COMPUTER SIMULATION OF REGENERATION PROCESSES FOR ION EXCHANGE RESINS USED IN WATER PURIFICATION

By

ATANU BASU

Bachelor of Chemical Engineering

Jadavpur University

Calcutta, India

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Thesis Approved:

Gary L. Foutch

Thesis Advisor

Martin S. High

Arland H. Johannes

Thomas C. Collins

Dean of the Graduate College

PREFACE

This work aims at modeling the important process of regeneration in ion exchange resins used for water purification. Regeneration involves solutions at high concentrations, and so local equilibrium between the stationary (resin) and mobile (solution) phase has been assumed at all points and at all times. The predictions obtained by ordinary equilibrium theory have been improved upon by the inclusion of the effect of axial dispersion in the model. The new model is called modified equilibrium theory. It reasonably predicted actual plant performances for regeneration and can be used to determine significant factors like technical feasibility, economic viability.

I want to express my deepest appreciation to my advisor, Dr. Gary L. Foutch, for his intelligent suggestions, constructive criticisms, effective guidance, and financial support during the entire period of this study. I am also very grateful to Dr. Arland H. Johannes and Dr. Martin S. High for readily agreeing to be in the advisory committee and for their technical assistance.

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NOMENCLATURE

c = ion concentration of hydrogen or hydroxide in solution, eq/m^3.

$\bar{c}$ = ion concentration of hydrogen or hydroxide in solid phase, eq/m^3.

C_{tot} = total concentration in solution, eq/m^3.

$\overline{C_{tot}}$ = total concentration in solid, eq/m^3.

D_a = axial dispersion or diffusion coefficient, m^2/s.

F = flowrate of regenerant, m^3/s.

L = column length, m

t = time, s.

u = empty-tube fluid velocity, m/s.

$u_i = \dfrac{F}{\Omega.\ \varepsilon} = \dfrac{u}{\varepsilon}$ = interstitial fluid velocity, m/s.

$x = \dfrac{c}{C_{tot}}$, N.D.

$y = \dfrac{\bar{c}}{\overline{C_{tot}}}$, N.D.

z = length along column, m.

Greek letters:

α = relative sorptivity of hydrogen with respect to sodium, N.D.

ε = intergrain porosity, N.D.

Ω = cross-sectional area of bed, m^2.

Superscript/Subcript:

i = index for space.

n = index for time.

CHAPTER I

INTRODUCTION

Ion exchange is practiced for water treatment throughout the world. Its industrial uses, to name a few, include important applications like softening, dealkalization, deionization, and high-purity water polishing. Ion exchange, and a few other processes, have also made possible the production of ultrapure water. Resin regeneration is reverse ion exchange occurring at high concentrations (more than 1N). Regeneration is important and needed for the reuse of resources. Resin reuse after exhaustion is necessary and practical for many industries due to economic considerations.

Ion Exchange Resins

In this work, the ion exchange materials of interest are synthetic polymeric-type resins. These are basically three-dimensional, cross-linked, hydrocarbon matrices carrying a charge (positive or negative) due to the deliberate incorporation of a functional group into the lattice. The functional groups generally used for cationic resins are sulfonic (most prevalent), carboxylic, phosphonic, phosphinic, and phenolic. Those for anionic resins typically include quaternary ammonium (strongly basic), and quaternary phosphonium (weakly basic). Styrene polymer chains interconnected by divinylbenzene (DVB) molecules typically constitute the hydrocarbon structure of a resin. For further details, Helfferich (1962), Kunin (1958), and Haub (1984) provide good references.

Ion Exchange, Mixed Bed Ion Exchange, and Regeneration

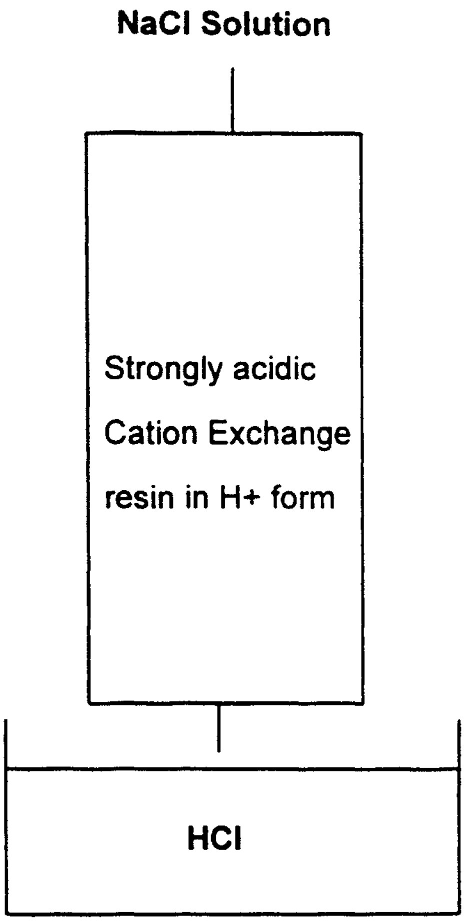
Ion exchange is the reversible reaction involving the interchange of ions (counter ions) between a solid (exchanger) phase and a liquid (solution) phase. To preserve electroneutrality, this process takes place stoichiometrically. For example, a typical cation exchange process can be represented as:

$$\text{R-B}^{v} \quad + \quad \text{A}^{v}\text{(solution)} \quad <\!\!=\!\!=\!\!=\!\!> \quad \text{R-A}^{v} \quad + \quad \text{B}^{v}\text{(solution)}$$

where R represents a stationary anionic site (of valence v) in the polyelectrolyte network of the exchanger phase. It should be realized that a divalent can also exchange with two monovalent sites. For a detailed description of the ion-exchange process, refer to Helfferich (1962).

Mixed bed ion exchange (MBIE) is simultaneous cation and anion exchange. Figure I-1 shows how salt water is impacted by ion exchange. Both units receive NaCl as feed. The left unit exchanges H^+ for Na^+ producing HCl. The right unit exchanges OH^- for Cl^- resulting in NaOH. In other words, the left unit removes Na^+ from the solution, whereas the right unit removes Cl^-. If the ion exchange resins were mixed intimately, the products (HCl and NaOH) would have been a single product without Cl^- or Na^+; HOH (water).

$$H^+ \quad + \quad OH^- \quad <\!\!=\!\!=\!\!=\!\!> \quad H_2O$$



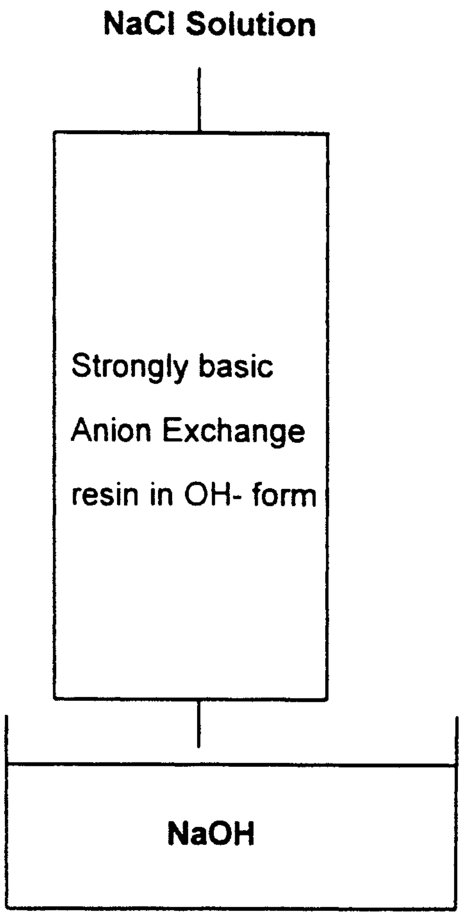


Figure I-1. Column Behavior of Cation and Anion Exchange Resins.

This is how MBIE generates high purity water.

After the service cycle (the time when an ion exchange unit is on-stream), the MBIE resin is almost exhausted and needs regeneration. Before regenerating, the bed is separated into its cationic and anionic counterparts. Each of these two beds is now regenerated with the appropriate high concentration solution. Here, the opposite (reverse) reaction of normal ion-exchange takes place, i.e.,

$$R\text{-}A^{v} \quad + \quad B^{v}(\text{solution}) \quad \Longleftrightarrow \quad R\text{-}B^{v} \quad + \quad A^{v}(\text{solution})$$

This thesis effort will be to simulate this regeneration process by the theory introduced below and developed in detail in Chapter III and IV.

Modified Equilibrium Theory

Exhaustion and regeneration constitutes a cycle for ion exchange operations, commonly carried out in fixed-bed columns. The performance of an ion exchange operation is governed by a combination of stoichiometric, equilibrium, rate relationships, and, of course, the process arrangement used. When only the first two factors are taken into account, "equilibrium" theory of ion exchange results in which local equilibrium is assumed between the two phases at any time and at all points. Given equilibrium data, feed composition, and initial composition of the bed alone; this theory can readily predict ideal process performance. Technical and economic feasibility of the process may be ascertained from this model. In this work regeneration is applied only to uniformly presaturated beds receiving feed of constant composition. Breakthrough curves show zones of constant (plateau zones) and varying composition (transition zones). Equilibrium theory can often predict acceptably the plateau-zone concentrations for systems operating under practical conditions. Mass transfer inefficiencies become relatively small for small particle size resin, low solution flow rate, and large ionic diffusivities. Transition-zone profiles predicted by equilibrium theory provide realistic approximations to actual profiles. The smaller the concentration gradient, the better the approximation. Non-equilibrium regions are often included in the equilibrium model to make it physically meaningful. With a less restrictive definition, equilibrium theory does not explicitly account for mass-transfer kinetics.

Tondeur and Bailly (1986) did not account for axial dispersion in their equilibrium based material balance equation across the bed. In the modified equilibrium theory documented later, axial dispersion is included and significant improvement in predictions has been observed when compared with the actual plant performances. Those will be discussed in detail in Chapter III and IV (with supplemental material in the Appendices).

Objectives

This thesis has very specific objectives, as follows:

- To simulate regeneration processes by ordinary equilibrium theory for normal ion exchange,
- To simulate regeneration processes by a modified equilibrium theory that takes into account the effect of axial dispersion,
- To compare predictions of the above theories, and demonstrate the superiority of the modified theory by showing the proximity of its results to real life cases,
- To perform a parametric analysis of the modified equilibrium model by varying the numerical value for axial dispersion coefficient (D_a) (due to the unavailability of dependable number), and

- To explain any deviations of the model predictions with actual plant performance, and recommend strategies needed to improve both the model and plant operation.

Chapter II

LITERATURE REVIEW

The amount of literature available specifically on regeneration of ion exchange resins is limited. For a detailed review on ion exchange literature in general, Haub's (1984) and Yoon's (1990) work provide good references. In this chapter, I will discuss, in brief, some of the important problems associated with ion exchange processes. These problems are to be taken into account for obtaining meaningful predictions from any mathematical model dealing with any kind of ion exchange. Some important recommendations available in the literature about regeneration conditions will also be discussed.

Recommendations for Regeneration Conditions

The conversion of both cation and anion resins to their original forms during regeneration is fundamental to the capability of MBIE beds to produce pure water. Regeneration of exhausted resins is generally carried outside the service vessels in order to avoid the contamination of the feed system with the regenerant chemicals (Bates, 1994). The regeneration cycle usually involves the following:

- separation of the resins
- regenerant flow
- rinse flow
- air mixing prior to transferring the resins back to the service vessel.

A backwash flow is used to separate the cation and anion resins when the smaller and lighter anion beads rise up through the larger and heavier cation beads. The cross contamination of the regenerant can take place in a single vessel regeneration system due to poor collector design, poor resin separation, and/or incorrect resin level. Bulk contamination with sulfuric acid because of incorrect valve operation or poor centre lateral design can be eluded easily by shifting the anion resin to a separate regeneration vessel. Air mixing, carried out after regeneration and rinsing, evenly distributes the resins throughout the bed. The bed should be drained to within 6" of the top of the resin prior to air mixing in order to allow enough movement for good blending without allowing re-separation as the bed settles (Bates, 1994). Improved regeneration techniques (like Tripol, Triobed, Conesep) are being adapted by the condensate polishing plants (CPP) nowadays to minimize contamination of resins with wrong regenerant as this is the major cause of impurity release from CPP.

Regeneration flow rate and concentration are important and should conform to the design specifications and resin manufacturers' recommendations. In industrial practice, influent conditions frequently vary from the design specifications. Mechanical constraints also sometimes make it impractical to adjust flow rate and concentration accordingly. In these situations, the manufacturers of the equipment and resin should be consulted for suggestions. The following four tables (Table II-1, 2, 3, and 4) give some guidelines to the operating conditions of a regeneration column. They depict the conventional case of downflow (cocurrent) regeneration unless stated otherwise. For sulfuric acid, the following data are meant to provide the maximum possible average regenerant concentration and the minimum possible regeneration flow rate within safe limits to elude calcium sulfate precipitation.

Table II-1 (Davies, 1994)

SUGGESTED REGENERANT FLOW RATES.

Regenerant	Flow Rate Range (gal/min-ft^3)
HCl	0.5 to 1.0
NaOH	0.25 to 0.5
H_2SO_4	0.5 to 1.5

Table II-2 (Davies, 1994)

REGENERANT CONCENTRATION RANGES.

Regenerant	Concentration Range(%)
HCl	4-10
NaOH	4-7
H_2SO_4	see Tables III, IV

Table II-3 (Davies, 1994)

REGENERANT FLOW RATE SCHEDULE FOR H_2SO_4.

Influent % Calcium	Flow Rate (gal/min-ft^3)
0	0.5
25	0.5
50	1.0
75	1.5
100	2.0

Table II-4 (Davies, 1994)

PERMISSIBLE H_2SO_4 CONCENTRATION.

% Calcium in Water [(Ca/(Ca + Mg + K)) X 100]	H_2SO_4 Concentration Permissible
0	10
20	4
40	3
60	2
100	1

Commonly Encountered Problems

The problems that will be mentioned here (Table II-5) apply to ion exchange operation (strong acid cation exchange and strong base anion exchange only) in general. These are the things that can not be taken into account in a mathematical model based on the fundamental principles and often call for empirical relations.

Table II-5 (Davies, 1994)

ION EXCHANGE PROBLEMS: CAUSES AND EFFECTS

Problems	**Sources/Causes**	**Effects**
Higher sodium leakage	• Occurs in strong acid cation exchange resin units when the spent regenerant (loaded with sodium) from the cation component of a polishing mixed bed is used for series regeneration.	• Sodium deposition might take place in the lead cation unit resulting in the failure to produce specified quality water.
Hardness leakage	• Occurs in strong acid cation exchange units mainly due to calcium sulfate precipitation when sulfuric acid is the regenerant.	• Deterioration in the quality of water produced.

Thermal instability	• Occurs mainly in strong base anion exchange units as these resins are prone to degradation above around 125 °F. Loss of strong base functionality might take place due to oxidation.	• Silica leakage may take place with the consequent drop in the quality of water.
Organic fouling	• Occurs predominantly in anion exchange resins.	• Degradation in the quality of treated water takes place due to higher silica leakage resulting from incomplete NaOH regeneration (for steric hindrance of the foulants). • Rinse quantities increase due to the amphoteric effect of the foulant. • Throughput capacity also decreases.
In-situ organic fouling	• Occurs also in anion exchange resins when the water to be treated contains oxidants like ozone, free chlorine residuals, or heavy metals.	• Organic sulfonates can be produced causing the quality of the treated water to deteriorate.
Iron fouling	• Occurs in ion exchange resins when the water to be treated contains some form of iron (ferrous iron, ferric iron, ferrous hydroxide, ferric hydroxide, organic iron complexes).	• Insoluble iron remains suspended and adversely effects the quality of water and also increases the pressure drop across the resin bed. • Gelatinous ferric hydroxide coats the resin beads leading to a decrease in capacity.

Oil fouling	• Occurs in ion exchange resins due to oil contamination of the water.	• Oil film formation takes place around the resin films hindering basic ion exchange reactions. The quality of water suffers.
Mud fouling	• Occurs in ion exchange resins due the absence or malfunctioning of the pretreatment plant for the water to be treated via ion exchange.	• Suspended solids form a filter cake on the resin bed leading to channeling and excessive pressure drop.
Algae/bacteria fouling	• Occurs in some ion exchange resins.	• Hampers flow patterns and interferes with the internal distribution system.
Calcium sulfate precipitation.	• Occurs in ion exchange resins and underbed collection systems due to incorrect regeneration conditions.	• Highly insoluble calcium sulfate accumulates around underbed collection systems leading to blocking and pressure drop problems.
Silica fouling	• Occurs in strong base anion exchange resins due to incomplete regeneration.	• Affects the capacity by building up on the resin. • Affects the quality of produced water.
Barium sulfate fouling	• Occurs due to the presence of barium in the water to be treated with strong acid cation exchange resin regenerated with sulfuric acid.	• Fouls the water produced. • Collects on and around underbed distributors/strainers causing higher pressure drop.
Resin fines	• Occur in the resin bed due to reasons like mechanical attrition, thermal shock, physical shock.	• Forms a filter cake which in turn causes channeling, and higher pressure drop.

Corrosion products	- Occur in vessel walls, inlet distribution system, and underbed collection system.	- Adversely affects the purity of the water produced. - Increases the pressure drop of the system

There are many other minor problems associated with ion exchange (Bates, 1994). Conscientious knowledge about the particular system in use will go a long way in correctly interpreting the model predictions, and incorporating necessary adjustments both to the model and plant operating conditions.

