottom at a given time, and it is expected that the breakthrough comes earlier at the temperature under the same feed conditions.

With the change of flow rates, the shape and tendency of the curves (in Figures IV-6 and IV-7) are similar. The exchange rate shown in Figure IV-7 is a little fast at higher flow rate, but is not influenced significantly by the change of flow rates in the range of calculation.

Conclusions

The model is essentially correct and demonstrates the feasibility of modeling the behavior of the boron sorption in BTRS since all parameters were determined independently and were referenced from related experiment results in the literature. This study shows the very steep shape of the breakthrough curves resulting from a very favorable sorption equilibrium condition of boron on OH form anion resin. Lower temperature is in favor of the sorption. Results calculated by simplification of the linear driving force give a good estimation and did not result in a serious error by comparison of using more complicated diffusion models (Figure IV-8). In addition, Fick's law is acceptable to use for the kinetic study of the boron sorption in BTRS.

The kinetics of the desorption of boron from a borate form resin needs to be a future study, which gives a complete description of BTRS operation in combination with this study. Experimental and operation data need to verify the predictions of the model.

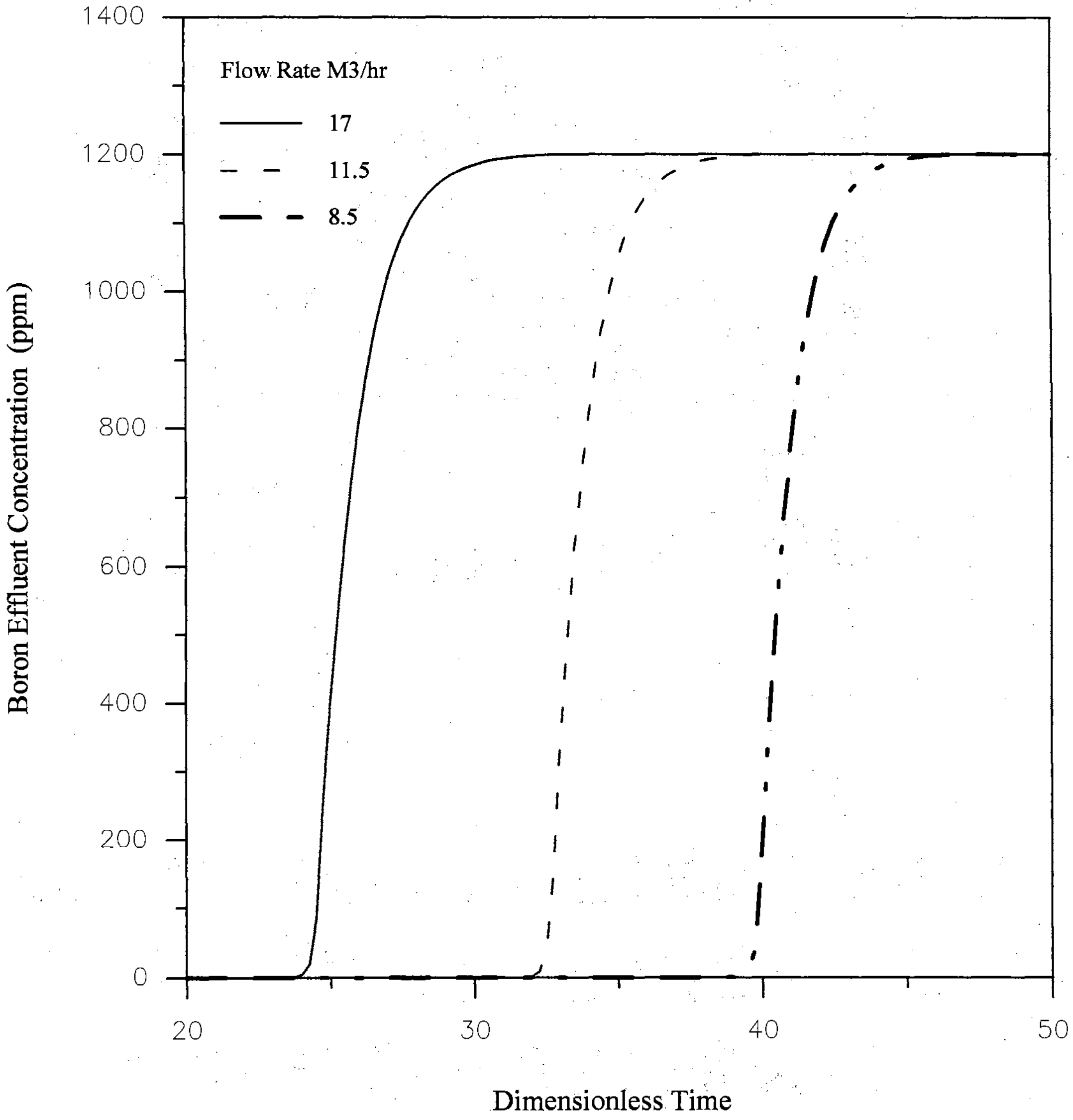

Figure IV-6 Effects of flow rate on boron sorption on OH form anion resin with the total feed concentration of boron 1200 ppm, at the flow rate 17 M3/hr (left), 11.5 M3/hr, and 8.5 M3/hr(right), respectively.

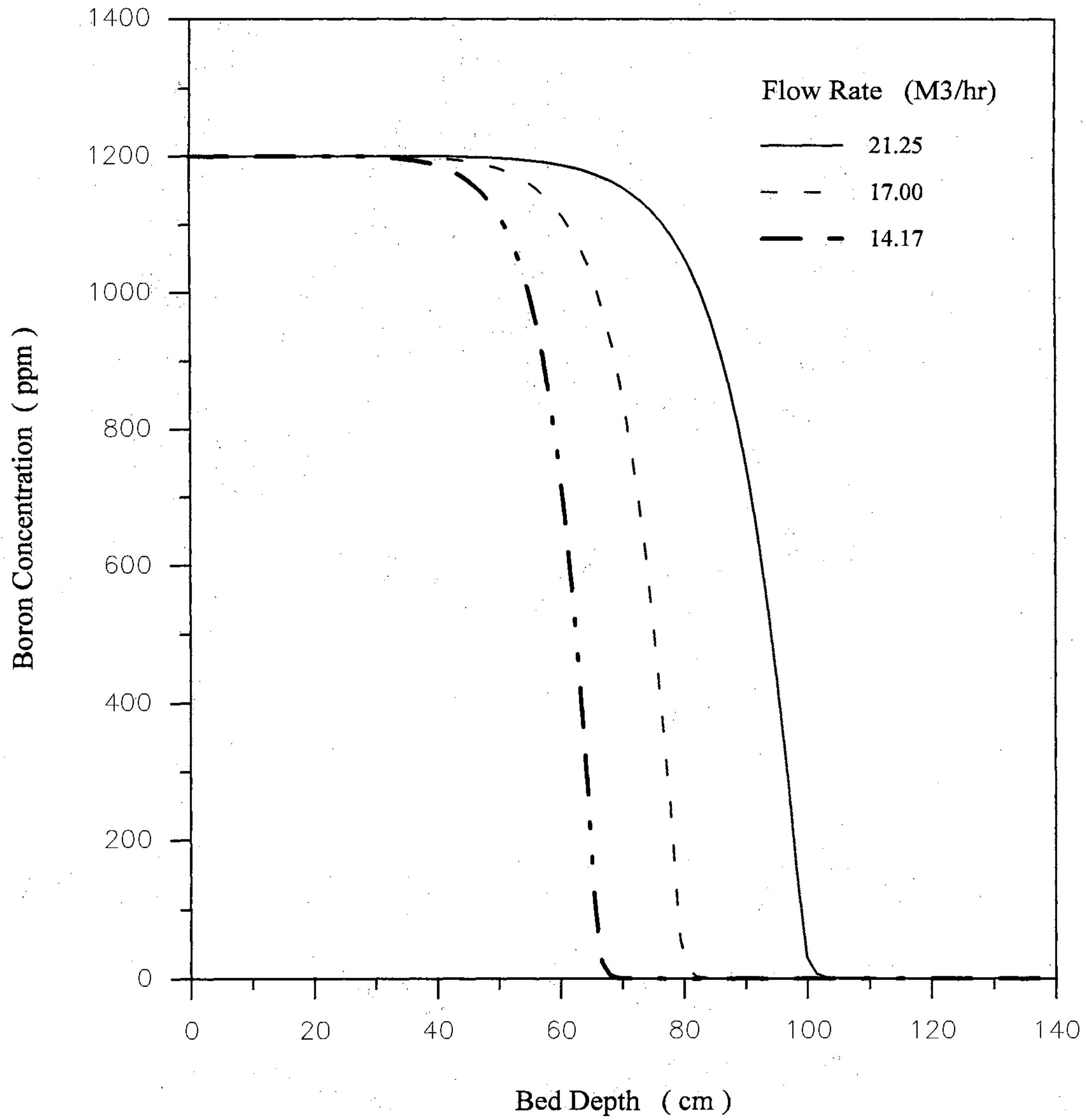

Figure IV-7 Effects of flow rate on the column dynamics during the boron sorption process with the conditions C = 1200 ppm boron, and T = 10 C.

REFERENCES

Acrivos, A. (1958). Solution of the laminar boundary layer energy equation at hgih Prandle number, Phys. Fluids, 3, 657-658.

Blickenstaff, R. A., Wagner, J. D. and Dranoff, J. S. (1967a). The kinetics of ion exchange accompanied by irreversible reaction. I. Film diffusion controlled neutralization of a strong acid exchanger by strong bases, J. Phys. Chem., 71 (5), 1665-1669.

Blickenstaff, R. A., Wagner, J. D. and Dranoff, J. S. (1967b). The kinetics of ion exchange accompanied by irreversible reaction. II. Intraparticle diffusion controlled neutralization of a strong acid exchanger by strong bases, J. Phys. Chem., 71 (5), 1670-1674.

Costa, J. I. and Glueckauf, E. (1947). Theory of chromatography. III. Experimental separation of two solutes and comparison with theory. J. Chem. Soc. (London), 1308-1314.

Dranoff, J. S. and Lapidus, L. (1958). Multicomponent ion exchange column calculations. Ind. Eng. Chem., 50, 1648-1653.

Dranoff, J. S. and Lapidus, L. (1958). Ion exchange in ternary systems. Ind. Eng. Chem., 53, 71-76.

Dwivedi, P. N. and Upadhyay, S. N. (1977). Particle-fluid mass transfer in fixed and fluidized beds. Ind. Eng. Chem., Process Des. Dev., 16(2), 157-165.

Franzreb, M., Höll, W. H., and Eberle, S. H. (1995). Liquid-phase mass transfer in multicomponent ion exchange. 2. Systems with irreversible chemical reactions in the film. Ind. Eng. Chem. Res., 34, 2670-2675.

Furnas, C. C. (1930). Heat transfer from a gas stream to a bed of broken solids, Trans. Am. Inst. Chem. Eng. 24, 142.

Glueckauf, E. (1955). Theory of chromatography. Trans. Faraday Soc. 51, 1540.

Hansen, K. W. (1971). Analysis of transient models for catalytic tubular reactors by orthogonal collocation. Chem. Eng. Sci., 26, 1555-1569.

Haub, C. E. and Foutch, G. L. (1986a). Mixed-bed ion exchange at concentrations approaching the dissociation of water. 1. Model development. Ind. Eng. Chem. Fund., 25, 373-381.

Haub, C. E. and Foutch, G. L. (1986b). Mixed-bed ion exchange at concentrations approaching the dissociation of water. 2. Column model Applications. Ind. Eng. Chem. Fund., 25, 381-385.

Helfferich, F. G. (1962). Ion Exchange. McGraw-Hill, Inc., New York, NY.

Helfferich, F. G.(1965). Ion-exchange kinetics. V. Ion exchange accompanied by reactions, J. Phys. Chem., 69 (4), 1178-1187.

Helfferich, F. G. (1983). Ion exchange kinetics—Evolution of a theory. In Mass Transfer and Kinetics of Ion Exchange. (Liberti, L and Helfferich, F. G., ed.), NATO ASI Series, Martinus Nijhoff Publishers, Hague.

Karanth, N. G. and Hughes, R. (1974). Simulation of an adiabatic packed bed reactor. Chem. Eng. Sci., 29, 197-205.

Kataoka, T., Yoshida, H., and Shibahara, Y. (1976). Liquid phase mass transfer in ion exchange accompanied by chemical reaction. J. Chem. Eng. Jpn., 9, 130.

Kataoka, T., Yoshida, H., and Ozasa, Y. (1976). Intraparticle ion exchange mass transfer accompanied by irreversible reaction. Chem. Eng. Sci., 32, 1237-1240.

Kataoka, T. and Yoshida, H. (1988). Kinetics of ion exchange accompanied by neutralization reaction. AIChE J., 34(6), 1020-1026.

Klinkenberg, A. (1954). Heat transfer in cross-flow heat exchangers and packed beds. Ind. Eng. Chem. 46, 2285.

Koloini, T., Plazl, I., and Zumer, M. (1990). Kinetics of Na^+-H^+ ion exchange in concentrated buffer solutions of sodium tetraborate and boric acid. Chem. Eng. Comm., 96, 127-139.

Kononova, G. N., O. A. Plotnikova, A. L. Martyushin and O. Yu. Odinstov (1987), Kinetics of the sorption of boron by the ANB-11G resin, Russ. J. Phys. Chem., 61 (5), 705-707.

Liapis, A. I. and Rippin, D. W. T. (1978). The simulation of binary adsorption in activated carbon columns using estimates of diffusional resistance with the carbon particles derived from batch experiments. Chem. Eng. Sci., 33, 593.

Lin, K. H. (1973). Use of ion exchange for the treatment of liquids in nuclear power plants, Report ORNL-4792, Oak Ridge, TN.

Lou, J. (1993). Simulation of Borate Ion Exchange and Radial Flow for Reactor Water Clean Up Systems. Master thesis, Oklahoma State University, Stillwater, OK.

Meichik, N. R., Leikin, Y. A., Galitskaya, N. B., and Kosaeva, A. E. (1989). Kinetics of the sorption of boron by anion-exchange resins. Russ. J. Phys. Chem., 63(3), 1871.

Mesmer, R. E., Baes Jr., and Sweeton, F. H. (1972a). Boric acid equilibria and pH in PWR coolants, Proceedings of the 32nd International Water Conference, Pittsburgh, PA, 55-62.

Mesmer, R. E., Baes Jr., and Sweeton, F. H. (1972b). Acidity Measurement at elevated temperatures. VI. Boric acid equilibria. Inorg. Chem., 11(3), 537-543.

Omatete, O. O., Clazie, R. N., and Vermeulen, T. (1980). Column dynamics of ternary ion exchange. Part II: Solution mass transfer controlling. Chem. Emg. J., 19, 241-250.

Périé, M, J. Périé, and M. Chemla (1991). Nuclear grade resins: Kinetics of isotopic and ionic exchange for borate and chloride anions, J. Electroanal. Chem., 303, 105-124.

Peterka, F. (1980). Selection of anion exchange resins for boron thermal regeneration systems, J. of Chromatography, 201, 359-370.

Raghavan, N. S. and Ruthven, D. M. (1983). Numerical simulation of a fixed-bed adsorption column by the method of orthogonal collocation. AIChE J., 29 (6), 922-925.

Rosen, J. B. (1952). Kinetics of a fixed bed system for solid diffusion into spherical particles, J. Chem. Phys., 20, 387.

Rosen, J. B. (1954). General numerical solution for solid diffusion in fixed beds, Ind. Eng. Chem., 46(8), 1590.

Ruthven, D. M. (1984). Principles of Adsorption and Adsorption Processes, John Wiley & Sons, New York.

Schlögl, R. and Helfferich, F. (1957). Comment on the significance of diffusion potentials in ion exchange. J. Chem. Phys., 26, 5.

Tomizawa, T. (1981). Studies on the absorption of boric acid on anion exchange resins: IV. Kinetics of the absorption of boric acid on OH^- form anion exchange resins, Denki Kagaku, 49 (8), 503-510.

Tomizawa, T. (1982). Studies on the absorption of boric acid on anion exchange resins: III. Kinetics of desorption of boric acid from borate-form anion exchange resins, Denki Kagaku, 50 (11), 886-891.

Wagner, J. D. and Dranoff, J. S. (1967). The kinetics of ion exchange accompanied by irreversible reaction. III. Film diffusion controlled neutralization of a strong acid exchanger by a weak base. J. Phys. Chem., 71, 4551-4553.

Walter, J. E. (1945). Multiple adsorption from solutions, J. Chem. Phys. 13 (6), 229-332

CHAPTER V

MIXED BED ION EXCHANGE FOR SORPTION OF LITHIUM AND BORON SOLUTION IN PRIMARY CIRCUIT OF PRESSURED WATER REACTOR SYSTEM

Introduction

Water, due to its low cost and effectiveness, has been chosen as heat transfer medium, moderator, and shield in large-scale nuclear reactors since 1943 (Smyth, 1945). In parallel with these useful functions, however, other processes occur. While transporting heat from source to sink, the water also transports particles and gases from the reactor to other parts of the system. The important process of slowing down neutrons is accompanied by neutron and proton capture, thus producing undesirable radioactive species in the coolant. The useful absorption of radiant energy is accompanied by dissociation reactions. In addition, water reacts chemically with almost all materials within the reactor, which contaminates water in the coolant circuit. It is from these side reactions that reactor water technology problems arise.

On the other hand, reactor water technology is not limited to coping with the undesirable properties of water. It also includes the exploitation of water properties to achieve improvements in reactor design and performance. For instance, the use of chemical poisons and mixtures of light and heavy water for reactivity control in pressurized water reactors. As mentioned in previous Chapters, boron, or its compounds, is used for purposes such as chemical shim control. Some metals, lithium for instance, are added to coolant for pH control to minimize corrosion. Therefore, water purification is inevitably required in the coolant circuit for the removal of contaminates or for the recovery of useful materials from the coolant. Ion exchange meets such requirements (Cohen, 1969).

Mixed bed ion exchange, an intimate mixture of cation and anion exchange resins, is used for the removal of impurities from solution. In H and OH form resins, cations are replaced with hydrogen ions, while anions are replaced with hydroxide. The hydrogen and hydroxide released react to form water, thus maintaining the low hydrogen and hydroxide concentrations in the solution to give strongly favorable equilibrium for cation and anion exchange through the column. This action accounts for the extraordinary ability of mixed-bed strong acid/strong base resins to produce very high purity water in relatively short beds at high flow rates.

Much progress in the study of kinetics and performance of mixed bed ion exchange has been made since the 1950's. Early investigation of mixed bed ion exchange (McGarvey and Kunin, 1951; Cadell and Moison, 1954; Frisch and Kunin, 1960) justified the use of the stagnant film diffusion model and the linear driving force simplification. Attention to the effects of chemical reactions and reversible change began when Helfferich (1965) proposed such effects to show their importance on neutralization and complex formation. Helfferich's postulation was confirmed experimentally in anion or cation exchanger bed by Blickenstaff et al. (1967a, b), Wagner and Dranoff (1967), Kataoka et al. (1976, 1977), and Kalinichev et al. (1981), etc. The influence of reversible change and water dissociation on the rate of change in mixed bed ion exchange was first investigated by Haub and Foutch (1986a, b). They emphasized that the neutralization reaction can occur in the bulk liquid, the film and at the interface so that it influences ion exchange process. Their research implied that the assumption of irreversible change is no longer valid at the cases of the concentration of impurity approaching the dissociation products of water, which are often required in power produced and semiconductor related industries. More general kinetic approaches of mixed bed ion exchange with multicomponent systems were reported by Zecchini and Foutch (1991) for a ternary system with cation resin in amine form, Hwang and Helfferich (1987) for the systems with fast, reversible reactions, and Franzreb et al. (1995) for the systems with irreversible reactions in the film. These works concluded that exchange kinetics was controlled by the diffusion processes. Moreover, the Nernst-Planck model was applied to describe ion exchange, and Fick's law was used for neutral species.

For the system of interest in this work, the weak dissociated boric acid participates in the boron transport from one phase to the other and gives a dominant contribution to the boron sorption on anion exchanger. Chemical reactions involved in the ion exchange process are neutralization, dissociation and association of boric acid, and complex polyborate formations. The direction of ionization of boric acid that is indicated by Eq. (4-4),

$$\alpha B(OH)_3 + \beta OH^- \xleftrightarrow{K_{\beta\alpha}} B_\alpha (OH)_{\beta+3\alpha}^{\beta-} \qquad (4\text{-}4)$$

and the amount of borates produced strongly depend on temperature, concentration and pH. Boron sorption equilibrium varies with the degree of polyborate formation inside the resins, and is a function of temperature and the feed concentration of boron. No quantitative and theoretical studies have previously been advanced for these interesting effects of boron solutions in mixed bed ion exchange.

The objective of this work is to investigate the kinetics of mixed bed ion exchange for solutions containing boron and alkalis and to develop a model for the prediction of the operation system with these solutions. The model developed here addresses general situation for such systems, but will focus on the system operating with a typical condition of the coolant in the primary circuit of pressurized water reactors (PWR). The coolant typically contains low concentration of alkalis (about 10^{-4} M lithium, sodium, or amine, etc.) and varying amounts of boric acid (2000 to 1 ppm as boron) in boron PWR system (Cohen, 1969, Bates, 1993). Therefore, the following conditions will be of interest in this work.

- Concentration ranges: boron from 1 to 2000 ppm; lithium from 0.5 to 3.5 ppm; chloride from 0 to 1 ppm; sodium from 0 to 1 ppm.
- Operation temperature ranges 40 to 60 °C.
- OH form strong base anion resin mixed with H form strong acid cation resin.

The equations derived in the model are solved numerically. A computer code developed for the calculation of this model will be given in Appendix J. Parameters and conditions of a calculation example will be also listed in Appendix J.

Theoretical Approach

The model developed in this work is based on the information provided in Chapters II, III, IV and the discussion above. The topics addressing various issues involved are highlighted.

Assumptions of Model Development

The theoretical treatment will be based on the following assumptions for the simplification of the derivation. The number of assumptions involved with the development is limited to produce as general a model as possible.

Boric acid is a weak acid with a very low degree of dissociation in the range of pH 5 - 7. Consequently, most of boron is carried by the neutral molecule-boric acid in the solution. Because the sorption of neutral species gives a predominant contribution of the boron sorption on anion resin, borates considered during the exchange process, for simplicity, are merely the major species as the tetrahedral $B(OH)_4^-$ and the triborate $B_3(OH)_{10}^-$ (or alternate $B_3O_3(OH)_4^-$). The other ionic species considered in the system are lithium, sodium, hydrogen, chloride, and hydroxide.

Exchange processes for both cation and anion exchangers are governed by the diffusion, which was clarified in Chapter IV. Though the feed concentration of boron, sorption on anion resin, may reach as high as 2000 ppm, the concentration of the total ionic species is relatively low, only about several ppm (for both cations and anions). In the cation exchange point of view, the concentration of cationic species involved in the cation exchange is relatively low because boric acid molecules do not participated in cation exchange. It is reasonable, therefore, to consider that the rate of cation exchange is controlled by the liquid side diffusion.

The anion exchange can be more complicated in the boron sorption on ion exchange than ordinary ion exchange. As discussed in Chapter IV, the reaction plane is located at the interface between the liquid film and the anion resin. The free ion OH^-, released by the anion resin is consumed by the ionization of boric acid at the reaction plane. The interface concentration of the free ion OH^- is hence at, or near zero, as long as the solution still contains boric acid molecules. The ionization reaction at the interface also converts boric acid molecules to various borate ions. The conversion is almost complete at least before the minimum capacity of the anion resin is consumed. The reasons for almost complete ionization of boric acid molecules at the entry of the anion resin are high pH (about 9-14, Tomizawa, 1979) and high boron concentration, which were illustrated in Chapter II. The first reason dominates the beginning of exchange, and the contribution of the latter increases as the free OH^- released by the anion resin is nearly consumed, which leads to a pH decrease from its peak value.

The postulation of completed conversion of boric acid at the interface implies a special feature of the boron sorption on OH^- form anion exchanger that is a) the diffusion of boric acid molecules as the major boron carriers characterizes the migration of boron from the liquid side to the interface; b) then boric acid molecules are ionized to borates through chemical reaction; and c) the diffusion of these borates, produced by the ionization, as the main boron carriers characterizes the transport of boron from the interface to the site inside the resin. The ionization reaction at the interface does not interfere with the intraparticle diffusion of borate ions produced by the reaction, but does affect the inter-diffusion of borates in the liquid solution and the boundary condition at the interface. Due to the minor contribution of borates in the solution to the boron sorption on the anion resin, that situation is a similar case to the type I reaction with particle diffusion control described by Helfferich (1965).

This postulation of completed ionization of boric acid molecules at the interface results in the assumption of zero boric acid concentration at the interface, which gives the maximum driving force for diffusion from the bulk liquid to the interface. Therefore, as long as the migration of boric acid molecules in the liquid side is the predominant contribution to the boron sorption on anion resin, it is acceptable to assume that anion exchange is governed by the intraparticle diffusion of borates at a relative high concentration (above 100 ppm).

In addition, local equilibrium reaches the interface. The selectivity coefficient, which relates the interface concentrations at both sides, can be used to determine the interface concentrations for the cation exchange, while local equilibrium at the anion surface obeys the relationship specified by Equation (3-28). Both the Nernst-Planck equation and Fick's first law are applied in this work to describe the fluxes of ionic species and molecule diffusion, respectively. The simplification of the linear driving force will be adopted in the model, which is indicated for the film model:

$$\frac{d\bar{q}_n}{dt} = k_{L,n} a_s \Delta C_n \qquad (5\text{-}1)$$

or the particle model

$$\frac{d\bar{q}_n}{dt} = k_{P,n} a_s \Delta q_n \qquad (5\text{-}2)$$

Where the subscript *n* indicates any species involved in the exchange.

If *k* denotes ionic species with any charge, *i* and *j* indicate counter ion and co-ion, respectively, the conditions of no electrical current and electroneutrality can be expressed in Equations (5-3) and (5-4), respectively.

- No net current

$$\sum_k z_k J_k = 0 \tag{5-3}$$

- Electroneutrality

$$C_{NT} = \sum_i z_i C_i = -\sum_j z_j C_j \tag{5-4}$$

where the C_{NT} is the total equivalent concentration of ionic species.

Due to the complete Donnan exclusion at the resin surface, no uptake of co-ions means zero flux of co-ions in the Nernst film surrounding the resin.

$$J_j = 0 \tag{5-5}$$

Combine this assumption with the condition in Equation (5-3) to result in

$$\sum_i z_i J_i = 0 \tag{5-6}$$

This is not a serious assumption in most cases involving chemical reactions and is not necessary for particle diffusion resistance controlled models.

The other assumptions commonly applied in the study of ion exchange kinetics are listed as follows:

- Pseudo steady state diffusion in the Nernst film

Since the Nernst film is quite thin, it is more important to consider the diffusion with distance than with time in the film. This implies that the concentration of species in the film does not depend on time as an approximation. Moreover, as diffusion crosses the Nernst film, if species consumed or produced by reactions are negligible or the reaction rate is independent of the spatial variable, its flux is independent of the spatial variable too. This assumption thus leads to a constant flux within the film. Otherwise, the mathematical expression of the kinetic model will become very complicated if the Nernst-Planck equation for flux is applied.

- Uniform localized resin surface concentrations.
- Plug flow
- Binary selectivity data may be extended to multicomponent for the determination of the interface concentrations
- Uniform resins and bed properties; i.e., constant d_p, ε, etc.,
- Isothermal and isobaric operation conditions

Sorption mechanism

For the system considered, the cations involved are Na^+, Li^+, and H^+. H^+ is the free ion originally existing inside the cation resin and is exchanged by Na^+ and Li^+. The hydrogen ion released by the cation resin is consumed by neutralization reactions with hydroxide ion to form water, and possibly with the tetrahedral $B(OH)_4^-$ to form the neutral boric acid molecule and water (recalling Eq. 2-4). The other ionic species are not involved in these reactions, nor does the boric acid molecule due to its Lewis acid behavior. Therefore, the ion exchange reaction for cations may be indicated as follows:

$$\overline{RH} + Li^+ + Na^+ + OH^- + B(OH)_4^- \longleftrightarrow \overline{R(Li,Na)} + H_2O + B(OH)_3 \qquad (5\text{-}4)$$

The sorption of boron on OH form anion resin seems to be governed by a different mechanism, which was postulated in Chapter IV. Cited here for convenience, these are:

Process I: Consumption of the counterion released by the ion exchanger.

$$\overline{RA} + B \longleftrightarrow \overline{RAB} \tag{4-18}$$

$$\overline{RA} + P + B \longleftrightarrow \overline{RP} + AB \tag{4-19}$$

Process II: Ion exchange with the initial counterion and replacement of the tetrahedral ion by polyborates according to selectivity.

$$\overline{RA} + AB \longleftrightarrow \overline{RAB} + A \tag{4-20}$$

$$\overline{RAB} + P \longleftrightarrow \overline{RP} + AB \tag{4-21}$$

Process III: Complex formation at sites

$$\overline{RAB} + (n-1)B \longleftrightarrow \overline{RAB_n} \tag{4-22}$$

where A denotes the counter-ion initially contained in the resin (here OH^-), B indicates the boric acid molecule, AB is the tetrahedral $B(OH)_4^-$, and P represents polyborates. These exchange processes may occur simultaneously in the system. Discussion about the mechanism was given in the section - Kinetics of Sorption, Chapter IV.

Mathematical Development of the Model

The expressions of the flux and the average particle rate of conversion will be derived in this section based on the assumptions and discussion given in the previous sections. The desired form of the flux will be expressed by the product of the concentration gradient of counter ion and its effective diffusivity that incorporates the effects of the electrical potential and the interactions among species on diffusion. The effective diffusivity De and the correction factor Ri of non-ionic mass transfer coefficient are also given in this section. Since the governing process and sorption mechanism of cation exchange differs from that of anion exchange, their mathematical expressions of the flux and the average particle rate of conversion for cation and anion exchange will be derived separately.

I. For cation resin

A convenient form of the Nernst-Planck equation that applies to the flux of any ionic species *k* in the film can be written as (Newman, 1973)

$$J_k = -D_k\left[\frac{\partial C_k}{\partial r} + \frac{z_k C_k F}{RT}\frac{\partial \Phi}{\partial r}\right] \tag{5-7}$$

Change notations and rewrite for counter-ions

$$J_i = -D_i\left[\frac{\partial C_i}{\partial r} + \frac{z_i C_i F}{RT}\frac{\partial \Phi}{\partial r}\right] \tag{5-8}$$

and for co-ions

$$J_j = -D_j\left[\frac{\partial C_j}{\partial r} + \frac{z_j C_j F}{RT}\frac{\partial \Phi}{\partial r}\right] \tag{5-9}$$

The condition of no co-ion flux described by Equation (5-5) and the introduction of the equivalent ionic change, which is defined as,

$$z^* = \frac{\sum z_j^2 C_j}{\sum z_j C_j} \tag{5-10}$$

can be used to eliminate the electric potential and co-ion concentration gradient in Equation (5-8). The resulting form of Equation (5-8) is

$$J_i = -D_i\left[\frac{dC_i}{dr} + n_i\frac{C_i}{C_{NT}}\frac{dC_{NT}}{dr}\right] \tag{5-11}$$

Where n_i is defined as

$$n_i = -\frac{z_i}{z^*} \tag{5-12}$$

The assumptions of pseudo steady state and only significant diffusion in the normal direction allow us to use ordinary derivatives instead of using partial derivatives in Equation (5-11).

Because of the independence of the flux on the space, Equation (5-13) can be obtained by differentiating Equation (5-11) with respect to the space variable *r* and rearranging.

$$\frac{d^2C_i}{dr^2} + \frac{n_i}{C_{NT}}\frac{dC_{NT}}{dr}\frac{dC_i}{dr} - \frac{n_i C_i}{C_{NT}^2}\left(\frac{dC_{NT}}{dr}\right)^2 + \frac{n_i C_i}{C_{NT}}\frac{d^2C_{NT}}{dr^2} = 0 \tag{5-13}$$

For counter ions of uni-valences (the same as in this case), the summation of Equation (5-13) leads to,

$$\frac{d^2C_{NT}}{dr^2} = 0 \tag{5-14}$$

and the resulting form of Equations (5-13) and (5-14) can be expressed as

$$C_{NT}^2 \frac{d^2C_i}{dC_{NT}{}^2} + n_i C_{NT}\frac{dC_i}{dC_{NT}} - n_i C_i = 0 \tag{5-15}$$

It is not difficult to solve this Euler's differential equation for its general solution,

$$C_i = a_i C_{NT} + b_i C_{NT}^{-n_i} \tag{5-16}$$

Apply the boundary conditions

$$r = R + \delta, \qquad C_i = C_i^o, \qquad \text{and } C_{NT} = C_{NT}^o \tag{5-17}$$

$$r = R, \qquad C_i = C_i^*, \qquad \text{and } C_{NT} = C_{NT}^* \tag{5-18}$$

on Equation (5-16) to obtain these coefficients

$$a_i = \frac{x_i^o - x_i^* \Gamma^{n_i+1}}{1 - \Gamma^{n_i+1}} \tag{5-19}$$

$$b_i = \left(x_i^* - \frac{x_i^o - x_i^* \Gamma^{n_i+1}}{1 - \Gamma^{n_i+1}} \right) C_{NT}^{*\ n_i+1} \tag{5-20}$$

where

$$x_i^o = \frac{C_i^o}{C_{NT}^o}; \quad x_i^* = \frac{C_i^*}{C_{NT}^*}; \quad \text{and} \quad \Gamma = \frac{C_{NT}^*}{C_{NT}^o} \tag{5-21}$$

And it is easy to see that these coefficients meet the conditions

$$\sum a_i = 1; \qquad \sum b_i = 0 \tag{5-22}$$

Equation (5-16) gives the relationship between C_i and C_{NT}. By substitution the Equation (5-16) and its derivative into Equation (5-11), the following result can be obtained by an appropriate rearrangement of the substitution.

$$J_i = -D_i a_i (n_i + 1) \frac{dC_{NT}}{dr} \tag{5-23}$$

With the counter ion of uni-valences in systems, note

$$n_i \equiv 1 \tag{5-24}$$

Integration of Equation (5-23) gives

$$J_i = -\frac{(n_i + 1)}{\delta} D_i a_i (C_{NT}^o - C_{NT}^*) \tag{5-25}$$

Summing the resulting form of Equation (5-25) by multiplying the charge valence and applying the conditions of no net current and no co-ion flux, the total equivalent concentration of counter ions at the interface can be eliminated from Equation (5-25) to give

$$J_i = -\frac{(n_i + 1)}{\delta} D_i a_i C_{NT}^{o} [1 - \Gamma] \tag{5-26}$$

where

$$\Gamma = \left[\frac{\sum_{i=1}^{n} D_i x_i^{o}}{\sum_{i=1}^{n} D_i x_i^{*}} \right]^{\frac{1}{n_i+1}} \tag{5-27}$$

A desired form of the flux for each ionic species can be written as:

$$J_i = -D_e \frac{dC_i}{dr} \tag{5-28}$$

Its integrated form with respect to the space variable r is

$$J_i = -\frac{D_e}{\delta} \left(C_i^{o} - C_i^{*} \right) \tag{5-29}$$

Comparing Equation (5-29) with Equation (5-26) here yields the expression of the effective diffusivity accounting for the effects of the electrical potential and the interactions among diffusing species

$$D_e = \frac{(n_i + 1)}{\left(C_i^{o} - C_i^{*} \right)} D_i a_i C_{NT}^{o} [1 - \Gamma] \tag{5-30}$$

Therefore, the flux expression can be written as

$$J_i = -\frac{(n_i + 1)}{\left(C_i^{o} - C_i^{*} \right)} D_i a_i C_{NT}^{o} [1 - \Gamma] \frac{dC_i}{dr} \tag{5-31}$$

A detailed derivation of the flux expression Equation (5-31) will be given in Appendix D.

