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MATHEMATICAL THEORY OF ELECTROCHEMICAL DEMINERALIZATION IN FLOWING SYSTEMS

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MATHEMATICAL THEORY OF ELECTROCHEMICAL DEMINERALIZATION IN FLOWING SYSTEMS

CHAPTER I

INTRODUCTION

A process for the desalination of water by the electrically-induced adsorption of ions on porous carbon electrodes has been under study at the University of Oklahoma for several years (1-4). The object of the present research is to arrive at a mathematical theory for the concentration changes occurring in a demineralization cell employing such a process.

The problem is to find relationships for the concentration distributions inside the cell as a function of time. Other investigators have obtained equations describing gas adsorption and ion-exchange column operations which are similar in that they also involve the transfer of matter between a moving fluid phase and a stationary solid phase. Discussion of these systems will illustrate some of the problems involved in the demineralization system.

Vermuelen (5) and McLeod (6) have pointed out that for the gas adsorption system the problem of finding the relationship for the concentration distribution involves the

mass balance equation, the equilibrium relationship between adsorbed and solution phases and the mass transfer rate equation. In the demineralization system under study here the mass balance equation and the equilibrium relationship present no problem. The equilibrium isotherm has been assumed to be linear. Although this was found to be a poor assumption in the case of gas adsorption (6), it has been adequate for electrically-induced adsorption of ions. Of the several experimental conditions investigated in this research; however, this assumption may be questionable for conditions involving the highest applied potential.

The mass transfer rate equation presents a more difficult problem, and one which has been of interest for many years to investigators working with electrode reactions. The velocity of electrochemical reactions on the surface of an electrode is governed both by the rate of transfer of ions to the electrode and by the rate of the electrode reactions themselves. The assumption is made in the present research that the rate of the electrode reactions is much faster than the rate of transfer to the electrode.

Three mechanisms are usually assumed for the transport of ions: diffusion, electrical migration, and convection. Early investigators in the field of electrode reactions simplified the problem of mass transfer by choosing conditions such that one or more of these mechanisms was of negligible

importance. This was done because the mass transfer rate expression becomes quite complex when all three are considered together. Work on mass transfer was reported as early as 1879 and for many years consisted of a treatment of diffusion only, as was done by Rosebrugh and Miller (7), and Sand (8).

Other pertinent work on the subject of mass transfer was reported by Levich (9-14), Tobias, Eisenberg and Wilke (15-18), Wagner (19-21), and Agar (22). Levich (11) and Eucken (23) were the first to consider the general case with all three components of flux within the solution and to apply the principles of hydrodynamics to concentration changes.

Most of the earlier work has been reviewed in detail by Agar (22) in 1947 and Tobias, Eisenberg, and Wilke (15) in 1952. The previous papers were not only collected and compared, but Agar also attempted to express concentration changes in terms of dimensionless Reynold's, Nusselt's and Prandlt's numbers. The Pecklet number was added to these three by Levich (14) in a similar change to dimensionless numbers. Tobias, Eisenberg, and Wilke included a discussion of all models previously used in the development of the various mathematical theories.

In the present research the complex nature of the carbon electrode system makes the derivation of the mass transport equations very difficult. Because of this a simplified model is chosen to represent the demineralization

cell for purposes of obtaining the mass transport equations.
The demineralization cell is represented by a series of solution compartments enclosed by permselective membranes, some
of which are closed compartments of fixed volume. The compartments of fixed volume represent the electrodes. Their fixed volume gives them a finite capacity. This system has been treated from the standpoint of non-equilibrium thermodynamics by Murphy and Taber (24).

The mass balance equation and transport equations for the model given above, when combined and solved, yield the concentration, time, and cell geometry relationships for the demineralization cell. The method employed in the solution of equations is one used by T. E. W. Schumann (25) to solve similar equations for heat transfer between a flowing fluid and a stationary solid, and by Boyd, Meyers, and Adamson (26) for an ion-exchange problem. They showed that the differential mass balance equations for the solid and the fluid can be solved in terms of a modified Bessel function of the first kind of zero order and its derivatives. Using the boundary conditions for the demineralization cell with this method, an equation is found which can be used to find the concentration distribution inside the cell, as well as the concentrationtime curve for the effluent from the cell. This equation is in terms of dimensionless concentration ratios and dimensionless cell geometry and time parameters, all of which can be

related to the measured quantities through constants derived from the model. Goldstein (27) discussed the application of this type to exchange processes.

The equations derived have been tested against experiments performed under several sets of conditions.

An important application of this theory concerns the calculation of the faraday efficiency. In order to calculate the faraday efficiency, the amount of salt removed from the solution which has passed through the cell, as well as that amount removed from solution remaining in the cell, must be known. It is experimentally difficult, if not impossible, to measure the latter quantity; however, equations given by the theory have been used to calculate this quantity and consequently the faraday efficiency. Using the theory, the faraday efficiency for several sets of conditions have been determined.

CHAPTER II

MATHEMATICAL DEVELOPMENT

The mathematical formulation of the theory of the concentration changes occurring in the demineralization cell during the demineralization phase begins with the establishment of the equations for the conservation of matter in the cell and the mass transfer rate. These are derived from the model representing the cell. The actual demineralization cell is described below. The model used to represent the cell was described previously.