Equilibrium Models in Brief

The process of ion exchange, occurring during the regeneration of exhausted resins, involves high concentrations (often more than 1N). So, the rate (kinetic) theories that are necessary for accurate quantitative predictions of ion exchange processes for ultra pure water production (concentrations in ppm or even ppb), are not imperative for the case of regeneration. Here, equilibrium models should provide acceptable predictions for most practical purposes. The later stages of regeneration are very sensitive and might need additional criteria (like local value of the slope of the equilibrium isotherm) for accurate handling. An excellent treatise on the equilibrium approach to ion exchange, in general, has been published by Tondeur and Bailly (1986). Their work can be seen as an extension of the idea of local equilibrium, between the solid (exchanger) and the liquid (solution) phase throughout the entire column, as proposed by De Vault (1943). In fact the early theories proposed by Wicke (1939), Wilson (1940), Weiss (1943) and Gluckauf (1946) also dealt with local equilibrium between the mobile and stationary phases. Tondeur and Bailly qualitatively developed the equilibrium theory, without taking into consideration the effect of axial dispersion, and applied it to lab scale ion exchange columns under controlled conditions (low flow rate, relatively less variation in the shape and size of resin beads). A theoretical analysis of equilibrium theories in predicting multicomponent ion exchange in fixed beds has been presented by Klein et al. (1967) and Tondeur et al. (1967). Variable-separation factor and constant-separation factor systems are respectively considered in the these two papers. Helfferich (1967, 1968) proposed the physical concept of "coherence" of concentration waves and the mathematical "h-transform" tool for constant separation factor ion exchange systems. Helfferich and Klein (1970) published a comprehensive treatise on multicomponent equilibrium theory for sorption processes in general and ion exchange in particular. A more mathematical discussion on multicomponent chromatography but with Langmuir-type adsorption systems can be obtained from Rhee et al. (1970). Hwang and co-workers (1988) extended multicomponent equilibrium theory to ion exchange systems involving reactions in either or both phases. Their approach starts with a methodology to determine the thermodynamic variance of the system and then formulates a general mathematical model to obtain compositions at the grid points by appropriate numerical methods.

Regeneration Model

Again, almost nothing specific is available in the literature on the modeling of regeneration processes; my effort in this thesis is to apply an equilibrium theory for general ion exchange to the case of regeneration and modify it (if necessary) to acceptably predict real-life plant performances. For binary regeneration and the high concentrations involved, the equilibrium theory discussed by Tondeur and

Bailly (1986) appears suitable. The process of regeneration is modeled with actual plant conditions by this equilibrium theory. Suitable equilibrium isotherm is supplied to the model to account for the specificity of the ion exchange system involved. This model fails to provide us with realistic predictions, as shown in Chapter III, and so necessitates the incorporation of column dynamics associated with dispersive effects. This is reasonable at the high flow rates encountered during real-life plant operations.

Lapidus and Amundson (1952) proposed a linear dispersion model for general sorption and chromatographic processes. An analytical solution has also been offered (for sufficiently long times) to the material balance equation by them and Lightfoot et al. (1962). This analytical solution involved error functions, and is impractical for real-life process calculations. Moreover, linear equilibrium isotherm is observed generally during chromatographic processes involving low concentrations. For high concentrations (as in regeneration), the equilibrium isotherms are mostly nonlinear. In this thesis, when ordinary equilibrium theory fails, the regeneration of ion exchange resins is simulated by incorporating the effect of axial dispersion in the equilibrium theory. So, this work involves simultaneous application of equilibrium and dispersion theories to the regeneration processes necessary in the ion exchange columns used for water treatment.

Numerical Techniques

The models in this work include a material balance equation, its initial condition and boundary condition(s), and equilibrium relationships particular to the exchange taking place. Finite difference methods for partial differential equations are applied to numerically integrate the systems considered. As discussed in detail in Chapter III, an explicit upstream method will be adapted in preference to an implicit scheme because of the former's ability to closely follow the moving concentration profile involved. Explicit methods are also used as they can handle the nonlinearity effectively at the small timesteps used here without forsaking the speed of computation. Implicit methods here would require the time-consuming solution of a nonlinear algebraic equation at the end of each timestep and this process is susceptible to the initial guess(es) supplied. The only things that are to be cautiously selected for an explicit method are the time and distance stepsizes in order to maintain the stability of the scheme. The codes will offer suggestions for the suitable choice of the stepsizes. The results obtained show that the explicit method performs satisfactorily.

Chapter III

SIMULATION OF REGENERATION PROCESSES WITH EQUILIBRIUM THEORY

Abstract

The process of regeneration of ion exchange resins used in water purification has been modeled using the equilibrium theory proposed by Tondeur and Bailly (1986) for ordinary ion exchange processes. The case of regeneration of ion exchange resins by separating the MBIE bed into its anionic and cationic counterparts has been simulated. For equilibrium relations, the proposed model assumes constant relative sorptivity for simple cationic regeneration and uses a fourth order polynomial as the best fit of the isotherm for simple anionic regeneration. The predictions obtained by this model are significantly less than that observed during actual plant performance. Tondeur and Bailly's work also shows the need for a modified equilibrium theory for better predictions, at least for regeneration.

Introduction

Equilibrium theory can be broadly defined as a model, without rate relationships, for ion exchange processes . It assumes equilibrium between the exchanger (solid) phase and solution (liquid) phase at any time and at all points. It can be used to ascertain the ideal performance of the process. When supplied with dependable phase equilibrium data, initial composition of the bed, and feed composition, equilibrium theory can predict the limiting behavior of the bed that can be used to determine the technical feasibility and economic viability of the proposed process. An equilibrium model should be used with caution when the process is suspected to be kinetically controlled.

Background

Tondeur and Bailly (1986) conducted experiments to determine the effluent histories of simple cationic exchanges involving Na^+ and H^+. Figure III-1 shows the plots of experimental concentrations against effluent volume at the outlet of two similar ion exchange columns. Figure III-1a is for the elution by hydrochloric acid of a bed initially equilibrated with a NaCl solution. Figure III-1b shows the fixation of Na^+ on the same column and under similar conditions. A closer look at these two figures reveals that the exchange front of Figure III-1a is relatively spread out, but that of Figure III-1b is precipitous (due to significant kinetic contributions). These breakthrough curves can be seen as images at the column outlet of what is actually going on throughout the bed. Tondeur and Bailly also gave the schematic evolution of the internal profiles corresponding to Fig. III-1a and III-1b respectively (Figure III-2). This figure shows that the overall shape of these curves is approximately mirror image of the breakthrough curves. The following two distinctive features are evident:

- In Figure III-2a, the concentration for Na^+ spreads more and more as it approaches the column end: spreading behavior.
- In Figure III-2b, the concentration for Na^+ sharpens itself and takes a steep, constant shape as it moves toward the column end: self-sharpening, or non-spreading, or constant-pattern behavior.

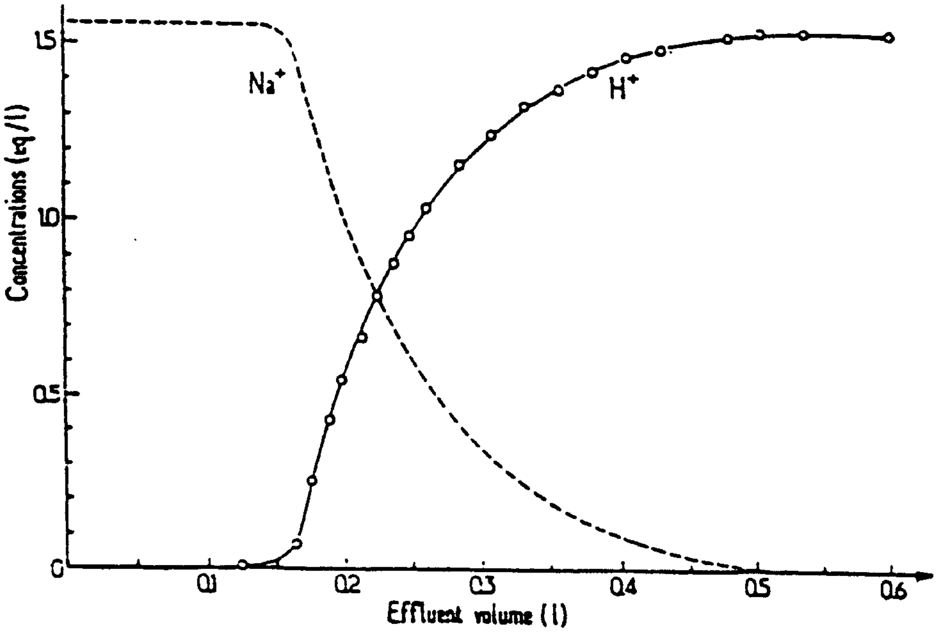


Figure III-1a. Experimental effluent history of a bed of cation exchanger initially in Na^+ form, receiving as feed HCl 1.49N (resin: Duolite C20; bed: 0.36m length, 0.29 equiv. capacity; flowrate: 10ml/min). [Tondeur and Bailly, 1986] [with permission]

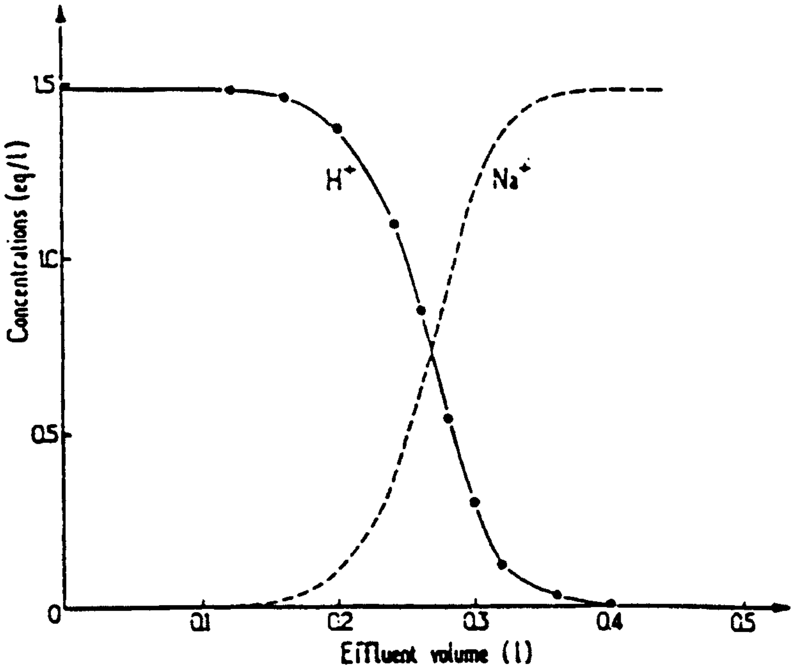


Figure III-1b. Experimental effluent history of a bed of cation exchanger in H^+ form receiving as feed NaCl 1.55N (same conditions as in Fig. III-1a). [Tondeur and Bailly, 1986] [with permission]

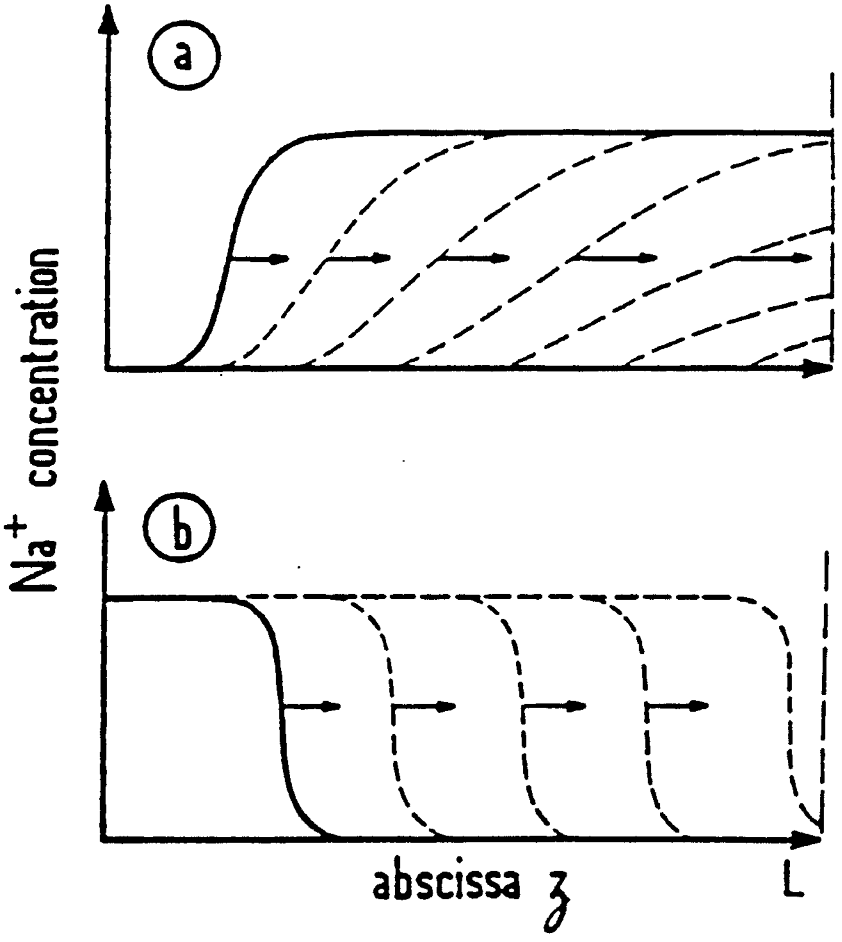


Figure III-2. Internal concentration profiles corresponding to experiments of Figure III-1. [Tondeur and Bailly, 1986] [with permission]

In the breakthrough curves of Figure III-1, equilibrium can be assumed for the plateau regions. The initial plateau is formed by what comes out until the column has felt the effect of the incoming ions (retained in the first layers of the column). The final plateau starts when the resin has consumed all the incoming ions it could, and is saturated or equilibrated with the feed. As the composition is practically constant for all species in these plateau regions, equilibrium can be rationally assumed. Had there been no equilibrium, mass transfer would have occurred between the two phases and composition would have changed. On the other hand, in the exchange fronts (joining the initial and final plateau regions) composition changes. It will be shown that departure from the thermodynamic equilibrium can be taken as the driving force for cationic (R-Na + HCl, R-Na + H_2SO_4) and anionic regeneration (R-Cl + NaOH). Tondeur and Bailly (1986) concluded that, generally, when a weakly retained ionic species replaces by a strongly retained one, the front spreads and a constant pattern front is observed when a strongly retained species replaces a weakly retained one. So, the trends seen in Figure III-1 are due to the preference of the ion exchange resin for Na^+ over H^+ ions.

Model Development

Material balance (Tondeur, 1986) on an elemental slice, of the regeneration column, perpendicular to the main flow gives

$$\varepsilon \frac{\partial c}{\partial t} + (1-\varepsilon)\frac{\partial \bar{c}}{\partial t} + u\frac{\partial c}{\partial z} = \frac{\partial}{\partial z}[D_a \frac{\partial c}{\partial z}] \qquad (3\text{-}1)$$

The first two terms on the left of (3-1) represent accumulation in the slice over a differential time interval. The third term is the net convective transfer flux. The term on the right is for axial diffusion (dispersion) flux. The equilibrium model neglects the contribution of the axial dispersion term and assumes that local equilibrium prevails between the exchanger phase concentration ($\bar{c}$) and the solution phase concentration (c). It also assumes this equilibrium can be expressed by some algebraic relation.

In the binary case of regeneration, the solid phase concentration ($\bar{c}$) can be eliminated through equilibrium as follows:

$$\frac{\partial \bar{c}}{\partial t} = \frac{d\bar{c}}{dc}\frac{\partial c}{\partial t} \tag{3-2}$$

After some algebraic manipulations, the material balance reduces to (see Appendix A for details)

$$\frac{\partial c}{\partial t} + u_c \frac{\partial c}{\partial z} = 0 \tag{3-3}$$

$$\text{where } u_c = \frac{u/\varepsilon}{1 + \frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc}} = \frac{u_i}{1 + \lambda \frac{dy}{dx}} \tag{3-4}$$

<u>Note</u>: $\lambda = \frac{1-\varepsilon}{\varepsilon}\frac{\overline{C_{tot}}}{C_{tot}}$ = capacity ratio, and $u_i = \frac{F}{\Omega\varepsilon} = \frac{u}{\varepsilon}$

Equation (3-3) can be viewed as a "wave equation" describing the propagation of any given value c of liquid phase concentration.

The following initial and boundary conditions apply:

I.C.:

$t = 0,\ z > 0$

$c = c_0 =$ constant throughout the column (3-5)

B.C.:

$t > 0,\ z = 0$

$c = c_f$ (3-6)

An equilibrium relation is still needed for solving (3-3) numerically.

Cationic Regeneration:

For obtaining the equilibrium relation, Tondeur and Bailly (1986) defined constant relative sorptivity as follows:

$$\alpha_j^i = \frac{y_i / x_i}{y_j / x_j} \qquad (3\text{-}7)$$

$$y_i = \frac{\alpha_n^i x_i}{\Sigma(\alpha_n^j x_j)} \tag{3-8}$$

$$x_i = \frac{\alpha_i^n y_i}{\Sigma(\alpha_j^n y_j)} \tag{3-9}$$

$$\alpha_n^1 > \alpha_n^2 > \ldots\ldots\ldots > \alpha_n^{n-1} > 1 \tag{3-10}$$

$$\alpha_k^i = \alpha_j^i \alpha_k^j \tag{3-11}$$

$$\alpha_k^i = 1 \big/ \alpha_i^k \tag{3-12}$$

Figure III-3 shows the equilibrium isotherm for Na^+/H^+ exchange at room temperature. This isotherm can be approximated by (3-7) with $\alpha_H^{Na} = 2$. Its slope, $\frac{dy_{Na}}{dx_{Na}}$, is a decreasing function of y_{Na} or x_{Na}. From (3-4), we see that the higher x_{Na} values have higher velocities, i.e., high Na^+ concentrations propagate faster than low ones. In Figure III-2a, this implies that the exchange front is spreading more and more as it travels. The spreading behavior is thus implied in the change with composition of the slope of the equilibrium isotherm.