With the assumption of linear driving force indicated in Equation (5-1), the average particle rate for *i*th species can be expressed as

$$\frac{d\bar{q}_i}{dt} = k_{L,i} R_i a_s (C_i^o - C_i^*) \tag{5-32}$$

Where R_i is the correction factor of non ionic mass transfer coefficient $k_{L,i}$ in the rate expression, which is given by:

$$Ri = \left(\frac{De}{D_i}\right)^{\frac{2}{3}} = \left[\frac{a_i(n_i+1)C_{NT}^o}{\left(C_i^o - C_i^*\right)}(1-\Gamma)\right]^{\frac{2}{3}} \tag{5-33}$$

For the spherical geometry of the resin, the specific surface a_s is

$$a_s = \frac{6}{d_p} \tag{5-34}$$

Then the particle rate after substitution of Equations (5-33) and (5-34) into Equation (5-32) can be expressed by Equation (5-35):

$$\frac{d\bar{q}_i}{dt} = 6\frac{k_{L,i}}{d_p}\left\{\frac{a_i(n_i+1)C_{NT}^o}{\left(C_i^o - C_i^*\right)}[1-\Gamma]\right\}^{\frac{2}{3}}(C_i^o - C_i^*) \tag{5-35}$$

The non-ionic mass transfer coefficient $k_{L,i}$ in the liquid side is determined by correlation in literature, for instance, the Dwivedi-Upadhyay correlation (Dwivedi and Upadhyay, 1977), which is given by:

$$J_d = \frac{1}{\varepsilon}\left(\frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}\right) \tag{5-36}$$

The mass transfer coefficient k_L can be related to the mass transfer factor J_d by the definition:

$$J_d = \frac{k_L}{u}(Sc)^{2/3} \tag{5-37}$$

This correlation will be used in this work for the calculation of mass transfer coefficient.

The interface concentration must be determined before Equations (5-31) and (5-35) can be solved. For the cation exchange, the interface concentrations of cationic species at both sides can be related by the selectivity coefficient. No explicit expression of the interface concentration, however, has been reported so far for a multicomponent system with arbitrary valence species. Franzreb et al. (1993) used the trial and error method to determine the total interfacial concentration and then its fractions of each ionic species involved. There seems no better method dealing with such systems. A similar way is used in this study and the detailed work is given in Appendix C. For systems with equal-valence species, however, the determination of the interfacial concentration is straightforward. While referencing the derivation in Appendix C, the procedure of determining the interface concentration can be illustrated as:

1. Use the binary selectivity coefficients to determine the interface concentration fractions of ionic species, given by

$$x_i^* = \frac{K_i^n y_i^*}{\sum_{j=1}^{n} K_j^n y_j^*} \tag{5-38}$$

Where *n* denotes the original free ion existing in the resin and the *n*th counter ion. In the film model the interface concentration fraction at the resin side y_i^* can be replaced by the average concentration fraction of the species in the resin phase.

2. As soon as the interface concentration fractions at the liquid side are obtained, Equation (5-27) and the definition in Equation (5-21) can be used to determine the total ionic interface concentration C_{NT}^{*}, which is

$$C_{NT}^{*} = \Gamma \cdot C_{NT}^{o} = \left[\frac{\sum_{i=1}^{n} D_i x_i^{o}}{\sum_{i=1}^{n} D_i x_i^{*}} \right]^{\frac{1}{n_i+1}} \cdot C_{NT}^{o} \qquad (5\text{-}39)$$

3. The interface concentration of each species can then be determined by applying the results of Equations (5-38) and (5-39).

$$C_i^{*} = x_i^{*} \cdot C_{NT}^{*} \qquad (5\text{-}39)$$

The rate of the cation exchange given in Equation (5-35) can be obtained readily as the interfacial concentrations are determined.

II. For anion resin

The situation of the anion exchange differs from that in Chapter IV due to the presence of other cations rather than the hydrogen ion considered in Chapter IV only. The presence of other cations raises pH in the solution. As a result, the dissociation degree of boric acid increases and higher borate concentrations can be expected. This is a general tendency. The pH range is wide from 6.0 to 9.0 (Bates, 1993; Riddle, 1993). Table V-1 gives part of the list.

Based on boron concentration and pH, the conditions in Table V-1 may be divided into two groups: one with higher boron concentration (above 400 ppm) and lower pH (less than 7); and the other with lower concentration and higher pH. Since the amount of borate depends on concentration and pH (See Figures V-1 to V-5), the various situations lead to the different consideration in development of the rate of anion exchange.

TABLE V-1

Influent Concentrations and the Other Conditions

Temperature °C	Boron (ppm)	Cation (ppm)	pH
40	2000	3.54	5.96
40	1600	2.77	6.08
40	1200	2.2	6.25
40	800	2.2	6.57
40	400	2.2	6.99
40	300	2.04	7.11
40	200	1.58	7.19
40	100	1.13	7.36
35	7	8.45	8.19
60	7	8.45	7.91

With higher boron concentration and lower pH, as discussed above, the intraparticle diffusion resistance of solutes was assumed more important than that on the liquid side so that the particle model is applied for the anion exchange. The general form of the average particle rate under the assumption of the linear driving force was indicated in Equation (5-2). Since it is hard to account for the rate of individual boron forms due to the unknown inter dependence, their magnitudes, and other resin conditions on time, the equivalent conversion rate is used in this work.

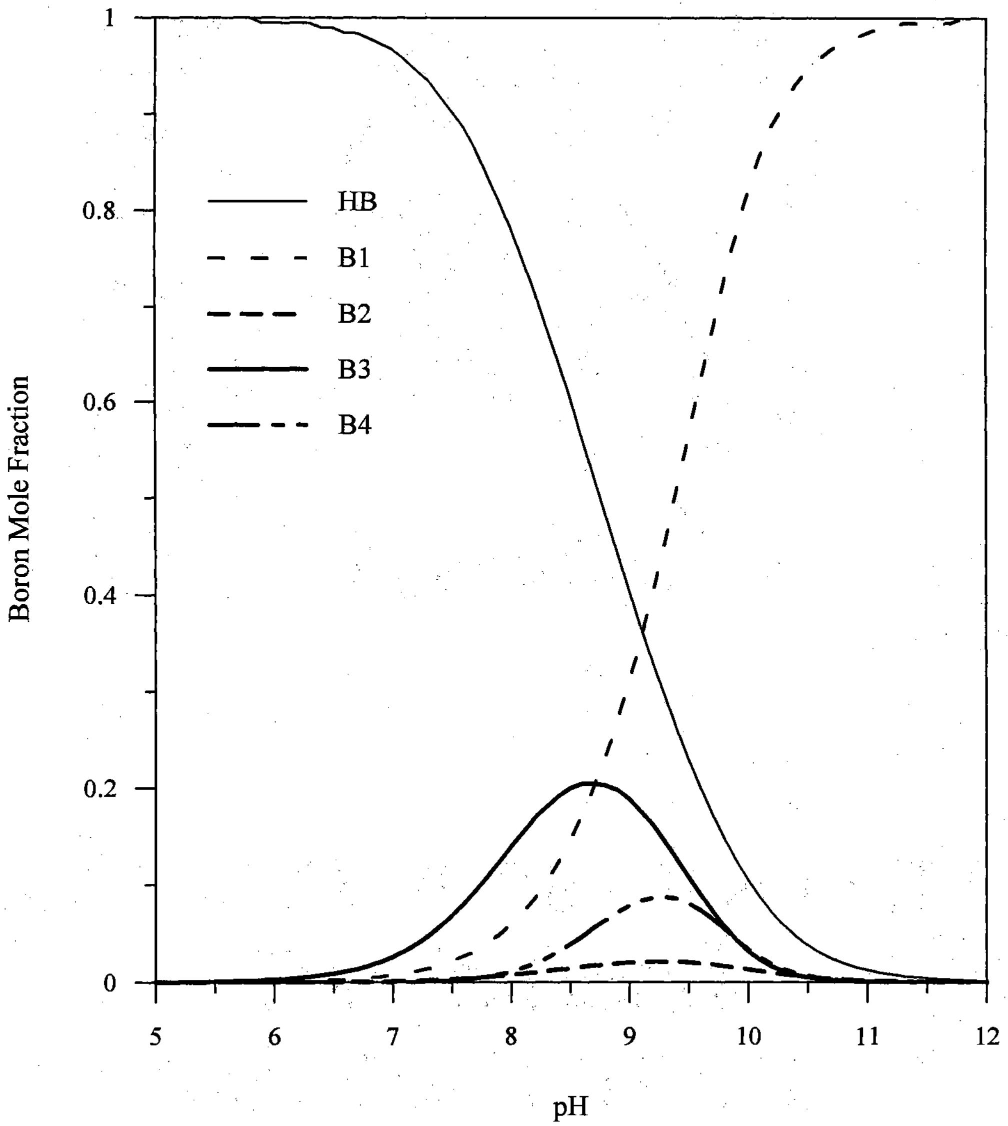

Figure V-1 Distribution of boron forms in boric acid solution as a function of the total boron concentration, temperature, and pH with the conditions: Boron = 2000 ppm, T = 40 C, (HB - boric acid, B1 - monoborate, B2 - dimer, B3 - trimer, B4 - tetramer borates).

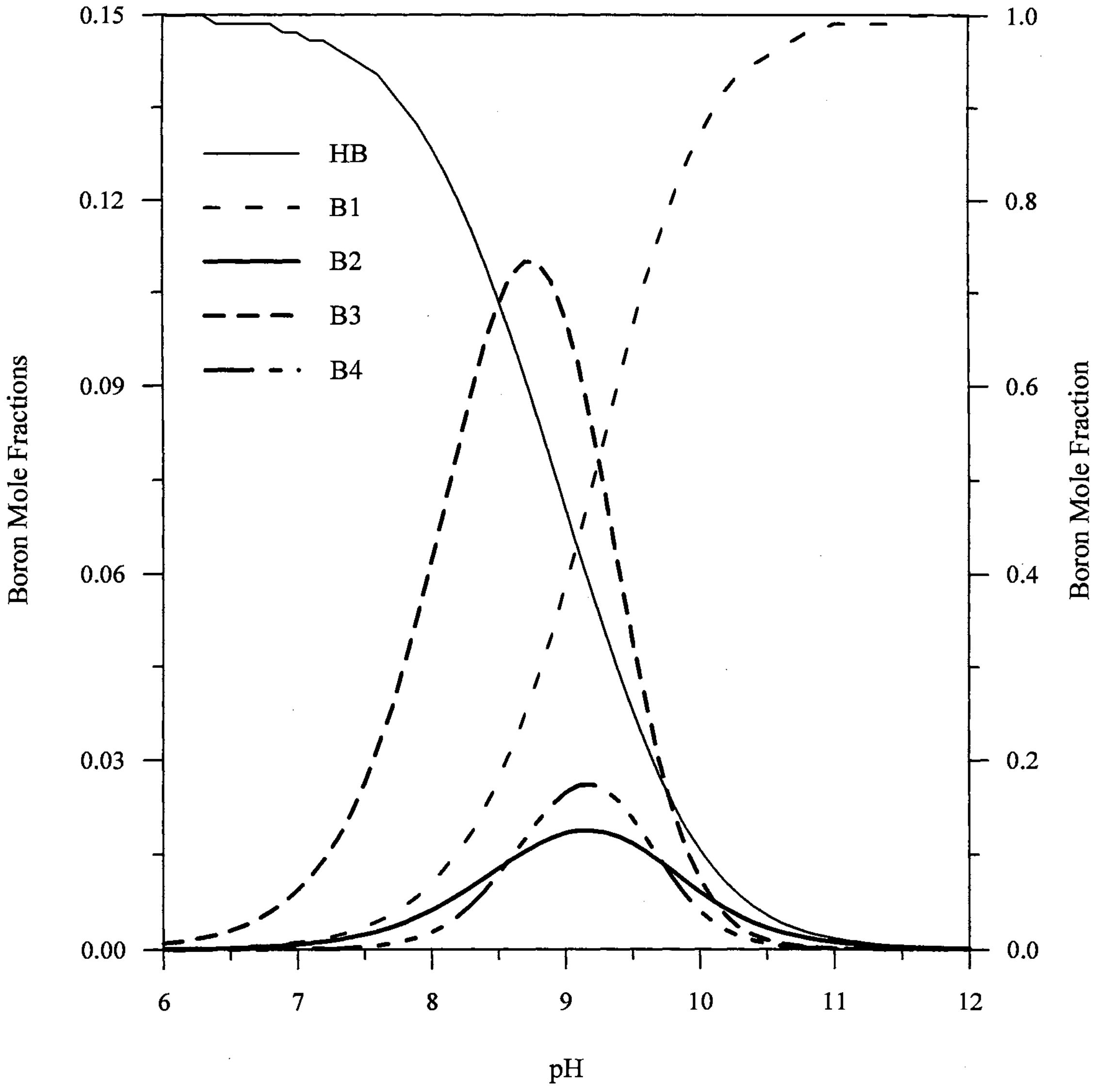

Figure V-2 Distribution of boron forms in solution as a function of the total boron concentration, temperature, and pH with the conditions: Boron = 1200 ppm, T = 46 C. (HB-boric acid, B1- monoborate, use right side y-axil; B2-dimer, B3-trimer, B4-tetramer borates, use left side y-axil)

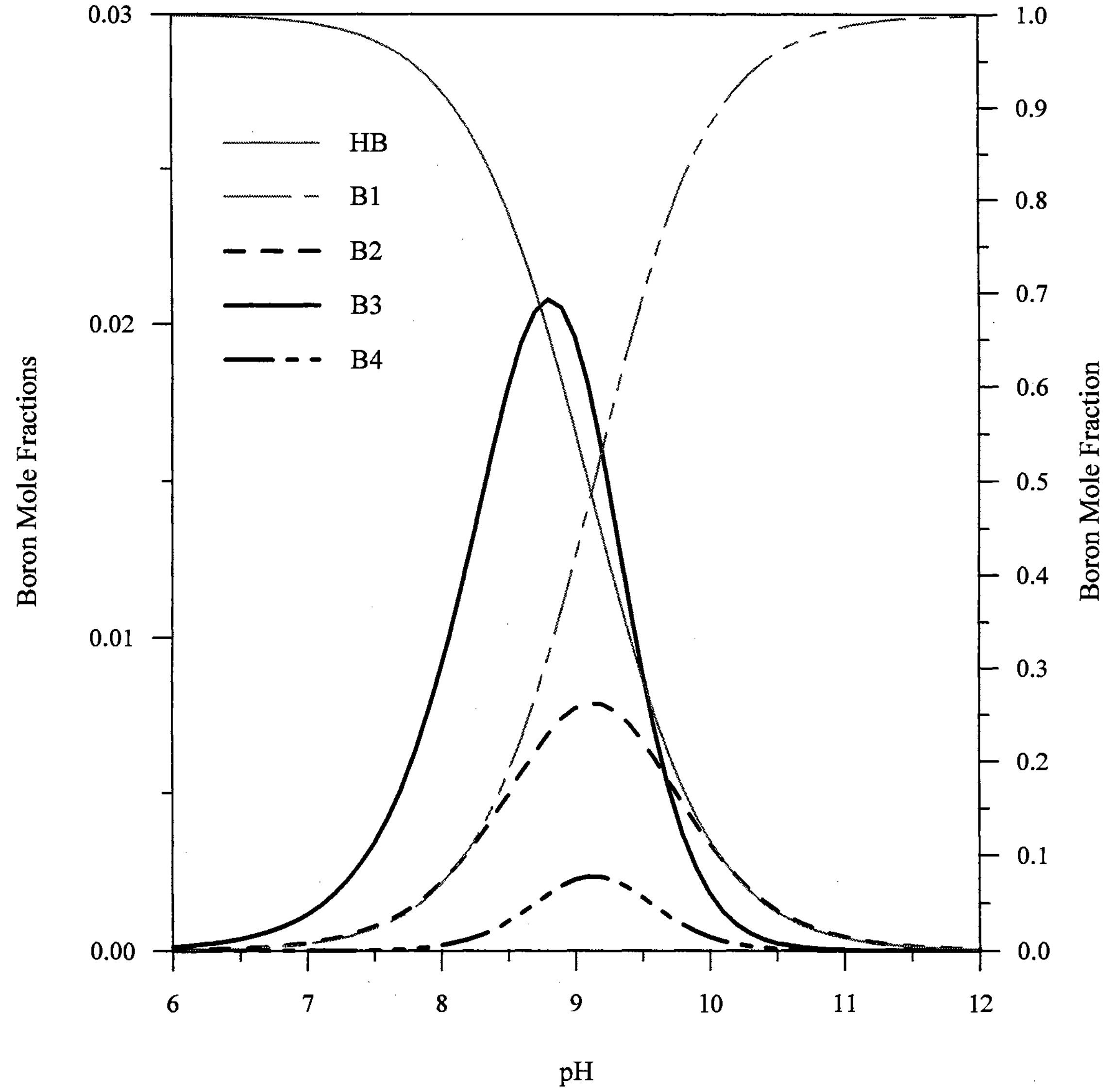

Figure V-3 Distribution of boron forms in boric acid solution as a function of the total boron concentration, temperature, and pH with the conditions: Boron = 400 ppm, T = 40 C. (HB-boric acid, B1-monoborate, use the right y-axil; B2-dimer, B3-trimer, B4-tetramer, use the left y-axil)

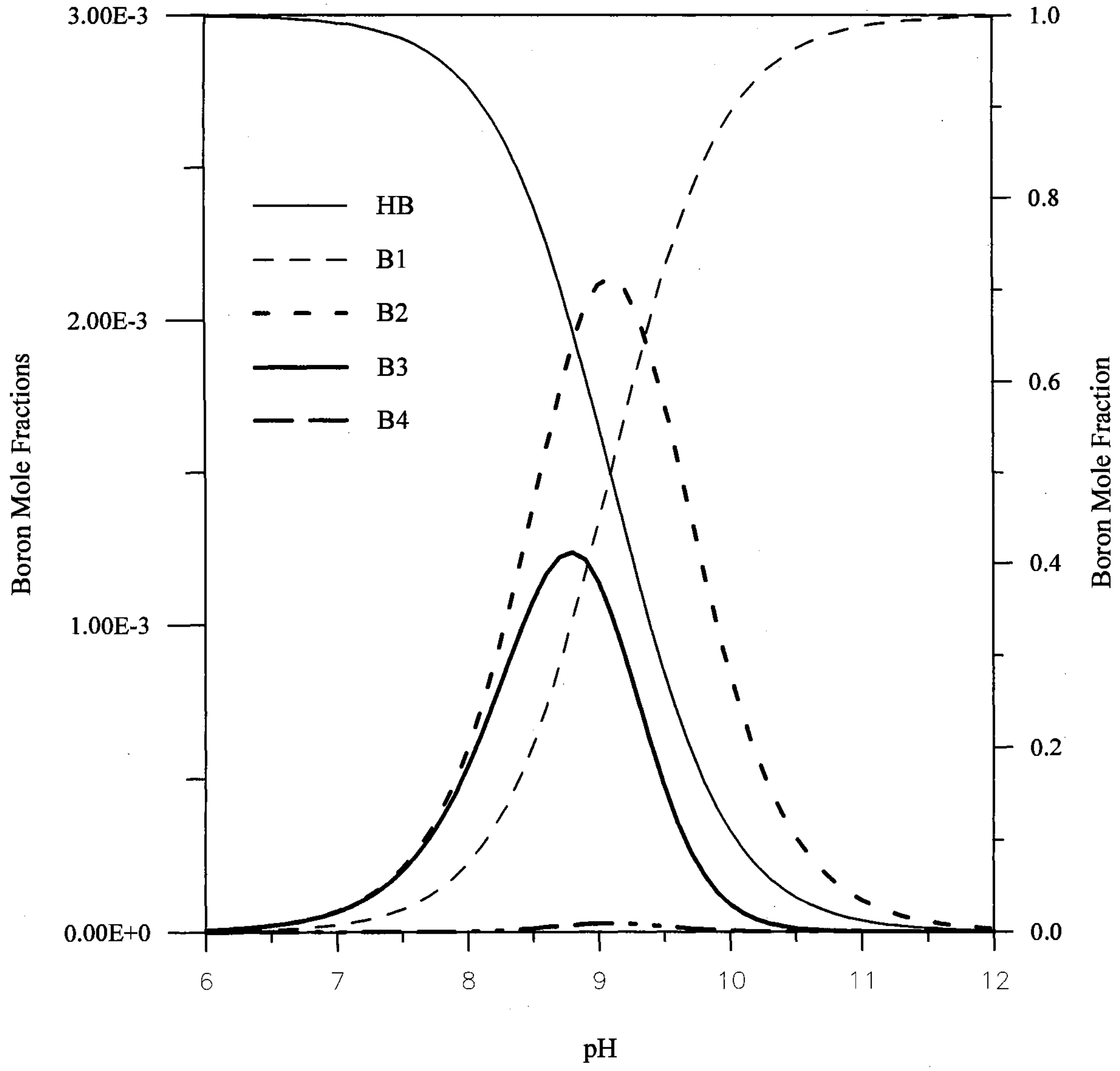

Figure V-4 Distribution of boron forms in solution as a function of the total boron concentration, temperature, pH value with the conditions, Boron = 100 ppm, T = 46 C. (HB-boric acid, B-monoborate, use right side y-axil; B2-dimer, B3-trimer, B4-tetramer borates, use left side y-axil)

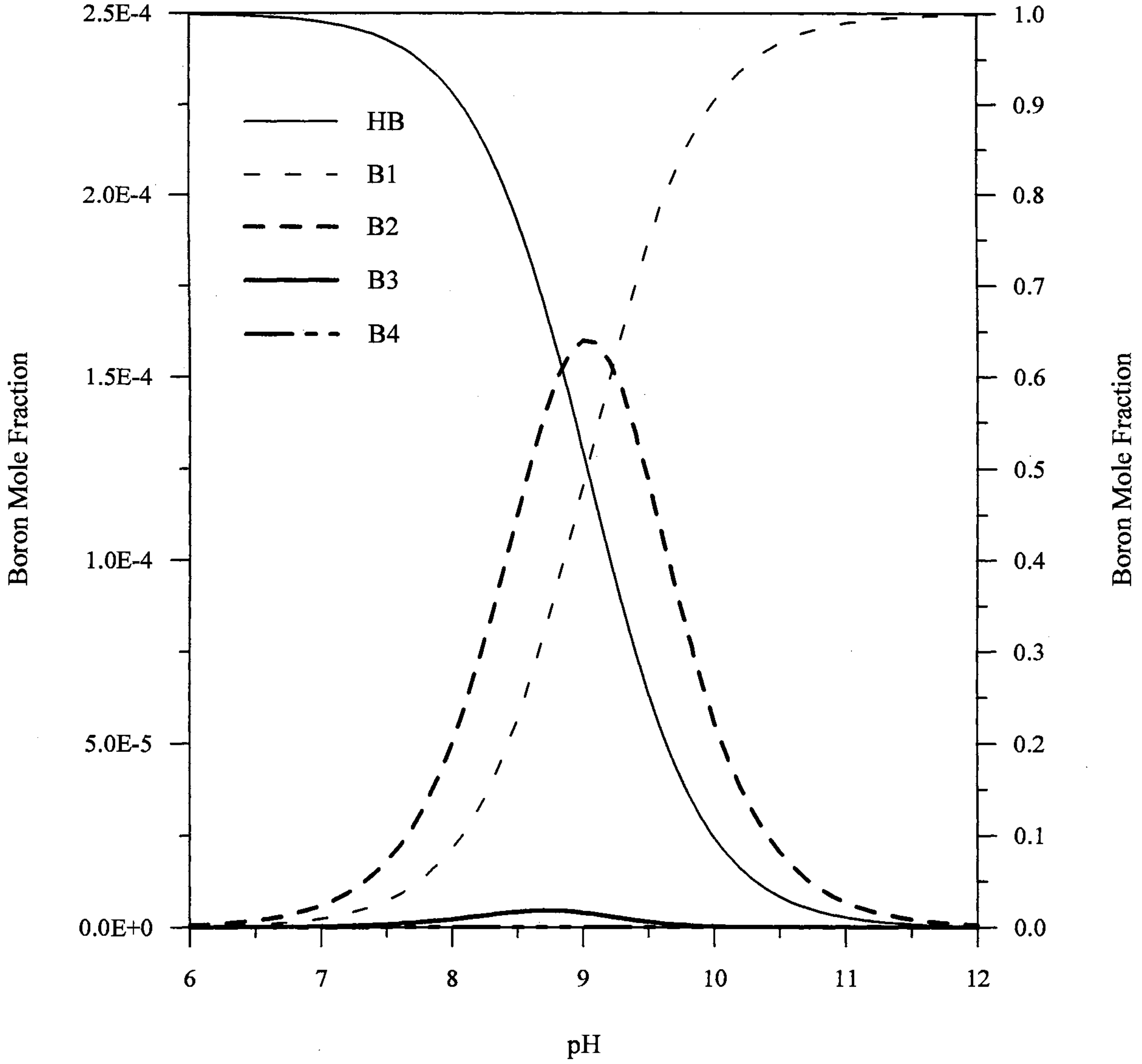

Figure V-5 Distribution of boron forms in boric acid solution as a function of the total boron concentration, temperature, and pH with the conditions: Boron=7 ppm, T=60 C. (HB-boric acid, B1-monoborate, use the right y-axil; B2-dimer, B3-trimer, B4-tetramer borates, use the left y-axil)

The rate may be written by

$$\frac{d\bar{q}_B}{dt} = k_{p,B} \cdot a_s \cdot (q_B^* - \bar{q}_B) \qquad (5\text{-}40)$$

where the product of $k_{p,B}a_s$ can be given approximately by:

$$k_{p,B}a_s = 60\frac{\bar{D}_{eff,B}}{d_p^2} \qquad (5\text{-}41)$$

For the other species, except boron forms, the rate expression is given by

$$\frac{d\bar{q}_i}{dt} = 60\frac{\bar{D}_{eff,i}}{d_p^2} \cdot (q_i^* - \bar{q}_i) \qquad (5\text{-}42)$$

Then the total particle rate is given by the summation of Equations (5-40) and (5-42):

$$\frac{d\bar{q}}{dt} = \frac{60}{d_p^2} \cdot \left[\bar{D}_{eff,B}(q_B^* - \bar{q}_B) + \sum \bar{D}_{eff,i}(q_i^* - \bar{q}_i)\right] \qquad (5\text{-}43)$$

The selectivity coefficient relation is a common way to determine the interface concentrations of species. The relation reflects a type of the Langmuir equilibrium. It is not consistent with the equilibrium relation suggested for boron sorption in Chapter III, which is closer to Freundlich's isotherm expression. This situation makes the sorption equilibrium on the anion resin in such system more complicated. Due to the lack of experimental information on the determination of equilibrium, however, Equation (3-28) is a good approximation to determine the interfacial boron concentration for the cases of predominant boron concentration in solution. The relation of the selectivity coefficient is used for other species. For comparable boron concentration with that of the other species, the selectivity coefficient is still recommended to determine the interfacial concentrations of species involved.

According to Equation (3-28), the interface concentration of boron can be expressed by

$$q_B^* = a \cdot (C_B^o)^\eta \exp[-(bT + cT^2)] \tag{5-44}$$

while the interface concentration of the other species can be obtained approximately by

$$q_i^* = Q \frac{K_{OH}^i C_i^o}{\sum K_{OH}^i C_i^o + q_B^*} \tag{5-45}$$

For the situations with low boron concentration and higher pH, the borate concentration increases to a comparable level with the boric acid concentration. Since the concentration of borates at the interface is relative high due to the ionization of boric acid, the diffusion resistance of borates in the liquid increases so that it becomes important to the exchange rate.

Equations (5-31) and (5-35) derived from the Nernst-Planck equation and the linear driving force can also be applied to the determination of the flux and the exchange rate of anionic species in the liquid film. The diffusion of the neutral molecule – boric acid – is described by applying Fick's first law. This is

$$J_{HB} = -D_{HB} \frac{dC_{HB}}{dr} \tag{5-46}$$

The average rate of exchange for boric acid is

$$\frac{d\overline{q}_{HB}}{dt} = k_{L,HB} a_s \left(C_{HB}^o - C_{HB}^* \right) \tag{5-47}$$

The concentrations of anionic species, boric acid, and hydrogen in the bulk solution should be determined simultaneously by solving a set of algebra equations resulting from the mass balance, charge balance, and the dissociation relationships of boric acid and water. The procedure to obtain the concentrations of these species is given in Appendix A.

The interface concentration of total boron may be determined by modifying Equation (3-28).

$$C_{BT}^{*} = \left[\frac{\overline{q}_B}{a \cdot \exp(bT + cT^2)} \right]^{\frac{1}{\eta}} = \overline{Y}_{BT}^{1/\eta} \cdot C_{BT}^{f} \qquad (4\text{-}48)$$

The previous determination of the interface concentration for each species is difficult due to lack of information about the degree of boric acid ionization, which reflects the conditions inside resin with time. An approximate estimation, by assuming the complete conversion of boric acid to monoborate at the interface, may be obtained based on the relationship of the selectivity coefficients, which is expressed as:

$$C_i^{*} = C_T^{*} \frac{K_{OH}^{i} \overline{Y}_i^{o}}{\sum K_{OH}^{i} \overline{Y}_i^{o}} \qquad (5\text{-}49)$$

These ionic species include the forms of OH^-, $B(OH)_4^-$, $B_3(OH)_{10}^-$ and the other ionic species, chloride in this case. The result of this assumption leads to zero interfacial boric acid concentration.

Column Material Balance

The concentration profile within the column and its effluent concentration history are determined by the overall column material balance obtained from the equation of continuity under the assumptions made for this system. As mentioned above, plug flow is assumed and the effects of axial dispersion are neglected in the derivation of the column material balance. Based on these assumptions, for a steady state flow system, the column material balance for each species yields the well-known relationship

$$\frac{\partial C_i}{\partial t}+f_r\frac{(1-\varepsilon)}{\varepsilon}\frac{\partial \overline{q}_i}{\partial t}+\frac{u_s}{\varepsilon}\frac{\partial C_i}{\partial z}=0 \tag{5-50}$$

This form needs to be simplified further for computation purpose. Follow Kataoka to define dimensionless variables in time and distance as:

$$\tau=\frac{k_i C_T^f}{d_p Q}\left(t-\frac{\varepsilon z}{u_s}\right) \tag{5-51}$$

and

$$\xi=\frac{k_i(1-\varepsilon)}{d_p u_s}z \tag{5-52}$$

The form of column material balance expressed in dimensionless variables is given in Equation (5-53).

$$\frac{\partial X_i}{\partial \xi}+f_r\frac{\partial Y_i}{\partial \tau}=0 \tag{5-53}$$

Since there are multiple species involved in the system and the material balance needs to be solved using the same steps in τ and ξ, a reference species is chosen (chloride in this work) and dimensionless variables in terms of the reference species are used, which are defined as:

$$\tau=\tau_r=\frac{k_r C_T^f}{d_{pa} Q_a}\left(t-\frac{\varepsilon z}{u_s}\right) \tag{5-54}$$

and

$$\xi=\xi_r=\frac{k_r(1-\varepsilon)}{d_{pa} u_s}z \tag{5-55}$$

Equation (5-53) can then be expressed as follows:

$$\frac{\partial X_i}{\partial \xi_r} + \mathrm{FRC}\frac{\partial Y_i}{\partial \tau_r} = 0 \tag{5-56}$$

Correspondingly, the average particle rate of species can be corrected similarly in terms of the reference species.

For the other anions

$$\frac{d\overline{Y}_i}{d\tau_r} = \frac{6k_i}{k_r}\left\{\frac{a_i(n_i+1)C_T^o}{\left(C_i^o - C_i^*\right)}\left[1-\Gamma\right]\right\}^{\frac{2}{3}}(X_i^o - X_i^*) \tag{5-57}$$

and for cations

$$\frac{d\overline{Y}_i}{d\tau_r} = \frac{6k_i}{k_r}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c}\left\{\frac{a_i(n_i+1)C_T^o}{\left(C_i^o - C_i^*\right)}\left[1-\Gamma\right]\right\}^{\frac{2}{3}}(X_i^o - X_i^*) \tag{5-58}$$

Use the cation resin volume fraction FRC replacing f_r for cationic species and the anion resin volume fraction FRA replacing f_r for anionic species respectively in computation. The constant FRC and FRA must be specified for any given mixed bed column. The detailed derivation of Equations (5-53) and (5-56) to (5-57) is given in Appendix E.

Computation Results and Discussion

The system chosen for testing is from the Sizewell CVCS plant, Nuclear Electric in England. Main details of the system are listed in Table V-II.