For binary ion exchange between species A and B, (3-8) gives

$$y_A = \frac{\alpha_B^A x_A}{\alpha_B^A x_A + 1 - x_A} \tag{3-13}$$

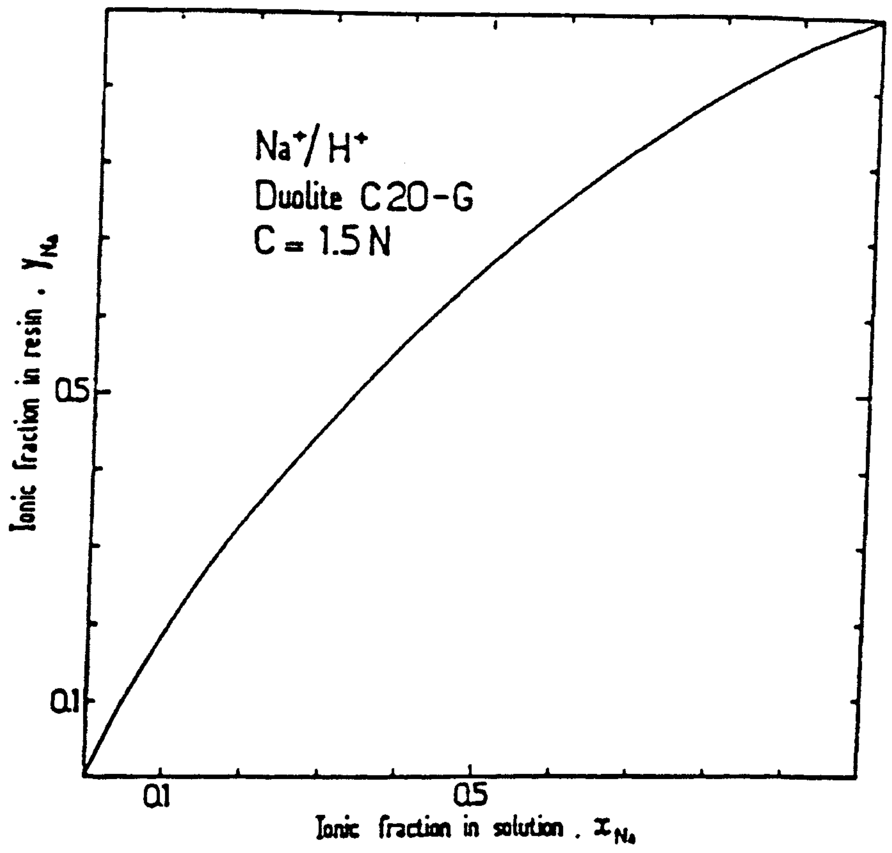


Figure III-3. Equilibrium isotherm for Na^+/H^+ exchange at room temperature. [Tondeur and Bailly, 1986] [with permission]

$$\therefore \frac{dy_A}{dx_A} = \frac{\alpha_B^A}{\left[1 + x_A(\alpha_B^A - 1)\right]^2} \qquad (3\text{-}14)$$

Substituting H for A and Na for B in (14), we get

$$\frac{dy_H}{dx_H} = \frac{\alpha_{Na}^H}{\left[1 + x_H(\alpha_{Na}^H - 1)\right]^2} \qquad (3\text{-}15)$$

$$\Rightarrow \frac{dy}{dx} = \frac{\alpha C_{tot}^2}{\left[C_{tot} + c(\alpha - 1)\right]^2} \qquad (3\text{-}16)$$

Equations (3-3), (3-5), (3-6), and (3-16) constitute a set that can be solved numerically provided the α value is known.

Anionic Regeneration:

The equilibrium isotherm (Figure III-4) for Cl^-/OH^- exchange (on Duolite A 102 D) had been fitted by Rodrigues and Tondeur (1975) with the following fourth degree polynomial:

$$y_{Cl} = -2.5x_{Cl}^4 + 7.5x_{Cl}^3 - 7.5x_{Cl}^2 + 3.5x_{Cl} \qquad (3\text{-}17)$$

Simplifying and differentiating, we get the following in terms of OH:

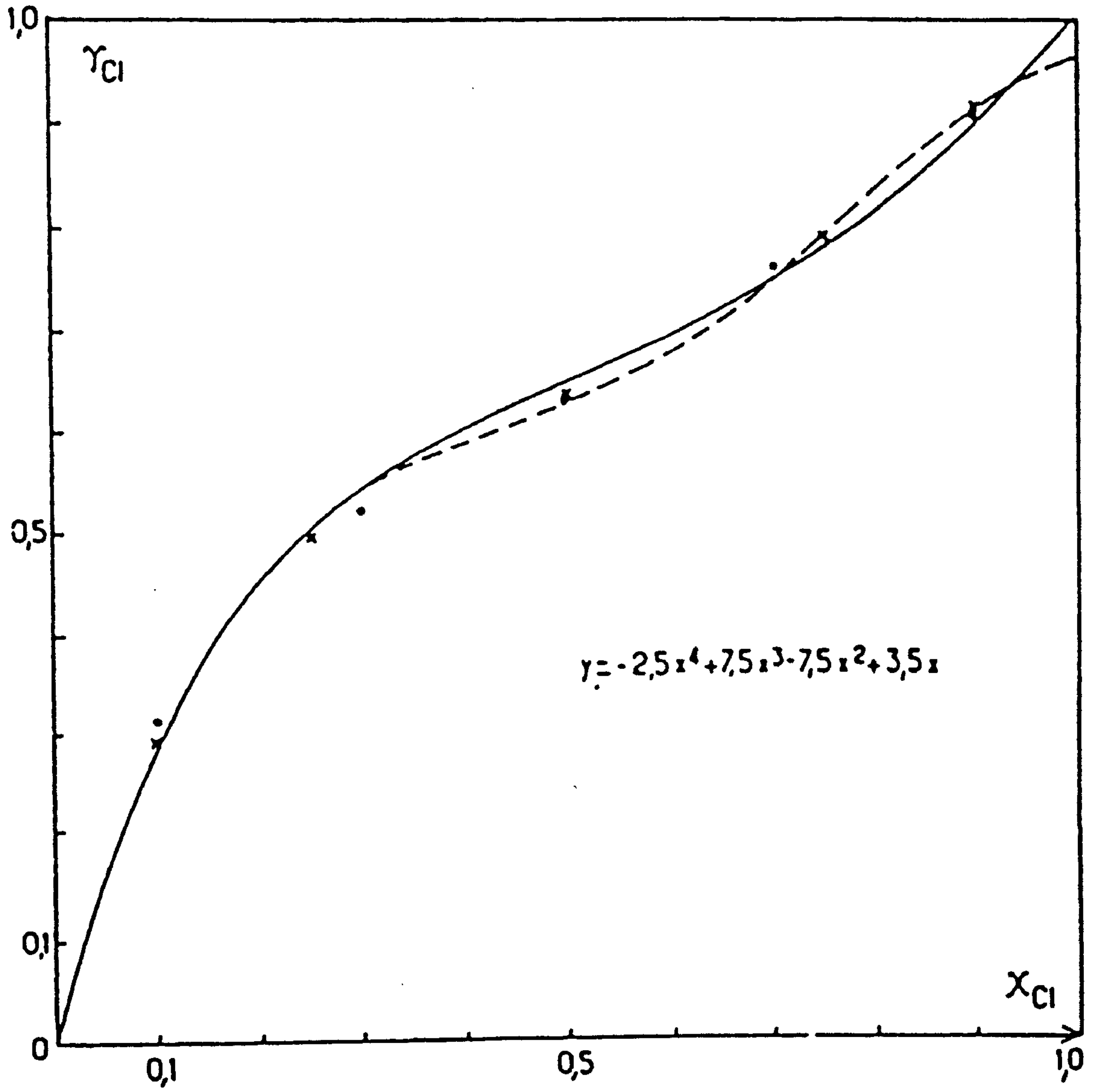


Figure III-4. Equilibrium isotherm for Cl^-/OH^- exchange on Duolite A 102 D.
x : Concentration 0.01N.
• : Concentration 1N.
[Rodrigues and Tondeur, 1975] [with permission]

$$\frac{dy}{dx} = \frac{10c^3 - 7.5c^2 C_{tot} + C_{tot}^3}{C_{tot}^3} \tag{3-18}$$

Equations (3-3), (3-5), (3-6), and (3-17) are numerically solved to obtain the breakthrough for anionic regeneration.

Results

The equilibrium model proposed above has been tested with the following data (Table III-1):

Table III-1.

OPERATING CONDITIONS: CATIONIC REGENERATION (R-Na + HCl)

$$\alpha_{Na}^{H} = \frac{1}{\alpha_{H}^{Na}} = 0.5$$

$$c_0 = 0.0001 \text{ eq} / l$$

$$c_f = 1.5 \text{ eq} / l$$

$$C_{tot} = 1.5 \text{ eq} / l$$

$$\overline{C_{tot}} = 1.3 \text{ eq} / l$$

$$F = 200 \text{ gpm}$$

$$\text{Column diameter} = 2.5 \text{ m}$$

$$\varepsilon = 0.35$$

CATIONIC REGENERATION (R-Na + H_2SO_4):

$c_f = 1.0$ eq / l

$C_{tot} = 1.0$ eq / l

Everything else remains the same as Table III-1.

ANIONIC REGENERATION (R-Cl + NaOH):

$F \approx 127$ gpm

Everything else is the same as in Table III-1.

All the flowrates and feed concentrations are chosen according to the suggestions offered in Davies (1993). Figures III-5, III-6,and III-7 represent the above three cases respectively. They show the times required to attain 99.98% regeneration.

Figure III-5 depicts the results for Table III-1. It shows how the residual loading of the bed changes as regeneration progresses. The time taken by the hydrogen ion to reach 99.98% of the cation resin capacity of the bed is more than 17 minutes. The nature of the curves satisfies the expectation as the spreading nature is observed.

Figure III-6 shows the concentration of ions in the same bed (but for different flow rate and influent concentration) during cationic regeneration with sulfuric acid. Here, the time required to acquire 99.98% regeneration is almost 24 minutes. The spreading nature is again observed as in Figure III-5.

Figure III-7 is for the case of anionic regeneration. The nature of the curves tally with that expected from the equilibrium isotherm equation. The time taken

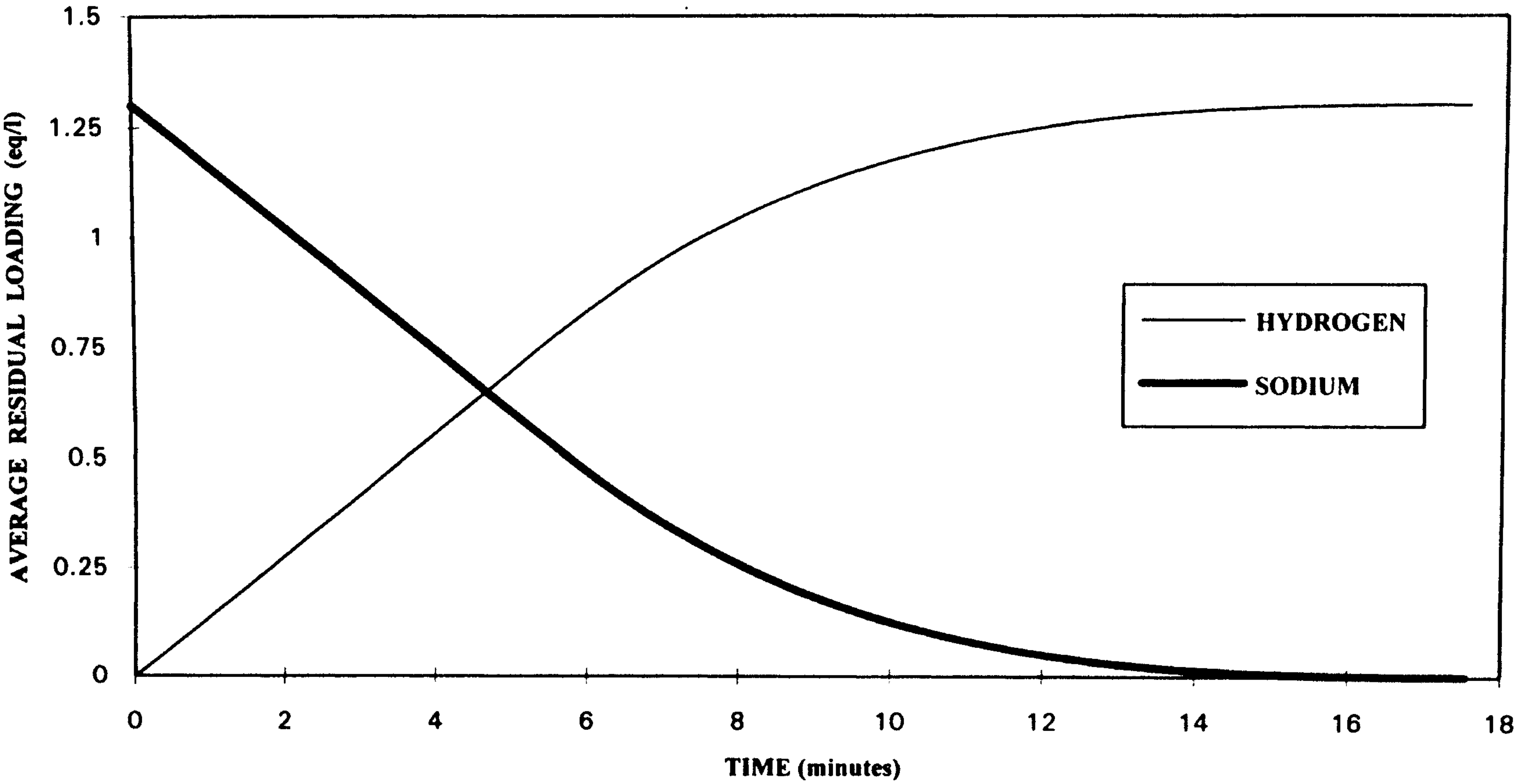


Figure III-5. Cationic regeneration (R-Na + HCl), by ordinary equilibrium theory.

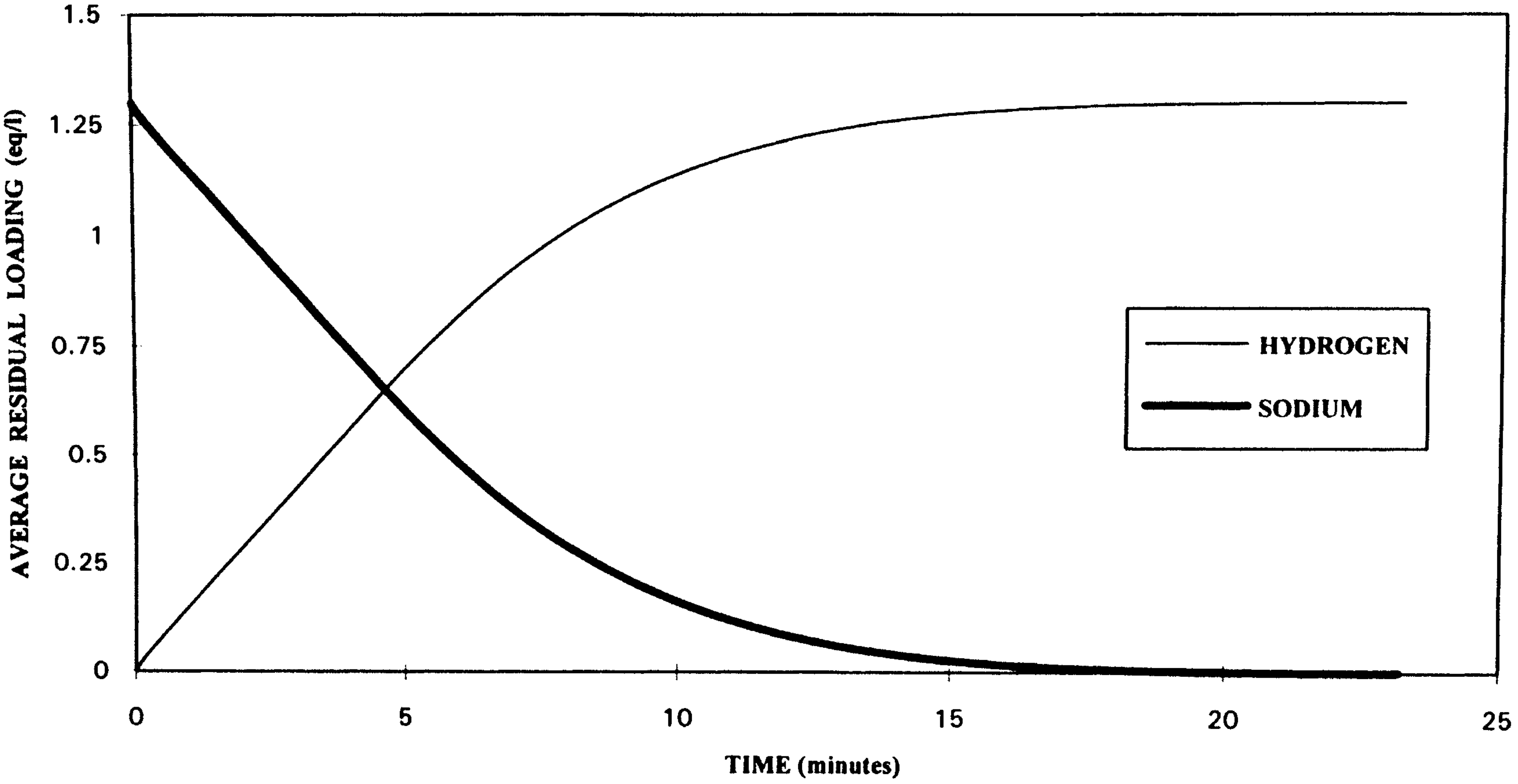


Figure III-6. Cationic regeneration (R-Na + H_2SO_4), by ordinary equilibrium theory.

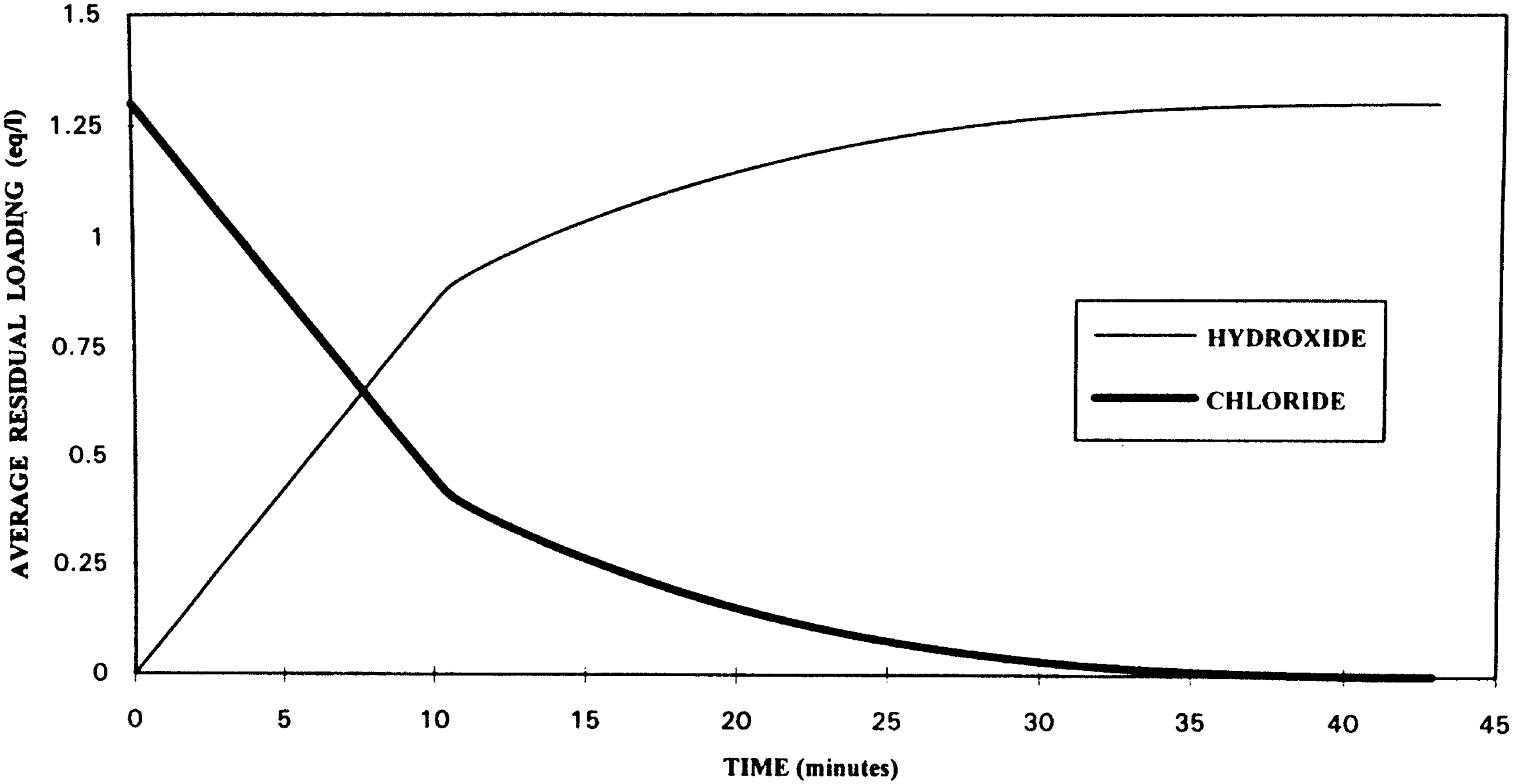


Figure III-7. Anionic regeneration (R-Cl + NaOH), by ordinary equilibrium theory.

by the bed to adsorb hydroxyl ion upto 99.98% of its total capacity is almost 43 minutes.

Discussion

An explicit, upstream method is used to numerically integrate the nonlinear PDE (3-3), with its I.C. (3-5), B.C. (3-6), and algebraic (equilibrium) relation {(3-16) or (3-17)}. This method is used with a small timestep to follow closely the moving concentration profile. The small timestep also helps in effectively accounting for the nonlinearity. Implicit methods, while allowing for larger timestep, may "jump over" the phenomenon of interest. Implicit schemes also involve solving a nonlinear algebraic equation at the end of each timestep and thus may be susceptible to associated problems as the latter method is very sensitive to initial guess(es). For a detailed derivation of the numerical algorithm and a listing of the codes see Chapter V and Appendix B, respectively.

The times predicted by the codes appear somewhat less than that expected during actual plant performances under similar conditions. The trends of the breakthrough curves are similar to what we expected from the equilibrium isotherms (especially for Cl^-/OH^- exchange where the equilibrium isotherm displayed inflection points). [When applied to the case shown in Figure III-1(a), the equilibrium theory predictions reasonably tallied with the experimental data.]

Conclusions

The ordinary equilibrium theory, when applied to regeneration, predicted the column behavior satisfactorily for cationic regeneration in lab scale operating conditions (e.g. Figure III-1(a)), but falls short of expectations in the case of real-life situations for both cationic and anionic regeneration (see Chapter IV). So, equilibrium curvature does not singularly seem to govern the ion exchange at large scale, actual plant performances.

This equilibrium model should be modified by incorporating axial dispersion to obtain better predictions for ion exchange regeneration used for water purification. This will be demonstrated in Chapter IV. The ideal limiting behavior for regeneration by equilibrium theory described in this chapter, does not appear promising for predictive process calculations.

Chapter IV

SIMULATION OF REGENERATION PROCESSES WITH MODIFIED EQUILIBRIUM THEORY

Abstract

Regeneration of ion exchange resins used in water purification has been simulated by a modified version of the existing equilibrium theory discussed in detail in Chapter III. The contribution of axial dispersion to mass transfer in ion exchange processes has been taken into account and the consequent improvement in the predictions of the plant performance has been demonstrated. The axial dispersion coefficient is assumed to be independent of time and distance along the bed (due to the unavailability of relevant data and information in the literature). This modified equilibrium theory has predicted the actual plant performance reasonably well when tested with some real-life operating parameters.

Introduction

In Chapter III, while simulating the process of regeneration by the existing "equilibrium theory" proposed by Tondeur and Bailly (1986), the effect of axial dispersion was neglected. The elution of the last traces of the ion previously saturating the bed is very sensitive to both axial dispersion and the local value of the constant relative sorptivity. The latter is specific to the type of resin used to obtain the equilibrium isotherm for Na^+ / H^+ or Cl^- / OH^- exchange at room temperature. Here, I will again use the fourth order polynomial of Chapter III as the best-fit of the isotherm for simple anionic regeneration. In the modified theory, I will consider the effect of axial dispersion and demonstrate its significance in predicting plant performance.

Assumptions

This modified equilibrium theory for regeneration is based on the following assumptions:

- Local equilibrium exists between the solid phase concentration, $\bar{c}$, and liquid phase concentration, c, governed by some identified algebraic relation, at any time and at all points of the exchanger.
- The bed is homogeneous.
- The bed is uniformly presaturated and receives a feed of constant composition.
- The axial dispersion coefficient, D_a, remains fairly constant with respect to both time and distance along the bed.
- Neutralization, precipitation, complex formation, weak acid and weak base formation in the liquid phase, and other secondary processes are absent.

Model Development

As in Chapter III, the material balance on a differential slice of the regeneration column gives (Tondeur, 1986):

$$\varepsilon\frac{\partial c}{\partial t}+(1-\varepsilon)\frac{\partial \bar{c}}{\partial t}+u\frac{\partial c}{\partial z}=\frac{\partial}{\partial z}[D_a\frac{\partial c}{\partial z}] \qquad (4\text{-}1)$$

It will be shown how the incorporation of the axial diffusion term on the right side of (4-1) improves the predictions of actual plant performance.

For the binary case, $\bar{c}$ is eliminated from (4-1) through equilibrium:

$$\frac{\partial \bar{c}}{\partial t} = \frac{d\bar{c}}{dc}\frac{\partial c}{\partial t} \tag{4-2}$$

After a series of algebraic manipulations (please refer to Appendix A for details), (4-1) reduces to

$$\frac{\partial c}{\partial t} + a u_c^{'} \frac{\partial c}{\partial z} = b u_c^{'} \frac{\partial^2 c}{\partial z^2} \tag{4-3}$$

where

$a = u_i = \dfrac{F}{\Omega \varepsilon} = \dfrac{u}{\varepsilon}$,

$b = \dfrac{D_a}{\varepsilon}$,

$u_c^{'} = (1 + \lambda \dfrac{dy}{dx})^{-1}$, and

$\lambda = \dfrac{1-\varepsilon}{\varepsilon} \dfrac{\overline{C_{tot}}}{C_{tot}} =$ capacity ratio.

The next step is to numerically integrate this second order, nonlinear PDE with the following initial and boundary conditions:

I.C.:

$$t = 0,\ z > 0 \qquad c = c_0 = \text{ constant throughout the column} \tag{4-4}$$

B.C. # 1:

$$t > 0,\ z = 0 \qquad c = c_f \tag{4-5}$$

B.C.# 2:

$$t > 0,\ z = L \qquad \frac{\partial c}{\partial z} = 0 \tag{4-6}$$

(at z = L, concentration varies only with time)

Equilibrium relations:

Cationic Regeneration (Tondeur, 1986): (Resin Duolite C 20-G, $C_{tot} = 1.5N$)

$$y = \frac{\alpha x}{\alpha x + 1 - x} \tag{4-7}$$

$$\therefore \frac{dy}{dx} = \frac{\alpha C_{tot}^2}{[C_{tot} + c(\alpha - 1)]} \qquad (4\text{-}8)$$

Anionic Regeneration (Rodrigues, 1975): (Resin: Duolite A 102 D, $C_{tot} = 1N$)

$$y_{Cl} = -2.5x_{Cl}^4 + 7.5x_{Cl}^3 - 7.5x_{Cl}^2 + 3.5x_{Cl} \qquad (4\text{-}9)$$

$$\therefore \frac{dy}{dx} = \frac{10c^3 - 7.5c^2 C_{tot} + C_{tot}^3}{C_{tot}^3} \qquad (4\text{-}10)$$

(4-3), (4-4), (4-5), (4-6), (4-8) and (4-3), (4-4), (4-5), (4-6), (4-10) form two sets of equations that can be solved to obtain the breakthrough curves for cationic and anionic regeneration, respectively.

Results

The modified equilibrium model is tested with the following data:

Cationic Regeneration (R-Na + HCl):

$D_a = 0.7712 \text{ X } 10^{-4} \text{ m}^2/\text{s}$

Everything else is the same as in Table III-1.

Cationic Regeneration (R-Na + H_2SO_4):

$D_a = 0.7712 \text{ X } 10^{-4} \text{ m}^2 / \text{s}$

Now, see Table III-2.

Anionic Regeneration (R-Cl + NaOH):

$D_a = 0.7712 \text{ X } 10^{-4} \text{ m}^2 / \text{s}$

The other conditions are as in Table III-3.

The flowrates and feed concentrations have been selected according to Davies (1994). Figures IV-1, IV-2, and IV-3 represent the above three cases, respectively.

Figure IV-1 is for cationic regeneration with HCl. It shows that the time required by the bed to attain 99.98% regeneration is about 23 minutes. This is considerably larger than 17 minutes which is observed by the ordinary equilibrium model. This is also much closer to what is expected during actual plant operations under similar conditions.

Figure IV-2 shows the case of cationic regeneration with sulfuric acid with slightly different operating conditions. The time required by the hydrogen concentration to reach 99.98% of its capacity in the resin is about 32 minutes, compared to 24 minutes predicted by the ordinary equilibrium theory under similar circumstances. Again, the modified theory prediction is closer to real-life expectation with the same operating conditions.

Anionic regeneration with NaOH is shown in Figure IV-3, which predicts about 64 minutes to achieve 99.98% of the actual resin capacity. It should be

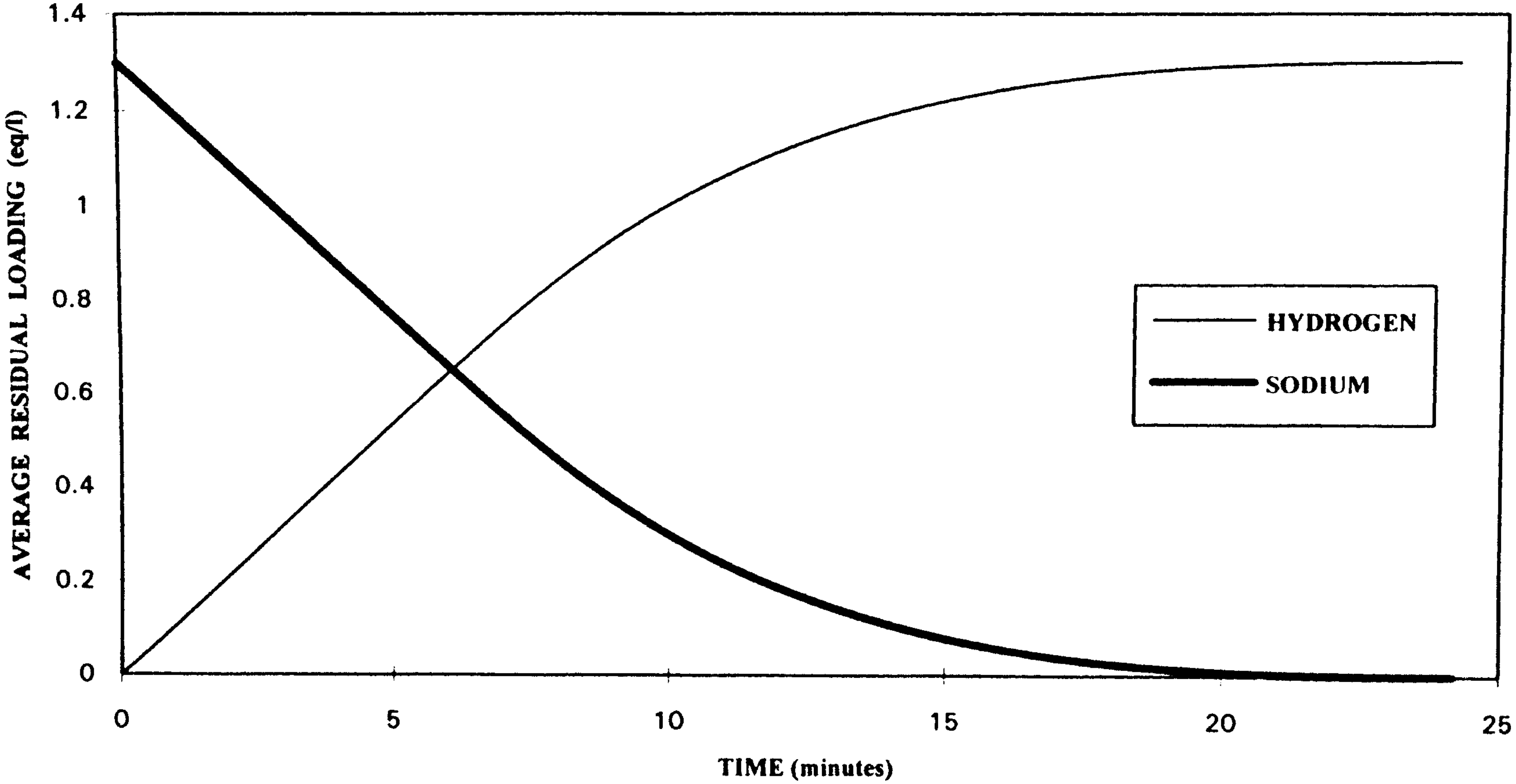


Figure IV-1. Cationic regeneration (R-Na + HCl), by modified equilibrium theory.

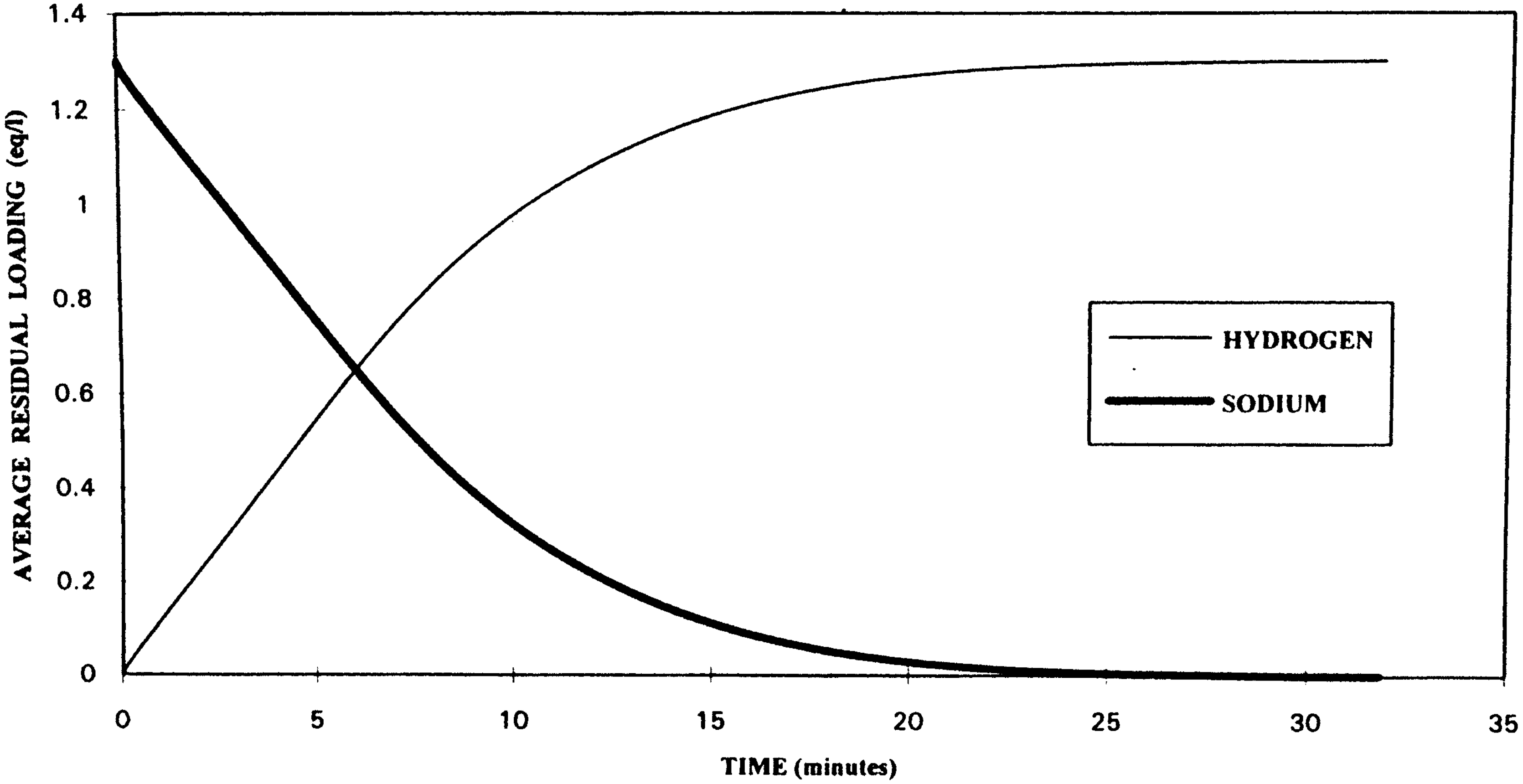


Figure IV-2. Cationic regeneration (R-Na + H_2SO_4), by modified equilibrium theory.