Table V-II

Conditions of Test Example

Items	Values	Items	Values
Circuit Volume	335 m^3	Cation Resin Vol.	0.283 m^3
Bed Volume	0.85 m^3	Cation Capacity	2.0 eq/dm^3
Bed Diameter	0.882 m	Cation Diameter	1.0 mm
Flow Rate	10 – 17 m^3/hr	Anion Resin Vol.	0.567 m^3
Temperature	40 – 46 °C	Anion Capacity	1.0 eq/dm^3
Boron	1200 ppm	Anion Diameter	0.66 mm
Lithium	2.2 ppm	Chloride	0.01-1.0 ppm
Sodium	0-0.5 ppm		

The resins are in H-OH forms. Selectivity data are from Riddle (1993).

Column dynamics

Figures V-6 and V-7 show the concentration distributions both in the bulk liquid and in the resin phases through the mixed bed. In the bulk liquid, the concentration front separates as two distinguished sections of cations and anions due to much higher feed concentrations of anions and boric acid and relatively low concentration of cations in the feed solution. Examine the concentration fronts of boron and chloride in Figure V-6. The chloride concentration front is much sharper than that of boron, due to the favorableness of chloride to boron sorption on the OH form strong anion resin. However,

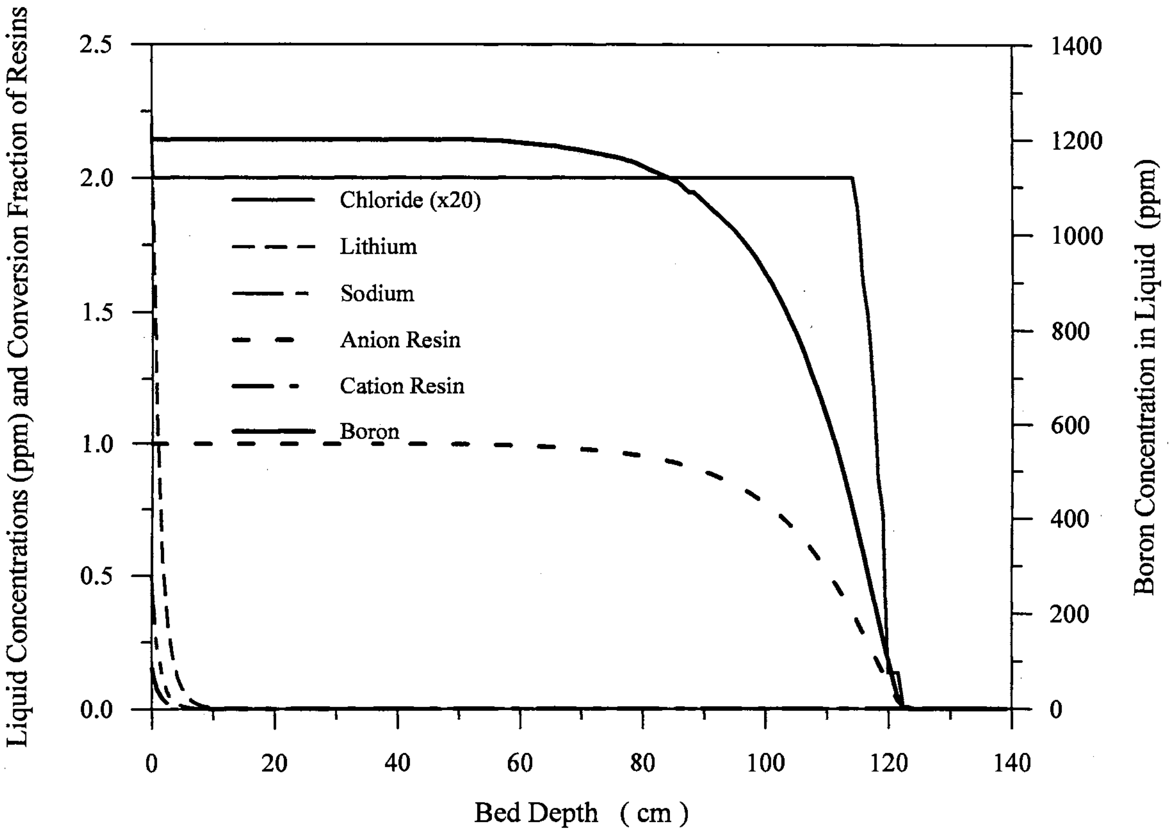

Figure V-6(a) Column dynamics of mixed bed ion exchange with lithium, boron chloride, and sodium solution under the conditions: T = 40 C, Flow Rate = 10 M3/hr, Boron = 1200 ppm, Chloride = 0.1 ppm, Lithium = 2.2 ppm, and Sodium = 0.5 ppm.

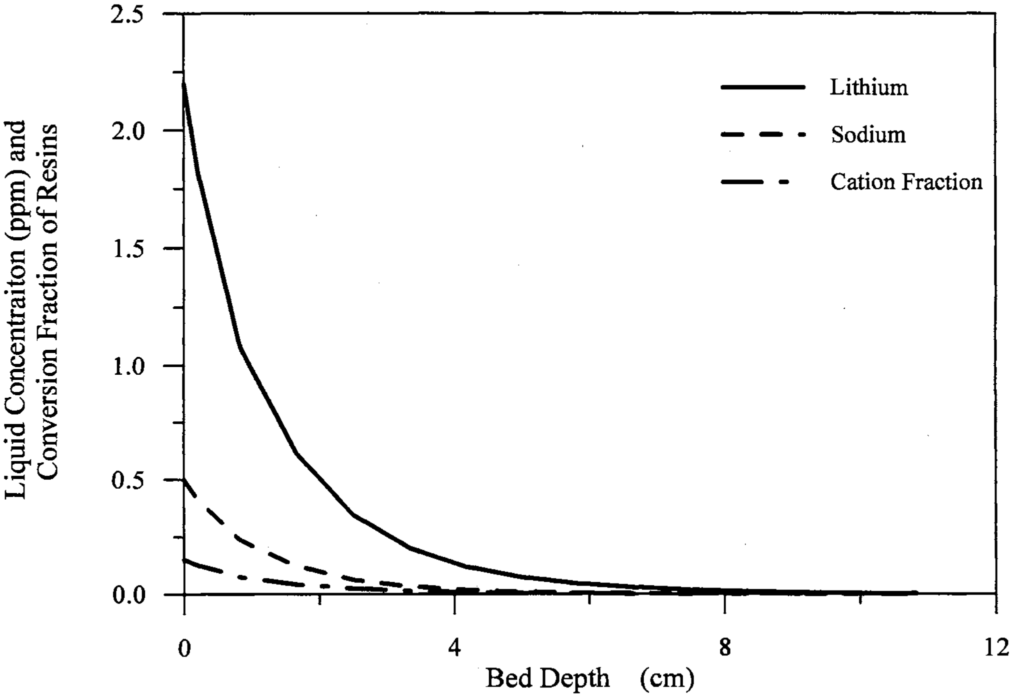

Figure V-6(b) Detailed on lithum, sodium, and cation resin conversion in Figure V-6(a)

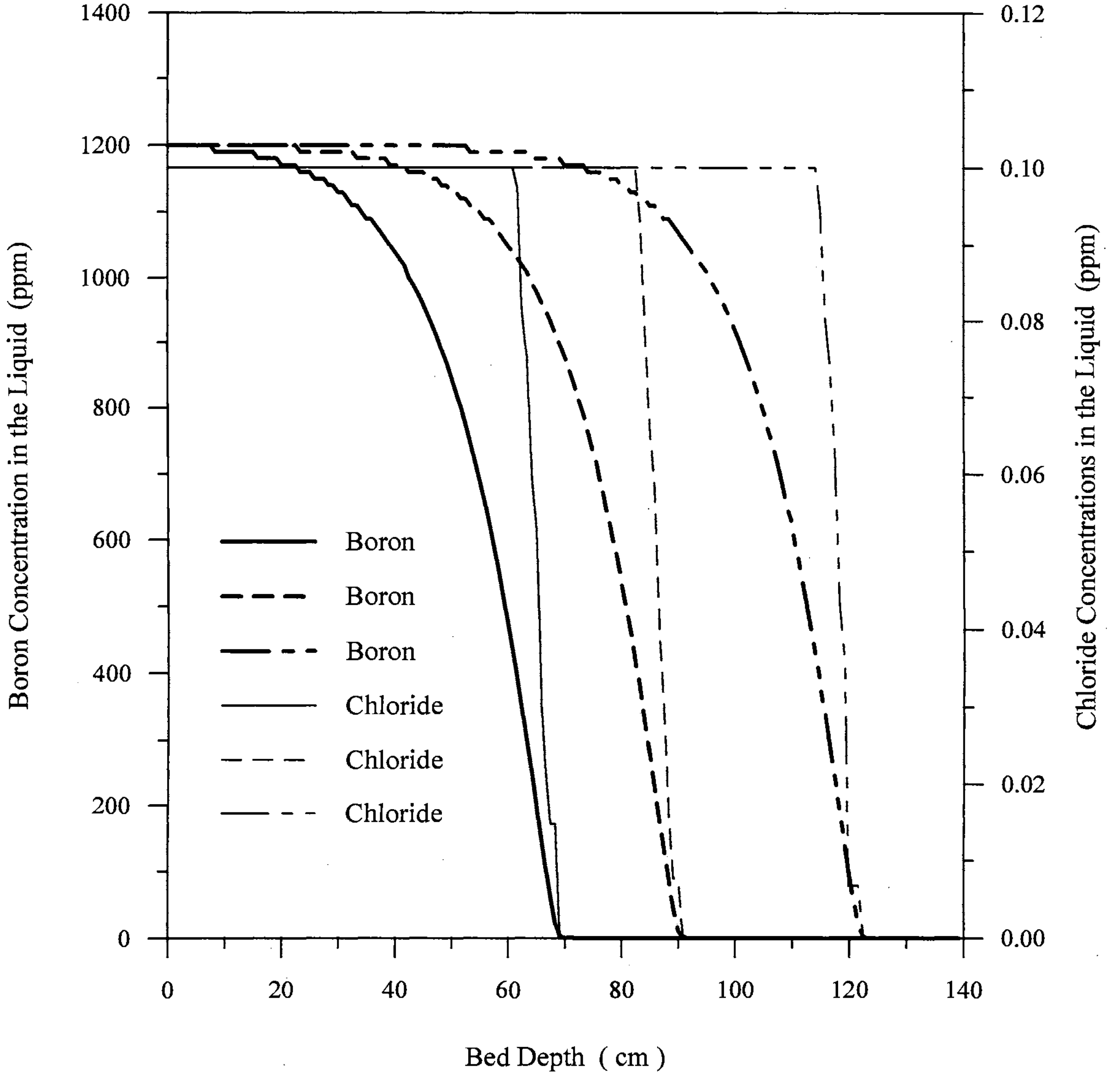

Figure V-7 Distributions of boron and chloride in the bulk liquid in the mixed bed ion exchange column under the conditions: Flow Rate = 10 M3/hr T = 40 C, Boron = 1200 ppm, Chloride = 0.1 ppm, Sodium = 0.5 ppm Lithium = 2.2 ppm; (lines from right to left indicating at the time 35%, 50%, and 70% of the total capacity exhausted).

the ionization reaction of boric acid results in high counterion concentration at the interface, which decreases chloride interfacial concentration. This is the reason that the chloride concentration front moves ahead of that for boron. By contrast, the front of lithium concentration in the bulk liquid is ahead of that for sodium due to the favorableness of sodium to lithium sorption on the cation resin.

The curvature of concentration fraction in the anion resin is similar to that of boron concentration in the bulk liquid. This is due to much higher boron concentration in the bulk liquid and the predominant boron sorption during the process. In other words, the behavior of boron sorption determines the behavior of the column dynamics of the system. This point is confirmed by the effluent concentration history given in Figure V-8.

Effects of concentrations

The effects of chloride concentration change on breakthrough are given in Figures (V-9) to (V-11). The effluent leakage of both cationic and anionic species increases with increasing chloride concentration. The higher the chloride concentration in the feed solution, the clearer the tendency, as indicated in these figures. Since the exchange of chloride on the anion resin is more favorable than boron, chloride reaches the breakthrough point immediately as boron is about to breakthrough.

With the breakthrough of boron, the concentration of boric acid in the bulk liquid increases dramatically so that the concentration of hydrogen is very high. The higher hydrogen concentration is not favorable for the exchange of cationic species on the cation resin and results in the sharp increase in cation leakage.

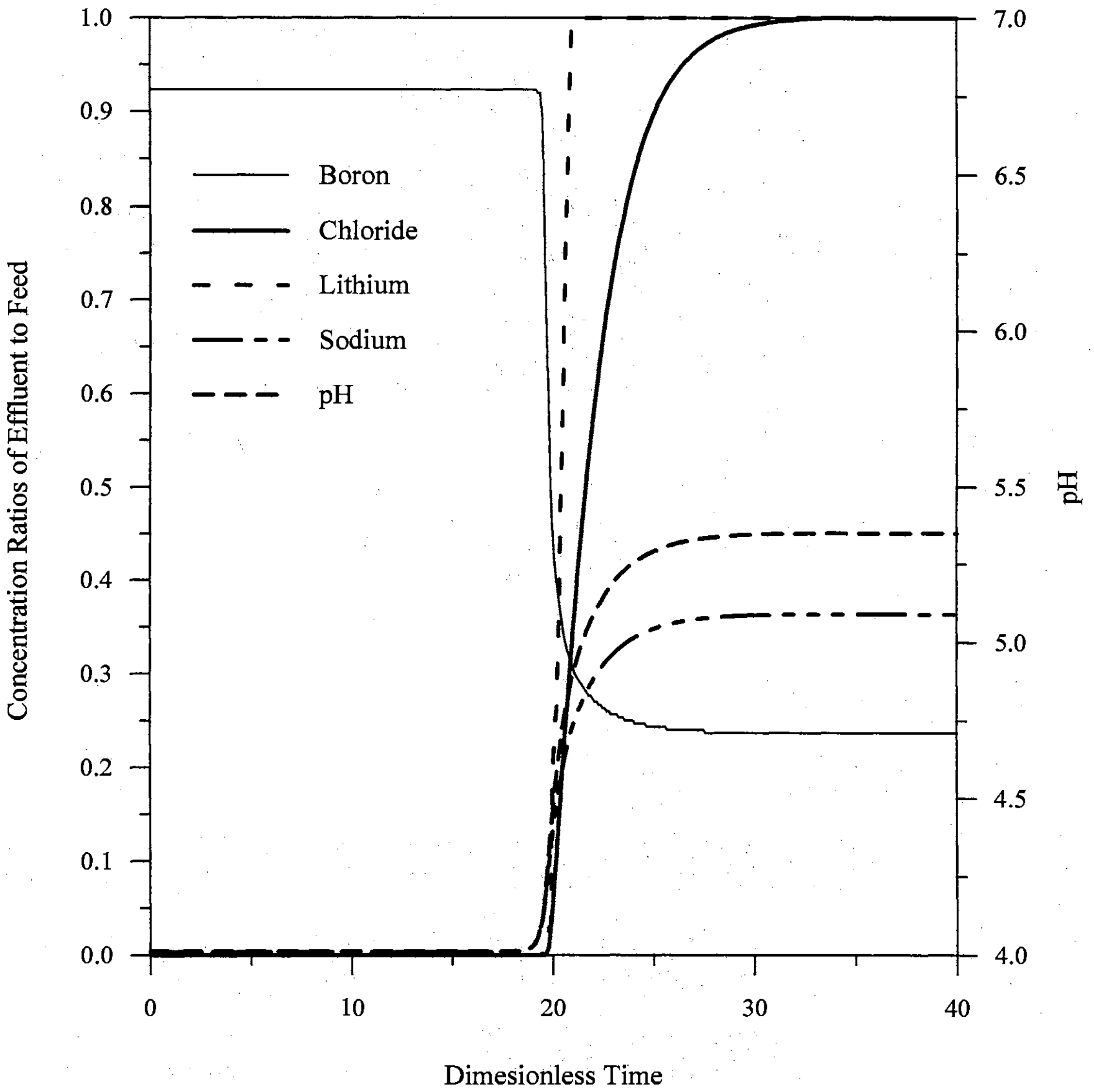

Figure V-8 History of effluent concentrations and pH from mixed bed column with the conditions: Flow Rate = 10 M3/hr, Temperature = 40 C, Boron = 1200 ppm, Chloride = 0.1 ppm, Lithium = 2.2 ppm, and Sodium = 0.5 ppm

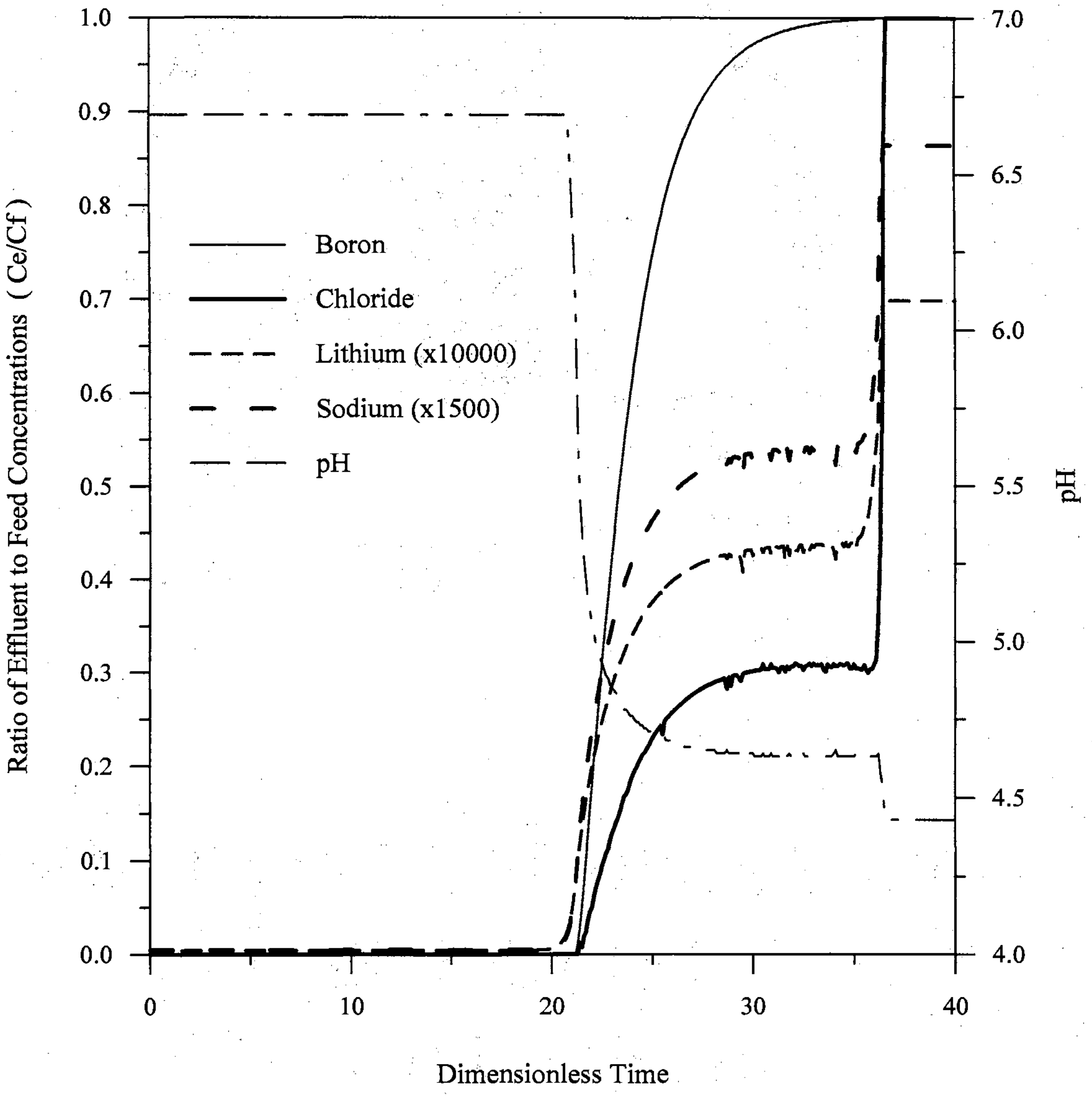

Figure V-9 History of effluent concentrations and pH from mixed bed column with the conditions: Flow Rate = 10 M3/hr, Temperature = 46 C Boron = 1200 ppm, Chloride = 1.0 ppm, Lithium = 2.2 ppm, and Sodium = 0.5 ppm.

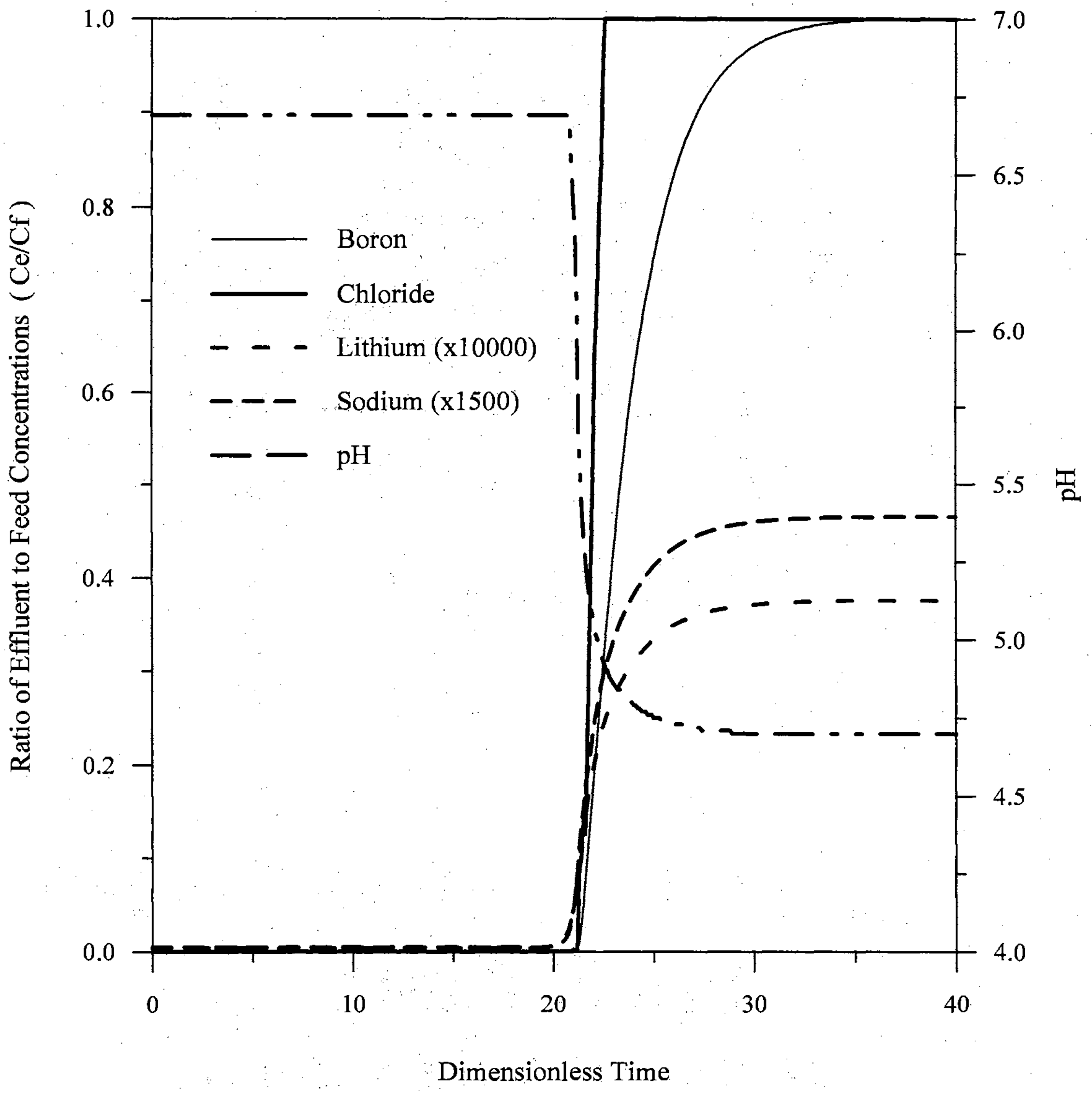

Figure V-10 History of effluent concentrations and pH from mixed bed column with the conditions: Flow Rate = 10 M3/hr, Temperature = 46 C Boron = 1200 ppm, Chloride = 0.1 ppm, Lithium = 2.2 ppm, and Sodium = 0.5 ppm.

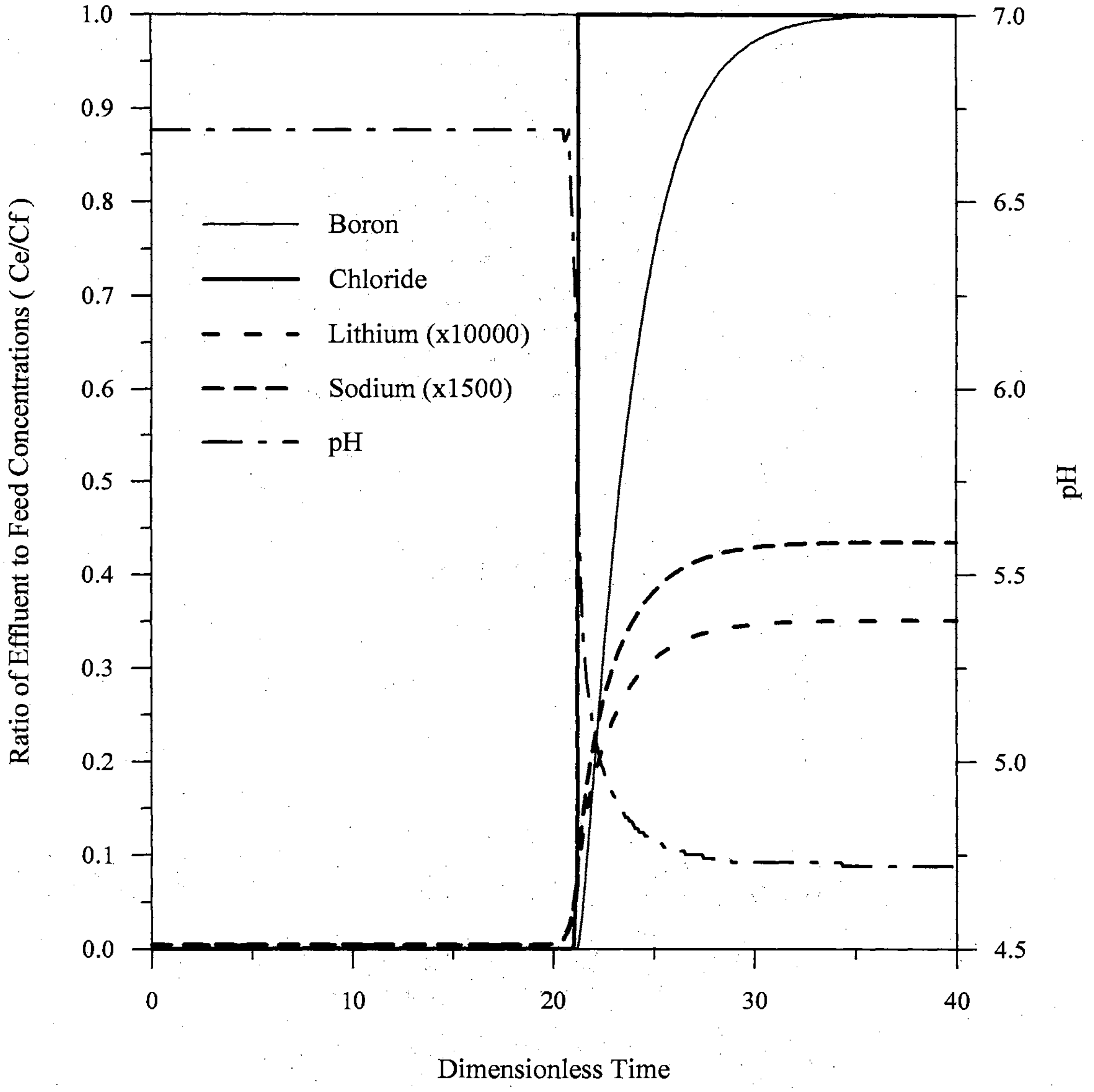

Figure V-11 History of effluent concentrations and pH from mixed bed column with the conditions: Flow Rate = 10 M3/hr, Temperature = 46 C Boron = 1200 ppm, Chloride = 0.01 ppm, Lithium = 2.2 ppm, and Sodium = 0.5 ppm.

As the feed concentration of chloride increases, the equilibrium concentration of chloride on the resin phase increases. The favorable situation for chloride in sorption on the anion resin leads to the replacement of boron by chloride in the resin phase until the equilibrium concentration of chloride is reached. With higher chloride feed concentration, therefore, a flatter chloride breakthrough curve can be expected. Continuously increasing the chloride feed concentration, there appears a concentration platform of chloride during boron breakthrough, which is shown in Figure (V-9). Moreover, with the testing conditions given, the lower the chloride feed concentration, the sharper the breakthrough curve of chloride, which can be obtained from the comparison of the breakthrough curves of chloride in Figures (V-9) to (V-11).

As the boron feed concentration decreases, the particle rate of boron exchange increases. The increase of the particle rate results from the decrease of the particle resistance to boron diffusion and the relative increase of the sorption capacity of the anion resin. The latter reason is because the decrease of the sorption capacity is proportional to a fractional exponential of the boron feed concentration, which was given in Equation (3-28). The decrease of 50 % in the feed concentration of boron, for example, only leads to the decrease of about 11 % in the sorption capacity of the anion resin toward boron under the same temperature. That also gives the explanation of the breakthrough point not proportional to the feed concentration of boron (Figure V-12).

The sharper boron breakthrough curve in Figure V-12 corresponding to the lower boron feed concentration reflects this increase of the particle rate. This also implies that the film diffusion will be the dominant controlling factor in the exchange process as the boron feed concentration continues to decrease. Meanwhile, in the resin phase, it is expected that the chloride equilibrium concentration increases with a decrease of the boron feed concentration, which leads to a flatter breakthrough curve of chloride with lower feed concentration of boron as discussed above.

Effects of temperature and flow rate

Figure V-13 shows the effect of temperature on boron sorption. As discussed in previous chapters, the increase of temperature results in the decrease of the boron sorption capacity of the anion resin. Earlier boron breakthrough corresponding to higher temperature is expected. Moreover, as the temperature increases, the overall rate of the ionization reaction of boric acid decreases. Slower diffusion of boric acid inside the anion resin leads to a decrease of the exchange rate. Correspondingly, the boron breakthrough curve becomes flatter due to the decrease of the particle rate of exchange.

The effect of flow rate on the rate of exchange is through the change of the mass transfer coefficient. The mass transfer coefficient increases with increasing flow rate. The overall effect of flow rate on the particle rate of exchange in this system is not significant comparing to that by the change of temperature and the feed concentration of boron.

It must be pointed out that effects of misdistribution of flow rate and eddy dispersion on exchange rate have not been considered in the model by the simplification of a plug flow pattern . The plug flow is an ideal flow pattern with uniform motion of liquid and, consequently, the bulk solution concentration is only a function of time and axial coordinator and is uniform in any horizontal plane in the column. In fact, misdistribution of flow exists in packet bed due to packing irregularities (and irregular packing material

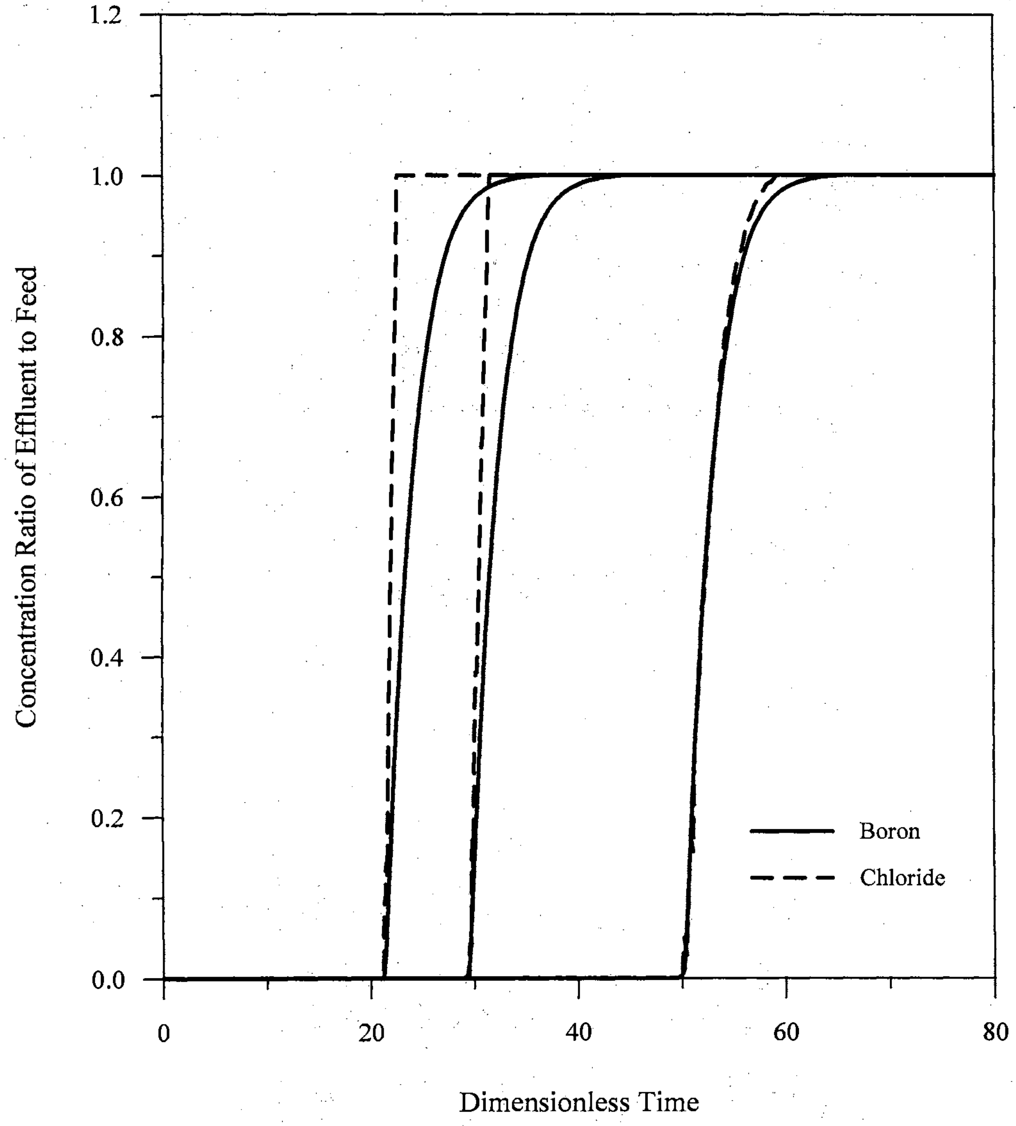

Figure V-12 Effects of the feed concentration of boron on the breakthrough curves of boron and chloride (The three sets of lines from right to left represent the feed concentration of boron at 1200 ppm, 800 ppm, and 400 ppm, respectively, chloride = 0.1 ppm).

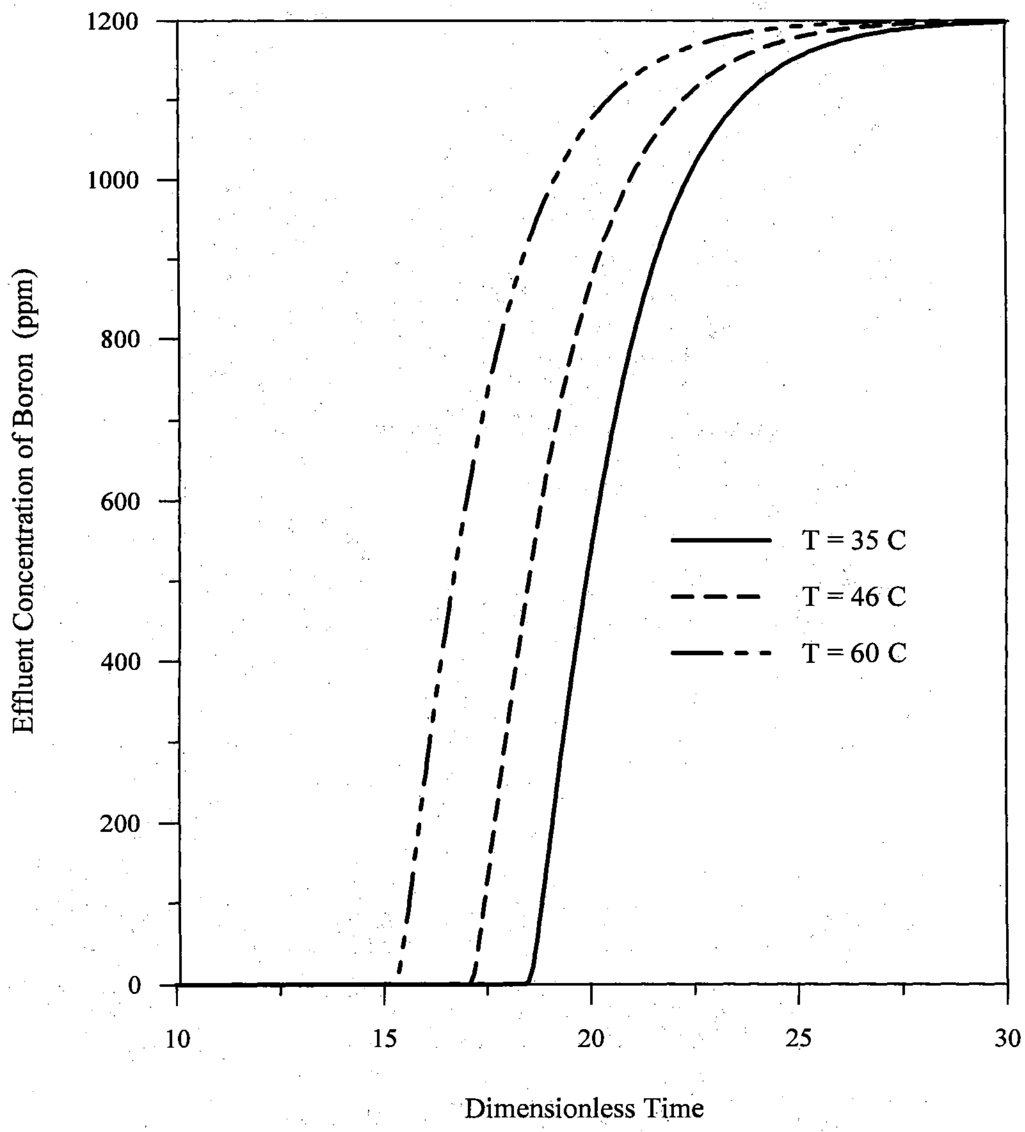

Figure V-13 Effects of temperature on the boron sorption in mixed bed ion exchange under the conditions: Flow Rate = 10 M3/hr, Boron = 1200 ppm, Chloride = 0.1 ppm, Lithium = 2.2 ppm, Sodium = 0.5 ppm.

for mixed bed), density and viscosity differences between adjacent bands. The neglect of dispersion term resulting from a plug flow in column material balance obviously leads to faster exchange rate and earlier breakthrough in ion exchange bed operation. For detailed discussion of hydrodynamic effects on exchange rate, both axial and eddy dispersions should be considered in model.

Conclusion

The mixed bed ion exchange model with the H-OH form resins for boron solution has been developed in this Chapter. The features of boron sorption on the ion exchange resin reflected by the calculation results of the model have been confirmed by the study in the previous Chapters. From this study, the effects of temperature and concentration on the process are:

- Higher chloride feed concentration leads to a decrease of the rate of exchange for boron and results in higher effluent leakage, not only of boron but also cationic species.
- The increase of sodium feed concentration leads to an increase of lithium leakage in the effluent.
- High temperature decreases the particle rate of exchange.
- Lower chloride feed concentration gives better boron sorption performance in mixed beds.

REFERENCES

Bates, C. (1993). SIZEWELL B primary circuit CVCS modeling, private communication.

Blickenstaff, R. A., Wagner, J. D. and Dranoff, J. S. (1967a). The kinetics of ion exchange accompanied by irreversible reaction. I. Film diffusion controlled neutralization of a strong acid exchanger by strong bases, J. Phys. Chem., 71 (5), 1665-1669.

Blickenstaff, R. A., Wagner, J. D. and Dranoff, J. S. (1967b). The kinetics of ion exchange accompanied by irreversible reaction. II. Intraparticle diffusion controlled neutralization of a strong acid exchanger by strong bases, J. Phys. Chem., 71 (5), 1670-1674.

Caddell, J. R. and Moison, R. L. (1954). Mixed-bed deionization at high flow rates Chem. Eng. Prog., Symp. Ser., 50 (14), 1-5.

Cohen, P. (1969). Water coolant Technology of Power Reactors. Gordon and Breach Science Publishers, New York.

Dwivedi, P. N. and Upadhyay, S. N. (1977). Particle-fluid mass transfer in fixed and fluidized beds. Ind. Eng. Chem., Process Des. Dev., 16(2), 157-165.

Franzreb, M., Höll, W. H., and Eberle, S. H. (1995). Liquid-phase mass transfer in multicomponent ion exchange. 2. Systems with irreversible chemical reactions in the film. Ind. Eng. Chem. Res., 34, 2670-2675.

Frisch, N. W. and Kuni, R. (1960). Kinetics of mixed-bed deionization: I. A.I.Ch.E. J., 6, 640.

Haub, C. E. and Foutch, G. L. (1986a). Mixed bed ion exchange at concentrations approaching the dissociation of water. 1. Model development. Ind. Eng. Chem. Fundam., 25, 373-381.

Haub, C. E. and Foutch, G. L. (1986b). Mixed bed ion exchange at concentrations approaching the dissociation of water. 2. Column model Applications. Ind. Eng. Chem. Fundam., 25, 381-385.

Helfferich, F. G. (1965). Ion-exchange kinetics. V. Ion Exchange Accompanied by Reactions. J. Phys. Chem., 69 (4), 1178-1187.

Helfferich, F. G. and Hwang, Y. L. (1985). Kinetics of acid uptake by weak base anion exchangers: Mechanism of proton transfer. A.I.Ch.E. SYMP. Ser., 81 (242), 17-27.

Hwang, Y. L. and Helfferich, F. G. (1987). Generalized model for multispecies ion exchange kinetics including fast reversible reactions. Reactive Polymers, 5, 237 -253.

Kalinichev, A. I., Semenovskaya, T. D., Kolotinskaya, E. V., Pronin, YA. and Chmutov, K. V. (1981). Investigation into the kinetics of ion-exchange processes accompanied by complex formation. Inorg. Nucl. Chem., 43, 787-789.

Kataoka, T, Yoshida, H. and Shibahara, Y. (1976). Liquid phase mass transfer in ion exchange accompanied by chemical reaction. J. Chem. Eng. Jpn., 9, 130.

Kataoka, T, Yoshida, H. and Ozasa, Y. (1977). Intraparticle ion exchange mass transfer accompanied by instantaneous irreversible reaction. Chem. Eng. Sci., 32, 1237-1240.

McGarvey, F. X. and Kunin, G. (1951). Monobed deionization with ion exchange resins, Ind. Eng. Chem., 43 (3), 734-740.

Riddle, J. M. (1993). Temperature effects on equilibrium leakage from ion exchange resins. EPRI Condensate Polishing Workshop, New Orleans, Louisiana.

Smyth, H. D. (1945). Atomic Energy for Military Purposes. Princeton University Press, Princeton, NJ.

Wagner, J. D. and Dranoff, J. S. (1967). The kinetics of ion exchange accompanied by irreversible reaction. III. Film diffusion controlled neutralization of a strong acid exchanger by a weak base. J. Phys. Chem., 71, 4551-4553.

Zecchini, E. J. and Foutch, G. L. (1991). Mixed bed ion exchange modeling with amine form cation resins. Ind. Eng. Chem. Res., 30, 1886-1892.

CHARPTE VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This work focuses on the sorption of boric acid by ion exchange. Both equilibrium of solution and resin phases and kinetics of sorption have been studied in detail. An equilibrium relationship of boron sorption on strong base anion exchange resins, given in Chapter III, was derived in this work. Parameters in the equation were determined quantitatively for seven types of anion exchange resins commonly used for boron sorption. Two kinetic models of ion exchange with boric acid solutions, one dealing with a homogeneous bed of anion resin for boron thermal regeneration and the other modeling demineralization of the coolant solution in mixed-beds, were developed in Chapters IV and V, respectively.

The relation describes the effects of not only temperature but also the influent concentration on boron sorption capacities of strong base anion exchange resins, particularly OH form anion resins. The form suggests that boron sorption on ion exchange resins is close to Freundlich's isotherm rather than Langmuir's isotherm. The characteristics of ion exchange resin and the conditional, complex formations of boron could be the major reasons resulting in this phenomenon. Satisfactory results comparing experimental data and model predictions verify the applicability of the model for determining bed capacity for boron sorption and the equilibrium concentrations at the resin surface.

The boron thermal regeneration model, developed in Chapter IV, considers both film and particle diffusion control. Though the example illustrated assumes particle diffusion, the model is easily to be extended to film diffusion control expected at low boron concentrations. Equation (4-33) gives the effective diffusivity of total boron. Similarly, the effective diffusivity of individual species can be obtained and particle rates of boron and each species determined by assuming a linear driving force in the film. For the particle diffusion-controlled cases, the model uses the linear driving force model for simplification, and the diffusion model, solved by the method of the orthogonal collocation, for more accurate, but also more complicated calculation. Moreover, in the example the only species considered is boric acid. The error caused by neglecting the contribution of borates in the liquid side much less than one percent, which can be concluded easily by comparing the concentrations of boric acid and the borates in solution from Figure II-1.

The mixed-bed model, given in Chapter V, deals with multicomponent systems containing weak electrolytes. Since the concentration of species sorption on anion resin is much higher than that on cation resin, different diffusion mechanisms were considered for the sorption of cation and anion resins in this model. That is, the situation certainly differing from the descriptions from other models reported in the literature. The model was applied to the demineralization of coolant in Sizewell CVCS, Nuclear Electric in England, but did not compared with the operating data.

Recommendations

The parameter values in the equilibrium model are better in a temperature range from 10 – 80 °C and boron concentration range of 1 ppm to 1500 ppm. More data are needed to determine these parameters accurately due to the sensitivity of the apparent capacity. Beyond these ranges these parameters must be recalculated.

Kinetic studies of boron desorption should be performed to complete the boron thermal regeneration model. The boron thermal regeneration model can be used to estimate the boron desorption process from borate form anion resin. However, more understanding of the resin phase conditions , pH and the dependency of degree of complex formations on concentration and temperature, for instance, is needed to develop a model dealing with boron desorption. The lack of diffusivity data of boron forms is part of the reason that boron desorption model has not been developed in this work.

The mixed-bed model should consider amine, and multi-valence species, sulfate, for instance, for generalized use in the demineralization of the coolant.

A common requirement of these models is experimental data for further test and validation.

APPENDIXES

APPENDIX A

DETERMINATION OF SPECIES CONCENTRATIONS IN BORIC ACID SOLUTION

Boric acid is a weak electrolyte. It may dissociate various types of borates along with boric acid molecule in its aqueous solution. The types of borates and the amount of these species in solution are dependent of temperature, boron concentration, and pH in the solution. In general, these species concentrations are obtained by solving a set of algebraic equations based on the equilibrium relations between boric acid and borates, water dissociation, charge balance, and mass balance. Practically, the set of equations has to be solved numerically and routinely. It costs computation time. The more species involved, the more time to be needed. In this work, it is not necessary to find out the solution concentration for every borate as did in Chapter II since some of them are quite insignificantly contained in the solution (See Figure II-1). Therefore, according to the problems chosen, the consideration of the monoborate $B(OH)_4^-$ and the trimer $B_3(OH)_{10}^-$ (or $B_3O_3(OH)_4^-$) are enough as discussed in Chapters III and IV.

Since the species involved and the conditions are different, the procedures to determine solution concentrations in BTRS and in demineralization are given separately in the following part I and part II.

Part I

In this part, the procedure to determine the solution concentrations of boric acid, $B(OH)_4^-$, and $B_3(OH)_{10}^-$ is given for the model calculation in Chapter IV. The relations used to determine the solution concentrations of these species are specified in Equations (A-1) to (A-5):

The equilibria conditions:

$$K_{11} = \frac{[H^+]\cdot[B_1^-]}{[HB]} = \frac{C_H \cdot C_{B_1}}{C_{HB}} \tag{A-1}$$

$$K_{13} = \frac{[H^+]\cdot[B_3^-]}{[HB]^3} = \frac{C_H \cdot C_{B_3}}{C_{HB}^3} \tag{A-2}$$

$$K_w = C_H \cdot C_{OH} \tag{A-3}$$

The total boron concentration in solution:

$$C_{BT} = C_{HB} + C_{B_1} + 3C_{B_3} \tag{A-4}$$

The condition of electroneutrality requires:

$$C_H = C_{OH} + C_{B_1} + C_{B_3} \tag{A-5}$$

In these equations, there are five unknowns — solution concentrations of boric acid C_{HB}, the orthoborate C_{B_1}, the trimer C_{B_3}, hydrogen C_H, and hydroxide C_{OH}. By manipulation, these unknowns can be solved explicitly.

I. The expression of C_H

Combine Eqs. (1), (2), (3) and (5) to give

$$C_H = \frac{K_w + K_{11}C_{HB} + K_{13}C_{HB}^3}{C_H} \tag{A-6}$$

or explicitly written as

$$C_H = (K_w + K_{11}C_{HB} + K_{13}C_{HB}^3)^{1/2} \tag{A-7}$$

II. The expression of C_{HB}

Equation (A-4) may be written as:

$$C_{BT} - C_{HB} = C_{B_1} + 3C_{B_3} \tag{A-8}$$

Substitution of Equations (A-1) and (A-2) into Equation (A-8) gives

$$C_{BT} - C_{HB} = \frac{K_{11}C_{HB} + 3K_{13}C_{HB}^3}{C_H} \tag{A-9}$$

Take square for both sides of Equation (A-9), and the resulting form is:

$$(C_{BT} - C_{HB})^2 = \frac{(K_{11}C_{HB} + 3K_{13}C_{HB}^3)^2}{C_H{}^2} \tag{A-10}$$

Substitution of Equation (A-7) into Equation (A-10) and rearrangement lead to the equation with only one unknown variable — the boric acid concentration in solution.

$$a_6C_{HB}^6 + a_5C_{HB}^5 + a_4C_{HB}^4 + a_3C_{HB}^3 + a_2C_{HB}^2 + a_1C_{HB} + a_0 = 0 \tag{A-11}$$

where

$$a_6 = 9K_{13}^2$$

$$a_5 = -K_{13}$$

$$a_4 = 6K_{11}K_{13} + 2K_{13}C_{BT}$$

$$a_3 = -(K_{13}C_{BT}^2 + K_{11})$$

$$a_2 = K_{11}^2 + 2K_{11}C_{BT} - K_w$$

$$a_1 = 2K_w C_{BT} - K_{11} C_{BT}^2$$

$$a_0 = -K_w C_{BT}^2$$

Equation (A-11) is a polynomial algebraic equation and it is ready to be solved to obtain boric acid concentration in solution by the Newton-Raphson method. Then, solve Equation (A-7) for hydrogen concentration, and the others are readily determined by applying Equations (A-1) to (A-3).

Part II

In this part, the procedure to determination of species concentrations in sodium, lithium, chloride, boric acid solution by the equilibria and electroneutrality conditions is given for the model calculation in Chapter V. The only borate species considered in the problem is the monoborate $B(OH)_4^-$. Similar to the part I, the relations based on the equilibrium and electroneutrality conditions and mass balance are given in Equations (A-1), (A-3), (A-12), and (A-13).

$$C_{BT} = C_{HB} + C_{B1} \qquad \text{(A-12)}$$

$$C_H + C_{Li} + C_{Na} = C_{B1} + C_{OH} + C_{Cl} \qquad \text{(A-13)}$$

In these equations, there are four unknowns — solution concentrations of boric acid C_{HB}, the monoborate C_{B_1}, hydrogen C_H, and hydroxide C_{OH}. Concentrations of the other species are known from the influent conditions at each slice of column set for numerical calculation of the column material balance. By manipulation, these unknowns can be also solved explicitly.

Combine Equations (A-1), (A-3), and (A-12) to give

$$C_{B1} = \frac{C_{BT} \cdot K_{11}}{C_H + K_{11}} \tag{A-14}$$

Substitution of Equations (A-3) and (A-14) into Equation (A-13) and rearrangement for solving C_H result in

$$b_0 C_H^3 + b_1 C_H^2 + b_2 C_H + b_3 = 0 \tag{A-15}$$

where

$$b_0 = 1$$

$$b_1 = \left(Ka + C_{Li} + C_{Na} - C_{Cl}\right)$$

$$b_2 = \left[\left(C_{Li} + C_{Na} - C_{Cl} - C_{BT}\right) \cdot K_{11} - Kw\right]$$

$$b_3 = -Kw \cdot K_{11}$$

Solve Equation (A-15) to obtain hydrogen concentration by Newton-Raphson method. Then, the concentrations of hydroxide C_{OH}, the monoborate C_{B_1}, and boric acid C_{HB} are easily determined by applying Equations (A-3), (A-12), and (A-14).

APPENDIX B

DERIVATION OF THE EFFECTIVE DIFFUSIVITY EXPRESSIONS OF BORATES

A derivation of the expression of Equation (4-33), describing the effective diffusivity of the total boron, is given in here. The flux of species across the Nernst film may be proceeded as follows:

The flux of the neutral species, boric acid, is

$$J_B = -D_B \frac{\partial C_B}{\partial r} \tag{B-1}$$

Fluxes of other ionic species are

N coions

$$J_j = -D_j \left[\frac{\partial C_j}{\partial r} + \frac{z_j C_j F}{RT} \frac{\partial \Phi}{\partial r} \right] \tag{B-2}$$

M counterions

$$J_i = -D_i \left[\frac{\partial C_i}{\partial r} + \frac{z_i C_i F}{RT} \frac{\partial \Phi}{\partial r} \right] \tag{B-3}$$

The condition of no net electrical current requires

$$\sum_{k=1}^{N+M} z_k J_k = 0 \tag{B-4}$$

For this application of the boron sorption by homogeneous anion resin bed, the only coion involved in the boric acid aqueous solution is hydrogen H^+, which is dissociated from water and released from the ionization of boric acid. If the assumption of complete Donnan exclusion is applied, the electrical potential term is eliminated from Equation (B-3) by applying the condition of no coion flux, and the resulting form of Equation (B-3) is.

$$J_i = -D_i \left[\frac{\partial C_i}{\partial r} - \frac{z_i C_i}{C_H} \frac{\partial C_H}{\partial r} \right] \tag{B-5}$$

For all borates, if K_{B_i} indicates the equilibrium constant of borate B_i with 'i' boron atom and valence z_i dissociated from boric acid, the dissociation constant may be expressed in this way:

$$K_{B_i} = \frac{C_{B_i} C_H^{|z_i|}}{C_B^i} \tag{B-6}$$

then

$$C_{B_i} = \frac{K_{B_i} C_B^i}{C_H^{|z_i|}} \tag{B-7}$$

Differentiation of Equation (B-7) leads to the concentration gradient relationship among borates, boric acid and hydrogen. This is

$$\frac{\partial C_{B_i}}{\partial r} = K_{B_i} \left(\frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \frac{\partial C_B}{\partial r} - \frac{|z_i| C_B^i}{C_H^{|z_i|+1}} \frac{\partial C_H}{\partial r} \right) \tag{B-8}$$

Substituting Equations (B-7) and (B-8) into Equation (B-5) with the change of subscript notation from ' i ' to ' B_i ', the borate flux can be expressed in terms of the concentration of boric acid, that is:

$$J_{B_i} = -D_{B_i} K_{B_i} \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \frac{\partial C_B}{\partial r} \tag{B-9}$$

The total boron flux is then given by:

$$J_T = J_B + \sum_{i=1}^{M-1} J_{B_i} = -\left(D_B + \sum_{i=1}^{M-1} D_{B_i} K_{B_i} \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \right) \frac{\partial C_B}{\partial r} \tag{B-10}$$

Comparing the form

$$J_k = -De_k \frac{\partial C_k}{\partial r} \tag{B-11}$$

The effective diffusivity of individual borate in terms of the concentrations of boric acid and hydrogen can be obtained as:

$$De_i = D_{B_i} K_{B_i} \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \tag{B-12}$$

and the effective diffusivity of the total boron, which was indicated in Equation (4-33), is expressed by:

$$De = \left(D_B + \sum_{i=1}^{M-1} D_{B_i} K_{B_i} \frac{i \cdot C_B^{i-1}}{C_H^{|z_i|}} \right) \tag{B-13}$$

Correspondingly, the fluxes of individual borate and the total boron are given in terms of the concentration gradient of boric acid. For borate, there is

$$J_{B_i} = -De_i \frac{\partial C_B}{\partial r} \tag{B-14}$$

and for the total boron, there is:

$$J_T = -De \frac{\partial C_B}{\partial r} \tag{B-15}$$

APPENDIX C

DETERMINATION OF SPECIES CONCENTRATIONS AT THE INTERFACE BY USING A LANGMUIR TYPE EQUILIBRIUM RELATION

The local equilibrium assumption allows determining species concentrations at the interface by applying some type of equilibrium isotherm equation. The equation (Eq. 3-28) developed in the Chapter III is a specific form for the boron sorption on strong base anion exchangers. Under the lack of the parameter data, a Langmuir type equilibrium relation,

$$Y^* = \frac{K \cdot X^*}{1 + X^*(K - 1)} \tag{C-1}$$

may be used to estimate the species concentrations at the interface between the liquid and the particle surface. If the equilibrium isotherm constant *K* in Eq. (C-1) is chosen as the selectivity coefficient of the resin for a species given, the relation is the same as the equation specifying selectivity coefficient for a binary system with uni-valence. Beyond this situation, the expressions are given in next part.

Expressions of the interface concentrations

For a binary system with arbitrary valence, the selectivity coefficient is defined in Equation (C-2):

$$K_A^B = \left(\frac{q_B^*}{C_B^*}\right)^{Z_A} \left(\frac{C_A^*}{q_A^*}\right)^{Z_B} \tag{C-2}$$

or

$$K_A^B = \left(\frac{Y_B^*}{X_B^*}\right)^{Z_A} \left(\frac{X_A^*}{1-Y_B^*}\right)^{Z_B} Q^{(Z_A-Z_B)} C_T^{*\,(Z_B-Z_A)} \tag{C-3}$$

The constant separation factors α may be defined by

$$\alpha_A^B = \left(\frac{Y_B^*}{X_B^*}\right)^{Z_A} \left(\frac{X_A^*}{Y_A^*}\right)^{Z_B} = \left(\frac{Y_B^*}{X_B^*}\right)^{Z_A} \left(\frac{X_A^*}{1-Y_B^*}\right)^{Z_B} \tag{C-4}$$

thus

$$\alpha_A^B = K_A^B \cdot Q^{-(Z_A-Z_B)} \cdot C_T^{*\,-(Z_B-Z_A)} \tag{C-5}$$

Solving for the fractional concentration of species B, Equation (C-4) may be rewritten as Equation (C-6):

$$X_B^* = X_A^{*\,Z_B/Z_A} (\alpha_A^B)^{-1/Z_A} Y_B^* \left(1-Y_B^*\right)^{-Z_B/Z_A} \tag{C-6}$$

or

$$X_B^* = \lambda_B{}' (X_A^*)^{Z_B/Z_A} \tag{C-7}$$

where

$$\lambda'_B = (\alpha_A^B)^{-1/Z_A} Y_B^* \left(1-Y_B^*\right)^{-Z_B/Z_A} \tag{C-8}$$

The α_A^B in Equation (C-8) is determined by Equation (C-5).

For a multicomponent system, rewriting Equation (C-4) for a multicomponent system gives

$$\alpha_i^n = \left(\frac{Y_n^*}{X_n^*}\right)^{Z_i} \left(\frac{X_i^*}{Y_i^*}\right)^{Z_n} \tag{C-9}$$

where the *n* represents the original free ion in the resin phase, which is hydroxide in this case; the *i* indicates the exchangeable species in the liquid phase. Rearranging Equation (C-9), we have

$$(\alpha_i^n)^{1/z_n} Y_i^* = \left(\frac{Y_n^*}{X_n^*}\right)^{z_i/z_n} X_i^* \tag{C-10}$$

Summary Equation (C-10) and apply the condition

$$\sum_{i=1}^{n} X_i^* = 1.0 \tag{C-11}$$

to have

$$\sum_{i=1}^{n} (\alpha_i^n)^{1/z_n} Y_i^* = \left(\frac{Y_n^*}{X_n^*}\right)^{z_i/z_n} \sum_{i=1}^{n} X_i^* = \left(\frac{Y_n^*}{X_n^*}\right)^{z_i/z_n} \tag{C-12}$$

Combining Equation (C-12) with Equation (C-10), we obtain

$$\sum_{i=1}^{n} (\alpha_i^n)^{1/z_n} Y_i^* = (\alpha_i^n)^{1/z_n} \frac{Y_i^*}{X_i^*} \tag{C-13}$$

Solving for the fractional concentration at the interface of the *i*th species, the more general form of solving fractional concentration of *i*th species is given by

$$X_i^* = \frac{(\alpha_i^n)^{1/z_n} Y_i^*}{\sum_{i=1}^{n} (\alpha_i^n)^{1/z_n} Y_i^*} \tag{C-14}$$

or to change notation for the summation to have the form of Equation (C-15).

$$X_i^* = \frac{(\alpha_i^n)^{1/z_n} Y_i^*}{\sum_{i=j}^{n} (\alpha_j^n)^{1/z_n} Y_j^*} \tag{C-15}$$

and

$$\alpha_j^n = K_j^n \cdot Q^{-(Z_n - Z_j)} \cdot C_T^{*\,-(Z_j - Z_n)} \tag{C-16}$$

Note: $\alpha_i^n = \frac{1}{\alpha_n^i}$ or: $\alpha_j^n = \frac{1}{\alpha_n^j}$

The selectivity coefficient K_A^B and the apparent capacity Q in Equations (C-7) and (C-15) are determined from experiment.

Determination of the total ionic concentration at the interface

For the film diffusion model, the interface concentration Y_B^* equals to the average concentration of species B in the resin, while X_B^* equals to the bulk concentration with the particle diffusion control. For both cases, the interface concentrations in Equations (C-7) and (C-15) are not able to be solved directly until the total ionic concentration C_T^* and X_A^* or Y_A^* have been determined.

In this system, the total ionic concentration equals to the concentration of hydrogen at the interface due to the charge balance, this is:

$$C_T^* = C_H^* = K_W / C_{OH}^* \tag{C-17}$$

and

$$X_n^* = C_{OH}^* / C_H^* \tag{C-18}$$

combining Equations (C-17) and (C-18) to give the total ionic concentration at the interface in terms of the fractional concentration of free ion released from the resin:

$$C_T^* = (K_W)^{1/2} (X_n^*)^{-1/2} \tag{C-19}$$

Substitute Equation (C-19) into Equation (C-7) and rearrange to have

$$X_i^* = \lambda_i (X_n^*)^{\beta_i} \tag{C-20}$$

where

$$\lambda_i = Y_i^* (K_i^n)^{1/z_n} \left(Y_n^*\right)^{-z_i/z_n} Q^{(z_n - z_i)/z_n} K_w{}^{(z_i - z_n)/z_n/2} \tag{C-21}$$

$$\beta_i = z_i / z_n - (z_i - z_n) / z_n / 2 \tag{C-22}$$

thus the material balance at the interface may be rewritten as

$$X_n^* + \sum_{i=1}^{n-1} \lambda_i (X_n^*)^{\beta_i} = 1.0 \tag{C-23}$$

Equation (C-23) is a polynomial in X_n^* and can be solved numerically by using the Newton-Raphson method. Once X_n^* has been determined, C_T^* and the concentrations of all ionic species at the interface can be determined by applying Equation (C-20).

APPENDIX D

DERIVATION OF THE FLUX EXPRESSION OF IONIC SPECIES IN MBIE

The flux of ionic species in mixed bed ion exchange can be described by the Nernst - Planck model. A convenient form of the Nernst - Planck equation that applies to the flux of any ionic species *k* in the film can be written as:

$$J_k = -D_k\left[\frac{\partial C_k}{\partial r} + \frac{z_k C_k F}{RT}\frac{\partial \Phi}{\partial r}\right] \qquad \text{(D-1)}$$

Change notations and rewrite for counter-ions

$$J_i = -D_i\left[\frac{\partial C_i}{\partial r} + \frac{z_i C_i F}{RT}\frac{\partial \Phi}{\partial r}\right] \qquad \text{(D-2)}$$

and for co-ions

$$J_j = -D_j\left[\frac{\partial C_j}{\partial r} + \frac{z_j C_j F}{RT}\frac{\partial \Phi}{\partial r}\right] \qquad \text{(D-3)}$$

The condition of no co-ion flux described by Equation (5-5) and the introduction of the equivalent ionic change, which is defined as,

$$z^* = \frac{\sum z_j^2 C_j}{\sum z_j C_j} \qquad \text{(D-4)}$$

can be used to eliminate the electric potential and co-ion concentration gradient in Equation (D-2). The resulting form of Equation (D-2) is

$$J_i = -D_i\left[\frac{dC_i}{dr} + n_i\frac{C_i}{C_{NT}}\frac{dC_{NT}}{dr}\right] \tag{D-5}$$

Where n_i is defined as

$$n_i = -\frac{z_i}{z^*} \tag{D-6}$$

The assumptions of pseudo steady state and only significant diffusion in the normal direction allow using ordinary derivatives instead of using partial derivatives in Equation (D-5).