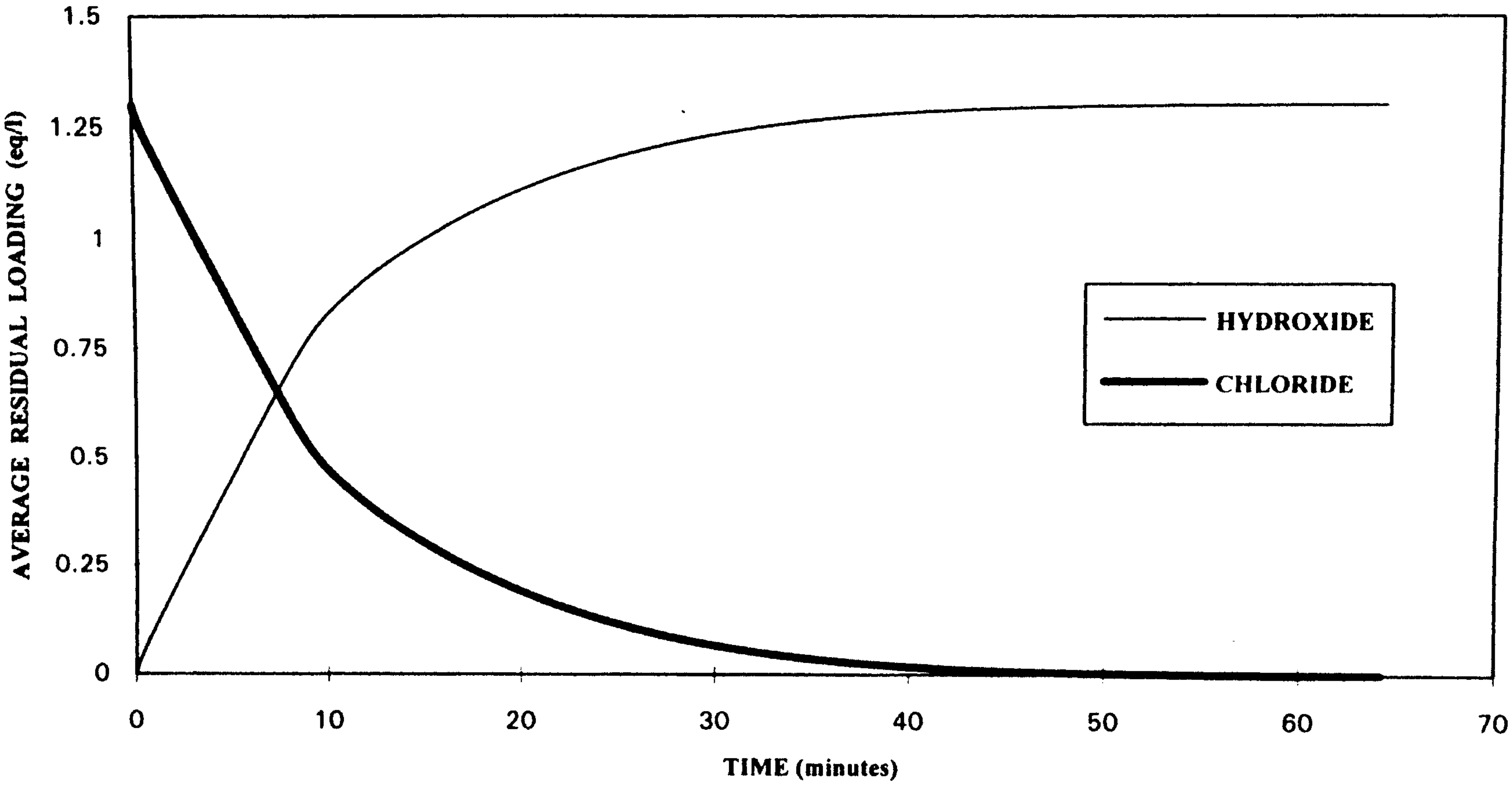


Figure IV-3. Anionic regeneration (R-Cl + NaOH), by modified equilibrium theory.

noted that this is much larger and more practical than the prediction by ordinary equilibrium theory (43 minutes). Like in Figure IV-1 and IV-2, the curves in this figure also correspond to the nature of the respective equilibrium isotherm.

Discussion

An explicit finite difference scheme has been devised for solving the complex, second order, nonlinear material balance PDE with its initial condition, boundary conditions and corresponding equilibrium relation. I chose an explicit method in preference to an implicit method for the same reasons as discussed in Chapter III. For a detailed description of the numerical method, refer to Chapter V. The times predicted by modified equilibrium theory are reasonable and seem to agree with those observed during real-life plant operations.

A parametric analysis has also been performed to observe the effect of the numerical value of D_a on the breakthrough curves for cationic regeneration (R-Na + HCl, Figure IV-4) and anionic regeneration (R-Cl + NaOH, Figure IV-5). It is found that the time required to achieve 99.98% regeneration increases with the increase of the numerical value for D_a. Also, the higher the value of D_a, the more the spreading of the breakthrough curve. These two phenomena are observed for both cationic and anionic regeneration.

In Figure IV-4, it is observed that when the magnitude of the axial dispersion is increased to 1.2 cm^2 / s, the time taken is about 27 minutes for the same operating conditions as in Figure IV-1. When the same is done for the operating conditions of Figure IV-3, the time required for 99.98% regeneration increases significantly to almost 76 minutes. So, the increase in the numerical

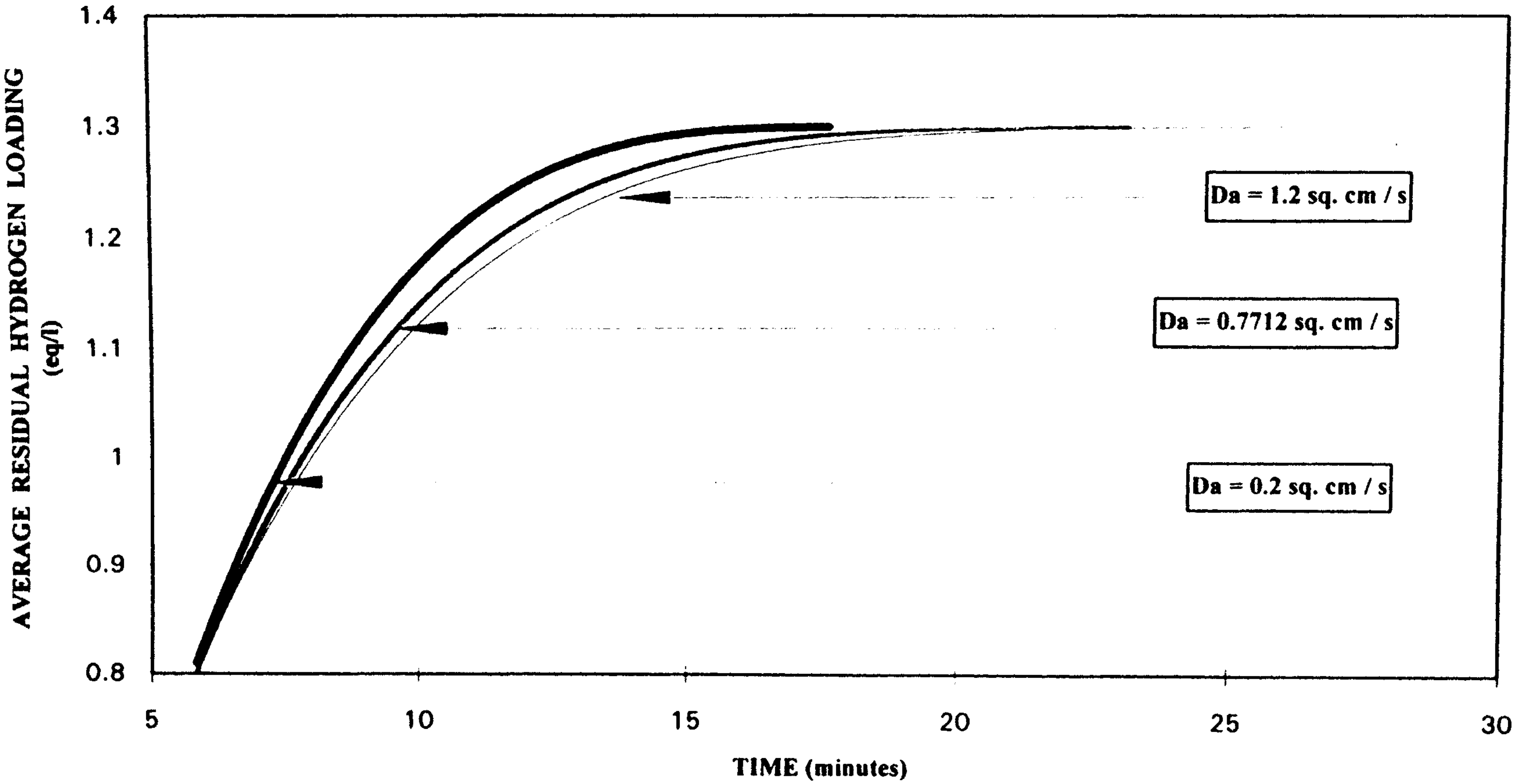


Figure IV-4. Effect of the numerical value of axial dispersion coefficient on cationic regeneration (R-Na + HCl).

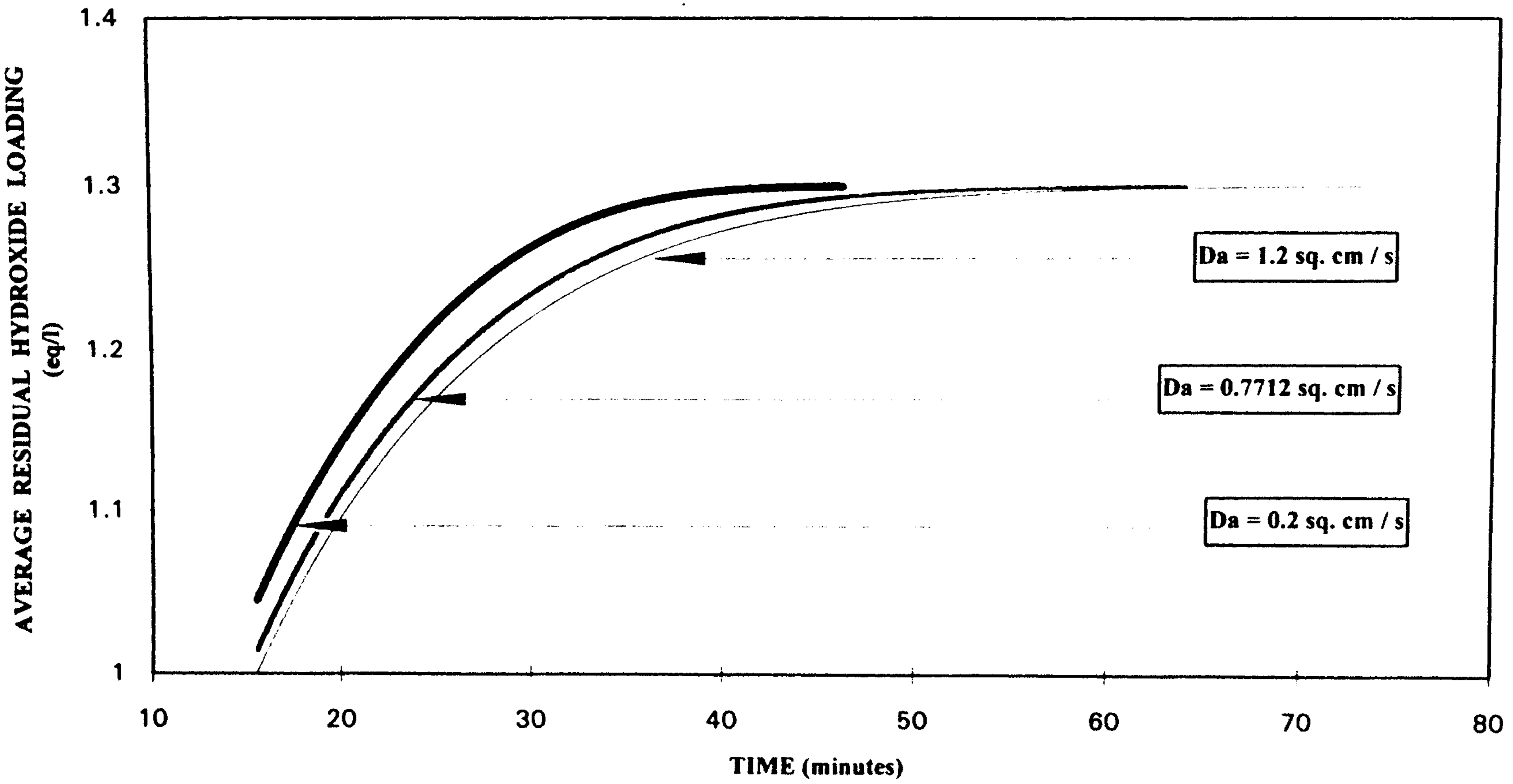


Figure IV-5. Effect of the numerical value of axial dispersion coefficient on anionic regeneration (R-Cl + NaOH).

value of the axial dispersion coefficient is found to increase the regeneration time and vice versa.

Figure IV-6 and IV-7 show the effect of regenerant concentration on regeneration. As expected, in both cases, the regeneration time increased with the decrease of concentration and vice versa. The effect of regenerant flow rate on regeneration has been documented in Figure IV-8 and IV-9 for cationic and anionic regeneration, respectively. The increase of flow rate is found to decrease the regeneration time and vice versa. This also is in accordance with what is expected in both cases. Thus the process of regeneration is sensitive to regenerant concentration and flow rate and these should be carefully monitored as a change in one or both can affect the regeneration characteristics significantly.

Conclusions and Recommendations

For better model predictions, one should run the model with more specific phase equilibrium data and axial dispersion coefficients. I think, the best way to obtain them is through experiments with the particular column on which the model is to be applied. Thermodynamic databases might also provide a short cut for obtaining equilibrium data for a particular combination of ions. It will be even better if the variation of D_a with time and/or distance can be incorporated into the model. D_a has been calculated from a Peclet Number ($= \frac{uL}{D_a}$) of 50, which is considered reasonable for ion exchange operations. The length of the regeneration column has been taken as L for this model. In fact, it is more accurately the actual ion exchange zone length; so the D_a value used in the model may be a little high. I

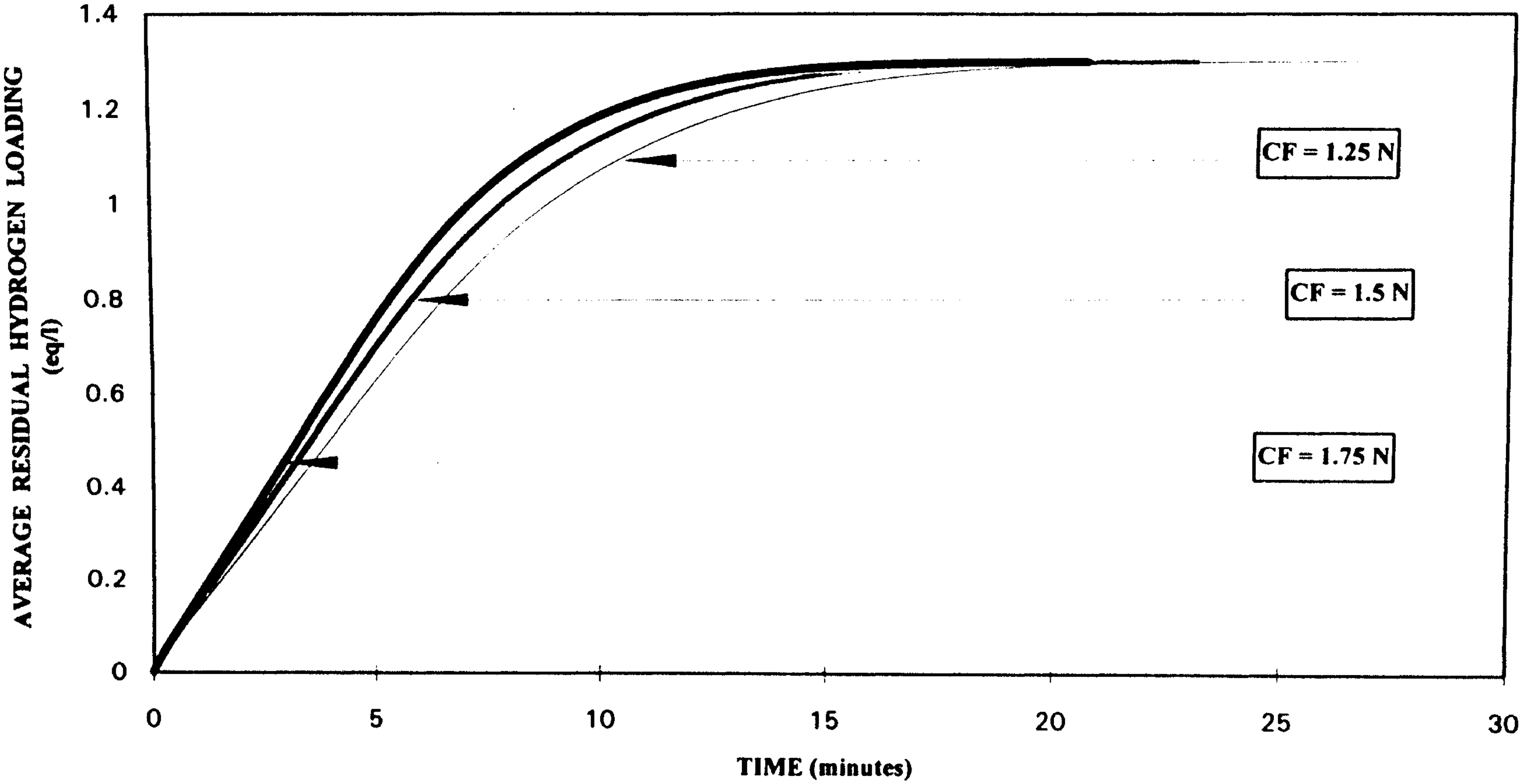


Figure IV-6. Effect of regenerant concentration on cationic regeneration (R-Na + HCl).

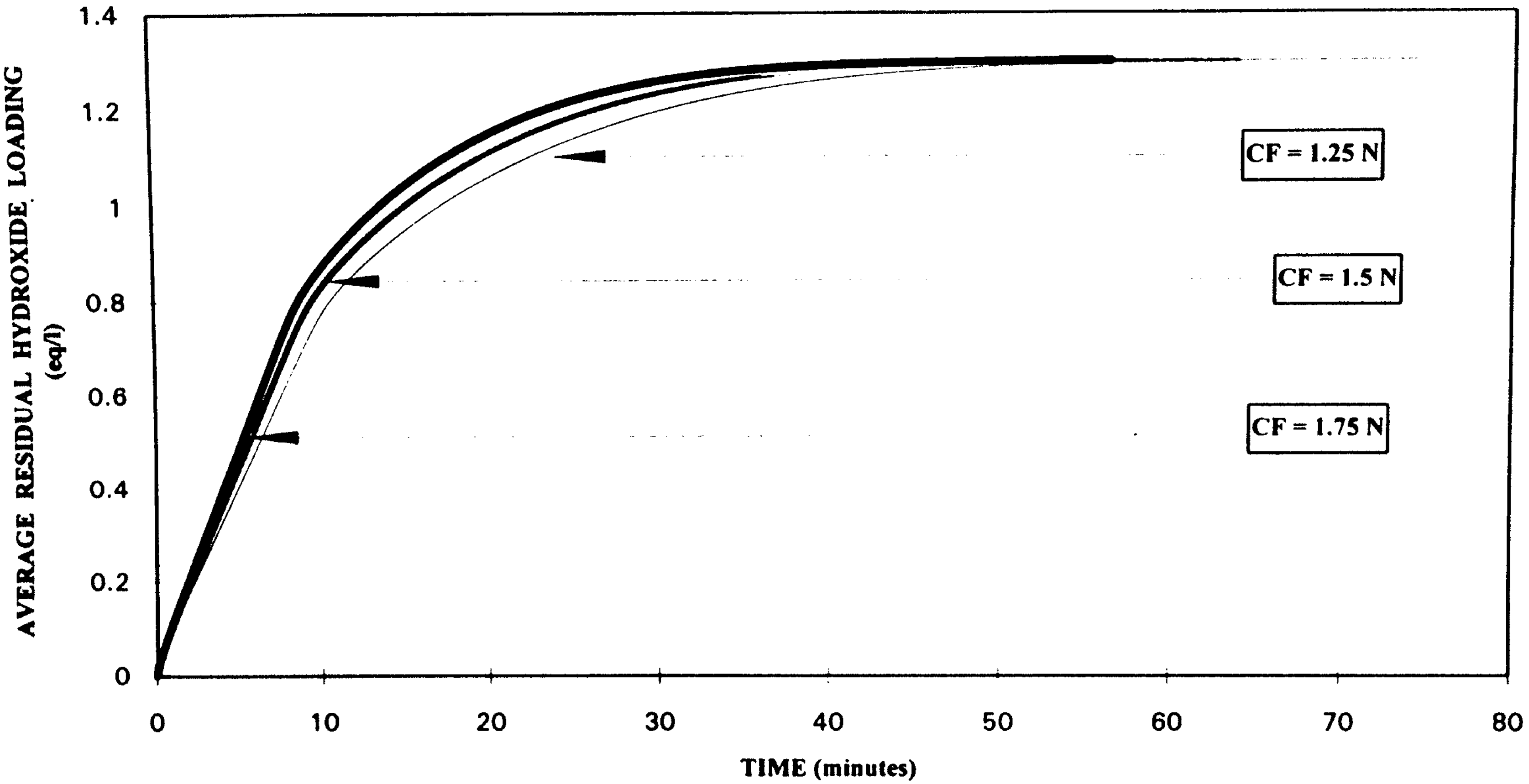


Figure IV-7. Effect of regenerant concentration on anionic regeneration (R-Cl + NaOH).

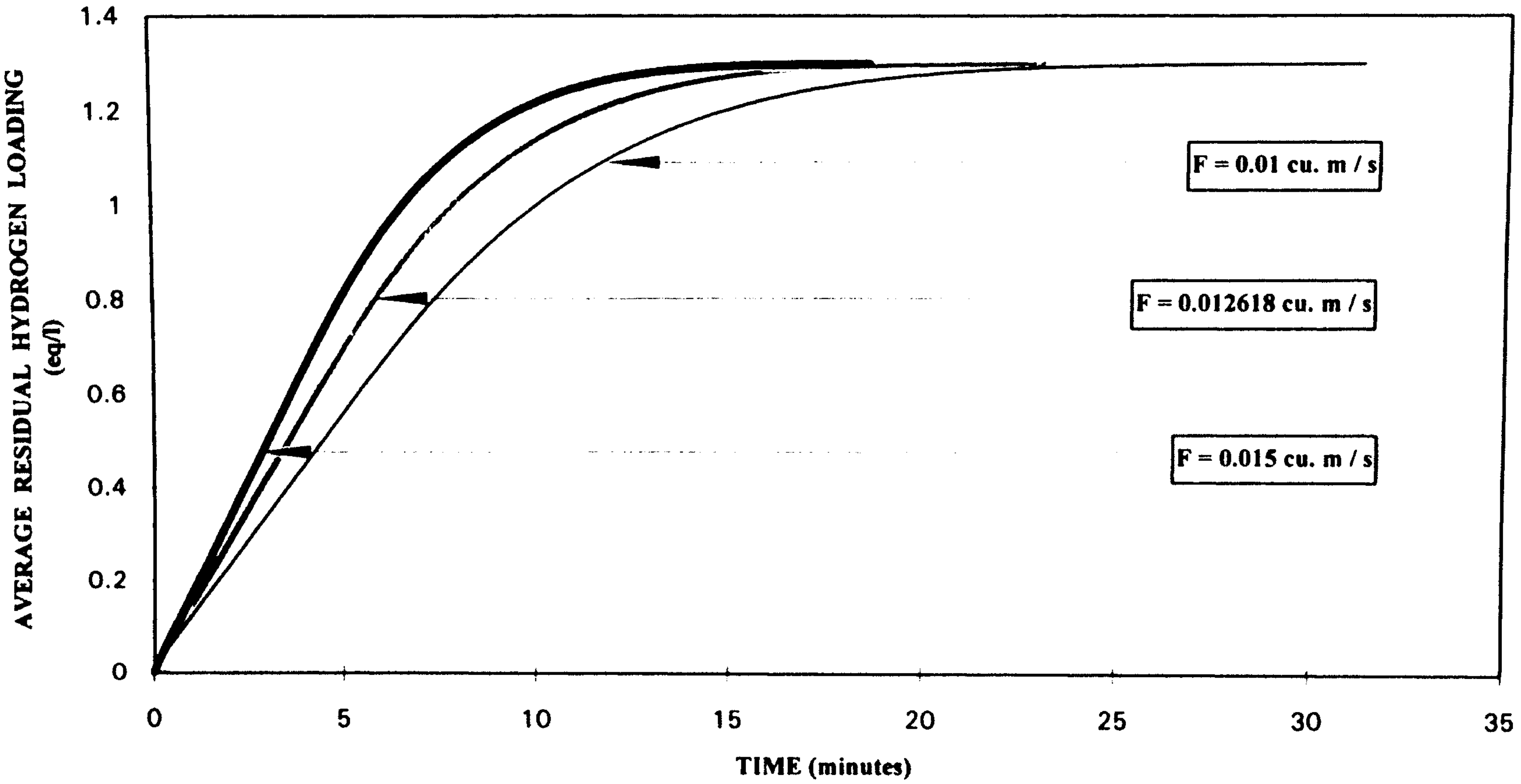


Figure IV-8. Effect of regenerant flow rate on cationic regeneration (R-Na + HCl).

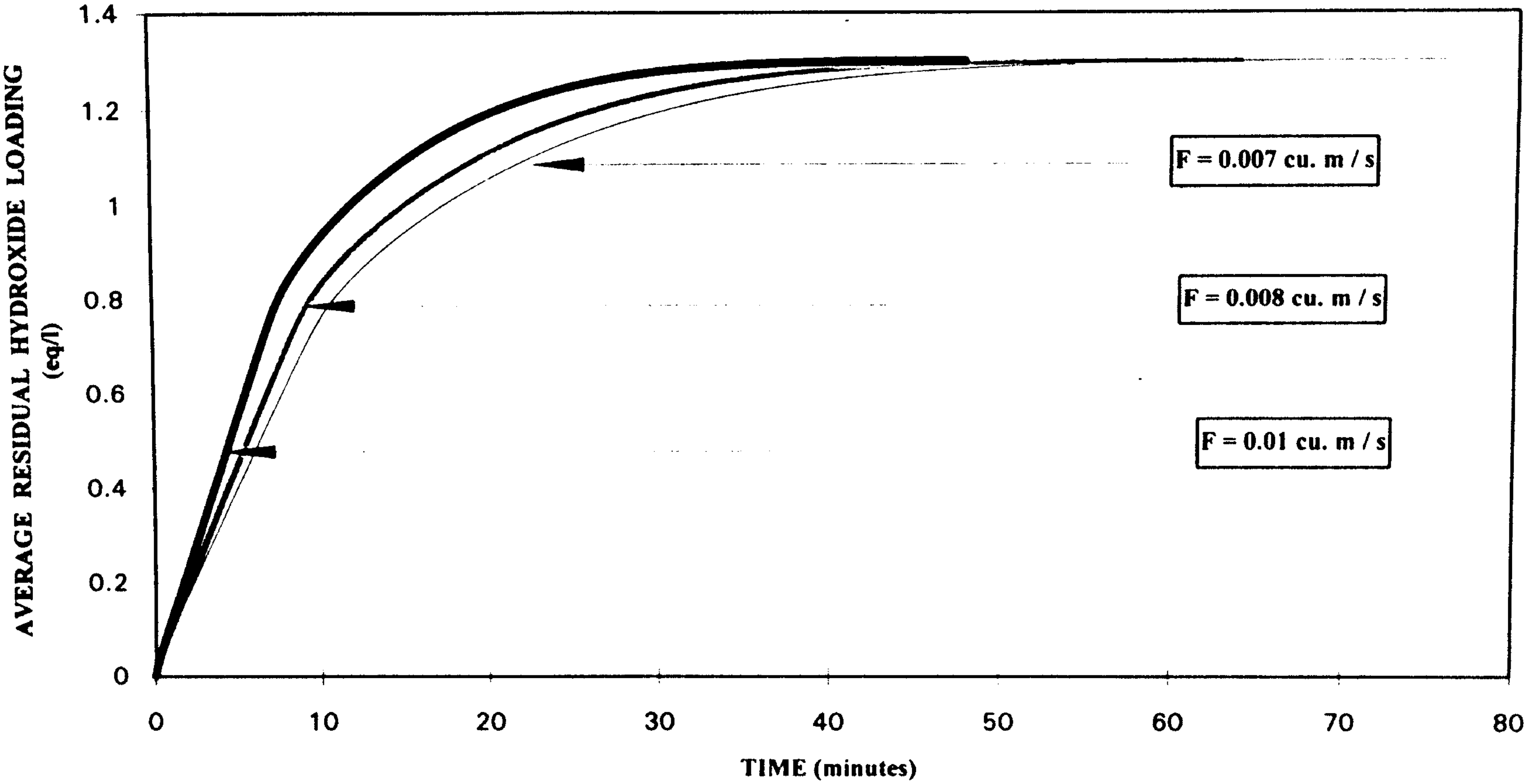


Figure IV-9. Effect of regenerant flow rate on anionic regeneration (R-Cl + NaOH).

believe that the local value of the slope of the equilibrium isotherm (near the origin) also plays an important role during the important last stages of the regeneration process. It is very difficult to get dependable data (or any data at all) about these local effects. The inclusion of the effect of the local slope will also enhance the accuracy of the prediction. It is pertinent to mention at this point that the best fitting curves used here did not fit the data precisely at the last stages of regeneration (near the origin of the equilibrium isotherm). One should also make sure that the following factors are accounted for before probing into any discrepancies in the model predictions:

- higher regeneration flow rate
- higher regenerant concentration
- higher sodium leakage
- hardness leakage
- calcium sulfate precipitation
- excessive pressure drop
- presence of different kinds of fouling (organic, iron, oil, mud, algae/bacteria, silica, barium sulfate).

Refer to Chapter II for a brief discussion on the above problems and to Davies (1994) for effective ways to circumvent them.

Chapter V

NUMERICAL ALGORITHMS

Introduction

The material balance equation along with its initial and boundary conditions, and equilibrium relation(s) have been formulated in Chapter III and IV for equilibrium theory and a modified equilibrium theory, respectively. Now, suitable numerical schemes are needed to obtain the breakthrough profiles for regeneration (for obvious reasons of enormous complexity and impracticability, analytical solutions are not considered). Finite difference methods are chosen in preference to finite element methods in order to simplify the procedure. Among the two broad categories of methods (explicit and implicit) available for the numerical solution of partial differential equations, I chose the explicit method for the reasons described in the following sections.

Numerical Scheme for Equilibrium Theory

The set to be solved here is as follows:

$$\frac{\partial c}{\partial t} + u_c \frac{\partial c}{\partial z} = 0 \tag{5-1}$$

with

$$u_c = \frac{u_i}{1+\lambda\frac{dy}{dx}} = ag(c), \text{ and}$$

$$a = u_i = \frac{F}{\Omega\varepsilon} = \text{ constant}$$

Note that u_c is a function of c alone.

I.C.:

$$t = 0,\ z > 0$$
$$c = c_0 = \text{ constant throughout the column} \quad (5\text{-}2)$$

B.C.:

$$t > 0,\ z = 0$$
$$c = c_f \quad (5\text{-}3)$$

(5-1) is a nonlinear equation as u_c is a function of the dependent variable c. Moreover, it can be looked upon as a "wave equation" describing the propagation of any given value of c. Since a moving concentration profile is involved, it is necessary to closely monitor its movement by using a small enough timestep. For small timesteps like this, explicit algorithms are faster and more stable than implicit ones for the same timestep. Implicit methods, while allowing for larger timestep, may "jump over" the phenomenon of actual interest. Another factor that contributed in favor of using the explicit, upstream method is its effective handling of nonlinearity due to the small size of the timestep involved. So, the error incurred through approximating the nonlinear term by its value at the previous timestep is very small. Implicit methods ask for solving a nonlinear algebraic equation at the end of each timestep and thus are susceptible to associated problems as the process of solving of nonlinear equation (or equations) is very sensitive to the initial guess(es) supplied. Once faced with unfavorable initial guess(es), the entire scheme stands the chance of being thrown off wildly or entering an infinite, futile, to and fro oscillation loop. The explicit method also saves on the number of arithmetic operations involved and hence computer time, for the same timestep.

While writing a finite difference scheme for (5-1), I used a forward difference approximation of error order $O(\Delta t)$ for $\frac{\partial c}{\partial t}$ and a backward difference approximation of error order $O(\Delta z)$ for $\frac{\partial c}{\partial z}$. As mentioned earlier, the nonlinear term (u_c) has been approximated by its value from the previous timestep.

$$\frac{c_i^{n+1} - c_i^n}{\Delta t} = -ag(c_i^n)\{\frac{c_i^n - c_{i-1}^n}{\Delta z}\} \tag{5-4}$$

$$\Rightarrow c_i^{n+1} = c_i^n - a(\frac{\Delta t}{\Delta z})g(c_i^n)(c_i^n - c_{i-1}^n) \tag{5-5}$$

The above methodology has been coded (Appendix B) with the incorporation of the suitable equilibrium relationship to obtain the breakthrough curves as predicted by ordinary equilibrium theory.

Numerical Scheme for Modified Equilibrium Theory

The set that is to be integrated here is:

$$\frac{\partial c}{\partial t} + au_c^{'}\frac{\partial c}{\partial z} = bu_c^{'}\frac{\partial^2 c}{\partial z^2} \tag{5-6}$$

with
$$a = u_i = \text{ constant,}$$
$$b = \frac{D_a}{\varepsilon} = \text{ constant, and}$$
$$u_c^{'} = (1+\lambda\frac{dy}{dx})^{-1} = g(c)$$

(5-2) and (5-3) also hold in this case as I.C. and B.C.#1, respectively.

B.C.#2:

$$t > 0,\ z = L$$
$$\frac{\partial c}{\partial z} = 0 \tag{5-7}$$

Again, an explicit, upstream method has been used with a small timestep to numerically integrate (5-6), a nonlinear, second order partial differential equation. Using forward difference of error order $O(\Delta t)$ for $\frac{\partial c}{\partial t}$, central difference of error order $O(\Delta z)^2$ for $\frac{\partial c}{\partial z}$, and central difference of error order $O(\Delta z)^2$ for $\frac{\partial^2 c}{\partial z^2}$, I obtained the following finite difference scheme for (5-6):

$$\frac{c_i^{n+1} - c_i^n}{\Delta t} = -ag(c_i^n)\{\frac{c_{i+1}^n - c_{i-1}^n}{2(\Delta z)}\} + bg(c_i^n)\{\frac{c_{i+1}^n - 2c_i^n + c_{i-1}^n}{(\Delta z)^2}\} \tag{5-8}$$

$$\Rightarrow c_i^{n+1} = c_i^n - \frac{a\Delta t}{2(\Delta z)} g(c_i^n)\{c_{i+1}^n - c_{i-1}^n\} + \frac{b\Delta t}{(\Delta z)^2} g(c_i^n)\{c_{i+1}^n - 2c_i^n + c_{i-1}^n\} \tag{5-9}$$

Equation (5-7) gives $\left.\frac{\partial c}{\partial z}\right|_{\substack{z=L \\ (i=m+1,\ say)}} = 0$

So, at z = L, using backward difference of error order $O(\Delta z)^2$ for $\frac{\partial c}{\partial z}$, I got:

$$\frac{3c_{m+1}^{n+1} - 4c_m^{n+1} + c_{m-1}^{n+1}}{2(\Delta z)} = 0 \tag{5-10}$$

$$\Rightarrow c_{m+1}^{n+1} = \frac{4c_m^{n+1} - c_{m-1}^{n+1}}{3} \tag{5-11}$$

The computer code written from the above algorithm is presented in Appendix C, and it satisfactorily predicts the actual plant performance for regeneration of ion exchange resins.