Because of the independence of the flux on the space, Equation (D-7) can be obtained by differentiating Equation (D-5) with respect to the space variable *r* and rearranging.

$$\frac{d^2C_i}{dr^2} + \frac{n_iC_i}{C_{NT}}\frac{d^2C_{NT}}{dr^2} + \frac{n_i}{C_{NT}}\frac{dC_{NT}}{dr}\frac{dC_i}{dr} - \frac{n_iC_i}{C_{NT}^2}\left(\frac{dC_{NT}}{dr}\right)^2 = 0 \tag{D-7}$$

For counter ions of uni-valences (the same as in this case), the summation of Equation (D-7) for all counterions leads to,

$$\begin{aligned}&\sum\frac{d^2C_i}{dr^2} + \frac{1}{C_{NT}}\frac{d^2C_{NT}}{dr^2}\sum n_iC_i + \frac{1}{C_{NT}}\frac{dC_{NT}}{dr}\sum n_i\frac{dC_i}{dr}\\ &-\frac{1}{C_{NT}^2}\left(\frac{dC_{NT}}{dr}\right)^2\sum n_iC_i = 0\end{aligned} \tag{D-8}$$

By applying the condition of Equation (5-4), the last two terms in the left side of Equation (D-8) are dropped, and Equation (D-8) leaves the form as:

$$\sum\frac{d^2C_i}{dr^2} + \frac{d^2C_{NT}}{dr^2} = 2\frac{d^2C_{NT}}{dr^2} = 0 \tag{D-9}$$

or

$$\frac{d^2C_{NT}}{dr^2} = 0 \tag{D-10}$$

Equation (D-10) indicates, for the cases of univalent counterions, that the gradient of the total equivalent concentration in the film is a constant, that is:

$$\frac{dC_{NT}}{dr} = \alpha \tag{D-11}$$

The constant gradient of the total equivalent concentration leads to the following transformation:

$$\frac{dC_i}{dr} = \frac{dC_i}{dC_{NT}} \cdot \frac{dC_{NT}}{dr} = \alpha \frac{dC_i}{dC_{NT}} \tag{D-12}$$

$$\frac{d^2C_i}{dr^2} = \frac{d}{dr}\left(\alpha \frac{dC_i}{dC_{NT}}\right) = \alpha \frac{d^2C_i}{dC_{NT}^2} \cdot \frac{dC_{NT}}{dr} = \alpha^2 \frac{d^2C_i}{dC_{NT}^2} \tag{D-13}$$

Substitution of Equations (D-10), (D-12), and (D-13) into Equation (D-7) results in the Euler's differential equation.

$$C_{NT}^2 \frac{d^2C_i}{dC_{NT}{}^2} + n_i C_T \frac{dC_i}{dC_{NT}} - n_i C_i = 0 \tag{D-14}$$

It is not difficult to solve this Euler's differential equation for its general solution,

$$C_i = a_i C_{NT} + b_i C_{NT}^{-n_i} \tag{D-15}$$

Apply the boundary conditions

$$r = R + \delta, \qquad C_i = C_i^o, \qquad \text{and} \quad C_{NT} = C_{NT}^o \tag{D-16}$$

$$r = R, \qquad C_i = C_i^*, \qquad \text{and} \quad C_{NT} = C_{NT}^* \tag{D-17}$$

on Equation (D-15) to obtain these coefficients

$$a_i = \frac{x_i^o - x_i^* \eta^{n_i+1}}{1 - \eta^{n_i+1}} \tag{D-18}$$

$$b_i = \left(x_i^* - \frac{x_i^o - x_i^* \eta^{n_i+1}}{1 - \eta^{n_i+1}} \right) \cdot C_T^{*\,n_i+1} \tag{D-19}$$

where

$$x_i^o = \frac{C_i^o}{C_T^o}; \qquad x_i^* = \frac{C_i^*}{C_T^*}; \qquad \text{and} \qquad \eta = \frac{C_T^*}{C_T^o} \tag{D-20}$$

And it is easy to see that these coefficients meet the conditions

$$\sum a_i = \frac{\sum x_i^o - \eta^{n_i+1}\sum x_i^*}{1-\eta^{n_i+1}} = \frac{1-\eta^{n_i+1}}{1-\eta^{n_i+1}} = 1 \tag{D-21}$$

$$\begin{aligned} \sum b_i &= \left(\sum x_i^* - \frac{\sum x_i^o - \eta^{n_i+1}\sum x_i^*}{1-\eta^{n_i+1}}\right)\cdot C_T^{*\,n_i+1} \\ &= \left(1 - \frac{1-\eta^{n_i+1}}{1-\eta^{n_i+1}}\right)\cdot C_T^{*\,n_i+1} = 0 \end{aligned} \tag{D-22}$$

Equation (D-15) gives the relationship between C_i and C_{NT}. Now one can apply these results to express the N-P flux equations of each counterion in the film with the total concentrations and their derivatives. Take derivative to Eq. (D-15) to give

$$\frac{dC_i}{dr} = a_i\frac{dC_T}{dr} - b_i C_T^{-2}\frac{dC_T}{dr} \tag{D-23}$$

With the univalent counterions in systems, note

$$n_i \equiv 1 \tag{D-24}$$

Substitute Equations (D-15) and (D-23) into Equation (D-5) to get

$$J_i = -D_i\left[a_i\frac{dC_T}{dr} - b_i C_T^{-2}\frac{dC_T}{dr} + \frac{a_i C_T + b_i C_T^{-1}}{C_T}\frac{dC_T}{dr}\right] \tag{D-25}$$

Cancel out the terms with b_i and rearrange to yields

$$J_i = -2D_i a_i\frac{dC_T}{dr} \tag{D-26}$$

Integrate the resulting equation with the boundary conditions in Equations (D-16) and (D-17) to obtain

$$J_i = -\frac{2}{\delta} D_i a_i (C_T^o - C_T^*) \tag{D-27}$$

where δ is the thickness of the Nernst film

The total equivalent concentration at the interface C_T^* in Equation (D-27) may be replaced by the total equivalent concentration in the liquid bulk and the fractions of counterion species both in the liquid bulk and at the interface. Multiplying Equation (D-26) by the charge valence, summating the resulting equation, and arranging gives

$$\sum_{i=1}^{n} z_i J_i = -2 \frac{dC_T}{dr} \sum_{i=1}^{n} D_i a_i z_i \tag{D-28}$$

Combining Equation (D-28) with Equation (5-6) leads to the following condition for counterions:

$$\sum_{i=1}^{n} D_i a_i z_i = 0 \tag{D-29}$$

Because all ionic species are uni-valence in this work, Equation (D-29) can be simplified as:

$$\sum_{i=1}^{n} D_i a_i = 0 \tag{D-30}$$

Substitute Equation (D-18) into Equation (D-30) and solve for η to give

$$\eta = \left[\frac{\sum_{i=1}^{n} D_i x_i^o}{\sum_{i=1}^{n} D_i x_i^*} \right]^{\frac{1}{2}} \tag{D-31}$$

Thus, with the definition of η, the final expression for C_T^* is

$$C_T^* = \left[\frac{\sum_{i=1}^{n} D_i x_i^o}{\sum_{i=1}^{n} D_i x_i^*} \right]^{\frac{1}{2}} C_T^o = \eta C_T^o \tag{D-32}$$

With this result, Equation (D-27) becomes

$$J_i = -\frac{2}{\delta} D_i a_i C_T^o [1 - \eta] \tag{D-33}$$

Comparing with

$$J_i = -\frac{De,i}{\delta} \left(C_i^o - C_i^* \right) \tag{D-34}$$

yields

$$De,i = \frac{2}{\left(C_i^o - C_i^* \right)} D_i a_i C_T^o [1 - \eta] \tag{D-35}$$

Therefore, the flux of *i*th ionic species can be expressed as the form of Equation (5-31) in Chapter V, this is:

$$J_i = -De,i \frac{dC_i}{dr} = -\frac{2}{\left(C_i^o - C_i^* \right)} D_i a_i C_T^o [1 - \Gamma] \frac{dC_i}{dr} \tag{D-36}$$

APPENDIX E

DERIVATION OF DIMENSIONLESS FORM OF COLUMN MATERIAL BALANCE

The column material balance for each species can be written as:

$$\frac{\partial C_i}{\partial t} + f_r \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \overline{q}_i}{\partial t} + \frac{u_s}{\varepsilon} \frac{\partial C_i}{\partial z} = 0 \qquad \text{(E-1)}$$

This form needs to be simplified further for computation purpose. Follow Kataoka to define dimensionless variables in time and distance as:

$$\tau = \frac{k_i C_T^f}{d_p Q}\left(t - \frac{\varepsilon z}{u_s}\right) \qquad \text{(E-2)}$$

and

$$\xi = \frac{k_i (1-\varepsilon)}{d_p u_s} z \qquad \text{(E-3)}$$

The form of column material balance expressed in dimensionless variables is given in Equation (E-4).

$$\frac{\partial X_i}{\partial \xi} + f_r \frac{\partial Y_i}{\partial \tau} = 0 \qquad \text{(E-4)}$$

Differentiate the above equations with respect to time and distance respectively to give the intermediate derivatives:

$$\frac{\partial \tau}{\partial t} = \frac{k_i C_T^f}{d_p Q}; \qquad \frac{\partial \tau}{\partial z} = -\frac{k_i C_T^f}{d_p Q}\frac{\varepsilon}{u_s}; \tag{E-5}$$

$$\frac{\partial \xi}{\partial t} = 0;\ \text{and} \qquad \frac{\partial \xi}{\partial z} = \frac{k_i(1-\varepsilon)}{d_p u_s} \tag{E-6}$$

By using the chain rule the original derivatives can be expressed in terms of the new variables as:

$$\frac{\partial C_i}{\partial t} = \frac{\partial C_i}{\partial \tau}\frac{\partial \tau}{\partial t} + \frac{\partial C_i}{\partial \xi}\frac{\partial \xi}{\partial t} = \frac{k_i C_T^f}{d_p Q}\frac{\partial C_i}{\partial \tau} + 0\frac{\partial C_i}{\partial \xi} = \frac{k_i C_T^f}{d_p Q}\frac{\partial C_i}{\partial \tau} \tag{E-7}$$

$$\frac{\partial \overline{q}_i}{\partial t} = \frac{\partial \overline{q}_i}{\partial \tau}\frac{\partial \tau}{\partial t} + \frac{\partial \overline{q}_i}{\partial \xi}\frac{\partial \xi}{\partial t} = \frac{k_i C_T^f}{d_p Q}\frac{\partial \overline{q}_i}{\partial \tau} + 0\frac{\partial \overline{q}_i}{\partial \xi} = \frac{k_i C_T^f}{d_p Q}\frac{\partial \overline{q}_i}{\partial \tau} \tag{E-8}$$

$$\frac{\partial C_i}{\partial z} = \frac{\partial C_i}{\partial \xi}\frac{\partial \xi}{\partial z} + \frac{\partial C_i}{\partial \tau}\frac{\partial \tau}{\partial z} = \frac{k_i(1-\varepsilon)}{d_p u_s}\frac{\partial C_i}{\partial \xi} - \frac{k_i C_T^f}{d_p Q}\frac{\varepsilon}{u_s}\frac{\partial C_i}{\partial \tau} \tag{E-9}$$

Replacing these results into Eq. (E-1) and transforming the dependent variables by

$$X_i = \frac{C_i}{C_T^f}, \qquad \text{and } Y_i = \frac{\overline{q}_i}{Q}$$

yields:

$$\frac{\partial X_i}{\partial \xi} + f_r\frac{\partial Y_i}{\partial \tau} = 0 \tag{E-10}$$

This resulting form is much conveniently carried out by numerical methods. Use the cation resin volume fraction FRC replacing fr for cationic species and the anion resin volume fraction FRA replacing fr for anionic species respectively in computation. The constant FRC and FRA must be specified for any given mixed bed column. The new independent variables τ and ξ are dependent upon a reference species as the basis since all of the material balance need to be solved using the same steps in τ and ξ. Choose a cationic species as the reference species in this work and specify as

$$\tau = \tau_r = \frac{k_r C_T^f}{d_{pc} Q_c}\left(t - \frac{\varepsilon z}{u_s}\right) \tag{E-11}$$

and

$$\xi = \xi_r = \frac{k_r(1-\varepsilon)}{d_{pc} u_s} z \tag{E-12}$$

Rewrite Eq. (E-10) in terms of the new independent variables τ and ξ for the reference ionic species as

$$\frac{\partial X_i}{\partial \xi_r} + \mathrm{FRC}\frac{\partial Y_i}{\partial \tau_r} = 0 \tag{E-13}$$

The partial derivatives of all other species in Eq. (E-13) can be expressed in terms of the reference ionic species as following:

for cations

$$\frac{\partial X_i}{\partial \xi_i} = \frac{\partial X_i}{\partial \xi_r}\frac{\partial \xi_r}{\partial \xi_i} = \frac{k_r}{k_i}\frac{\partial X_i}{\partial \xi_r} \tag{E-14}$$

$$\frac{\partial Y_i}{\partial \tau_i} = \frac{\partial Y_i}{\partial \tau_r}\frac{\partial \tau_r}{\partial \tau_i} = \frac{k_r}{k_i}\frac{\partial Y_i}{\partial \tau_r} \tag{E-15}$$

and for anions

$$\frac{\partial X_i}{\partial \xi_i} = \frac{\partial X_i}{\partial \xi_r}\frac{\partial \xi_r}{\partial \xi_i} = \frac{k_r}{k_i}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c}\frac{\partial X_i}{\partial \xi_r} \tag{E-16}$$

$$\frac{\partial Y_i}{\partial \tau_i} = \frac{\partial Y_i}{\partial \tau_r}\frac{\partial \tau_r}{\partial \tau_i} = \frac{k_r}{k_i}\frac{d_{pa}}{d_{pc}}\frac{Q_a}{Q_c}\frac{\partial Y_i}{\partial \tau_r} \tag{E-17}$$

Therefore, the partial derivatives of all other species can be determined by Equations (E-14) to (E-17) as soon as that of the reference ionic species has been calculated. The average particle rate of species in Equation (5-35) can be corrected by the similar way in a dimensionless form. That is

for cations

$$\frac{d\overline{Y}_i}{d\tau_i} = \frac{6k_i}{k_c}\left\{\frac{a_i(n_i+1)C_T^o}{\left(C_i^o - C_i^*\right)}[1-\Gamma]\right\}^{\frac{2}{3}}(X_i^o - X_i^*) \tag{E-18}$$

and for anions

$$\frac{d\overline{Y}_i}{d\tau_i} = \frac{6k_i}{k_c}\frac{d_{pc}}{d_{pa}}\frac{Q_c}{Q_a}\left\{\frac{a_i(n_i+1)C_T^o}{\left(C_i^o - C_i^*\right)}[1-\Gamma]\right\}^{\frac{2}{3}}(X_i^o - X_i^*) \tag{E-19}$$

APPENDIX F

COMPUTER CODES

PART I. THE DETERMINATION OF BORON FORM CONCENTRATIONS IN AQUEOUS SOLUTION

```
$debug

C  PROGRAM BOCOMP- was originally developed by Dr. Na (1993) and is adapted
C  here for calculating the solution concentrations of boron forms based on Beas and
C  Mesmer's form and parameters (1976). The general equilibrium relationship was
C  given in Eq.(4-4). Ionization equilibrium of boric acid to form B1, B2, B3, and B4
C  were given in Eqs. (4-6) to (4-13). The equilibrium constant of reaction KI is
C  determined by
C              logK=A/T+B+CT+DlogT                    log = log10 here
C
C       For B(OH)4-,         A = 1573.21; B = 28.6059; C = 0.012078; D = -13.2258
C       For B2(OH)7-,        A = 2756.1; B = -18.996; C = 0; D = 5.835
C       For B3(OH)10-,       A = 3339.5; B = -8.084; C = 0; D = 1.497
C       For B4(OH)14=,       A = 212820; B = -134.56; C = 0; D = 42.105

C       Reference Appendix A. for the determination procedure.
C
C       BT:          TOTAL CON. OF B(OH)3       MOL/L
C       HB:          CONCENTRATION. OF B(OH)3
C       B11:         CONCENTRATION. OF B(OH)4-
C       B21:         CONCENTRATION OF B2(OH)7-
C       B31:         CONCENTRATION OF B3(OH)10-
C       B42:         CONCENTRATION OF B4(OH)14=
C       H:           CONCENTRATION OF HYDROGEN ION
C       OH:          CONCENTRATION OF HYDROXYL ION
C       KW:          ION PRODUCT OF WATER
C       K11:         EQUILIBRIUM CONSTANT FOR B11
C       K21:         EQUILIBRIUM CONSTANT FOR B21
C       K31:         EQUILIBRIUM CONSTANT FOR B31
C       K42:         EQUILIBRIUM CONSTANT FOR B42
C       PH:          PH OF SOLUTION
```

```
C    TEMP:         TEMPERATURE
C    XB:           INITIAL BORON CONCENTRATION     IN ppm


     IMPLICIT REAL*8(A-H, K, O-Z)
     PARAMETER(NP=6,NU=8,NV=9)
     COMMON /EQUI/ KW, K11,K21,K31,K42
     COMMON /BORO/ TK, BT
     DIMENSION X(NP)

     OPEN(UNIT=NU, FILE='B1200_60.DAT', STATUS ='UNKNOWN')

C    Set initial conditions

     NTRIAL = 6000
     TOLX = 1.0D-15
     TOLF = 1.0D-30

     TEMP = 60.
     TK   =  273.15 + TEMP
        CALL CALROW (TK, ROH2O)
        CALL CALKW  (TK,ROH2O, KW)

        WRITE(nu,100) TEMP,KW
100     FORMAT(/10X, 'DISTRIBUTION OF BORON',//
   $       3X, 'TEMPERATURE  =', F10.1, ' C', /
   $            3x, 'Water Dissociation Constant Kw = ', e15.7,// )

        WRITE(nu,120)
120     FORMAT(2X,'xb',8x,'pH',8x,'hb',8x,'b1',8x,'b2',8x,'b3',8x,'b4',/)
c        XB, OH, HB, B11, B21, B31, B42

        DO 900 pch =  0.0, 14, 0.1    ! Calculating the concentration changes with pH
                                      ! If calculating the concentration changes with
                                      ! the total boron concentration, use the total boron
                                      !concentration to set routine and to give the initial
                                      !guess to hydroxide OH or hydrogen.
              ph   = pch
              xb   = 1200.0
              BT   = XB / 10811
              ch   = 10**(-ph)

C       INTIAL GUESS OF BORON FORM CONCENTRATIONS

     B11 = 1.D-3 * BT *(ph+1)
     B21 = 1.D-4 * BT *(ph+1)
```

```
      B31 = 1.D-5 * BT *(ph+1)**2
      B42 = 1.D-6 * BT *(ph+1)**3
      HB  = 9.D-1 * BT /(ph+1)
c     OH  = 1.D-9

      X(1) = B11
      X(2) = B21
      X(3) = B31
      X(4) = B42
      X(5) = HB
c      X(6) = OH

          oh = kw/ch

      CALL MNEWT (NTRIAL, NP, TOLX, TOLF, X, oh )

         B11 = X(1)
         B21 = X(2)
         B31 = X(3)
         B42 = X(4)
         HB  = X(5)
c          OH  = X(6)

Change the variable notation for writing file (units xb-ppm, rest MF)
          WHB  = HB*10811/XB                          !mole fraction in boron
          WB11 = B11*10811/XB
          WB21 = B21*10811/XB*2.
          WB31 = B31*10811/XB*3.
          WB42 = B42*10811/XB*4.

 900      WRITE(nu,950) XB, pH, WHB, WB11, WB21, WB31, WB42
 950      FORMAT(1X, F6.0, 6(1X, E9.4) )
 999      CLOSE(NU)
          STOP
          END


      SUBROUTINE USRFUN (F, DF, X, oh)            ! Called by Subroutine MNEWT
      IMPLICIT REAL*8(A-H,K,O-Z)
      PARAMETER (NP =6)
      COMMON /EQUI/ KW, K11, K21, K31, K42
      COMMON /BORO/ TK, BT
      DIMENSION DF(NP,NP), F(NP), X(NP)

         B11 = X(1)
         B21 = X(2)
```

```
      B31 = X(3)
      B42 = X(4)
      HB  = X(5)
c       OH  = X(6)

    CALL CALKB(TK,SI, K11,K21,K31,K42)       ! Calculating equilibrium constants

C       MASS BALNACE OF BORON
    F(1) = ( B11 + 2*B21 + 3*B31 + 4*B42 + HB ) - BT

C       EQUILIBRIUM EQUATION
    F(2) =  K11*HB*OH - B11
    F(3) =  K21*HB**2*OH - B21
    F(4) =  K31*HB**3*OH - B31
    F(5) =  K42*HB**4*OH**2 - B42

C       ELECTRONEUTRALITY EQUATION                 ! Add this Eq., if pH is
unknown
c     F(6) = ( B11 + B21 + B31 + 2*B42 + OH ) - KW/OH

    DO 10 I = 1, NP
      F(I) = -F(I)
10      CONTINUE

C       SET ELEMENTS OF JACOBIAN MATRICES

    DO 20 I = 1,NP
      DO 20 J = 1,NP
        DF(I,J) = 0.
  20 CONTINUE

C       For B11
        DF(1,1) =  1.
        DF(2,1) = -1.
C       DF(6,1) =  1.

C       For B21
        DF(1,2) =  2.
        DF(3,2) = -1.
C       DF(6,2) =  1.

C       For B31
        DF(1,3) =  3.
        DF(4,3) = -1.
C       DF(6,3) =  1.
```

```
C       For B42
        DF(1,4) =  4.
        DF(5,4) = -1.
C       DF(6,4) =  2.

C       For HB
        DF(1,5) = 1.
        DF(2,5) = K11*OH
        DF(3,5) = 2.*K21*HB *OH
        DF(4,5) = 3.*K31*HB**2*OH
        DF(5,5) = 4.*K42*HB**3*OH**2

        RETURN
        END


      SUBROUTINE CALROW (TK, ROH2O)
      IMPLICIT REAL*8 (A-H, K, O-Z)
C
C ********************************************************************
C     DENSITY OF WATER
C
C     F. FRANKS, "WATER A COMPREHENSIVE TREATISE", PLENUM PRESS
C     VOL. 1 (1972)
C     ROH2O : DENSITY OF PURE WATER   G/CC
C********************************************************************
      A0 =  5.0756897E02
      A1 =  3.2813464
      A2 = -4.6638625E-2
      A3 =  1.2941179E-4
      A4 = -1.7344969E-7
      A5 =  9.9308722E-11
      B  = -4.5854083E-3

      ROH2O =  (A0 + A1*TK + A2*TK**2 + A3*TK**3 + A4*TK**4 + A5*TK**5)
     $      / ( 1 + B*TK)
      ROH2O = 0.001 * ROH2O

      RETURN
      END

      SUBROUTINE CALKW (TK, ROH2O, KW)
      IMPLICIT REAL*8 (A-H, K, O-Z)
C
C ********************************************************************
C       IONIC PRODUCT OF WATER
```

```
C MARSHALL AND FRANK CORRELATION
C W. L. MARSHALL & E. U. FRANCK, "ION PRODUCT OF WATER SUBSTANCE,
C 0-1000 C, 1-10,000 BARS NEW INTERNATIONAL FORMULATION AND ITS
C BACKGROUND", J.PHYS. CHEM. REF. DATA, VOL. 10, NO. 2,
C PP. 295-304(1981)
C******************************************************************
C    ROH2O : G /CM3
C    TK    : ABSOLUTE TEMPERATURE

      A =   -4.098
      B = -3245.2
      C =    2.2362E5
      D =   -3.984E7
      E =   13.957
      F = -1262.3
      G =    8.5641E5
      KW =   A + B/TK + C/(TK**2) + D/(TK**3)
     $   + ( E + F/TK + G/(TK**2) ) * DLOG10(ROH2O)
      KW = 10.**KW

      RETURN
      END



      SUBROUTINE CALKB(TK, SI, K11, K21, K31, K42)
      IMPLICIT REAL*8 (A-H, K,O-Z)
C******************************************************************
C       EQULIBRIUM CONSTANTS OF BORATES
C
C    BY BEAS &MESMER,  THE HYDROLYSIS OF CATIONS, JOHN WILEY AND
C    SONS, NEW YORK, NY. 1976
C    TK:       ABSOLUTE TEMPERATURE
C******************************************************************

        K11 = 1573.21/TK + 28.6059 +  0.012078 * TK - 13.2258 * DLOG10(TK)
        K21 = 2756.1 /TK - 18.996 +  5.835  * DLOG10(TK)
        K31 = 3339.5 /TK - 8.084 + 1.497 * DLOG10(TK)
        K42 =12820. /TK -134.56 + 42.105 * DLOG10(TK)                 ?
        K53 =14099. /TK -118.115  + 36.237  * DLOG10(TK)

      K11 = 10.**K11
      K21 = 10.**K21
      K31 = 10.**K31
      K42 = 10.**K42
      K53 = 10.**K53
```

```
      RETURN
      END

      SUBROUTINE MNEWT(NTRIAL,N,TOLX,TOLF, X, OH)
C       W. H. PRESS, ET. AL., "NUMERICAL RECIPES THE ART OF SCIENTIFIC
C        COMPUTING", CAMBRIDGE, CAMBIRIDGE UNIVERSITY PRESS(1988)
C
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (NP=6)
      COMMON /BORO/ TK, BT
      DIMENSION X(NP),DF(NP,NP),F(NP),INDX(NP)

      DO 13  K=1,NTRIAL

      DO 5 I = 1, 5
       IF ( X(I) .LT. 0. ) X(I) = 1.D-14 * BT
       IF ( X(I) .GT. BT ) X(I) = BT
    5 CONTINUE
         CALL USRFUN (F, DF, X, OH)
         ERRF=0.

       DO 11 I=1,N
        ERRF=ERRF + DABS( F(I) )
   11  CONTINUE

C       PRINT *,(X(J),J=1,7)
       IF(ERRF.LE.TOLF) GO TO 15
       CALL LUDCMP(DF,N,NP,INDX,D)
       CALL LUBKSB(DF,N,NP,INDX,F)
       ERRX=0.
500      format(/,3x, 3(d12.6,3x),/)
       DO 12 I=1,N
         if(x(i)<=0.0) then
           if(i==1) x(i) = x(i+1)
           if(i==3) x(i) = x(i-1)
           if(i==4) x(i) = 1.0d-14
         endif
        ERRX = ERRX + DABS( F(I)/X(I) )
        X(I) = X(I) + F(I)
         if(x(i)<=0.0) then
                 if(i==1) x(i) = x(i+1)
                 if(i==3) x(i) = x(i-1)
                 if(i==4) x(i) = 1.0d-14
         endif
   12  CONTINUE
```

```
      IF(ERRX .LE. TOLX) GO TO 15
   13 CONTINUE

      WRITE(8,100)
         write(*,100)
  100 FORMAT ( /'  **** NO CONVERGENCE ****'/ )
  15 CONTINUE
C  15 WRITE(7,200) K
C 200 FORMAT ( /' ITERATION NO. =     ', I5/ )
      RETURN
      END

      SUBROUTINE LUBKSB(A,N,NP,INDX,B)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(NP,NP),INDX(N),B(N)
      II=0
      DO 12 I=1,N
        LL=INDX(I)
        SUM=B(LL)
        B(LL)=B(I)
        IF (II.NE.0)THEN
          DO 11 J=II,I-1
            SUM=SUM-A(I,J)*B(J)
11          CONTINUE
        ELSE IF (SUM.NE.0.) THEN
          II=I
        ENDIF
        B(I)=SUM
12    CONTINUE
      DO 14 I=N,1,-1
        SUM=B(I)
        IF(I.LT.N)THEN
          DO 13 J=I+1,N
            SUM=SUM-A(I,J)*B(J)
13          CONTINUE
        ENDIF
        B(I)=SUM/A(I,I)
14    CONTINUE
      RETURN
      END


      SUBROUTINE LUDCMP(A,N,NP,INDX,D)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (NMAX=100,TINY=1.0E-20)
```

```
      DIMENSION A(NP,NP),INDX(N),VV(NMAX)
      D=1.
      DO 12 I=1,N
        AAMAX=0.
        DO 11 J=1,N
          IF (DABS(A(I,J)).GT.AAMAX) AAMAX=ABS(A(I,J))
11        CONTINUE
        IF (AAMAX.EQ.0.) PAUSE 'Singular matrix.'
        VV(I)=1./AAMAX
12      CONTINUE
      DO 19 J=1,N
        IF (J.GT.1) THEN
          DO 14 I=1,J-1
            SUM=A(I,J)
            IF (I.GT.1)THEN
              DO 13 K=1,I-1
                SUM=SUM-A(I,K)*A(K,J)
13              CONTINUE
              A(I,J)=SUM
            ENDIF
14          CONTINUE
        ENDIF
        AAMAX=0.
        DO 16 I=J,N
          SUM=A(I,J)
          IF (J.GT.1)THEN
            DO 15 K=1,J-1
              SUM=SUM-A(I,K)*A(K,J)
15            CONTINUE
            A(I,J)=SUM
          ENDIF
          DUM=VV(I)*ABS(SUM)
          IF (DUM.GE.AAMAX) THEN
            IMAX=I
            AAMAX=DUM
          ENDIF
16        CONTINUE
        IF (J.NE.IMAX)THEN
          DO 17 K=1,N
            DUM=A(IMAX,K)
            A(IMAX,K)=A(J,K)
            A(J,K)=DUM
17          CONTINUE
          D=-D
          VV(IMAX)=VV(J)
        ENDIF
```

```
      INDX(J)=IMAX
      IF(J.NE.N)THEN
        IF(A(J,J).EQ.0.)A(J,J)=TINY
        DUM=1./A(J,J)
        DO 18 I=J+1,N
          A(I,J)=A(I,J)*DUM
18        CONTINUE
      ENDIF
19    CONTINUE
      IF(A(N,N).EQ.0.)A(N,N)=TINY
      RETURN
      END
```

PART II. LEAST SQUARE REGRESSION OF PARAMETERS IN EQUATIONS (3-28) AND (3-30)

```
$debug
C     PROGRAM NLSTSQM


C        THIS F77 PROGRAM OF O.T.HANNA (Hanna and Sandall, Computational
C        Methods in Chemical Engineering, Prentice Hall, NJ 1995) IS ADAPTED AND
C        MODIFIED FOR CALCULATION OF EQUATIONS (3-28) AND (3-30) IN
C        CHAPTER III.THE PROGRAM DOES LINEAR/NONLINEAR LEAST
C        SQUARES MULTIPLE REGRESSION.
C        FOR LINEAR PROBS. YP= G0(X(1),...,X(K)) + B(1)*G1(X(1),...,X(K)) +
C        + B(2)*G2(X(1),...,X(K))... + B(P)*GP(X(1),...,X(K)).
C        FOR NONLINEAR PROBS. YPRED = F(X(1),...,X(K),B(1),B(2),...,B(P)).
C        N=NUMBER OF DATA SETS X(I,J),Y(I).
C        P=NUMBER OF PARAMETERS TO BE DETERMINED.
C        K=NUMBER OF INDEPENDENT VARIABLES.
C        FOR N = P, PROGRAM DOES INTERPOLATION
C        CURRENT DIMENSIONING OF X1(I,J),ETC., REQUIRES N <= 50, K <= 4.
C        CASE=1 FOR LINEAR LST. SQ., CASE=2 FOR NONLINEAR LST. SQ.
C        PROGRAM GIVES OPTION TO CALCULATE PREDICTED FUNCTION.
C        BOTH ERROR LEAST-SQUARES AND ERROR-MAX. ARE GIVEN.
C        USER MUST SPECIFY NO. OF DATA SETS (N), NO. OF PARAMETERS (P),
C        AND NO. OF INDEPENDENT VARIABLES (K) IN *PARAMETER
C        STATEMENT* BELOW.
C        DATA GIVEN IN HERE ARE FOR AMBERLITE IRN78 RESIN
C        IF USER USES THE CODE FOR OTHER RESIN, DATA MUST BE
C        REPLACED BY USER.

C        FOR DESIRED DOUBLE PRECISION REMEMBER TO (I) GIVE
C        CONSTANTS AS (FOR EXAMPLE) 1.D0/7.D0, NOT 1./7., AND (II) SPECIFY
C        ANY NEW VARIABLES AS DOUBLE PRECISION TYPE.
C        IF REQUIRED FOR YOUR SYSTEM, CHANGE THE WRITE UNIT NO. (NU)
C        LOCATED IN THE *PARAMETER* STATEMENT BELOW.

C**********************************************************************
C*TO RUN, SPECIFY N = NO. OF DATA SETS, P = NO. OF PARAMETERS, AND
C*K = NO. OF INDEPENDENT VARIABLES IN PARAMETER STATEMENT
C*BELOW.      *
C*IN SUBROUTINE DATA AT END OF PROGRAM GIVE THE DATA SETS
C*Y(I),X1(I,J).*
C*FOR LINEAR CASE DEFINE P+1 FUNCTIONS G0,G(1)..G(P) IN SUB FUNC
C*AS IN LINEAR MODEL ABOVE. FOR NONLINEAR CASE DEFINE THE
C*FUNCTIONS*
```

```
C*G0=F(X,B), G(1)=DF/DB(1), G(2)=DF/DB(2)...G(P)=DF/DB(P)          *
C*********************************************************************

    IMPLICIT DOUBLE PRECISION (A-H,O-Z)
    INTEGER P,CASE,QUES

C***USER MUST SPECIFY NO. OF DATA SETS (N), NO. OF PARAMETERS(P),
C***AND NO. OF INDEPENDENT VARIABLES (K) IN PARAMETER
C***STATEMENT BELOW.
C   *************************************************************
    PARAMETER (NU = 8,N = 26, P = 4, K = 2)
C   *************************************************************
C   ***USER MAY NEED TO ALTER UNIT NO. NU IN PARAMETER statement
C   ***ABOVE

    DOUBLE PRECISION B(P),G(P),X(K),X1(N,K),Y(N),Z(N),Z1(N,1),D(N,P)
    DOUBLE PRECISION DT(P,N),A(P,P),B1(P,1),B2(P),DELTAB(P),YPRED(N)
    DOUBLE PRECISION E(N),E1(N),NRMCOR
    EXTERNAL DOT
    OPEN (UNIT=NU,FILE='OUTPUT.DAT',STATUS='UNKNOWN')

C   FIRST CHECK FOR PROBLEM CONSISTENCY TO BE SURE N >= P.
    IF (N .LT. P) THEN
      WRITE (*,*)'**ERROR--N < P'
      STOP
    END IF

    WRITE (*,*)  'INPUT CASE, LINEAR(1),NONLINEAR(2) ? '
    WRITE (NU,*) 'INPUT CASE, LINEAR(1),NONLINEAR(2) ? '
    READ*,CASE

        NNZ = CASE

    IF (CASE .EQ. 1) THEN
      WRITE (*,*)  'LINEAR CASE  '
      WRITE (NU,*)  'LINEAR CASE  '
    ELSE IF (CASE .EQ.2) THEN
      WRITE (*,*)  'NONLINEAR CASE  '
      WRITE (NU,*)  'NONLINEAR CASE  '
    END IF

    CALL DATA(NU,N,K,X1,Y,P,NNZ)

C...SET INITIAL PARAMETER VALUES B(I) FOR LIN. OR NONLIN. PROBLEM
    IF (CASE .EQ. 2) THEN
      WRITE (*,*)  'NONLINEAR PROB.,INPUT INITIAL VALUES OF B(I)'
```

```
      WRITE (NU,*) 'NONLINEAR PROB.,INPUT INITIAL VALUES OF B(I)'
      DO 10 I=1,P
        WRITE (*,12)'INPUT B(',I,')'
12       FORMAT(' ',A,I2,A)
        READ*,B(I)
        WRITE (*,15) 'B(',I,')=',B(I)
        WRITE (NU,15)'B(',I,')=',B(I)
15       FORMAT (' ',A,I2,A,D13.6)
10     CONTINUE
    ELSE
      DO 20 I=1,P
        B(I) = 0.D0
20     CONTINUE
    END IF

C*************************START OF MAIN LS CALCULATION LOOP
    DO 500 I1 = 1,1E6
C...CALCULATE NORMAL EQNS., (DTD)*DELTAB = DT*Z
C...SET MATRIX D: D(I,K) = GK(X1(I,1),X1(I,2),...,X1(I,K))
C...Z(I) = Y(I) - GO(X1(I,1),X1(I,2),...,X1(I,K))
      DO 30 I = 1,N
C...SET X VECTOR AT GIVEN DATA SET
        DO 32 J = 1,K
          X(J) = X1(I,J)
32       CONTINUE
        CALL FUNC(P,K,X,G0,G,B)
        Z(I) = Y(I) - G0
        Z1(I,1) = Z(I)
        DO 35 M = 1,P
          D(I,M) = G(M)
35       CONTINUE
30     CONTINUE

C...SET MATRIX TRANSPOSE DT: DT(K,I) = D(I,K)
      DO 40 I = 1,N
        DO 45 M = 1,P
          DT(M,I) = D(I,M)
45       CONTINUE
40     CONTINUE

C...FORM THE MATRIX DT*D = A AND THE VECTOR DT*Z = B2
    CALL MTXMLT(P,N,DT,N,P,D,A)
    CALL MTXMLT(P,N,DT,N,1,Z1,B1)
    DO 50 I=1,P
      B2(I) = B1(I,1)
50   CONTINUE
```

```
C...SOLVE NORMAL EQNS. (DT*D)*DELTAB = DT*Z TO GET CORR. DELTAB
C...TO B.
    CALL LNEQ(P,A,B2,DELTAB,DET,RELERR)
    DO 55 I=1,P
      B(I) = B(I) + DELTAB(I)
55  CONTINUE
    NRMCOR = DSQRT( DOT(P,DELTAB,DELTAB,NNZ) )

    IF (CASE .EQ. 2) THEN
      WRITE (*,70)  'NORM OF CORRECTIONS = ',NRMCOR
      WRITE (NU,70) 'NORM OF CORRECTIONS = ',NRMCOR
70      FORMAT (' ',A,D13.6)
    END IF
    WRITE (*,*)
    WRITE (NU,*)

C...USE STOP TEST FOR NONLINEAR PROBLEM
C...LOOP UNTIL CASE = 1 OR NRMCOR (NORM OF CORR) < 1.D-7
     IF ( (CASE .EQ. 1) .OR. (NRMCOR .LT. 1.D-10) ) GO TO 501
500   CONTINUE
501   CONTINUE

C...PRINT FINAL RESULTS
    DO 60 I = 1,P
      IF (CASE .EQ. 2) THEN
        WRITE (*,63)  'B(',I,') = ',B(I),'CORR(',I,') = ',DELTAB(I)
        WRITE (NU,63) 'B(',I,') = ',B(I),'CORR(',I,') = ',DELTAB(I)
63        FORMAT (' ',A,I2,A,D13.6,T30,A,I2,A,D13.6)
      ELSE
        WRITE (*,65)  'B(',I,') = ',B(I)
        WRITE (NU,65) 'B(',I,') = ',B(I)
65        FORMAT (' ',A,I2,A,D13.6)
      END IF
60  CONTINUE
    WRITE(*,*)
    WRITE(NU,*)

C...CALCULATE ERROR(EST. VARIANCE) AND RESIDUAL ERRORS E(I) IN
C...TERMS OF FUNCTION YPRED(X)
       EMAX  = 0.D0
           eimax = 0.d0
           sumei = 0.d0
       DO 80 I = 1,N
         DO 75 J = 1,K
           X(J) = X1(I,J)
```

```
75        CONTINUE
         CALL FUNC(P,K,X,G0,G,B)
         IF (CASE .EQ. 1) THEN
           YPRED(I) = G0 + DOT(P,B,G,NNZ)
         ELSE
           YPRED(I) = G0
         END IF
C...E(I) IS RESIDUAL
         E(I)  = Y(I) - YPRED(I)
             ei    = dabs(e(i))/y(i)
             if(ei.gt.eimax) eimax = ei
             sumei = sumei + ei
         IF (DABS(E(I)) .GT. EMAX)  EMAX = DABS(E(I))
         WRITE(*,77) 'Y(',I,')=',Y(I),'YPRED(',I,')=',YPRED(I),
   +       'E(',I,')=',E(I)
         WRITE(NU,77)'Y(',I,')=',Y(I),'YPRED(',I,')=',YPRED(I),
   +       'E(',I,')=',E(I)
77        FORMAT(' ',A,I2,A,D13.6,T24,A,I2,A,D13.6,T50,A,I2,A,D13.6)
80      CONTINUE
               averror = sumei/n
       WRITE (*,*)
       WRITE (NU,*)

C...SSE = SUM OF SQUARED RESIDUALS
       SSE = DOT(N,E,E,NNZ)
       IF (N .NE.P) THEN
         ERROR = SSE/(N - P)
         WRITE(*,85) 'ERROR=SSE/(N-P) =',ERROR,'MAX ERROR =',EMAX
         WRITE(NU,85)'ERROR=SSE/(N-P) =',ERROR,'MAX ERROR =',EMAX
             write(*,85)'AVERAGE ERROR = ', averror, 'MAX error =',eimax
             write(nu,85)'AVERAGE ERROR = ',averror,'MAX error =',eimax
85        FORMAT (' ',A,D13.6,T37,A,D13.6)
       ELSE
         WRITE (*,*) 'N=P,INTERPOLATION CALCULATION'
         WRITE (NU,*)'N=P,INTERPOLATION CALCULATION'
         IF (SSE.GT.1.D-7) WRITE(*,*)'CAREFUL,RESULTS MAY BE POOR!'
         WRITE (*,*)
         WRITE (NU,*)
       END IF
       WRITE (*,*)
       WRITE (NU,*)

C******************** END OF MAIN LEAST SQUARES CALCULATION

C...WE NOW EVALUATE  YPRED(X) VALUES VIA PROMPT.
    DO 1000 I2 = 1,1E6
```

```
          WRITE(*,*) 'PREDICTION DESIRED AT PARTICULAR X (NO-0,YES-1) ?'
          WRITE(NU,*)'PREDICTION DESIRED AT PARTICULAR X (NO-0,YES-1) ?'
          READ*,QUES
          IF (QUES .EQ. 1) THEN
            WRITE(*,*) 'SPECIFY K COMPONENTS OF VECTOR X()'
            WRITE(NU,*)'SPECIFY K COMPONENTS OF VECTOR X()'
            DO 90 I=1,K
              WRITE(*,95)'X(',I,')='
95             FORMAT(' ',A,I2,A)
              READ*,X(I)
90           CONTINUE
            DO 100 I=1,K
              WRITE(*,105)'X(',I,') =',X(I)
              WRITE(NU,105)'X(',I,') =',X(I)
105             FORMAT(' ',A,I2,A,D13.6)
100           CONTINUE
            CALL FUNC(P,K,X,G0,G,B)
            IF (CASE .EQ. 1) THEN
              YP = G0 + DOT(P,B,G,NNZ)
            ELSE
              YP = G0
            END IF
            WRITE (*,120) 'YPRED =',YP
            WRITE (NU,120)'YPRED =',YP
120           FORMAT (' ',A,D13.6)
            WRITE (*,*)
            WRITE (NU,*)
          END IF
1000  CONTINUE

        END

        SUBROUTINE MTXMLT(NR1,NC1,A1,NR2,NC2,A2,PROD)
C...THIS IS A GENERAL SUB FOR MATRIX MULTIPLICATION BY O.T.HANNA.
C...NR1,NC1 ARE NO. OF ROWS, COLS. FOR MATRIX A1,ETC.
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        DOUBLE PRECISION A1(NR1,NC1),A2(NR2,NC2),PROD(NR1,NC2)
        IF (NC1 .NE. NR2) THEN
          WRITE (*,*) '**ERROR,N0. COLS A1 .NE. N0. ROWS A2'
          STOP
        END IF
        DO 10 I=1,NR1
          DO 20 K=1,NC2
          PROD(I,K) = 0.D0
            DO 30 J=1,NC1
              PROD(I,K) = PROD(I,K) + A1(I,J)*A2(J,K)
```

```
30        CONTINUE
20      CONTINUE
10    CONTINUE
      RETURN
      END

      SUBROUTINE LNEQ(N,A,B,X,DET,RELERR)
C...THIS A SUB TO SOLVE LINEAR EQNS. AX = B BY O.T.HANNA. A IS A
C...MATRIX AND X, B ARE VECTORS. PROGRAM FOLLOWS SOMEWHAT THE
C...OUTLINE OF J.C.MASON. PROGRAM DOES ONE ITERATIVE
C...IMPROVEMENT TO IMPROVE ACCURACY AND ESTIMATE ERROR. SUB IS
C...SET UP FOR <= 50 EQNS.;FOR MORE, CHANGE DIMENSIONING.

      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION A(N,N),A1(50,50),B(N),B1(50),X(N),X1(50,2),
     +  RELERR(N),R(50),DET
      INTEGER L(50)
      PARAMETER(EPS = 1.D-10)

      DET = 1.D0
C...KEEP COPY OF ORIGINAL A,B IN A1,B1
      DO 3 I=1,N
        B1(I) = B(I)
        DO 5 J=1,N
          A1(I,J) = A(I,J)
5       CONTINUE
3     CONTINUE

C...PERFORM N CYCLES OF PIVOT/ELIMINATION ON MATRIX A
C...FIND LARGEST ABS(A(I,J)) IN COL. K; RECORD ROW NO. IN L(K)
      DO 100 K=1,(N-1)
        D = 0.D0
        DO 10 I=K,N
          C = DABS(A(I,K))
          IF (D .LT. C) THEN
            D = C
            L(K) = I
          END IF
10      CONTINUE
        IF (DABS(D) .LT. 1.D-14) THEN
          WRITE (*,*) '*** SINGULAR MATRIX ***'
          RETURN
        END IF

        L1 = L(K)
C...INTERCHANGE ROWS K AND L(K) IF NECESSARY
```

```
      IF (L1 .NE. K) THEN
C...THIS CHANGES SIGN OF DETERMINANT
        DET = -1.D0*DET
C...NOW INTERCHANGE ROWS K AND L(K) OF MATRIX A
        DO 20 J=K,N
          D = A(K,J)
          A(K,J) = A(L1,J)
          A(L1,J) = D
20        CONTINUE
      END IF
C...NOW CALC. MULTIPLIERS  AMULT(I,K) TO ELIM. A(I,K) FOR I > K
C...STORES AMULT IN NEWLY VACATED LOCATION A(I,K)
      DO 30 I=(K+1),N
        AMULT = -A(I,K)/A(K,K)
        A(I,K) = AMULT
C...PERFORM ROW OPERATIONS ON MATRIX A
        DO 40 J=(K+1),N
          A(I,J) = A(I,J) + AMULT*A(K,J)
40        CONTINUE
30      CONTINUE
100   CONTINUE
C...CALCULATE DETERMINANT DET OF MATRIX A
    DO 50 I=1,N
      DET = DET*A(I,I)
50    CONTINUE

    DO 150 I1=1,2
C...NOW INTERCHANGE ROWS K AND L(K) OF VECTOR B AS FOR MATRIX A
      DO 70 K=1,(N-1)
        L1 = L(K)
        IF (L1 .NE. K) THEN
          D = B(K)
          B(K) = B(L1)
          B(L1) = D
        END IF
C...PERFORM ROW OPERATIONS ON B
        DO 60 I=(K+1),N
          AMULT = A(I,K)
          B(I) = B(I) + AMULT*B(K)
60        CONTINUE
70      CONTINUE
C...CALCULATE X(N)...X(1) BY BACK SUBSTITUTION
      X(N) = B(N)/A(N,N)
      X1(N,I1) = X(N)
      DO 90 I=(N-1),1,-1
        D = B(I)
```

```
          DO 80 J=(I+1),N
            D = D - A(I,J)*X(J)
80          CONTINUE
          X(I) = D/A(I,I)
          X1(I,I1) = X(I)
90        CONTINUE
C...CALCULATE RESIDUAL VECTOR R = B - AX
        DO 110 I=1,N
          W = B1(I)
          DO 95 J=1,N
            W = W -A1(I,J)*X(J)
95          CONTINUE
          R(I) = W
          B(I) = R(I)
          B1(I) = B(I)
110       CONTINUE
150     CONTINUE
      DO 120 I=1,N
        X(I) = X1(I,1) + X1(I,2)
        RELERR(I) = DABS(X1(I,2))/(DABS(X(I)) + EPS)
120     CONTINUE
      RETURN
      END

      FUNCTION DOT(N,Y,Z,NNZ)
C...SUBROUTINE FOR DOT PRODUCT OF VECTORS Y(I) AND Z(I)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION Y(N),Z(N)
      DOT = 0.D0
      DO 10 I = 1,N
        DOT = DOT + Y(I)*Z(I)
10      CONTINUE
      RETURN
      END

      SUBROUTINE FUNC(P,K,X,G0,G,B)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER P
      DOUBLE PRECISION X(K),G(P),B(P)

C...SUB FUNC SPECIFIES THE MODEL FITTING FUNCTION.
C...HERE X IS THE VECTOR (X(1),X(2),...,X(K)).
C...FOR LINEAR PROBS. YPRED = G0(X)+C1*G1(X)+C2*G2(X)...+CP*GP(X).
C...FOR NONLINEAR PROBS. YPRED = F(X,B1,B2..BP) WITH GO = F,
C...G(1) = DF/DB1, G(2) = DF/DB2,...,G(P) = DF/DBP.
C...SPECIFY N=NO.OF DATA SETS,P=NO.OF PARAMETERS AND K=NO. OF
```

```
C...INDEPENDENT VARIABLES IN PARAMETER STATEMENT NEAR TOP OF
C...MAIN PROGRAM.
C...THE MARKS *** DESIGNATE USER SPECIFIED STATMENTS.


C***EQUATION (3-30) WHERE  YPRED = C1 + C2*LOG(X1)+[-(C3*X2 +
C4*X2**2)]
C***HERE P = 4.

        IF(NNZ==1) THEN

    G0 = 0.D0
    G(1) = 1.d0
    G(2) = dlog(X(1))
    G(3) = -X(2)
    G(4) = -X(2)**2

        ELSE
C***EXAMPLE OF NONLINEAR MODEL WHERE YPRED = F(X,B1,B2) =
C***G0(X,B1,B2),
C***G(1) = DF/DB1, AND G(2) = DF/DB2.
C***EXAMPLE IS  ypred = b1*x1**b2*exp(-(b3*x2+b4*x2**2))
C***HERE P = 4.

C               G0 =  YPRED
C               G1 =  X1**B2*EXP[-(B3*X2+B4*X2**2)]
C               G2 =  G0*LOG(X1)
C               AND SO ON

        a1  = b(1)
        a2  = x(1)**b(2)
        a3  = dexp(-(b(3)*x(2)+b(4)*x(2)**2))

        g0  = a1*a2*a3
        g(1) = a2*a3
        g(2) = g0*dlog(x(1))
        g(3) = -x(2)*g0
        g(4) = -(x(2)**2)*g0

        ENDIF

    RETURN
    END

    SUBROUTINE DATA(NU,N,K,X1,Y,P,NNZ)
C...HERE THE USER MUST SPECIFY THE DATA PAIRS X(I),Y(I).
```

```
C...THE MARKS *** DESIGNATE WHERE THE USER MUST MODIFY THE
C...PROGRAM.
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION X1(N,K),X2(50,4),Y(N),Y1(50)
      INTEGER Q,P

      WRITE (*,10)  'NUMBER OF PARAMETERS = ',P
      WRITE (NU,10) 'NUMBER OF PARAMETERS = ',P
10     FORMAT (' ',A,I2)
      WRITE (*,20)  'NUMBER OF DATA SETS = ',N
      WRITE (NU,20) 'NUMBER OF DATA SETS = ',N
20     FORMAT (' ',A,I2)
      WRITE (*,25)  'NUMBER OF INDEPENDENT VARIABLES = ',K
      WRITE (NU,25) 'NUMBER OF INDEPENDENT VARIABLES = ',K
25     FORMAT (' ',A,I2)
      WRITE (*,*)
      WRITE (NU,*)
      WRITE (*,*) 'ORIGINAL DATA'
      WRITE (NU,*)'ORIGINAL DATA'

C...GIVE HERE THE DATA SETS Y(I),X1(I,J) SPECIFIED; THE NO. OF DATA
C...SETS(N), THE NO. OF PARAMETERS(P), AND THE NO. OF INDEPENDENT
C...VARIABLES(K) MUST BE GIVEN IN THE PARAMETER STATEMENT IN THE
C...MAIN PROGRAM. WE CANNOT USE DUMMY VARIABLES X1(I,J),Y(I) IN
C...DATA STATEMENTS, SO USE X2(I,J),Y1(I) TO GIVE DATA;THEN CHANGE
C...BACK.

C...SPECIFY DATA SETS Y(I),X1(I,J) BELOW USING INDICATED FORMAT.
C...X1(I,J) IS ITH DATA VALUE FOR JTH INDEPENDENT VARIABLE.
C...I (NO. DATA SETS) GOES FROM 1 TO N; J (NO. INDEP'T VARIBLES) GOES
C...FROM 1 TO K. FOR EXAMPLE, IF K=4 AND THE FIRST DATA SET
C...CORRESPONDS TO Y(1)=8, X(1)=4, X(2)=3, X(3)=1 WE COULD WRITE
C...DATA Y1(1),X2(1,1),X2(1,2),X2(1,3) /8.D0,4.D0,3.D0,1.D0/
C...OR FOR LARGER K, IT MAY BE BETTER TO USE THE IMPLIED LOOP FORM
C...DATA Y1(1),(X2(I), J = 1,K) /8.D0,4.D0,3.D0,1.D0/

*********START OF DATA---SPECIFIED BY USER************************
C...EXAMPLE HERE IS FOR N=26, K=2.
C       DATA PROVIDED HERE ARE FOR REGRESION OF AMBERLITE IRN78
LC
C       RESIN AS AN EXAMPLE
        DATA Y1(1), X2(1,2), X2(1,1)  /19.41D0, 10.D0, 1.1154D-1/
        DATA Y1(2), X2(2,2), X2(2,1)  /24.31D0, 10.D0, 3.2481d-1/
        DATA Y1(3), X2(3,2), X2(3,1)  /28.63D0, 10.D0, 6.2235d-1/
        DATA Y1(4), X2(4,2), X2(4,1)  /32.50D0, 10.D0, 9.2864d-1/
        DATA Y1(5), X2(5,2), X2(5,1)  /36.05D0, 10.D0, 1.23980d0/
```

```
        DATA Y1(6 ),X2(6 ,2),X2(6,1)  /39.57D0, 10.D0, 1.58700d0/
        DATA Y1( 7),X2( 7,2),X2( 7,1) /16.72D0, 30.D0, 1.1148d-1/
        DATA Y1( 8),X2( 8,2),X2( 8,1) /19.98D0, 30.D0, 2.3676d-1/
        DATA Y1( 9),X2( 9,2),X2( 9,1) /22.78D0, 30.D0, 3.7027d-1/
        DATA Y1(10),X2(10,2),X2(10,1) /26.52D0, 30.D0, 6.8064d-1/
        DATA Y1(11),X2(11,2),X2(11,1) /29.80D0, 30.D0, 1.00350d0/
        DATA Y1(12),X2(12,2),X2(12,1) /32.25D0, 30.D0, 1.33080d0/
        DATA Y1(13),X2(13,2),X2(13,1) /32.54D0, 30.D0, 1.43990d0/
        DATA Y1(14),X2(14,2),X2(14,1) /16.17D0, 45.D0, 1.2457D-1/
        DATA Y1(15),X2(15,2),X2(15,1) /21.94D0, 45.D0, 3.8723d-1/
        DATA Y1(16),X2(16,2),X2(16,1) /25.10D0, 45.D0, 7.0658d-1/
        DATA Y1(17),X2(17,2),X2(17,1) /27.75D0, 45.D0, 1.04000d0/
        DATA Y1(18),X2(18,2),X2(18,1) /30.23D0, 45.D0, 1.39200d0/
        DATA Y1(19),X2(19,2),X2(19,1) /13.50D0, 60.D0, 1.4000d-1/
        DATA Y1(20),X2(20,2),X2(20,1) /15.67D0, 60.D0, 2.0038d-1/
        DATA Y1(21),X2(21,2),X2(21,1) /18.12D0, 60.D0, 3.4430d-1/
        DATA Y1(22),X2(22,2),X2(22,1) /19.51D0, 60.D0, 4.4125d-1/
        DATA Y1(23),X2(23,2),X2(23,1) /22.47D0, 60.D0, 7.2008d-1/
        DATA Y1(24),X2(24,2),X2(24,1) /25.20D0, 60.D0, 1.04580d0/
        DATA Y1(25),X2(25,2),X2(25,1) /27.39D0, 60.D0, 1.37910d0/
        DATA Y1(26),X2(26,2),X2(26,1) /28.61D0, 60.D0, 1.54150d0/
C*********END OF DATA*******************************************

C...NOW CHANGE DATA BACK TO Y(I),X1(I,J)
    DO 30 I=1,N
      Y(I) = Y1(I)
      DO 32 J=1,K
        X1(I,J) = X2(I,J)
32      CONTINUE
30    CONTINUE
    WRITE(*,*) 'OBSERVATIONS Y(I) AND XJ(I)'
    WRITE(NU,*)'OBSERVATIONS Y(I) AND XJ(I)'
    WRITE(*,35) 'Y','X1','X2','X3','X4'
    WRITE(NU,35)'Y','X1','X2','X3','X4'
35    FORMAT(' ',T9,A,T23,A,T37,A,T51,A,T67,A)
    DO 40 I=1,N
      WRITE(*,42)  Y(I),(X1(I,J),J=1,K)
      WRITE(NU,42) Y(I),(X1(I,J),J=1,K)
42      FORMAT(' ',5D14.6)
40    CONTINUE

    WRITE (*,*)
    WRITE (NU,*)
    WRITE (*,*)  'IS DATA TO BE TRANSFORMED?(NO-0,YES-1) '
    WRITE (NU,*) 'IS DATA TO BE TRANSFORMED?(NO-0,YES-1) '
    READ*,Q
```

```
   IF (Q .EQ. 1) THEN
C***USER MUST SPECIFY ANY DESIRED TRANSFORMATION BELOW

    WRITE (*,*) 'TRANSFORMED DATA,Y=Y,X=X'
    WRITE (NU,*)'TRANSFORMED DATA,Y=Y,X=X'
    DO 50 I = 1,N
C***       Y(I) = LOG( Y(I) )
C***       X1(I,1) = 1.D0/X1(I,1)
C***       ETC.

             equiv  = 61.811/3.

      IF(NNZ==1) THEN
c     for linear regression of Amberlite IRN78LC RESIN
      y(i)   = dlog(y(i)*61.811/10.811/equiv)
      x1(i,1) = x1(i,1)*61.811/10.811/equiv
       x1(i,2) = x1(i,2)+2.7315d2
      ELSE
c     for nonlinear regression
          y(i)    = y(i)*61.811/10.811/equiv
          x1(i,1) = x1(i,1)*61.811/10.811/equiv         !CONCENTRATION
          x1(i,2) = x1(i,2)+2.7315d2                    !TEMPERATURE
      ENDIF


50   CONTINUE
    WRITE(*,*) 'TRANSFORMED OBSERVATIONS Y(I) AND XJ(I)'
    WRITE(NU,*)'TRANSFORMED OBSERVATIONS Y(I) AND XJ(I)'
    WRITE(*,60) 'Y','X1','X2','X3','X4'
    WRITE(NU,60)'Y','X1','X2','X3','X4'
60   FORMAT(' ',T9,A,T23,A,T37,A,T51,A,T67,A)
    DO 70 I=1,N
      WRITE(*,75)  Y(I),(X1(I,J),J=1,K)
      WRITE(NU,75) Y(I),(X1(I,J),J=1,K)
75     FORMAT(' ',5D14.6)
70   CONTINUE
    WRITE (*,*)
    WRITE (NU,*)
   END IF

   RETURN
   END
```

PART III HOMOBTRS.FOR

```
$debug
C**********************************************************************
C      This program is developed to calculate column dynamic behavior
C      of Boron Thermal Regenerate System as a part of the project of boron
C      sorption by ion exchange in nuclear power plants in Chapter IV.
C      The model uses the isotherm derived in Chapter III, with LDF & plug
C      flow simplifications.
C                                                     By Jidong Lou
C                                                     October, 1996
C**********************************************************************
C
C      CHT_BED:   Height of column (cm)
C      CON_PPM:   Concentration in ppm
C      COI:       Bulk concentration of ith species.
C      CII:       Interfacial concentration of ith species.
C      CFBT:      The total boron concentration in the influent of column (meq/cm^3).
C      DE_PAR:    Effective diffusivity of boron in particle
C      DEN_SOLV:  Density of solution (g/cm^3)
C      DIA_ANI:   Diameter of anion resin particle (cm)
C      DIA_CAT:   Diameter of cation resin particle (cm)
C      DIA_BED:   Diameter of column (cm)
C      DIFFI:     Self-Diffusivity of ith species.
C      DKMN:      Equilibrium constants of reaction of borate, M – is the number of
C                 boron atom in the borate, N – is the charge number of the borate
C      DKLA:      Mass transfer coefficient of representative anion species in liquid.
C      DKWT:      Water formation equilibrium constant
C      HB:        Boric acid
C      Q_MIN:     The minimum capacity of resin (meq/cm^3 dry resin).
C      Q_APP:     The apparent (equilibrium) capacity of resin (meq/cm^3 dry resin).
C      TEMPC      Temperature in °C
C      TEMPK      Temperature in Kelvin
C      VCP_SOLV:  Viscosity of solution in CP.
C      VDF_BED:   Void fraction of bed
C      VELS:      Solution velocity              (cm/sec)
C      VOL_FLOW:  Volume flow rate through column (cm^3/sec).
C      XCBTI:     Concentration fraction of species BT at the interface.
C      XCBTB:     Concentration fraction of species BT in the bulk liquid.
C      YCBTA:     Average concentration fraction of species BT in the resin phase.
C      YCBTI:     Interfacial concentration fraction of species BT in the resin phase.

       implicit real*8 (a-h, o-z)
       common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
       common /data1/ vol_flow, vcp_solv, den_solv
       common /data2/dia_ani, dia_bed, cht_bed, vdf_bed
```

```
        common /data3/q_psuedo, cf_psuedo
        common /data4/ccsec,temp
        common /defltl/diffb1,diffb3,diffhb,diffoh,de_par
        common /equi_20/dk11,dk21,dk31,dk42,dkwt,dkla
        common /solconc/cooh,coch,cobt,cob1,cob3,cohb
        common /infconc/ata,cfbt
        common /consts1/tautot,tau,xi,taupr,nt,chtd,time
        common /coeffeq/ap,bp,cp

C      dimension xcbt(3000),ycat(3000)

     open(5,file='btrsn.dat',status='unknown')

        xi  = 0.025
        tau = 0.025
        CCSEC = 1.0

        write(*,*) 'give the value of TEMP '
        read (*,*) TEMP

Calling subroutines to fulfill the tasks

        call deflts
        call output
        call solver

        stop
        END                          !end the main program

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       Subroutine OUTPUT prints out the results calculated in this code
C       called by MAIN, print calculation conditions for results.
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
        subroutine output

        implicit real*8 (a-h, o-z)
        common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
        common /data1/ vol_flow, vcp_solv, den_solv
        common /data2/dia_ani, dia_bed, cht_bed, vdf_bed
        common /equi_20/dk11,dk21,dk31,dk42,dkwt,dkla
        common /defltl/diffb1,diffb3,diffhb,diffoh,de_par
        common /infconc/ata,cfbt
        common /consts1/tautot,tau,xi,taupr,nt,chtd,time
        common /coeffeq/ap,bp,cp

C       dimension xbtout(nt+1),ybtout(nt+1)
```

```
        write (5,10)
        write (5,12) YCBT
        write (5,13) dia_ani
        write (5,81) vdf_bed
        write (5,14) q_min, q_app
        write (5,15) cfbt, vol_flow
        write (5,83) dia_bed, chtd
        write (5,16) diffb1,diffhb
        write (5,84) diffb3,diffoh
        write (5,17) vcp_solv,den_solv
        area  = 3.141592*(dia_bed*dia_bed)/4.
        vels  = vol_flow/area

        write (5,19)
        write (5,21) tau, xi
        write (5,22) time, nt
        write (5,88) dkla
        write (5,23) vels

10  FORMAT(' BED SYSTEM PARAMETERS:',/)
c  12  FORMAT(' RESIN REGENERATION',3X,': YCO =',F5.3)
13  FORMAT(' RESIN PROPERTIES',5X,': PDA=',F6.4)
81  FORMAT(24X,'VD =', F6.4)
14  FORMAT(' RESIN CONSTANTS',6X,':QA =',E10.4,3X,'QAMAX =',E10.4)
82  FORMAT(24X,'TKCO=',F6.3)
15  FORMAT(' COLUMN PARAMETERS',4X,': CF =',E10.4,' FR =',E10.4)
83  FORMAT(24X,'DIA =',F6.2,5X,'CHT =',F6.1)
16  FORMAT(' IONIC CONSTANTS',6X,': DB1=',E10.4,2X,'DHB=,'E10.4)
84  FORMAT(24X,'DB3=',E10.4,' DOH=', E10.4)
17  FORMAT(' FLUID PROPERTIES', 5X,': CP =',F7.5,5X,'DEN=',F6.4)
19  FORMAT(/,' CALCULATED PARAMETERS',/)
21  FORMAT(' INTEGRATION INCREMENTS   : TAU=',F6.4,1X,'XI=',F6.4)
22  FORMAT(' TOTAL TIME AND  SLICE    : TIME=',F8.3,2X,'NT =',I4)
88  FORMAT(24X,'KLA =', E10.4)
23  FORMAT(' SUPERFICIAL VELOCITY     : VS =',F7.3)

        CLOSE(5)
        RETURN
        END



C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       Default values for calculating MTC, self-diffusivities, equilibrium
```

```
C      constants, dimensionless parameters, etc. are given in this sub-
C      routine. Other initial and operation conditions are also specified
C      in this subroutine.
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*

       subroutine deflts
       implicit real *8 (a-h,o-z)
       common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
       common /data1/ vol_flow, vcp_solv, den_solv
       common /data2/dia_ani, dia_bed, cht_bed, vdf_bed
       common /data3/q_psuedo, cf_psuedo
       common /data4/ccsec,temp
       common /deflt1/diffb1,diffb3,diffhb,diffoh,de_par
       common /equi_20/dk11,dk21,dk31,dk42,dkwt,dkla
       common /infconc/ata,cfbt
       common /consts1/tautot,tau,xi,taupr,nt,chtd,time
       common /coeffeq/ap,bp,cp

       nn = 3
       con_ppm  = 1200.0
       tempc    = temp  !10.0
       tempk    = tempc + 273.16
       vol_flow = 4722.0                          !cm3/sec
       time     = 120.0

       ap      = 7.93735d0
       bp      =-8.71998d-3
       cp      = 2.43548d-5
       ata     = 0.274489

       dia_ani  = 0.05              !diameter of anion resin bead  cm
       q_min    = 1.5               !capacity of anion resin meq/dry.cm37
       vdf_bed  = 0.35              !bed void fraction dimensionless
       ani_frc  = 1.0               !volume fraction of anion resin in MB
       dia_bed  = 88.2              !bed diameter   cm
       cht_bed  = 139.1             !effective bed height (resin height) cm
       vcp_solv = 1.23              !viscosity of water at tempc = 10 C

Come here specify the values of selectivities and charges of ionic species

       tkbo_mon  = 1.65
       tkbo_di   = 6.197
       tkbo_tri  = 10.8
       tkbo_tetri = 16.633

       zchn      = -1.0                 !charge number of hygroxide
```

```
        zchg_monb  = -1.0                        !charge number of mono-borate
        zchg_dib   = -1.0                        !charge number of di-borate
        zchg_trib  = -1.0
        zchg_tetrib= -2.0
```

Come to here specify the initial loading in the resin phase

```
        ycbi       = 0.001 !*100.

        call CALROW (tempk, ROH2O, KK)
        den_solv   = roh2o
        cfbt = con_ppm/10811.0*3.                !total inlet boron concentration meq/cm3
                                                 !MW of boron = 10.811
        de_par     = 3.3239d-7                   !the appear average diffusivity in resin
                                                 !under 1000 ppm solution concentration

        q_app   = ap*exp(-(bp*tempk+cp*tempk**2))*cfbt**ata
        cf_psuedo = 1200./10811.0*3.
        q_psuedo = ap*exp(-(bp*283.15+cp*283.15**2))*cf_psuedo**ata
```

Calculating the self-diffusivities

```
        rtf   = (8.931d-10)*tempk
        xlamh  = 221.7134 + 5.52964*tempc - 0.014445*tempc*tempc
        xlamoh = 104.74113 + 3.807544*tempc
        diffh  = rtf*xlamh
        diffoh = rtf*xlamoh
        diffhb = (1.412311 - 1.072404*cfbt + 0.745155*cfbt**2)*1.0D-5
        diffb1 = 1.61*1.0D-5           !FROM LANGEVIN,DESALINATION VOL. 68,
No.2
                                       ! pp.131-148(1988)
        diffb2 = rtf*27.
        diffb3 = rtf*27.
        diffb4 = rtf*30.7
        diffb5 = rtf*30.7
```

Calculating nonionic MTC of species in solution,take monoborate as base

```
        area  = 3.141592*(dia_bed*dia_bed)/4.
        vels  = vol_flow/area

        rena  = dia_ani*100.*vels*den_solv/((1.-vdf_bed)*vcp_solv)
        scna  = (vcp_solv/100.)/(den_solv*diffhb)
```