Conclusions

In both of the above cases, proper caution should be exercised in the selection of timestep and spatial increment in order to insure stability of the explicit method used. The codes in Appendix B and C will offer experienced suggestions while execution, though no hard and fast rule apply. Without going into a detailed discussion of the stability characteristics, it can be roughly stated that the numerical value of the timestep should be less than the spatial increment. For involved discussions on different stability criteria, refer to Carnahan et al. (1969), and Smith (1978).

Chapter VI

CONCLUSIONS AND RECOMMENDATIONS

Equilibrium Theory

The results obtained by simulating regeneration of ion exchange resins by ordinary equilibrium theory lead to the following conclusions:

- Equilibrium theory reasonably holds for small columns with low flowrates (lab scale apparatus, Figure III-1: Tondeur, 1986).
- It can also be used to find the ideal limiting behavior (like minimum time expected for required regeneration) of real-life regeneration columns.
- It is not recommended when a closer prediction of the plant performance is desired as its estimates are always shown to be significantly less.
- Its predictions can be improved by supplying system specific equilibrium data and axial dispersion coefficients to the model. It would be even better if the nature of variation of D_a with distance and/or time can be incorporated into the model.

Modified Equilibrium Theory

The equilibrium theory has been modified by incorporating the effect of axial dispersion in the mass transfer during regeneration. The improvement obtained in the predictions is significant. The times predicted by the modified equilibrium model appear very reasonable for actual plant performances under similar operating conditions. The following can be stated about the modified equilibrium model:

- Its predictions are much more realistic for the real-life plant performances than those by the ordinary equilibrium model. This establishes the fact that axial dispersion plays an important role, especially during the sensitive, last stages of regenration when mass transfer is comparatively slow.
- It can be used to determine the process characteristics before carrying out the actual regeneration. So, it can also help in ascertaining technical viability and economic feasibility of the process.
- As in the ordinary equilibrium model, the predictions for any particular system can be improved by providing the model with specific equilibrium data and D_a. The incorporation of the variation of D_a with space and/or time in the model will improve its predictions even further.
- The inclusion of some empirical relation(s) to take care of the associated problems discussed in Chapter II might also favorably affect the predictions.

If very accurate quantitative fitting is sought, kinetic models having rate relationships may be the way to go. But, this does not seem to be the case during regeneration where the modified equilibrium theory is found to be reasonably satisfactory. The equilibrium models, though not suitable for high purity condensate polishing predictions, appear satisfactory for simulating regeneration processes involving high concentrations. This work leaves open the scope for researchers in ion exchange to improve upon the modified model for regeneration proposed here by incorporating changes (theoretical and empirical) that might seem necessary after running it for a large number of actual plant conditions.

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APPENDIX A

Derivation of the Reduced Material Balance for Equilibrium Theory

Material balance:

$$\varepsilon\frac{\partial c}{\partial t}+(1-\varepsilon)\frac{\partial \bar{c}}{\partial t}+u\frac{\partial c}{\partial z}=\frac{\partial}{\partial z}[D_a\frac{\partial c}{\partial z}] \tag{3-1}$$

Elimination of solid phase through equilibrium:

$$\frac{\partial \bar{c}}{\partial t}=\frac{d\bar{c}}{dc}\frac{\partial c}{\partial t} \tag{3-2}$$

The above material balance now becomes (neglecting axial dispersion term):

$$\frac{\partial c}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc}\frac{\partial c}{\partial t}+\frac{u}{\varepsilon}\frac{\partial c}{\partial z}=0 \tag{A-1}$$

$$\Rightarrow\frac{\partial c}{\partial t}(1+\frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc})+\frac{u}{\varepsilon}\frac{\partial c}{\partial z}=0 \tag{A-2}$$

$$\Rightarrow \frac{\partial c}{\partial t} + [\frac{u/_{\varepsilon}}{(1 + \frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc})}]\frac{\partial c}{\partial z} = 0 \qquad \text{(A-3)}$$

$$\Rightarrow \frac{\partial c}{\partial t} + u_c \frac{\partial c}{\partial z} = 0 \qquad \text{(3-3)}$$

Derivation of Reduced Material Balance for Modified Equilibrium Theory

(3-1) and (3-2) of above also hold here. Assuming D_a does not vary with distance (z), the material balance becomes

$$\frac{\partial c}{\partial t} + (\frac{1-\varepsilon}{\varepsilon})\frac{d\bar{c}}{dc}\frac{\partial c}{\partial t} + \frac{u}{\varepsilon}\frac{\partial c}{\partial z} = \frac{D_a}{\varepsilon}\frac{\partial^2 c}{\partial z^2} \qquad \text{(A-4)}$$

$$\Rightarrow (1 + \frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc})\frac{\partial c}{\partial t} + \frac{u}{\varepsilon}\frac{\partial c}{\partial z} = \frac{D_a}{\varepsilon}\frac{\partial^2 c}{\partial z^2} \qquad \text{(A-5)}$$

$$\Rightarrow \frac{\partial c}{\partial t} + u_c \frac{\partial c}{\partial z} = \frac{D_a}{\varepsilon}(1 + \frac{1-\varepsilon}{\varepsilon}\frac{d\bar{c}}{dc})^{-1}\frac{\partial^2 c}{\partial z^2} \qquad \text{(A-6)}$$

$$\Rightarrow \frac{\partial c}{\partial t} + u_c \frac{\partial c}{\partial z} = \frac{D_a}{\varepsilon}(1 + \lambda\frac{dy}{dx})^{-1}\frac{\partial^2 c}{\partial z^2} \qquad \text{(A-7)}$$

$$\Rightarrow \frac{\partial c}{\partial t} + a u_c^{'} \frac{\partial c}{\partial z} = b u_c^{'} \frac{\partial^2 c}{\partial z^2} \qquad \text{(4-3)}$$

Note: $u_c = \frac{u/\varepsilon}{1 + \frac{1-\varepsilon}{\varepsilon} \frac{d\bar{c}}{dc}} = \frac{u_i}{1 + \lambda \frac{dy}{dx}}$

Derivations of Equilibrium Relationships(Chapter III) and g(c) (Chapter V)

Equilibrium Relationships for Cationic Regeneration (R-Na + HCl, or R-Na + H_2SO_4):

$$y = \frac{\alpha x}{\alpha x + 1 - x} \tag{3-13}$$

$$\frac{dy}{dx} = \frac{\alpha}{[1 + x(\alpha - 1)]^2} \tag{3-14}$$

$$\Rightarrow \frac{dy}{dx} = \frac{\alpha}{[1 + \frac{c}{C_{tot}}(\alpha - 1)]^2} \tag{A-8}$$

$$\Rightarrow \frac{dy}{dx} = \frac{\alpha C_{tot}^2}{[C_{tot} + c(\alpha - 1)]^2} \tag{3-16}$$

Equilibrium Relationships for Anionic Regeneration (R-Cl + NaOH):

$$y_{Cl} = -2.5x_{Cl}^4 + 7.5x_{Cl}^3 - 7.5x_{Cl}^2 + 3.5x_{Cl} \tag{3-17}$$

$$\Rightarrow (1-y) = -2.5(1-x)^4 + 7.5(1-x)^3 - 7.5(1-x)^2 + 3.5(1-x) \qquad \text{(A-9)}$$

$$\Rightarrow \frac{dy}{dx} = -10(1-x)^3 + 22.5(1-x)^2 - 15(1-x) + 3.5 \qquad \text{(A-10)}$$

$$\Rightarrow \frac{dy}{dx} = 10x^3 - 7.5x^2 + 1 \qquad \text{(A-11)}$$

$$\Rightarrow \frac{dy}{dx} = \frac{10c^3 - 7.5c^2C_{tot} + C_{tot}^3}{C_{tot}^3} \qquad \text{(3-18)}$$

g(c) calculation for cationic regeneration:

$$u_c' = g(c) = (1 + \lambda \frac{dy}{dx})^{-1} \qquad \text{(A-12)}$$

$$\Rightarrow g(c) = (1 + \frac{1-\varepsilon}{\varepsilon} \frac{\alpha C_{tot}\overline{C_{tot}}}{[C_{tot} + c(\alpha-1)]^2})^{-1} \qquad \text{(A-13)}$$

$$\Rightarrow g(c) = \frac{\varepsilon[C_{tot} + c(\alpha-1)]^2}{\varepsilon[C_{tot} + c(\alpha-1)]^2 + (1-\varepsilon)\alpha C_{tot}\overline{C_{tot}}} \qquad \text{(A-14)}$$

$$\Rightarrow g(c) = \frac{1}{1 + (\frac{1-\varepsilon}{\varepsilon})\frac{\alpha C_{tot}\overline{C_{tot}}}{[C_{tot} + c(\alpha-1)]^2}} \qquad \text{(A-15)}$$

g(c) calculation for anionic regeneration:

(A-12) also holds here. When combined with (3-18) it gives

$$g(c) = [1 + \frac{1-\varepsilon}{\varepsilon} \frac{\overline{C_{tot}}}{C_{tot}} (\frac{10c^3 - 7.5c^2 C_{tot} + C_{tot}^3}{C_{tot}^3})] \qquad \text{(A-16)}$$

(A-16) and (A-15) are used in the FORTRAN codes of Appendix B and C.

APPENDIX B

CODES FOR EQUILIBRIUM THEORY

```
C
C
C      SIMULATION OF CATIONIC REGENERATION
C          (R-Na + HCl) BY EQUILIBRIUM THEORY.
C
C
      PROGRAM  EQBMCAT
      IMPLICIT REAL*8 ( A-H, O-Z )
      REAL*8  L
C
C   Definition of variables and constants:
C
C   C = ionic concentration of hydrogen in solution.
C   CBR = ionic concentration of hydrogen in solid.
C   CBRN = ionic concentration of sodium in solid.
C   C0 = ionic concentration of hydrogen throughout the column, initially.
C   CF = ionic concentration of hydrogen in the feed.
C   CTOT = total concentration in solution.
C   CBRTOT = total concentration in solid.
C   Z = length along column.
C   DZ = spatial increment.
C   T = time.
C   DT = time increment.
C   ALPHA = relative sorptivity of hydrogen with respect to sodium.
C   EPS = fractional volume of solution in bed.
C   F = solution flowrate.
C   OMEGA = column cross-sectional area.
C   NSP = number of spatial increments.
C   NTM = number of time increments.
C   LPR = print frequency.
C   L = column length.
C   P = intermediate storage array for C.
C   Y = dummy variable for C in the function statement.
C
C   Units:: Length in meter, Time in second, Concentration in eq/m3.
C
      REAL*8  C(0:500), P(0:500), CBR(0:500), CBRN(0:500)
      DATA ALPHA, C0, CF / 0.5D0, 0.0000001D0, 1.5D-03 /
      DATA CTOT, CBRTOT / 1.5D-03, 1.3D-03 /
      DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 0.012618D0, 0.35 /
      DATA PI / 3.1415927D0 /
```

```
C
C   Function definition.
C
    G(Y) = 1.0D0 / ( 1.0D0 + (1.0D0-EPS)*ALPHA*CTOT*CBRTOT/(EPS*
   *    (CTOT + Y*(ALPHA-1.0D0))**2) )
C
C   Set NTM to a very high value.
C
    NTM = 5000000
C
    WRITE(*,*) 'ENTER NSP, DT, LPR'
    READ(*,*)  NSP, DT, LPR
C
    OPEN ( UNIT = 6, FILE = 'CTEQRS', STATUS = 'UNKNOWN' )

    DZ = L/DBLE(NSP)
    OMEGA = PI*((DIA/2.0D0)**2)
    A = F/(OMEGA*EPS)
    CONST = A*(DT/DZ)
    T = 0.0D0
    DO 5 K = 0, NSP
    C(K) = C0
 5  CONTINUE
    WRITE(6,11)
 11 FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER CATIONIC
    *REGENERATION: R-Na + HCl.')
    WRITE(6,12)
 12 FORMAT(//,6X,'TIME (min)',8X,'HYDROGEN (eq/l)',9X,'SODIUM
    *(eq/l)',//)
    WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20 FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
    DO 25 I = 1, NTM/LPR
    DO 10 J = 1, LPR
C
    T = T + DT
    DO 30 KK = 0, NSP
    P(KK) = C(KK)
 30 CONTINUE
    C(0) = CF
    SUMCBR = 0.0D0
    DO 15 K = 1, NSP
```

```
     C(K) = P(K) - CONST*G(P(K))*(P(K) - P(K-1))
     CBR(K) = ( ALPHA*C(K)*CBRTOT ) / ( ALPHA*C(K) + CTOT - C(K) )
     CBRN(K) = CBRTOT - CBR(K)
     SUMCBR = SUMCBR + CBR(K)
15   CONTINUE
10   CONTINUE
     AVGCBR = SUMCBR/DBLE(NSP)
     AVGCBRN = CBRTOT - AVGCBR
C
C     Exit condition (99.98% regeneration).
C
     CHECK = 0.9998D0*CBRTOT
     IF (AVGCBR .GT. CHECK) GOTO 26
C
     WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRN*1.0D+03
25   CONTINUE
26   STOP
     END
```

```
C
C
C     SIMULATION OF CATIONIC REGENERATION
C        (R-Na + H2SO4) BY EQUILIBRIUM THEORY.
C
C
      PROGRAM  EQBMCTS
      IMPLICIT REAL*8 ( A-H, O-Z )
      REAL*8  L
C
C   Definition of variables and constants:
C
C   C = ionic concentration of hydrogen in solution.
C   CBR = ionic concentration of hydrogen in solid.
C   CBRN = ionic concentration of sodium in solid.
C   C0 = ionic concentration of hydrogen throughout the column, initially.
C   CF = ionic concentration of hydrogen in the feed.
C   CTOT = total concentration in solution.
C   CBRTOT = total concentration in solid.
C   Z = length along column.
C   DZ = spatial increment.
C   T = time.
C   DT = time increment.
C   ALPHA = relative sorptivity of hydrogen with respect to sodium.
C   EPS = fractional volume of solution in bed.
C   F = solution flowrate.
C   OMEGA = column cross-sectional area.
C   NSP = number of spatial increments.
C   NTM = number of time increments.
C   LPR = print frequency.
C   L = column length.
C   P = intermediate storage array for C.
C   Y = dummy variable for C in the function statement.
C
C   Units:: Length in meter, Time in second, Concentration in eq/m3.
C
      REAL*8  C(0:500), P(0:500), CBR(0:500), CBRN(0:500)
      DATA ALPHA, C0, CF / 0.5D0, 0.0000001D0, 1.0D-03 /
      DATA CTOT, CBRTOT / 1.0D-03, 1.3D-03 /
      DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 0.012618D0, 0.35 /
      DATA PI / 3.1415927D0 /
```

```
C
C   Function definition.
C
      G(Y) = 1.0D0 / ( 1.0D0 + (1.0D0-EPS)*ALPHA*CTOT*CBRTOT/(EPS*
     *    (CTOT + Y*(ALPHA-1.0D0))**2) )
C
C   Set NTM to a very high value.
C
      NTM = 5000000
C
      WRITE(*,*) 'ENTER NSP, DT, LPR'
      READ(*,*)  NSP, DT, LPR
C
      OPEN ( UNIT = 6, FILE = 'CTEQRS', STATUS = 'UNKNOWN' )

      DZ = L/DBLE(NSP)
      OMEGA = PI*((DIA/2.0D0)**2)
      A = F/(OMEGA*EPS)
      CONST = A*(DT/DZ)
      T = 0.0D0
      DO 5 K = 0, NSP
      C(K) = C0
 5    CONTINUE
      WRITE(6,11)
 11   FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER CATIONIC
     *REGENERATION: R-Na + H2SO4.')
      WRITE(6,12)
 12   FORMAT(//,6X,'TIME (min)',8X,'HYDROGEN (eq/l)',9X,'SODIUM
     *(eq/l)',//)
      WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20   FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
      DO 25 I = 1, NTM/LPR
      DO 10 J = 1, LPR
C
      T = T + DT
      DO 30 KK = 0, NSP
      P(KK) = C(KK)
 30   CONTINUE
      C(0) = CF
      SUMCBR = 0.0D0
      DO 15 K = 1, NSP
```

```
    C(K) = P(K) - CONST*G(P(K))*(P(K) - P(K-1))
    CBR(K) = ( ALPHA*C(K)*CBRTOT ) / ( ALPHA*C(K) + CTOT - C(K) )
    CBRN(K) = CBRTOT - CBR(K)
    SUMCBR = SUMCBR + CBR(K)
 15 CONTINUE
 10 CONTINUE
    AVGCBR = SUMCBR/DBLE(NSP)
    AVGCBRN = CBRTOT - AVGCBR
C
C    Exit condition (99.98% regeneration).
C
    CHECK = 0.9998D0*CBRTOT
    IF (AVGCBR .GT. CHECK) GOTO 26
C
    WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRN*1.0D+03
 25 CONTINUE
 26 STOP
    END
```

```
C
C
C    SIMULATION OF ANIONIC REGENERATION (R-Cl + NaOH)
C                  BY EQUILIBRIUM  THEORY.
C
C
     PROGRAM  EQBMAN
     IMPLICIT REAL*8 ( A-H, O-Z )
     REAL*8  L
C
C    Definition of variables and constants:
C
C    C = ionic concentration of hydroxide in solution.
C    CBR = ionic concentration of hydroxide in solid.
C    CBRC = ionic concentration of chloride in solid.
C    C0 = ionic concentration of hydroxide throughout the column, initially.
C    CF = ionic concentration of hydroxide in the feed.
C    CTOT = total concentration in solution.
C    CBRTOT = total concentration in solid.
C    Z = length along column.
C    DZ = spatial increment.
C    T = time.
C    DT = time increment.
C    ALPHA = relative sorptivity of hydroxide with respect to sodium.
C    EPS = fractional volume of solution in bed.
C    F = solution flowrate.
C    OMEGA = column cross-sectional area.
C    NSP = number of spatial increments.
C    NTM = number of time increments.
C    LPR = print frequency.
C    L = column length.
C    P = intermediate storage array for C.
C    Y = dummy variable for C in the function statement.
C
C    Units:: Length in meter, Time in second, Concentration in eq/m3.
C
     REAL*8  C(0:500), P(0:500), CBR(0:500), CBRC(0:500)
     DATA C0, CF / 0.0000001D0, 1.5D-03 /
     DATA CTOT, CBRTOT / 1.5D-03, 1.3D-03 /
     DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 8.0D-03, 0.35 /
     DATA PI / 3.1415927D0 /
```

```
C
C    Function definition.
C
     G(Y) = EPS*(CTOT**4) / ( (1.0D0 - EPS)*CBRTOT*(10.0D0*(Y**3) -
    *      7.5D0*Y*Y*CTOT + CTOT**3) + EPS*(CTOT**4) )
C
C    Set NTM to a very high value.
C
     NTM = 5000000
C
     WRITE(*,*) 'ENTER NSP, DT, LPR'
     READ(*,*)  NSP, DT, LPR
C
     OPEN ( UNIT = 6, FILE = 'ANEQRS', STATUS = 'UNKNOWN' )

     DZ = L/DBLE(NSP)
     OMEGA = PI*((DIA/2.0D0)**2)
     A = F/(OMEGA*EPS)
     CONST = A*(DT/DZ)
     T = 0.0D0
     DO 5 K = 0, NSP
     C(K) = C0
 5   CONTINUE
     WRITE(6,11)
 11  FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER ANIONIC
    *REGENERATION: R-Cl + NaOH.')
     WRITE(6,12)
 12  FORMAT(//,6X,'TIME (min)',8X,'HYDROXIDE (eq/l)',9X,'CHLORIDE
    *(eq/l)', //)
     WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20  FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
     DO 25 I = 1, NTM/LPR
     DO 10 J = 1, LPR
C
     T = T + DT
     DO 30 KK = 0, NSP
     P(KK) = C(KK)
 30  CONTINUE
     C(0) = CF
     SUMCBR = 0.0D0
     DO 15 K = 1, NSP
```

```
     C(K) = P(K) - CONST*G(P(K))*(P(K) - P(K-1))
     CBR(K) = CBRTOT*( 2.5D0*(C(K)**4) - 2.5*CTOT*(C(K)**3) +
    *        C(K)*(CTOT**3) ) / (CTOT**4)
     CBRC(K) = CBRTOT - CBR(K)
     SUMCBR = SUMCBR + CBR(K)
  15 CONTINUE
  10 CONTINUE
     AVGCBR = SUMCBR/DBLE(NSP)
     AVGCBRC = CBRTOT - AVGCBR
C
C    Exit condition (99.98% regeneration).
C
     CHECK = 0.9998D0*CBRTOT
     IF (AVGCBR .GT. CHECK) GOTO 26
C
     WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRC*1.0D+03
  25 CONTINUE
  26 STOP
     END
```