C-Dwivedi and Upadhyay'S CORRELATION

```
        FA = vels*scna**(-2/3)*(1.957/rena**0.82+1.685/rena**0.444)
        dkla  = FA
C
CALCULATE TOTAL NUMBER OF STEPS IN DISTANCE (NT)
C
        CHTD  = dkla * (1.-vdf_bed)*cht_bed/vels/dia_ani
        nt    = JFIX(chtd/xi)             !TOTAL SLICES
        mt    = nt + 1                    !TOTAL DISTANCE ROUTINE STEPS
        WRITE(*,*) 'TOTAL SLICES NT =', NT

CALCULATING TIME(TOTAL, DIMENSIONLESS)

        taun   = dkla*cfbt*((time*60.)-vdf_bed*cht_bed/vels) !*FAR
        taud   = (dia_ani*q_psuedo)
        TAUPR  = taun/taud

        tmaxan = q_app*3.142*((dia_bed/2.)**2)*cht_bed*vdf_bed*ani_frc
        tmaxad = (vol_flow*cfbt*60.)
        TMAXA  = tmaxan/tmaxad
        TMAX = TMAXA

        taumaxan = dkla*cfbt*((tmaxa*60.)-vdf_bed*cht_bed/vels)
        taumaxad = (dia_ani*q_app)
        TAUMAXA  = taumaxan/taumaxad
        TAUMAX  =  TAUMAXA

        WRITE (*,*)'TAUMAX,taupr=',TAUMAX,taupr
        WRITE (*,222)
        WRITE (*,223) TMAX
        WRITE (*,224)

 222  FORMAT(' PROGRAM RUN TIME IS BASED ON TOTAL RESIN CAPACITY')
 223  FORMAT(' AND FLOW CONDITIONS. THE PROGRAM WILL RUN
FOR',F9.1)
 224  FORMAT(' MINUTES OF COLUMN OPERATION FOR CURRENT
CONDITIONS.')

    Return
    End

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       Sub. SOLVER completes the numerical counterparts of the coupled
C       differential equations derived from model, called by main.
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
    subroutine solver
        implicit real *8 (a-h, o-z)
```

```
      common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
      common /data2/dia_ani, dia_bed, cht_bed, vdf_bed
      common /data3/q_psuedo, cf_psuedo
      common /data4/ccsec,temp
      common /defltl/diffb1,diffb3,diffhb,diffoh,de_par
      common /equi_20/dk11,dk21,dk31,dk42,dkwt,dkla
      common /solconc/cooh,coch,cobt,cob1,cob3,cohb
      common /infconc/ata,cfbt
      common /consts1/tautot,tau,xi,taupr,nt,chtd,time
      common /coeffeq/ap,bp,cp

      dimension ycbti(nt+1),ycbta(3,nt+1),ycbtn(nt+1)
      dimension xcbtb(nt+1),xcbti(nt+1),cohbb(nt+1)
      dimension cobtb(nt+1),rate(nt+1),xcbtn(nt+1)

C     Initialize     values

      j = 1
      tautot = 0.0
      mt  = nt + 1
      kkk = 1
      kki = 0
      kcount = 1
      do 1001 im = 1, mt
            ycbta(1,im)  = 0.1d-6  !ycbi
1001  continue

      coeff_eq = ap*exp(-(bp*tempk+cp*tempk**2))
      gamma    = de_par*coeff_eq*(cfbt)**(ata-1.)/(dia_ani*dkla)

Come here begin a loop to increment time and check program restraints

      do while(tautot<=taupr)

            if(j==3) then
                  jd = 1
            else
                  jd = j + 1
            endif

      ratio_yystar = 1.- exp(-60.*gamma*tautot)

Come here set column inlet conditions

            cobt = cfbt
            xcbtb(1) = cobt/cfbt
```

```
Come here begin a loop to increment distance

         do 400 k = 1, nt

                cbt1 = cobt
                yt  = ycbta(j,k)

     if(ycbta(j,k)<0.999) then
            call intercon(yt,cbt1,xystar,ri)
                if(ycbta(j,k)<0.5*q_min/q_app) then
                      xcbti(k) = xystar
                            if(xcbti(k)>xcbtb(k)) xcbti(k) = xcbtb(k)
                else
                         ycbti(k) = xystar
                endif
          else
                 xcbti(k) = xcbtb(k)
                 ycbti(k) = ycbta(j,k)
          endif

Calculate the particle rate

                if(ycbta(j,k)<q_min/q_app) then
                         rate (k) = 6.*ri*(xcbtb(k)-xcbti(k)) !*(q_psuedo/q_app)
                else
                         rate (k) = 60.*gamma*(ycbti(k) - ycbta(j,k))
                endif
                ycbta(jd,k) = ycbta(j,k) + tau*rate(k)

        if(ycbta(jd,k)>0.999) then
                ycbta(jd,k) = 0.999
                rate(k)=(ycbta(jd,k) - ycbta(j,k))/tau
        endif

        if(k<=3) then
                if(ycbta(j,k)<=0.5*q_min/q_app) then
                         f1c = xi*6.*ri*(xcbtb(k)-xcbti(k))
                         f2c = xi*6.*ri*(xcbtb(k)+f1c/2.-xcbti(k))
                         f3c = xi*6.*ri*(xcbtb(k)+f2c/2.-xcbti(k))
                         f4c = xi*6.*ri*(xcbtb(k)+f3c - xcbti(k))
                else
                         f1c = xi*60.*gamma*(ycbti(k)-ycbta(j,k))
                         f2c = xi*60.*gamma*(ycbti(k)+f1c/2.-ycbta(j,k))
                         f3c = xi*60.*gamma*(ycbti(k)+f2c/2.-ycbta(j,k))
                         f4c = xi*60.*gamma*(ycbti(k)+f3c - ycbta(j,k))
```

```
            endif
          xcbtb(k+1)=xcbtb(k)-(f1c+2.*f2c+2.*f3c+f4c)/6.
      else
          coec_bt =  55.0*rate(k) - 59.0*rate(k-1) + 37.0*rate(k-2) - 9.0*rate(k-3)
          xcbtb(k+1) = xcbtb(k) - (1./24.)*coec_bt*xi
      endif
        if(xcbtb(k+1)<0.0   xcbtb(k+1) = xcbtb(k)
        cobt = xcbtb(k+1)*cfbt

come to here redefine the concentration fractions in the liquid phase

400   continue                    ! end of space routine

C     Reset the conditions for next time step calculation
      call solcon
      cohbb(nt) = cohb
      cobtb(nt) = cobt

            do 410 kin = 1, nt
                  ycbtn(kin)  = ycbta(jd,kin)
                  xcbtn(kin)  = xcbtb(kin)
410    continue

C     Print out results
       open(9,file='ctbreaky.dat',access='append',status='unknown')
       open(11,file='ctdistrc.dat',access='append',status='unknown')

      if(tautot<tau) then
            write(9,430)
            write(9,441)
            write(9,442)
            write(11,440)
            write(11,431)
      endif
      ttq = (q_psuedo/q_app)

      if(tautot>0.250*taupr*ttq.and.tautot<(0.250*taupr+tau)*ttq) then
            write(11,435)
            kot = 0
            do 423 i = 1, nt+1
                  za  =  float(nt)
                  zb  =  float(i-1)
                  z   =  zb*cht_bed/za
                  kot =  kot+1
                  if(kot==1.or.kot==(nt+1).or.kot==(kot/10*10)) then
                        cbt =  xcbtb(i)*con_ppm
```

```
                         write(11,445) z,cbt,ycbtn(i)
                    endif
423     continue
       endif

       kkk = kcount - 1

       if(kcount==1.or.kkk==kkk/10*10) then
       tautotout = tautot/(q_psuedo/q_app)
       cobtout = cobt/cfbt*con_ppm
       write(9,4)tautotout,cobtout,ycbtn(nt)
       write(*, 444) cobtout, ycbtn(nt), tautotout
       endif

430    format(/,12x,' Concentration Distributions in Resins',/)
431    format(3x,' Z ',15x,'CBT',18x,'ycbt',//)
432    format('Concentration Distribution in Column at 10% Total Time',/)
433    format('Concentration Distribution in Column at 20% Total Time',/)
434    format(//)
435    format('Concentration Distribution in Column at 50% Total Time',/)
440    format(/,16x,' Effluent Concentrations',/)
441    format(2x,' Time',14X,'COBT',17x,'YCBT')
442    format(//)
4      format(3x,f7.3,10x,2(d10.5,10x)) !,d13.7,1x,d13.7,1x,d13.7)
444    format('cobt,yt,tautot=:',3(e10.5,5x))
445    format(3x,f10.3,10x,2(e12.5,10x))

       if(j==3) then
         j = 1
       else
         j = j + 1
       endif
       tautot = tautot + tau
       kcount = kcount + 1

       open (16,file='btrsny.dat',access='append',status='unknown')

       if(tautot==tau) write(16,200)
        kount = 0

      DO 300 kk = 1, nt+1
              ybbt= ybbt + ycbtn(kk)
300     continue
         ybtfr = ybbt/((nt+1)*q_app)
         write(16,201) tautot, ybtfr
         ybbt = 0.0
```

```
200  FORMAT(2X,' Z (cm)', 18X, ' YBT  ')
201  FORMAT(2X,E8.3,12X, F15.7)

    enddo                   ! end of time loop

    return
        End

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       This subroutine is used for the determinations of the average
C       rate of the total boron concentration and the distributions of the
C       total boron concentration in the resin phase. Called by SOLVER.
C
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C
        subroutine intercon(yt,cbt1,xystar,ri)
        implicit real *8 (a-h,o-z)
        common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
        common /infconc/ata,cfbt

        ystar = (cbt1/cfbt)**ata
        if(yt<=0.5*q_min/q_app) then
         xstar = 0.
        else
         xstar = yt*cfbt**(ata-1.)
        endif

        if(yt<=q_min/q_app) then
                xystar = xstar
        else
                xystar = ystar
        endif
        ri = 1.0
        return
        end

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       This subroutine is used to determine the concentrations of species
C       in solution based on equilibrium relationship (See Appendix A).
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*

        Subroutine solcon
        implicit real *8 (a-h,o-z)
        common /data0/tempk,tempc,q_min,con_ppm,ycbi,q_app
        common /equi_20/dk11,dk21,dk31,dk42,dkwt,dkla
        common /solconc/cooh,coch,cobt,cob1,cob3,cohb
```

```
        common /infconc/ata,cfbt
        common /consts1/tautot,tau,xi,taupr,nt,chtd,time
```

Convergent criteria specified

```
        tolelim = 1.0d-6
```

Calculating solution concentrations of the all species

```
        tk = tempk
        cohb = 0.92*cobt                ! initial guess for B(OH)3

          call CALROW (TK, ROH2O, KK)
          call CALKW (TK, ROH2O, dkwt)
          call CALKB (TK, SI,dkwt,dK11, dK21, dK31, dK42)
          call fundi(cobt, cohb, funct, fdiff)
```

Calculating the neutral species (Eq.7) by Newton method

```
    cnhb  = cohb - funct/fdiff
        error = (cnhb - cohb)/cnhb
        nit = 1

        do
          if(dabs(error)<tolelim.or.nit>=50) exit
          cohb = cnhb
          call fundi(cobt, cohb, funct, fdiff)
          cnhb  = cohb - funct/fdiff
          error = (cnhb - cohb)/cnhb
          nit = nit + 1
        enddo

        cohb = cnhb
        if (cohb>=cobt) cohb = 0.92*cobt
```

Calculating the concentration of hydrogen in solution

```
        coch = sqrt(dkwt + dk11*cohb + dk31*cohb**3)
```

Calculating the concentrations of the other species

```
        cooh = dkwt/coch                        !hydroxide
        cob1 = dk11*cohb/coch                   !monoborate B(OH)4
        cob3 = dk31*cohb**3/coch                !triborate  B3(OH)10
        return
        end
```

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

        subroutine     fundi(cobt, cohb, funct, fdiff)          !Called by Subroutine Solcon
        implicit real*8 (a-h, o-z)
        common/equi_20/dk11,dk21,dk31,dk42,dkwt,dkla

Calculating the coefficients of the function

        coa6 = 9.0*dk31**2
        coa5 = -dk31
        coa4 = 6.0*dk11*dk31+2.0*dk31*cobt
        coa3 = -(dk31*cobt**2+dk11)
        coa2 = 2.0*dk11*cobt - dkwt + dk11**2
        coa1 = 2.0*dkwt*cobt - dk11*cobt**2
        coa0 = -dkwt*cobt**2

Calculating the coefficients of the differential equation

        dcoa5 = 6.0*coa6
        dcoa4 = 5.0*coa5
        dcoa3 = 4.0*coa4
        dcoa2 = 3.0*coa3
        dcoa1 = 2.0*coa2
        dcoa0 = 1.0*coa1

Calculating the function

        func1 = coa6*cohb**6 + coa5*cohb**5
        func2 = coa4*cohb**4 + coa3*cohb**3
        func3 = coa2*cohb**2 + coa1*cohb + coa0
        funct = func1 + func2 + func3

Calculating the differential equation

        fdif1 = dcoa5*cohb**5 + dcoa4*cohb**4
        fdif2 = dcoa3*cohb**3 + dcoa2*cohb**2
        fdif3 = dcoa1*cohb + dcoa0
        fdiff = fdif1 + fdif2 + fdif3

        return
        End
```

```
C****************************************************************
C     THIS SUBROUTINE SERVES FOR DETERMINING THE DENSITY OF
C     WATER UNDER THE GIVEN TEMPERATURE BASED ON (1)THE
C     CORRERATION OF F.FRANKS, FROM 'WATER A COMPREHENSIVE
C      TREATISE', FLENUM PRESS VOL. 1 (1972), (2) J.F.KEENAN AND
C      F.G.KEYS, 'THERMODYNAMIC PROPERTIES OF STEAM', JOHN WILLEY
C     & SON, INC., NEW YORK (1936).
C****************************************************************
C           Called by Subroutine Solcon
      SUBROUTINE CALROW (TK, ROH2O, KK)
      IMPLICIT REAL*8 (A-H, O-Z)

         IF(KK.EQ.1) THEN

        A0 =  5.0756897E02
        A1 =  3.2813464
        A2 = -4.6638625E-2
        A3 =  1.2941179E-4
        A4 = -1.7344969E-7
        A5 =  9.9308722E-11
        B  = -4.5854083E-3

        XIGMA = (A0+A1*TK+A2*TK**2+A3*TK**3+A4*TK**4+A5*TK**5)
        ROH2O = XIGMA / (1. + B*TK)

        ELSE

        VC =  3.1975
        AA = -0.3151548
        BB = -1.203374E-3
        CC =  7.489081E-13
        DD =  0.1342489
        EE = -3.946263E-3

        T1 =  374.11 - (TK - 273.15)
        T2 =  T1**(1./3.)
        ROH2O = (1.0+DD*T2+EE*T1)/(VC+AA*T2+BB*T1+CC*T1**4)

        ENDIF

     return
     End
```

```
C*********************************************************************
C       THIS SUBROUTINE SERVES FOR OBTAINING THE IONIC PRODUCT OF
C       WATER BASED ON MARSHALL AND FRANK CORRELATION, FROM
C       'ION PRODUCT OF WATER SUBSTANCE, 0-1000 C, 1-10,000 BARS NEW
C       INTERNATIONAL FORMULATION AND ITS BACKGROUND,  J. PHYS.
C       CHEM. REF.DATA,  VOL.10 NO. 2, PP. 295-304(1981).
C*********************************************************************

        SUBROUTINE CALKW (TK, ROH2O, AKW)
        IMPLICIT REAL*8 (A-H, O-Z)

        A  = -4.098
        B  = -3245.2
        C  =  2.2362E5
        D  = -3.984E7
        E  =  13.957
        F  = -1262.3
        G  =  8.5641E5

    AKW=A+B/TK+C/(TK**2)+D/(TK**3)+(E+F/TK+G/(TK**2))*DLOG10(ROH2O)
    AKW = 10.**AKW

    return
    End


C*********************************************************************
C       THIS SUBROUTINE IS USED TO DETERMINE THE EQUILIBRIUM
C       CONSTANTS OF BORATES, BASED ON MESMER, BAES & SWEETON,
C       'BORIC ACID EQUILIBRIUM AND PH IN PWR COOLANTS',
C       PROCEEDINGS OF THE 32ND INTERNATIONAL WATER COMFERENCE,
C       PITTSBURGHS, PA(1972)
C*********************************************************************
      SUBROUTINE CALKB (TK, SI,dkwt,dK11, dK21, dK31, dK42)
      IMPLICIT REAL*8 (A-H, O-Z)

        IF(SI.NE.0.) THEN

        FI   = (0.325 - 0.00033*TK)*SI - 0.0912*SI**1.5
        AK11 =  1573.21/TK+28.6059+0.012078*TK-13.2258*DLOG10(TK)+FI
        AK21 =  2756.1/TK-18.7322-0.00033*TK+5.835*DLOG10(TK)-FI
        AK31 =  3339.5/TK-7.85-0.00033*TK+1.497*DLOG10(TK)-FI
        AK42 =  12820./TK-134.33-0.00033*TK+42.105*DLOG10(TK)-FI
        AK53 =  14099./TK-118.115+36.237*DLOG10(TK)
```

```
    ELSE

    AK11 =  1573.21/TK+28.8397+0.011748*TK-13.2258*DLOG10(TK)
    AK21 =  2756.1/TK-18.966+5.835*DLOG10(TK)
    AK31 =  3339.5/TK-8.048+1.497*DLOG10(TK)
    AK42 =  12820./TK-134.56+42.105*DLOG10(TK)
    AK53 =  14099./TK-118.115+36.237*DLOG10(TK)

    ENDIF

    AK11 = 10.**AK11
    AK21 = 10.**AK21
    AK31 = 10.**AK31
    AK42 = 10.**AK42
    AK53 = 10.**AK53

    dk11 = ak11*dkwt
    dk21 = ak21*dkwt
    dk31 = ak31*dkwt
    dk42 = ak42*dkwt**2

return
End
```

PART IV. BONMBIE.FOR

```
$debug
C********************************************************************
*
C  THIS PROGRAM IS DEVELOPED TO MODEL MULTI-COMPONENT MIXED
C  BED ION EXCHANGE WITH THREE ANIONS, THREE CATIONS, AND ONE
C  UNDISSOCIATED MOLECULE SPECIES (OH,B(OH)4,Cl; H,Li,Na; AND BORIC
C  ACID B(OH)3).  IT IS USED FOR THE CALCULATION OF THE MODEL IN
C  CHAPTER V.  THE MIXED BED (H-OH) RESINS WERE USED FOR Li AND
C  BORON SORPTION.
C  A EXAMPLE IS USING THE KASHIWAI DATA TO PREDICT THE RATE OF
C  CHLORIDE BREAKTHROUGH WITH A 1 ppm INPUT OPERATING AT 1200
C  ppm B AND 2.2 ppm Li AT TEMERATURE 46 C.
C                                                BY  JIDONG LOU
C                                                January, 1997
C********************************************************************
C
C       CHT_BED:     Height of column (cm)
C       CON_PPM:     Concentration in ppm
C       COI:         Bulk concentration of ith species.
C       CII:         Interfacial concentration of ith species.
C       CFBT:        The total boron concentration in the influent of column (meq/cm3).
C       DE_PAR:      Effective diffusivity of boron in particle
C       DEN_SOLV:    Density of solution (g/cm3)
C       DIA_ANI:     Diameter of anion resin particle (cm)
C       DIA_CAT:     Diameter of cation resin particle (cm)
C       DIA_BED:     Diameter of column (cm)
C       DIFFI:       Self-Diffusivity of ith species.
C       DKMN:        Equilibrium constants of reaction of borate, M – is the number of
C                    boron Atom in the borate, N – is the charge number of the borate
C       DKLA:        Mass transfer coefficient of representative anion species in liquid.
C       DKWT:        Water formation equilibrium constant
C       HB:          Boric acid
C       Q_MIN:       The minimum capacity of resin (meq/cm3 dry resin).
C       Q_APP:       The apparent (equilibrium) capacity of resin (meq/cm3 dry resin).
C       TEMPC        Temperature in oC
C       TEMPK        Temperature in Kelvin
C       VCP_SOLV:    Viscosity of solution in CP.
C       VDF_BED:     Void fraction of bed
C       VOL_FLOW:    Volume flow rate through column (cm3/sec).
C       XCBTI:       Concentration fraction of species BT at the interface.
C       XCBTB:       Concentration fraction of species BT in the bulk liquid.
C       YAAT:        Total average concentration fraction of anionic species in resin
C                    phase
```

```
C       YAB1:           Concentration fraction of borate B(OH)4- in resin phase
C       YACL:           Concentration fraction of chloride ion in resin phase
C       YAHB:           Concentration fraction of pseudo molecule in resin phase
C       YCAT:           Total average concentration fraction of cationic species in the resin
C                       phase.
C       YCBTI:          Interfacial concentration fraction of species BT in the resin phase.
C       zchg_I:         Charge numbers of ith species

        implicit real*8 (a-h, o-z)
        common /data_00/tempk,tempc,qa_min,qa_app,con_ppm
        common /data_10/vol_flow,vcp_solv,den_solv
        common /data_20/dia_cat,dia_ani,dia_bed,cht_bed,vdf_bed
        common /data_30/cap_cat,cap_ani,frc_cat,frc_ani
        common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
        common /chargea/zchg_b1,zchg_b3,zchg_cl,zchg_oh,zchn
        common /chargec/zchg_na,zchg_li,zchg_h
        common /dfcoef1/diffb1,diffb3,diffhb,diffoh,diffcl
        common /dfcoef2/diffh,diffli,diffna
        common /dfcoef3/par_bde,par_clde
        common /equi_20/dkb1,dkb3,dkwt
        common /mtceff1/dklarf,dklcli,dklcna
        common /mtceff2/dklab1,dklab3,dklacl,dklahb
        common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
        common /infconc/cioh,cib1,cib3,cihb,cibt,cich,cicl,cina,cili
        common /ratiode/rhb,rb1,rb3,rcl,rli,rna
        common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
        common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
        common /consts3/ppmb,ppmcl,ppmli,ppmna
        common /yconsts/yci,ap,bp,cp,ata,nn

        dimension xb1(20000),xcl(20000),xhb(20000),ycat(20000)
        dimension xli(20000),xna(20000),ycct(20000)
        nn  = 3
        open(5,file='mixlib35.dat',status='unknown')

        write (*,*) ' Give the increments XI, TAU = '
        read  (*,*) xi,tau

Calling subroutines to fulfill the tasks

        call deflts
        call solver(xb1,xcl,xhb,ycat,xli,xna,ycct)
        call output(xb1,xcl,xhb,ycat,xli,xna,ycct)

        stop
        END                     !end the main program
```

```
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C      Default values for calculating MTC, self-diffusivities,equilibrium
C      constants, dimensionless parameters, etc. are given in this sub-
C      routine. Other initial and operation conditions are also specified
C      in this subroutine.
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
       subroutine deflts
       implicit real *8 (a-h,o-z)
       common /data_00/tempk,tempc,qa_min,qa_app,con_ppm
       common /data_10/vol_flow,vcp_solv,den_solv
       common /data_20/dia_cat,dia_ani,dia_bed,cht_bed,vdf_bed
       common /data_30/cap_cat,cap_ani,frc_cat,frc_ani
       common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
       common /chargea/zchg_b1,zchg_b3,zchg_cl,zchg_oh,zchn
       common /chargec/zchg_na,zchg_li,zchg_h
       common /dfcoef1/diffb1,diffb3,diffhb,diffoh,diffcl
       common /dfcoef2/diffh,diffli,diffna
       common /dfcoef3/par_bde,par_clde
       common /equi_20/dkb1,dkb3,dkwt
       common /mtceff1/dklarf,dklcli,dklcna
       common /mtceff2/dklab1,dklab3,dklacl,dklahb
       common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
       common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
       common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
       common /consts3/ppmb,ppmcl,ppmli,ppmna
       common /yconsts/yci,ap,bp,cp,ata,nn

       ppmb     = 1200.0
       ppmcl    = 0.10
       ppmli    = 2.2
       ppmna    = 0.5
       tempc    = 46.0
       vol_flow =    4722.0      !cm3/sec
       time     = 100.0               !min

       ap      = 7.93735d0     !parameters used in the corrolation
       bp      =-8.71998d-3    !for calculating the apparent
       cp      = 2.43548d-5    !capacity of Amberlite IRN78LC
       ata     = 0.274489      !qa_app

       dia_cat  = 0.085       !diameter of cation resin bead  cm
       dia_ani  = 0.05       !diameter of anion resin bead  cm
       cap_cat  = 2.0        !capacity of cation resin meq/dry.cm3
       cap_ani  = 1.2        !capacity of anion resin Ambertile IRN78LC (meq/dry.cm3)
       vdf_bed  = 0.35         !bed void fraction dimensionless
```

```
frc_cat   = 0.33              !volume fraction of cation resin in MB
frc_ani   = 1.0 - frc_cat     !volume fraction of anion resin in MB
dia_bed   = 88.2              !bed diameter   cm
cht_bed   = 139.1             !effective bed height (resin height) cm
vcp_solv  = 0.65              !viscosity of water at tempc = 46 C
```

Come here specify the values of selectivities and charges of ionic species

```
tkb1_oh   = 1.65
tkb3_oh   = 10.8
tkcl_oh   = 22.0
tkli_h    = 0.85
tkna_h    = 1.5

zchn      =  1.0                  !charge number of hydrogen
zchg_b1   = -1.0                  !charge number of mono-borate
zchg_b3   = -1.0                  !charge number of tri-borate
zchg_oh   = -1.0                  !charge number of hydroxide
zchg_cl   = -1.0                  !charge number of chloride
zchg_na   =  1.0                  !charge number of sodium
zchg_li   =  1.0                  !charge number of lithium
zchg_h    =  1.0                  !charge number of hydrogen
```

Come to here specify the initial loading in the resin phase

```
yci       = 0.001             !initial condition
```

Give the feed conditions

```
Tempk = tempc + 273.16
call CALROW (tempk, ROH2O, KK)
call CALKW (tempk, ROH2O, dkwt)
den_solv   = roh2o
cfbt = ppmb/10811.0*3.        !total inlet boron concentration meq/cm3
                                  !MW of boron = 10.811
cfli = ppmli/6941.                !lithium feed concentration    in meq/cm3
cfna = ppmna/23000.               !sodium feed concentration in meq/cm3
cfcl = ppmcl/35453.               !chloride feed concentration in meq/cm3
```

Calculate the acid equilibria constant

```
tk = tempk
ak11 = 1573.21/TK + 28.8397 + 0.012078*TK - 13.2258*DLOG10(TK)
ak31 = 3339.5/TK - 8.084 + 1.497*DLOG10(TK)

ak11 = 10.**ak11
```

```
ak31 = 10.**ak31

dkb1 = ak11*dkwt
dkb3 = ak31*dkwt
```

Determine other species concentrations in feed

```
cobt  = cfbt
cona  = cfna
coli  = cfli
cocl  = cfcl
```

Set initial boric acid and borate concentrations based on charge and material balance

```
call solu_con
cfhb  = cohb
cfat  = cfcl + cob1 + cooh
cfct  = cfna + cfli + coch
```

Calculation of the apparent capacity of the anion resin

```
ratioca = (cfbt/(cfhb+cfat))
qa_min  = cap_ani
qa_app  = ap*exp(-(bp*tempk+cp*tempk**2))*cfbt**ata*ratioca
write(*,*) 'qa_app =', qa_app
```

Appearent particle diffusion coefficients

```
par_bde  = 5.3239d-7          !the appear average diffusivity in resin phase
                              !correponding 1000 ppm solution concentration
par_clde = 5.4870d-7          !chloride self-diffusivity in resin
```

Calculating the self-diffusivities

```
rtf    = (8.931d-10)*tempk
xlamh  = 221.7134 + 5.52964*tempc - 0.014445*tempc*tempc
xlamoh = 104.74113 + 3.807544*tempc
xlamna = 23.00498 + 1.06416*tempc + 0.0033196*tempc*tempc
xlamcl = 39.6493 + 1.39176*tempc + 0.0033196*tempc*tempc

diffh  = rtf*xlamh
diffoh = rtf*xlamoh
diffna = rtf*xlamna
diffcl = rtf*xlamcl

diffhb = (1.412311 - 1.072404*cfbt + 0.745155*cfbt**2)*1.0D-5
```

```
        diffb1 = 1.61*1.0D-5  !FROM LANGEVIN,DESALINATION VOL. 68, No.2
                  ! pp.131-148(1988)
        diffli = rtf*38.7*(tempk/334/vcp_solv)
            ! The third term as temperature correction if not at 25 C
            ! 1.621d-5
        diffb3 = rtf*27.

Calculate nonionic MTC of species in solution,take Chloride as base

        area  = 3.141592*(dia_bed*dia_bed)/4.
        vels  = vol_flow/area/vdf_bed

        rena   = dia_ani*100.*vels*den_solv/((1.-vdf_bed)*vcp_solv)
        renc   = dia_cat*100.*vels*den_solv/((1.-vdf_bed)*vcp_solv)

        scnc   = (vcp_solv/100.)/(den_solv*diffh)
        scna   = (vcp_solv/100.)/(den_solv*diffcl)

C-Dwivedi and Upadhyay'S CORRELATION

        FA = vels*scna**(-2/3)*(1.957/rena**0.82+1.685/rena**0.444)
        FC = vels*scnc**(-2/3)*(1.957/renc**0.82+1.685/renc**0.444)

        dkla  = FA
        dklc  = FC

C
CALCULATE TOTAL NUMBER OF STEPS IN DISTANCE (NT)
C
        CHTD  = dkla * (1.-vdf_bed)*cht_bed/vels/dia_ani
        nt    = JFIX(chtd/xi)              !TOTAL SLICES
        mt    = nt + 1                     !TOTAL DISTANCE ROUTINE STEPS

CALCULATING TIME(TOTAL, DIMENSIONLESS)

        taun   = dkla*(cfat+cfhb)*((time*60.)-vdf_bed*cht_bed/vels) !*FAR
        taud   = (dia_ani*qa_app)
        TAUPR  = taun/taud

        tmaxan = qa_app*3.142*((dia_bed/2.)**2)*cht_bed*vdf_bed*frc_ani
        tmaxad = (vol_flow*(cfat+cfhb)*60.)
        TMAXA  = tmaxan/tmaxad

        tmaxcn = cap_cat*3.142*((dia_bed/2.)**2)*cht_bed*vdf_bed*frc_cat
        tmaxcd = (vol_flow*cfct*60.)
        TMAXC  = tmaxcn/tmaxcd
```

```
      IF(TMAXA.GT.TMAXC) THEN
         TMAX = TMAXC
      ELSE
         TMAX = TMAXA
      ENDIF

      taumaxan = dkla*(cfat+cfhb)*((tmaxa*60.)-vdf_bed*cht_bed/vels)
      taumaxad = (dia_ani*qa_app)
      TAUMAXA  = taumaxan/taumaxad !*VDF*FAR

      taumaxcn = dklc*cfct*((tmaxc*60.)-vdf_bed*cht_bed/vels)
      taumaxcd = (dia_cat*cap_cat)
      TAUMAXC  = taumaxcn/taumaxcd !*VDF*FCR

      IF(TAUMAXA.GT.TAUMAXC) THEN
         TAUMAX  =  TAUMAXC
      ELSE
         TAUMAX  =  TAUMAXA
      ENDIF

      WRITE (*,*)'TAUMAX,taupr=',TAUMAX,taupr
      WRITE (*,222)
      WRITE (*,223) TMAX
      WRITE (*,224)

222 FORMAT(' PROGRAM RUN TIME IS BASED ON TOTAL RESIN CAPACITY')
223 FORMAT(' AND FLOW CONDITIONS. THE PROGRAM WILL RUN:',F9.1)
224 FORMAT(' MINUTES OF COLUMN OPERATION FOR CURRENT
&               CONDITIONS.')

Calculating the liquid side mass transfer coefficient for individuals

      dklarf  = dkla                        !MTC of the reference species CL

      dklacl  = dklarf
      dklab1  = dklarf*((diffb1/diffcl)**(2./3.))
      dklahb  = dklarf*((diffhb/diffcl)**(2./3.))

      dklcli  = dklarf*(((diffli/diffcl)*(dia_ani/dia_cat))**(2./3.))
      dklcna  = dklarf*(((diffna/diffcl)*(dia_ani/dia_cat))**(2./3.))

      return
      End

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
```

```
C       Subroutine OUTPUT prints out the results calculated in this code
C       called by MAIN
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
        subroutine output(xb1,xcl,xhb,ybtout,xli,xna,ycct)

        implicit real*8 (a-h, o-z)
        common /data_00/tempk,tempc,qa_min,qa_app,con_ppm
        common /data_10/vol_flow,vcp_solv,den_solv
        common /data_20/dia_cat,dia_ani,dia_bed,cht_bed,vdf_bed
        common /data_30/cap_cat,cap_ani,frc_cat,frc_ani
        common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
        common /dfcoef1/diffb1,diffb3,diffhb,diffoh,diffcl
        common /dfcoef2/diffh,diffli,diffna
        common /dfcoef3/par_bde,par_clde
        common /mtceff1/dklarf,dklcli,dklcna
        common /mtceff2/dklab1,dklab3,dklacl,dklahb
        common /ratiode/rhb,rb1,rb3,rcl,rli,rna
        common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
        common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
        common /consts3/ppmb,ppmcl,ppmli,ppmna

        dimension xb1(nt+1),xcl(nt+1),xhb(nt+1),ybtout(nt+1)
        dimension xli(nt+1),xna(nt+1),ycct(nt+1)

        area  = 3.141592*(dia_bed*dia_bed)/4.
        vels  = vol_flow/area

        write (5, 10)
        write (5, 13) dia_ani,dia_cat
        write (5, 81) vdf_bed
        write (5, 14) cap_ani,cap_cat
        write (5, 82) tkb1_oh,tkcl_oh
        write (5,182) tkli_h,tkna_h
        write (5, 15) cfbt, vol_flow
        write (5, 83) dia_bed, chtd
        write (5, 16) diffb1,diffhb
        write (5,161) diffcl,diffoh,diffb3
        write (5, 84) diffli,diffna,diffh
        write (5, 17) vcp_solv,den_solv
        write (5,19)
        write (5,21) tau, xi
        write (5,22) time, nt
        write (5,88) dklarf
        write (5,23) vels

 10 FORMAT(' MIXED BED SYSTEM PARAMETERS:',/)
```

```
 13  FORMAT(' RESIN PROPERTIES',5X,': PDA=',F6.4,2X,': PDC=',F6.4)
 81  FORMAT(24X,'VD =', F6.4)
 14  FORMAT(' RESIN CONSTANTS',6X,': QA =',E10.4,2x,': QC =',E10.4)
 82  FORMAT(24X,'TKOB = ',F7.4,3x,'TKOC = ',F7.4)
182  FORMAT(24X,'TKHL = ',F7.4,3x,'TKHN = ',F7.4)
 15  FORMAT(' COLUMN PARAMETERS',4X,': CF =',E10.4,' FR =',E10.4)
 83  FORMAT(24X,'DIA =',F6.2,5X,'CHT =',F6.1)
 16  FORMAT(' IONIC CONSTANTS',6X,': DB1=',E10.4,2X,'DHB=,'E10.4)
161     FORMAT(24X,'DCL=',E10.4,'  DOH=', E10.4, ' :DB3=',E10.4)
 84  FORMAT(24X,'DLI=',E10.4,'  DNA=', E10.4,2X,':DH =',E10.4)
 17  FORMAT(' FLUID PROPERTIES', 5X,': CP =',F7.5,5X,'DEN=',F6.4)
 19  FORMAT(/,' CALCULATED PARAMETERS',/)
 21  FORMAT(' INTEGRATION INCREMENTS   : TAU=',F6.4,1X,'XI=',F6.4)
 22  FORMAT(' TOTAL TIME AND  SLICE    : TIME=',F8.3,2X,'NT =',I4)
 88  FORMAT(24X,'KLA_CL =', E10.4)
 23  FORMAT(' SUPERFICIAL VELOCITY     : VS =',F7.3)

CONCENTRATION PROFILES

    WRITE(5,200)
       kount = 0
       if(nt>4000) nt = 4000
     DO 300 K = 1, nt+1
      za  =  float(nt)
      zb  =  float(k-1)
      z   =  zb*cht_bed/za
      kount = kount+1
       if(kount==1.or.kount==(nt+1).or.kount==(kount/10*10)) then
              cbt  = (xb1(k)+xhb(k))*ppmb*(cfhb+cfat)/cfbt
              cli  = xli(k)*ppmli*cfct/cfli
              cna  = xna(k)*ppmna*cfct/cfna
              ccl  = xcl(k)*ppmcl*(cfhb+cfat)/cfcl
              yaat = ybtout(k)
              ycat = ycct(k)
              write(5,201) z, cbt,ccl,cli,cna,yaat,ycat
       endif
300      continue
200  FORMAT(2x,'Z(cm)',6x,'ppm_b',5x,'ccl',7x,'cli',7x,'cna',7x,'yaat',
   &7x,'ycct')
201  FORMAT(1x,e8.3,1x,6(e9.4,1x))

     CLOSE(5)
     RETURN
     END

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

```
C     THIS SUBROUTINE SERVES FOR DETERMINING THE DENSITY OF
C     WATER UNDER THE GIVEN TEMPERATURE BASED ON (1)THE
C     CORRERATION OF F.FRANKS, FROM 'WATER A COMPREHENSIVE
C     TREATISE', FLENUM PRESS VOL. 1 (1972), (2) J.F.KEENAN AND
C     F.G.KEYS, 'THERMODYNAMIC PROPERTIES OF STEAM', JOHN WILLEY
C     & SON, INC., NEW YORK (1936).
C*********************************************************************
C
      SUBROUTINE CALROW (TK, ROH2O, KK)
      IMPLICIT REAL*8 (A-H, O-Z)

        IF(KK.EQ.1) THEN

                A0 =  5.0756897E02
                A1 =  3.2813464
                A2 = -4.6638625E-2
                A3 =  1.2941179E-4
                A4 = -1.7344969E-7
                A5 =  9.9308722E-11
                B  = -4.5854083E-3

                XIGMA =
(A0+A1*TK+A2*TK**2+A3*TK**3+A4*TK**4+A5*TK**5)
                ROH2O = XIGMA / (1. + B*TK)

        ELSE

                VC =  3.1975
                AA = -0.3151548
                BB = -1.203374E-3
                CC =  7.489081E-13
                DD =  0.1342489
                EE = -3.946263E-3

                T1 =  374.11 - (TK - 273.15)
                T2 =  T1**(1./3.)
                ROH2O = (1.0+DD*T2+EE*T1)/(VC+AA*T2+BB*T1+CC*T1**4)
        ENDIF

        return
        End

C*********************************************************************
*
C     THIS SUBROUTINE SERVES FOR OBTAINING THE IONIC PRODUCT OF
WATER
```

```
C     BASED ON MARSHALL AND FRANK CORRELATION, FROM 'ION
PRODUCT OF
C     WATER SUBSTANCE, 0-1000 C, 1-10,000 BARS NEW INTERNATIONAL
C     FORMULATION AND ITS BACKGROUND;,  J.PHYS.CHEM.REF.DATA,
VOL.10
C     NO. 2, PP. 295-304(1981).
C*******************************************************************

      SUBROUTINE CALKW (TK, ROH2O, AKW)
      IMPLICIT REAL*8 (A-H, O-Z)

      A  = -4.098
      B  = -3245.2
      C  =  2.2362E5
      D  = -3.984E7
      E  =  13.957
      F  = -1262.3
      G  =  8.5641E5

   AKW=A+B/TK+C/(TK**2)+D/(TK**3)+(E+F/TK+G/(TK**2))*DLOG10(ROH2O)
   AKW = 10.**AKW

      return
      End

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C     Sub. SOLVER completes the numerical counterparts of the coupled
C     differential equations derived from model, called by main.
C                                                     Jidong Lou
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C
    subroutine solver(xab1b,xaclb,xahbb,yatn,xclib,xcnab,yctn)
      implicit real *8 (a-h, o-z)
      common /data_00/tempk,tempc,qa_min,qa_app,con_ppm
      common /data_20/dia_cat,dia_ani,dia_bed,cht_bed,vdf_bed
      common /data_30/cap_cat,cap_ani,frc_cat,frc_ani
      common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
      common /chargea/zchg_b1,zchg_b3,zchg_cl,zchg_oh,zchn
      common /chargec/zchg_na,zchg_li,zchg_h
      common /dfcoef1/diffb1,diffb3,diffhb,diffoh,diffcl
      common /dfcoef2/diffh,diffli,diffna
      common /dfcoef3/par_bde,par_clde
      common /equi_20/dkb1,dkb3,dkwt
      common /mtceff1/dklarf,dklcli,dklcna
      common /mtceff2/dklab1,dklab3,dklacl,dklahb
      common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
```

```
        common /infconc/cioh,cib1,cib3,cihb,cibt,cich,cicl,cina,cili
        common /ratiode/rhb,rb1,rb3,rcl,rli,rna
        common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
        common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
        common /consts3/ppmb,ppmcl,ppmli,ppmna
        common /yconsts/yci,ap,bp,cp,ata,nn

        dimension yab1(3,nt+1),yacl(3,nt+1),yahb(3,nt+1),yabt(3,nt+1)
        dimension ycli(3,nt+1),ycna(3,nt+1),yctn(nt+1),yatn(nt+1)
        dimension rateli(nt+1),ratena(nt+1),cch(nt+1),xch(nt+1)
        dimension rateb1(nt+1),ratecl(nt+1),ratehb(nt+1),ratebt(nt+1)
        dimension xab1b(nt+1),xaclb(nt+1),xahbb(nt+1),xabtb(nt+1)
        dimension xclib(nt+1),xcnab(nt+1)

C       Initialize values

        j = 1
        tautot = 0.0
        mt  = nt + 1
        kkk = 1
        kki = 0
        kcount = 0
        do 1001 im = 1, mt
                yab1(1,im) = yci/3.
                yacl(1,im) = yci/3.
                yahb(1,im) = yci/3.
                yabt(1,im) = yab1(1,im)+yahb(1,im)
                ycna(1,im) = yci/2.
                ycli(1,im) = yci/2.

                yat  = yci
                yct  = yci
1001    continue

          cobt  = cfbt
          cocl  = cfcl
          cona  = cfna
          coli  = cfli

          call solu_con

          cfhb  = cohb
          cfat  = cfcl + cob1 + cooh
          cfct  = cfna + cfli + coch
          pH    = - dlog10(coch*1.0d-14/dkwt)
```

```
    coeffb        = (cfct/(cfat+cfhb))
    coeffc        = 6.0*dia_ani/dklarf/dia_cat
    coeffq        = qa_app/cap_cat
    coeffqca      = qa_app/(cfat+cfhb)
    coeffp        = 60.*coeffqca/dia_ani/dklarf
    dkebt         = (10.*par_bde/dia_ani)
    pcbt          = par_bde*coeffp
    pccl          = par_clde*coeffp

    rkbt          = dklarf/dkebt
    rkb           = dklarf/dklahb
    rkb1          = dklarf/dklab1
    rkli          = dklarf/dklcli*(dia_ani/dia_cat)
    rkna          = dklarf/dklcna*(dia_ani/dia_cat)
```

Come here begin a loop to increment time and check program restraints

```
    do while(tautot<=taupr)
        if(j==3) then
            jd = 1
        else
            jd = j + 1
        endif
```

Come here set column inlet conditions

```
    cobt  = cfbt
    cocl  = cfcl
    cona  = cfna
    coli  = cfli

    call solu_con

    cfhb    = cohb
    cfat    = cfcl + cob1 + cooh
    cfct    = cfna + cfli + coch
    cch(1)  = coch

    xab1b(1) = cob1/(cfat+cfhb)
    xaclb(1) = cocl/(cfat+cfhb)
    xahbb(1) = cohb/(cfat+cfhb)
    xabtb(1) = cobt/(cfat+cfhb)

    xclib(1) = coli/(cfct+cfhb)
    xcnab(1) = cona/(cfct+cfhb)
    xch(1)   = coch/(cfct+cfhb)
```

```
        catb    = cfat
        cctb    = cfct
        cobt    = cfbt
        if(cfbt>0.02775) kkai = 1      ! boron>100ppm using particle model
```

Come here begin a loop to increment distance

```
        do 400 k = 1, nt

            ki   = k
            kni  = 0
            cat1 = catb
            cct1 = cctb
            cbt1 = cobt

      if(yatn(k)<0.999) then

       if(kkai==1) then
```

Calculating the interface concentrations of boron and chloride

```
          sumkyp = cocl*tkcl_oh+cobt*tkb1_oh+cooh
                yibt = (cobt/(cfhb+cfat))**ata
                yicl = (cocl*tkcl_oh)/sumkyp
```

Calculating the particle rate based on the particle model

```
                if(yibt<yabt(j,k)) yibt = yabt(j,k)
                if(yicl<yacl(j,k)) yicl = yacl(j,k)

                ratebt(k)  = pcbt*(yibt - yabt(j,k))
                if(ratebt(k)*xi*frc_ani>xabtb(k)) then
                    ratebt(k) = 0.95*xabtb(k)/xi/frc_ani
                    kni = 1
                endif
                ratecl(k)  = pccl*(yicl - yacl(j,k))
                if(ratecl(k)*xi*frc_ani>xaclb(k)) then
                    ratecl(k) = 0.95*xaclb(k)/xi/frc_ani
                endif
                yabt(jd,k) = yabt(j,k) + ratebt(k)*tau
                yacl(jd,k) = yacl(j,k) + ratecl(k)*tau
```

Correction if the total fraction exceeds unity.

```
                yat = yabt(jd,k) + yacl(jd,k)
```

```
                  if(yat>0.999) then
                        yabt(jd,k) = yabt(jd,k)/(yat/0.999)
                        yacl(jd,k) = yacl(jd,k)/(yat/0.999)
                        yat      = 0.999
                  endif

        else          ! choice of model
```

Calculating the interface concentrations

```
          yab1p = yab1(j,k)
          yaclp = yacl(j,k)
          yahbp = yahb(j,k)
              call ainfcon(catb,yab1p,yaclp,yahbp)
              xab1i = cib1/(cfat+cfhb)
              xacli = cicl/(cfat+cfhb)
              xahbi = cihb/(cfat+cfhb)
                    if(xab1i > xab1b(k)) xab1i = xab1b(k)
                    if(xacli > xaclb(k)) xacli = xaclb(k)
                    if(xahbi > xahbb(k)) xahbi = xahbb(k)
```

Calculating the rate based on the film model

```
            rateb1(k)  = 6.*rb1*dklab1*(xab1b(k)-xab1i)/dklarf
            ratecl(k)  = 6.*rcl*dklacl*(xaclb(k)-xacli)/dklarf
            ratehb(k)  = 6.*rhb*dklahb*(xahbb(k)-xahbi)/dklarf

            yab1(jd,k) = yab1(j,k) + rateb1(k)*tau
            yacl(jd,k) = yacl(j,k) + ratecl(k)*tau
            yahb(jd,k) = yahb(j,k) + ratehb(k)*tau
```

Correction if the total fraction exceeds unity.

```
            yat = yab1(jd,k) + yacl(jd,k) + yahb(jd,k)
            if(yat>0.999) then
                  yabt(jd,k) = yabt(jd,k)/(yat/0.999)
                  yacl(jd,k) = yacl(jd,k)/(yat/0.999)
                  yahb(jd,k) = yahb(jd,k)/(yat/0.999)
                  yat      = 0.999
            endif
        endif                   ! endif for model choice
```

Calculating the change of concentration fractions in the liquid

```
          if(k<=3) then
            if(kkai==1) then
```

```
                    xabtb(k+1) = xabtb(k) - ratebt(k)*xi*frc_ani
               else
                    xab1b(k+1) = xab1b(k) - rateb1(k)*xi*frc_ani
                    xahbb(k+1) = xahbb(k) - ratehb(k)*xi*frc_ani
               endif
                    xaclb(k+1) = xaclb(k) - ratecl(k)*xi*frc_ani
             else
              if(kkai==1) then
               coec_bt =  55.0*ratebt(k) - 59.0*ratebt(k-1) + 37.0*ratebt(k-2) -
9.0*ratebt(k-3)
             else
               coec_b1 =  55.0*rateb1(k) - 59.0*rateb1(k-1) + 37.0*rateb1(k-2) -
9.0*rateb1(k-3)
               coec_hb =  55.0*ratehb(k) - 59.0*ratehb(k-1) + 37.0*ratehb(k-2) -
9.0*ratehb(k-3)
             endif
               coec_cl =  55.0*ratecl(k)   - 59.0*ratecl(k-1)
  &              +  37.0*ratecl(k-2) - 9.0*ratecl(k-3)
            if(kkai==1) then
               xabtb(k+1) = xabtb(k)-(xi/24.)*coec_bt*frc_ani
            else
               xab1b(k+1) = xab1b(k)-(xi/24.)*coec_b1*frc_ani
               xahbb(k+1) = xahbb(k)-(xi/24.)*coec_hb*frc_ani
             endif
               xaclb(k+1) = xaclb(k) - (xi/24.)*coec_cl*frc_ani
               endif
               if(xaclb(k+1)>xaclb(k))        xaclb(k+1)= xaclb(k)
               if(xabtb(k+1)>xabtb(k))        xabtb(k+1)= xabtb(k)

          else              !

             if(kkai==1) then
                     yabt(jd,k) = yabt(j,k)
             else
                     yab1(jd,k) = yab1(j,k)
                     yahb(jd,k) = yahb(j,k)
               yabt(jd,k) = yab1(jd,k) + yahb(jd,k)
             endif
                     yacl(jd,k) = yacl(j,k)

                  yat       = yabt(jd,k) + yacl(jd,k)

              if(kkai==1) then
               xabtb(k+1) = xabtb(k)
              else
               xab1b(k+1) = xab1b(k)
```

```
                xahbb(k+1) = xahbb(k)
                          endif
                xaclb(k+1) = xaclb(k)

          endif

             if(xab1b(k+1)<0.0) xab1b(k+1) = xab1b(k)
             if(xaclb(k+1)<0.0) xaclb(k+1) = xaclb(k)
             if(xahbb(k+1)<0.0) xahbb(k+1) = xahbb(k)
             if(xabtb(k+1)<0.0) xabtb(k+1) = xabtb(k)

             if(kkai==1) then
               xabt = xabtb(k+1)
               else
               xabt = xab1b(k+1) + xahbb(k+1)
             endif

c___________________________________________________________________________

Come here to calculate the material balance for the cationic species
c___________________________________________________________________________

     if(yct<0.999) then

           yclip  = ycli(j,k)
           ycnap  = ycna(j,k)
           coli   = xclib(k)*(cfct+cfhb)
           cona   = xcnab(k)*(cfct+cfhb)
           coch   = xch(k)*(cfct+cfhb)

           call cinfcon(cctb,yclip,ycnap)
                 xclii = cili/(cfct+cfhb)
                 xcnai = cina/(cfct+cfhb)

     else

                 xclii = xclib(k)
                 xcnai = xcnab(k)
      endif

           coefft = coeffc*coeffq

           rateli(k)  = rli*dklcli*coefft*(xclib(k)-xclii)
           ratena(k)  = rna*dklcna*coefft*(xcnab(k)-xcnai)
```

```
          ycli(jd,k) = ycli(j,k)  + rateli(k)*tau

          ycna(jd,k) = ycna(j,k)  + ratena(k)*tau

          yct       = ycli(jd,k) + ycna(jd,k)

        if(k<=3) then
          xclib(k+1)=xclib(k) - rateli(k)*xi*frc_cat*rkli
          xcnab(k+1)=xcnab(k) - ratena(k)*xi*frc_cat*rkna
        else
          coec_li =  55.0*rateli(k)   - 59.0*rateli(k-1)
     &        +  37.0*rateli(k-2) - 9.0*rateli(k-3)
          coec_na =  55.0*ratena(k)   - 59.0*ratena(k-1)
     &        +  37.0*ratena(k-2) - 9.0*ratena(k-3)

       xclib(k+1) = xclib(k) - (xi/24.)*coec_li*frc_cat
       xcnab(k+1) = xcnab(k) - (xi/24.)*coec_na*frc_cat
        endif
          if(xclib(k+1)<0.or.xclib(k+1)>xclib(k)) then
                 xclib(k+1) = xclib(k)
          endif
          if(xcnab(k+1)<0.) xcnab(k+1) = xcnab(k)
```

Renew the bulk concentrations of species for next calculation of Subs.SOLU_CON

```
         cocl = xaclb(k+1)*(cfat+cfhb)
         cobt = xabt*(cfhb+cfat)
         coli = xclib(k+1)*(cfct+cfhb)
         cona = xcnab(k+1)*(cfct+cfhb)
```

come to here redefine the concentration fractions in the liquid phase

```
         call solu_con

          if(kkai==1) then
            xabtb(k+1) = cobt/(cfat+cfhb)
          else
                xab1b(k+1) = (cobt-cohb)/(cfat+cfhb)
                xahbb(k+1) = cohb/(cfhb+cfat)
          endif

              cctb      = coli + cona + coch
          catb       = cctb
          cch(k+1)   = coch
          xch(k+1)   = coch/(cfct+cfhb)
400      continue
```

Output results for comparison

```
      do 410 kki = 1, nt
         yctn(kki) = ycli(jd,kki) + ycna(jd,kki)
        if(kkai==1) then
         yatn(kki) = yabt(jd,kki) + yacl(jd,kki)
            else
              yatn(kki) = yab1(jd,kki) + yahb(jd,kki) + yacl(jd,kki)
        endif
410   continue

       open(9,file='mcony35.dat',status='unknown')
       open(11,file='mconc35.dat',status='unknown')
       open(12,file='mbreak35.dat',status='unknown')

      if(tautot<tau) then
              write(9,430)
              write(9,441)
              write(9,442)
              write(11,440)
              write(11,431)
        write(12,588)
        write(12,589)
      endif

      if(tautot>0.25*taupr.and.tautot<(0.25*taupr+tau).or.
      & tautot>0.35*taupr.and.tautot<(0.35*taupr+tau).or.
   & tautot>0.50*taupr.and.tautot<(0.50*taupr+tau)) then
         write(11,432)
         kot = 0
         do 421 i = 1, nt+1
          za  =  float(nt)
     zb  =  float(i-1)
     z   =  zb*cht_bed/za
     if(kot==1.or.kot==(nt+1).or.kot==(kot/4*4)) then
          if(kkai==1) then
            cbt = xabtb(i)*ppmb*((cfat+cfhb)/cfbt)
          else
            cb1 =  xab1b(i)*ppmb*((cfat+cfhb)/cfbt)
                chb =  xahbb(i)*ppmb*((cfat+cfhb)/cfbt)
            cbt =  cb1 + chb
          endif
                ccl =  xaclb(i)*ppmcl*((cfat+cfhb)/cfcl)
                     cli =  xclib(i)*ppmli*((cfat+cfhb)/cfli)
                     cna =  xcnab(i)*ppmna*((cfat+cfhb)/cfna)
```

```
              write(11,445) z,cbt,ccl,cli,cna,yatn(i),yctn(i)
            endif
                kot =  kot+1
421         continue
          write(11,434)
          endif

          if(kcount==0.or.kcount==kcount/4*4) then
           cbt  = cobt/cfbt*ppmb
           tt   = tautot
          write(9,4)tt,yctn(1),yatn(1),yab1(jd,1),yacl(jd,1),yahb(jd,1)
          endif

          ph = - dlog10(coch)
          write(*, 444) ph, cob1, cocl, cohb, cobt,tautot

            if(kcount==0.or.kcount==kcount/2*2) then
              cbt = cobt/cfbt !*ppmb
              clb = cocl/cfcl !*ppmcl
              cli = coli/cfli !*ppmli
              cna = cona/cfna !*ppmna
              write(12,590) tautot,cbt,clb,cli,cna,ph
              write(*, 444) ph, cli, cna, cbt
            endif

430     format(/,12x,' Concentration Distributions in Resins',/)
431     format(2x,' Z ',7x,'CBT',7x,'CCl',7x,'CLI',7x,'CNA',6x,'ycat',//)
432     format('Concentration Distribution in Column at 25% Total Time',/)
433     format('Concentration Distribution in Column at 50% Total Time',/)
434       format(//)
435     format('Concentration Distribution in Column at 75% Total Time',/)
436     format('Concentration Distribution in Column at 85% Total Time',/)
440       format(/,16x,' Effluent Concentrations',/)
441       format('  Time',4X,'ycct',7x,'ycat',6x,'yb1a',7x,'ycla',6x,'yhba')
442       format(//)
4         format(f7.2,1x,6(d9.4,1x))
444       format(' ch,b1,cl,hb,bt=:',f5.2,1x,4(e8.3,1x),1x,f7.2)
44        format('ch,o,b1,cl,h,t=:',6(e8.3,1x))
445       format(1x,f6.2,2x,e11.6,1x,3(e9.4,1x),2(f8.4,1x))
446       format(1x,f6.2,2x,e11.6,1x,4(e9.4,1x),f8.2)
498       format(//)
499       format('  Z',9x,'B1',9x,'Cl',9x,'HB',9x,'Li',9x,'Na',6x,'pH',/)
588       format(//,12x,'The Effluent Concentration History',//)
589       format('  Time',7x,'cbt',8x,'ccl',8x,'cli',8x,'cna',9x,'pH',//)
590       format(1x,f7.2,1x,e11.6,1x,3(e10.5,1x),2x,f6.2)
```

```
          if(j==3) then
            j = 1
          else
            j = j + 1
          endif
       tautot = tautot + tau
          kcount = kcount + 1

      enddo

      return
         End

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       Sub. SOLCON determines the concentrations of species in the bulk
C       liquid phase based on the equilibrium conditions, charge balance,
C       and material balance as well.  It is called by SOLVER.
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C     FUNCTION
C        FUNC(CHO)   = CHO**3 + (DKB1+CNA+CLI-CCL)*CHO**2
C                             + (DKB1*(CNA+CLI-CCL-CBT)-DKWT)*CHO
C                - DKWT*DKB1
C     DIREVATIVE
C       FPRIME(CHO) = 3.*CHO**2 + 2.*(DKB1+CNA+CLI-CCL)*CHO
C                              + (DKB1*(CNA+CLI-CCL-CBT)*DKB1-DKWT)
C
C     DETERMINE THE HYDROGEN CONCENTRATION BY N-R METHOD

      SUBROUTINE SOLU_CON
         IMPLICIT REAL*8 (A-H,O-Z)
         common /equi_20/dkb1,dkb3,dkwt
         common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
         TOL  = 1.E-6
         DALT = 1.E-10
         NUMB = 1
         U2   = 1.0

         BB = (DKB1+CONA+COLI-COCL)
         CC = (DKB1*(CONA+COLI-COCL-COBT)-DKWT)
         DD = -DKWT*DKB1
         ee =  (4.*BB**2.-12.*CC)

         CHOO=(-2.*BB+ee**0.5)/6.+DALT
125  DO
       IF (ABS(U2)<TOL.AND.NUMB>50) EXIT
           FUNC = CHOO**3.+BB*CHOO**2.+CC*CHOO+DD
```

```
        DERI = 3.*CHOO**2.+2*BB*CHOO+CC
        CHO  = CHOO - FUNC/DERI
        U2   = (CHO-CHOO)/CHO
        CHOO = CHO
        NUMB = NUMB + 1
      ENDDO

      COCH  = CHO
      COOH  = DKWT/COCH
      COB1 = (COBT * DKB1)/(COCH + DKB1)
      COHB = (COB1*COCH)/DKB1

      RETURN
      END

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C     This subroutine serves to determine the concentration of each
C     species at the interface of the resin and the liquid based on
C     the equilibrium relationship at the interface
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
      Subroutine cinfcon(cctb,yclip,ycnap)
      implicit real *8 (a-h,o-z)
      common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
      common /dfcoef2/diffh,diffli,diffna
      common /mtceff1/dklarf,dklcli,dklcna
      common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
      common /infconc/cioh,cib1,cib3,cihb,cibt,cich,cicl,cina,cili
      common /ratiode/rhb,rb1,rb3,rcl,rli,rna
      common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
      common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
      common /consts3/ppmb,ppmcl,ppmli,ppmna
      common /yconsts/yci,ap,bp,cp,ata,nn

      dimension ycia(nn), xcii(nn),tkih(nn)
      dimension aac(nn), xcib(nn),diff(nn)

      icount = 0
      ni = nn
      sigmayci = 0.0
      tolelim = 1.0d-8

      ycia(1) = yclip
      ycia(2) = ycnap

      xcib(1) = coli/cctb
      xcib(2) = cona/cctb
```

```
        xcib(3) = coch/cctb

        diff(1) = diffli
        diff(2) = diffna
        diff(3) = diffh

        tkih(1) = tkli_h
        tkih(2) = tkna_h

        do 5 ia = 1, ni-1
           sigmayci = sigmayci + ycia(ia)
5       continue
        ycha = 0.999 - sigmayci

Correction of YCHA if there is unrealistic value due to numerical error

        if(ycha<=0.0) then
                ycha = 0.001
            do 10 ib = 1, ni-1
                        ycia(ib) = ycia(ib)*0.999/(sigmayci+ycha)
10          continue
        end if

Calculate concentration fractions at the interface for uni-valence

                sumxi = 0.0
                sumky = 0.0
                do 11 ic = 1, ni-1
                        sumky = sumky + ycia(ic)/tkih(ic)
11              continue
                sumky = sumky + ycha

                do 12 ic2 = 1, ni-1
                        xcii(ic2) = ycia(ic2)/tkih(ic2)/(sumky)
                        sumxi = sumxi + xcii(ic2)
12              continue
                xcii(3) = 1.0 - sumxi     !hydrogen

Calculate the total concentration at the interface

                sumdxib = 0.0
                sumdxii = 0.0
            do 21 id = 1, ni
              sumdxib = sumdxib + diff(id)*xcib(id)
              sumdxii = sumdxii + diff(id)*xcii(id)
21               continue
```

```
            rs = sumdxib/sumdxii
                  ccti = (rs)**(0.5)*cctb
```

Come here to specify the interface concentrations of all species

```
                  cili  = ccti*xcii(1)
                  cina  = ccti*xcii(2)
                  cich  = ccti*xcii(3)
```

Calculate Ri

```
                  rtbi = (ccti/cctb)**2
                  do 41 ie = 1, ni-1
              if(rtbi==1) then
               aac(ie) = 0.0
              else
               aac(ie) = ((xcii(ie)*rtbi - xcib(ie))/(rtbi - 1.0))
               if(aac(ie)<0.0) aac(ie) = 0.0
              endif
41                continue


          ra  = 2.0/3.0
          dli =  (coli - cili)
          dna = (cona - cina)
          if(dli<0.0)  dli = 0.0
          if(dna<0.0)  dna = 0.0

          if(ccti>cctb) then
            rli = 0.0
       rna = 0.0
          else
       if(dli==0.0.or.dna==0.0) then
              if(dli==0.0.and.dna==0.0) then
               rli = 0.0
               rna = 0.0
              else
               if(dli==0.0) then
                rli = 0.0
                rna = ((2.0*aac(2)*cctb/dna)*(1.0-(ccti/cctb)))**ra
               else
                rna = 0.0
                rli = ((2.0*aac(1)*cctb/dli)*(1.0-(ccti/cctb)))**ra
               endif
              endif
            else
```

```
        rli = ((2.0*aac(1)*cctb/dli)*(1.0-(cctI/cctb)))**ra
        rna = ((2.0*aac(2)*cctb/dna)*(1.0-(ccti/cctb)))**ra
                endif
          endif


        return
        end

C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
C       This subroutine serves to determine the concentration of ionic
C       species at the interface of the resin and the liquid based on
C       the equilibrium relationship at the interface
C*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*
        Subroutine ainfcon(catb,yab1p,yaclp,yahbp)
        implicit real *8 (a-h,o-z)
        common /data_40/tkb1_oh,tkb3_oh,tkcl_oh,tkna_h,tkli_h
        common /dfcoef1/diffb1,diffb3,diffhb,diffoh,diffcl
        common /equi_20/dkb1,dkb3,dkwt
        common /mtceff1/dklarf,dklcli,dklcna
        common /mtceff2/dklab1,dklab3,dklacl,dklahb
        common /solconc/cooh,coch,cobt,cohb,cona,coli,cocl,cob1,cob3
        common /infconc/cioh,cib1,cib3,cihb,cibt,cich,cicl,cina,cili
        common /ratiode/rhb,rb1,rb3,rcl,rli,rna
        common /consts1/tautot,taupr,tau,xi,nt,chtd,time,taumax
        common /consts2/cfbt,cfat,cfct,cfli,cfcl,cfna,cfhb,cfb1,cfb3
        common /consts3/ppmb,ppmcl,ppmli,ppmna
        common /yconsts/yci,ap,bp,cp,ata,nn

        dimension yaia(nn+1), xaii(nn+1),tkioh(nn+1)
        dimension aaa(nn+1),xaib(nn+1),diff(nn+1)

        icount = 0
        ni = nn
        sigmayai = 0.0
        tolelim = 1.0d-8

        yaia(1) = yab1p
        yaia(2) = yahbp
        yaia(3) = yaclp
        yaia(4) = 1.0 - yab1p - yahbp - yaclp

        xaib(1) = cob1/(catb + cohb)          !fraction of species
        xaib(2) = cohb/(catb + cohb)          !under the basis of
        xaib(3) = cocl/(catb + cohb)          !solution concentration
        xaib(4) = cooh/(catb + cohb)          !of the slice
```

```
      diff(1) = diffb1
      diff(2) = diffhb
      diff(3) = diffcl
      diff(4) = diffoh

      tkioh(1) = tkb1_oh
      tkioh(2) = tkb1_oh                              !use the tkb1_oh for HB
      tkioh(3) = tkcl_oh
      tkioh(4) = 1.0                                  !for hydroxide itself

      yoha = yaia(4)
```

Correction of YOHA if there is unrealistic value due to numerical error

```
      if(yoha<=0.0) then
            yoha = 0.001
         do 10 ib = 1, ni
                  yaia(ib) = yaia(ib)*0.999/(yaclp+yab1p+yahbp+yoha)
10       continue
      end if
```

Calculate concentration fractions at the interface for uni-valence

```
            sumxi = 0.0
            sumky = 0.0
            do 11 ic = 1, ni
                  sumky = sumky + yaia(ic)/tkioh(ic)
11          continue
            sumky = sumky + yoha

            do 12 ic2 = 1, ni
                  xaii(ic2) = yaia(ic2)/tkioh(ic2)/(sumky)
                  sumxi = sumxi + xaii(ic2)
12          continue
            xaii(4) = 1.0 - sumxi    !hydroxide
```

Calculate the total concentration at the interface

```
            sumdxib = 0.0
            sumdxii = 0.0
         do 21 id = 1, ni+1
           sumdxib = sumdxib + diff(id)*xaib(id)
           sumdxii = sumdxii + diff(id)*xaii(id)
21          continue
```

```
                cati = ((sumdxib/sumdxii)**(0.5))*(catb + cohb)

Come here to specify the interface concentrations of all species

                cib1 = cati*xaii(1)
                cihb = cati*xaii(2)
                cicl = cati*xaii(3)
                cioh = cati*xaii(4)

                cbtstare = cfbt*(yahbp+yab1p)**(1.0/ata)
                cbtstarc = cib1 + cihb

Calculate Ri

                rtbi = (cati/(catb+cohb))**2
                do 41 ie = 1, ni
                        aaa(ie) = ((xaib(ie) - xaii(ie)*rtbi)/(1.0 - rtbi))
                        if(aaa(ie)<0.0) aaa(ie) = 0.0
41              continue

          ra  = 2.0/3.0
          rc  = cati/(catb+cohb)
          cot = catb + cohb

          db1 = (cob1-cib1)
          dcl = (cocl-cicl)
          dhb = (cohb-cihb)

          if(db1<0.0) db1 = 0.0
          if(dcl<0.0) dcl = 0.0
          if(dhb<0.0) dhb = 0.0

          if(rc>=(1.0+10.**(-20))) then
                rb1 = 0.0
                rcl = 0.0
                rhb = 0.0
          else
            if(db1==0.0.or.dcl==0.0.or.dhb==0.0) then
              if(db1==0.0.and.dcl==0.0.and.dhb==0.0) then
                rb1 = 0.0
                rcl = 0.0
                rhb = 0.0
              else
                if(db1==0.0.and.dhb==0.0) then
                  rb1 = 0.0
                  rhb = 0.0
```

```
                rcl = ((2.0*aaa(2)*cot/dcl)*(1.0-rc))**ra
              else
                          if(dhb==0.0.and.dcl==0.0) then
                  rhb = 0.0
                  rcl = 0.0
                  rb1=((2.0*aaa(1)*cot/db1)*(1.0-rc))**ra
                else
                            if(db1==0.0.and.dcl==0.0)then
                    rb1 = 0.0
                    rcl = 0.0
                    rhb = ((2.0*aaa(1)*cot/dhb)*(1.0-rc))**ra
                  endif
                endif
              endif
            endif
          else
        rcl = ((2.0*aaa(2)*cot/dcl)*(1.0-rc))**ra
        rb1 = ((2.0*aaa(1)*cot/db1)*(1.0-rc))**ra
            rhb =       ((2.0*aaa(1)*cot/db1)*(1.0-rc))**ra
                endif
         endif
2005     continue
                rhb = 1.0
        return
        end
```

VITA

Jidong Lou

Candidate for the Degree of

Doctor of Philosophy

Thesis: MODELING OF BORON SORPTION EQUILIBRIUM AND KINETIC STUDIES OF ION EXCHANGE WITH BORON SOLUTION

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Changzhou, Jiangsu, The People's Republic of China(PRC), July 2, 1955, the son of Chenyi Lou and Shangzhi Po.

Education: Graduated from BeiMa High School, Lishui, Jiangsu, PRC, in January 1973; received Bachelor of Engineering Degree in Chemical Engineering Mechanism from Jiangsu Institute of Chemical Technology at Changzhou in May 1982; completed requirements for the Master of Science degree at Oklahoma State University in May, 1993; completed requirements for Doctor of Philosophy degree at Oklahoma State University in December 1997.

Professional Experience: Employed as a teaching assistant, lecturer, associate researcher with Jiangsu Institute of Petrochemical Technology, Sinopec, PRC, 1982-1991; employed as a part time engineer for Yong-Hong Industrial Company, PRC, 1983-1985; employed as a teaching assistant and a research associate, School of Chemical Engineering, Oklahoma State University, September 1991, to August 1997.