APPENDIX C

CODES FOR MODIFIED EQUILIBRIUM THEORY

```
C
C
C    SIMULATION OF CATIONIC REGENERATION (R-Na + HCl) BY
C    MODIFIED EQUILIBRIUM THEORY (WITH AXIAL DISPERSION)
C
C
      PROGRAM  DIFFCAT
      IMPLICIT REAL*8 ( A-H, O-Z )
      REAL*8  L
C
C     Definition of variables and constants:
C
C     C = ionic concentration of hydrogen in solution.
C     C0 = ionic concentration of hydrogen throughout the column, initially.
C     CF = ionic concentration of hydrogen in the feed.
C     CTOT = total concentration in solution.
C     CBRTOT = total concentration in solid.
C     DA = axial diffusion or dispersion coefficient.
C     Z = length along column.
C     DZ = spatial increment.
C     T = time.
C     DT = time increment.
C     ALPHA = relative sorptivity of hydrogen with respect to sodium.
C     EPS = fractional volume of solution in bed.
C     F = solution flowrate.
C     OMEGA = column cross-sectional area.
C     NSP = number of spatial increments.
C     NTM = number of time increments.
C     LPR = print frequency.
C     L = column length.
C     P = intermediate storage array for C.
C     Y = dummy variable for C in the function statement.
C
C     Units:: Length in meter, Time in second, Concentration in eq/m3.
C
      REAL*8  C(0:500), P(0:500), CBR(0:500), CBRN(0:500)
      DATA ALPHA, C0, CF / 0.5D0, 0.0000001D0, 1.5D-03 /
      DATA CTOT, CBRTOT / 1.5D-03, 1.3D-03 /
      DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 0.012618D0, 0.35 /
      DATA DA, PI / 7.712D-05, 3.1415927D0 /     !!
C
```

```
C    Function definition.
C
      G(Y) = 1.0D0 / ( 1.0D0 + (1.0D0-EPS)*ALPHA*CTOT*CBRTOT/
     *     (EPS*(CTOT + Y*(ALPHA-1.0D0))**2) )
C
C    Set NTM to a very high value.
C
      NTM = 50000000
C
      WRITE(*,*) 'ENTER NSP, DT, LPR'
      READ(*,*)  NSP, DT, LPR
C
      OPEN ( UNIT = 6, FILE = 'CTDFRS', STATUS = 'UNKNOWN' )
C
      DZ = L/DBLE(NSP)
      OMEGA = PI*((DIA/2.0D0)**2)
      A = F/(OMEGA*EPS)
      B = DA/EPS
      CONST1 = A*DT/(2.0D0*DZ)
      CONST2 = B*DT/((DZ)**2)
      T = 0.0D0
      DO 5 K = 0, NSP
      C(K) = C0
 5    CONTINUE
      WRITE(6,11)
 11   FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER CATIONIC
     *REGENERATION: R-Na + HCl.')
      WRITE(6,12)
 12   FORMAT(//,6X,'TIME (min)',8X,'HYDROGEN (eq/l)',9X,'SODIUM (eq/l)',
     * //)
      WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20   FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
      DO 25 I = 1, NTM/LPR
      DO 10 J = 1, LPR
C
      T = T + DT
      DO 30 KK = 0, NSP
      P(KK) = C(KK)
 30   CONTINUE
      C(0) = CF
      SUMCBR = 0.0D0
```

```
      DO 15 K = 1, NSP-1
      C(K) = P(K) - CONST1*G(P(K))*(P(K+1) - P(K-1)) + CONST2*G(P(K))*
     *      (P(K+1) - 2.0D0*P(K) + P(K-1))
      CBR(K) = ( ALPHA*C(K)*CBRTOT ) / ( ALPHA*C(K) + CTOT - C(K) )
      CBRN(K) = CBRTOT - CBR(K)
      SUMCBR = SUMCBR + CBR(K)
   15 CONTINUE
      C(NSP) = (4.0D0*C(NSP-1) - C(NSP-2))/3.0D0
      CBR(NSP) = (ALPHA*C(NSP)*CBRTOT) / (ALPHA*C(NSP) + CTOT -
     *        C(NSP))

      CBRN(NSP) = CBRTOT - CBR(NSP)
      SUMCBR = SUMCBR + CBR(NSP)
   10 CONTINUE
      AVGCBR = SUMCBR/DBLE(NSP)
      AVGCBRN = CBRTOT - AVGCBR
C
C     Exit condition (99.98% regeneration).
C
      CHECK = 0.9998D0*CBRTOT
      IF (AVGCBR .GT. CHECK) GOTO 26
C
      WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRN*1.0D+03
   25 CONTINUE
   26 STOP
      END
```

```
C
C
C     SIMULATION OF CATIONIC REGENERATION (R-Na + H2SO4) BY
C     MODIFIED EQUILIBRIUM THEORY (WITH AXIAL DISPERSION)
C
C
      PROGRAM  DIFFCTS
      IMPLICIT REAL*8 ( A-H, O-Z )
      REAL*8  L
C
C     Definition of variables and constants:
C
C     C = ionic concentration of hydrogen in solution.
C     C0 = ionic concentration of hydrogen throughout the column, initially.
C     CF = ionic concentration of hydrogen in the feed.
C     CTOT = total concentration in solution.
C     CBRTOT = total concentration in solid.
C     DA = axial diffusion or dispersion coefficient.
C     Z = length along column.
C     DZ = spatial increment.
C     T = time.
C     DT = time increment.
C     ALPHA = relative sorptivity of hydrogen with respect to sodium.
C     EPS = fractional volume of solution in bed.
C     F = solution flowrate.
C     OMEGA = column cross-sectional area.
C     NSP = number of spatial increments.
C     NTM = number of time increments.
C     LPR = print frequency.
C     L = column length.
C     P = intermediate storage array for C.
C     Y = dummy variable for C in the function statement.
C
C     Units:: Length in meter, Time in second, Concentration in eq/m3.
C
      REAL*8  C(0:500), P(0:500), CBR(0:500), CBRN(0:500)
      DATA ALPHA, C0, CF / 0.5D0, 0.0000001D0, 1.0D-03 /
      DATA CTOT, CBRTOT / 1.0D-03, 1.3D-03 /
      DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 0.012618D0, 0.35 /
      DATA DA, PI / 7.712D-05, 3.1415927D0 /    !!
C
```

```
C    Function definition.
C
     G(Y) = 1.0D0 / ( 1.0D0 + (1.0D0-EPS)*ALPHA*CTOT*CBRTOT/
    *     (EPS*(CTOT + Y*(ALPHA-1.0D0))**2) )
C
C    Set NTM to a very high value.
C
     NTM = 50000000
C
     WRITE(*,*) 'ENTER NSP, DT, LPR'
     READ(*,*)  NSP, DT, LPR
C
     OPEN ( UNIT = 6, FILE = 'SCTDFRS', STATUS = 'UNKNOWN' )
C
     DZ = L/DBLE(NSP)
     OMEGA = PI*((DIA/2.0D0)**2)
     A = F/(OMEGA*EPS)
     B = DA/EPS
     CONST1 = A*DT/(2.0D0*DZ)
     CONST2 = B*DT/((DZ)**2)
     T = 0.0D0
     DO 5 K = 0, NSP
     C(K) = C0
 5  CONTINUE
     WRITE(6,11)
 11  FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER CATIONIC
    *REGENERATION: R-Na + H2SO4.')
     WRITE(6,12)
 12  FORMAT(//,6X,'TIME (min)',8X,'HYDROGEN (eq/l)',9X,'SODIUM (eq/l)',
    * //)
     WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20  FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
     DO 25 I = 1, NTM/LPR
     DO 10 J = 1, LPR
C
     T = T + DT
     DO 30 KK = 0, NSP
     P(KK) = C(KK)
 30  CONTINUE
     C(0) = CF
     SUMCBR = 0.0D0
```

```
      DO 15 K = 1, NSP-1
      C(K) = P(K) - CONST1*G(P(K))*(P(K+1) - P(K-1)) + CONST2*G(P(K))*
     *      (P(K+1) - 2.0D0*P(K) + P(K-1))
      CBR(K) = ( ALPHA*C(K)*CBRTOT ) / ( ALPHA*C(K) + CTOT - C(K) )
      CBRN(K) = CBRTOT - CBR(K)
      SUMCBR = SUMCBR + CBR(K)
   15 CONTINUE
      C(NSP) = (4.0D0*C(NSP-1) - C(NSP-2))/3.0D0
      CBR(NSP) = (ALPHA*C(NSP)*CBRTOT) / (ALPHA*C(NSP) + CTOT -
     *         C(NSP))

      CBRN(NSP) = CBRTOT - CBR(NSP)
      SUMCBR = SUMCBR + CBR(NSP)
   10 CONTINUE
      AVGCBR = SUMCBR/DBLE(NSP)
      AVGCBRN = CBRTOT - AVGCBR
C
C     Exit condition (99.98% regeneration).
C
      CHECK = 0.9998D0*CBRTOT
      IF (AVGCBR .GT. CHECK) GOTO 26
C
      WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRN*1.0D+03
   25 CONTINUE
   26 STOP
      END
```

```
C
C
C   SIMULATION OF ANIONIC REGENERATION (R-Cl + NaOH) BY
C   MODIFIED EQUILIBRIUM THEORY (WITH AXIAL DISPERSION)
C
C
      PROGRAM  DIFFAN
      IMPLICIT REAL*8 ( A-H. O-Z )
      REAL*8  L
C
C    Definition of variables and constants:
C
C    C = ionic concentration of hydroxide in solution.
C    CBR = ionic concentration of hydroxide in solid.
C    CBRC = ionic concentration of chloride in solid.
C    C0 = ionic concentration of hydroxide throughout the column, initially.
C    CF = ionic concentration of hydroxide in the feed.
C    CTOT = total concentration in solution.
C    CBRTOT = total concentration in solid.
C    DA = axial diffusion or dispersion coefficient.
C    Z = length along column.
C    DZ = spatial increment.
C    T = time.
C    DT = time increment.
C    EPS = fractional volume of solution in bed.
C    F = solution flowrate.
C    OMEGA = column cross-sectional area.
C    NSP = number of spatial increments.
C    NTM = number of time increments.
C    LPR = print frequency.
C    L = column length.
C    P = intermediate storage array for C.
C    Y = dummy variable for C in the function statement.
C
C    Units:: Length in meter, Time in second, Concentration in eq/m3.
C
      REAL*8  C(0:500), P(0:500), CBR(0:500), CBRC(0:500)
      DATA  C0, CF / 0.0000001D0, 1.5D-03 /
      DATA CTOT, CBRTOT / 1.5D-03, 1.3D-03 /
      DATA L, DIA, F, EPS / 1.5D0, 2.5D0, 8.0D-03, 0.35 /
      DATA DA, PI / 7.712D-05, 3.1415927D0 /     !!
```

```
C
C   Function definition.
C
    G(Y) = EPS*(CTOT**4) / ( (1.0D0 - EPS)*CBRTOT*(10.0D0*(Y**3) -
   *       7.5D0*Y*Y*CTOT + CTOT**3) + EPS*(CTOT**4) )
C
C   Set NTM to a very high value.
C
    NTM = 5000000
C
    WRITE(*,*) 'ENTER NSP, DT, LPR'
    READ(*,*)  NSP, DT, LPR
C
    OPEN ( UNIT = 6, FILE = 'DFANRS', STATUS = 'UNKNOWN' )
C
    DZ = L/DBLE(NSP)
    OMEGA = PI*((DIA/2.0D0)**2)
    A = F/(OMEGA*EPS)
    B = DA/EPS
    CONST1 = A*DT/(2.0D0*DZ)
    CONST2 = B*DT/((DZ)**2)
    T = 0.0D0
    DO 5 K = 0, NSP
    C(K) = C0
 5  CONTINUE
    WRITE(6,11)
 11 FORMAT(/,6X,'RESIDUAL LOADING OF THE BED AFTER ANIONIC
   *REGENERATION: R-Cl + NaOH.')
    WRITE(6,12)
12  FORMAT(//,6X,'TIME (min)',8X,'HYDROXIDE (eq/m)',7X,'CHLORIDE
   *(eq/l)', //)
    WRITE(6,20) T/60.0D0, C0*1.0D+03, (CBRTOT-C0)*1.0D+03
 20 FORMAT ( 2X, F12.5, 8X, F12.8, 11X, F12.8 )
    DO 25 I = 1, NTM/LPR
    DO 10 J = 1, LPR
C
    T = T + DT
    DO 30 KK = 0, NSP
    P(KK) = C(KK)
 30 CONTINUE
    C(0) = CF
```

```
      SUMCBR = 0.0D0
      DO 15 K = 1, NSP-1
      C(K) = P(K) - CONST1*G(P(K))*(P(K+1) - P(K-1)) + CONST2*G(P(K))*
     *      (P(K+1) - 2.0D0*P(K) + P(K-1))
      CBR(K) = CBRTOT*( 2.5D0*(C(K)**4) - 2.5*CTOT*(C(K)**3) +
     *         C(K)*(CTOT**3) ) / (CTOT**4)
      CBRC(K) = CBRTOT - CBR(K)
      SUMCBR = SUMCBR + CBR(K)
   15 CONTINUE
      C(NSP) = (4.0D0*C(NSP-1) - C(NSP-2))/3.0D0
      CBR(NSP) = CBRTOT*( 2.5D0*(C(NSP)**4) - 2.5D0*CTOT*(C(NSP)**3)
     *    + C(NSP)*(CTOT**3) ) / (CTOT**4)
      CBRC(NSP) = CBRTOT - CBR(NSP)
      SUMCBR = SUMCBR + CBR(NSP)
   10 CONTINUE
      AVGCBR = SUMCBR/DBLE(NSP)
      AVGCBRC = CBRTOT - AVGCBR
C
C     Exit condition (99.98% regeneration).
C
      CHECK = 0.9998D0*CBRTOT
      IF ( AVGCBR .GT. CHECK ) GOTO 26
C
      WRITE(6,20) T/60.0D0, AVGCBR*1.0D+03, AVGCBRC*1.0D+03
   25 CONTINUE
   26 STOP
      END
```

VITA

Atanu Basu

Candidate for the Degree of

Master of Science

Thesis: COMPUTER SIMULATION OF REGENERATION PROCESSES FOR ION EXCHANGE RESINS USED IN WATER PURIFICATION

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Calcutta, India, on March 3, 1969, the son of Prativa and Kanan Basu.

Education: Graduated from Patha Bhavan High School, Calcutta, India in May 1987; received Bachelor of Chemical Engineering degree from Jadavpur University, Calcutta, India in June 1991. Completed the requirements for the Master of Science degree in Chemical Engineering at Oklahoma State University in May 1994.

Professional Experience: Employed as a Junior Engineer in Tata Iron & Steel Company, India from June 1991 to July 1992; employed by Oklahoma State University, School of Chemical Engineering as a Research Assistant from August 1992 to present.

Professional Memberships: American Institute of Chemical Engineers, Society for Industrial and Applied Mathematics, and Association for Computing Machinery.