The cell consists of two electrically conductive but chemically inert end plates, against which the electrodes are held. The electrodes are composed of inert fibrous material on which carbon blacks, charcoals or mixtures of these materials are deposited from slurries. The end plates, with electrodes in place, are pressed together with a separator between them so that a small solution space remains between the electrodes. Solution is pumped through the cell from bottom to top and the electrodes are connected to the power supply through connections on the end plates. This cell is compared with the model in Figure 1. In the model ions entering the α compartment from the β compartment are balanced by counter

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Figure 1. Demineralization Cell Compared with the Model Used in the Mathematical Development of the Theory. ions entering from the other side of the α compartment. The equivalents of salt in the β compartment change only by transfer of salt out through the membrane or out of the cell by flow of solution through the cell; therefore, the sum of these changes must equal the change in equivalents of salt in the β compartment, or

$$\frac{\partial \xi^{\beta}}{\partial t} = -u \frac{\partial \xi^{\beta}}{\partial x} - \frac{\partial \xi^{\alpha}}{\partial t}$$
(1)

where the symbol, ξ , represents equivalents of salt. This is the equation for conservation of matter in the cell. It can be rearranged and put into the following form by multiplying each term by the unit ratio, V^{β}/V^{β} or V^{α}/V^{α} , as the case may be,

$$\Lambda_{\beta} \left[\frac{9C_{\beta}}{9t} \right] + n\Lambda_{\beta} \left[\frac{9C_{\beta}}{9x} \right] + \Lambda_{\alpha} \left[\frac{9C_{\alpha}}{9t} \right] = 0$$
 (5)

In order to solve this equation for the required relationship between C^{α} , C^{β} , x and t, an expression for $\partial C^{\alpha}/\partial t$ must be known. The model provides this expression in the equation for the flux of salt from one compartment to another. The flux of salt across the membranes, as given by Murphy and Taber (24), is

$$-\underline{J} = D_{\alpha} \left[\frac{\partial C^{\alpha}}{\partial t} \right] = \frac{\tau \Lambda C^{\beta}}{D_{\beta} F} \left[\Delta E - \frac{2RT}{F} \ln \frac{C^{\alpha}}{C^{\beta}} \right]$$
(3)

The ΔE shown here is the potential difference between the probe electrodes; however, for a system of electrodes instead of solution compartments, it would be the difference between the potential at the probe electrodes and the standard cell

potential, E° , for the probe electrodes. For identical probe electrodes E° would be zero; however, for a pair of unlike probe electrodes E° will have a value.

Combining Equations 1 and 2 and making the further assumption that $\ln(C^{\alpha}/C^{\beta})$ may be approximated by $(C^{\alpha}/C^{\beta} - 1)$, the resulting mass balance equation is

$$\frac{\partial C^{\beta}}{\partial t} = -u \frac{\partial C^{\beta}}{\partial x} - \frac{\tau \Lambda}{D_{\beta}^{2} F} C^{\beta} \Delta E - \frac{2 \tau R T \Lambda}{D_{\beta}^{2} F^{2}} (C^{\beta} - C^{\alpha})$$
(4)

Although this equation was arrived at by considering the flux of salt through a membrane, it should be noted that a similar mass balance equation could in principle be developed by considering such mechanisms as migration, diffusion and convection. Tobias, Eisenberg, and Wilke (15) give the flux of salt from a planar-electrode in the absence of fluid turbulence to be

$$J_{t} = -cU\frac{\partial\phi}{\partial z} + D\frac{\partial c}{\partial z} - V_{z}c$$
 (5)

where: $J_t = \text{total rate of transfer, gram ions/cm}^2-\text{sec}; c = \text{concentration, gram ions/cm}^3; U = \text{mobility, cm}^2/\text{sec-v}; \phi = \text{potential, v}; z = \text{distance to the electrode, cm}; D = \text{diffusion coefficient, cm}^2/\text{sec}; V_z = \text{velocity of the bulk fluid toward the electrode. This flux corresponds to the flux of salt across the membranes in the treatment above. The third, or convection term in this equation, is assumed to be negligibly small, since the bulk solution velocity toward the electrode to be zero. All other fluxes except migration$

and diffusion toward the electrode are assumed to be negligible here.

In the case where solution is being pumped past the electrode, another flux parallel to the electrode arises

$$J_{p} = -V_{x}c \tag{6}$$

This flux corresponds to the flux of salt due to the flowing solution in the previous treatment.

To convert Equation 5 from a flux to a concentration change with respect to time, consider a differential volume of the β compartment dV^{β} with faces of area dA on the membranes. The equivalents of salt gained by the volume dV^{β} by transfer through the membrane will be $J_t dA$. This corresponds to a concentration change of $J_t dA/dV^{\beta}$ or J_t/D_{β} , since $dV^{\beta} = D_{\beta} dA$. With a similar argument a concentration change with respect to time in the differential volume dV^{β} can be obtained in the form $(J_p^{\text{in}} - J_p^{\text{out}})/dx$ where $dV^{\beta} = dxdA'$. Combining these two expressions and substituting for J_t and J_p yields the concentration change with respect to time as

$$\frac{\partial c^{\beta}}{\partial t} = -V_{x} \frac{\partial c^{\beta}}{\partial x} - \frac{c^{\beta}U}{D_{\beta}} \frac{\partial \phi}{\partial z} + \frac{D}{D_{\beta}} \frac{\partial c^{\beta}}{\partial z}$$
(7)

With some assumptions concerning the potential and concentration gradients, the terms of Equation 7 correspond to those of Equation 4. The first term on the right of Equation 7 corresponds to the first term on the right of Equation 4; therefore, which is proper, since they are both linear flow rates. If the potential gradient of Equation 7 is linear, then

$$U = \tau \Lambda / F$$

The third term on the right of Equation 7 corresponds to the third term on the right of Equation 4 if the concentration gradient in Equation 7 is assumed to be linear. Comparing these terms, the diffusion coefficient in Equation 7 is given by

$D = 2\tau RTA/F^2$

The relationship of the concentration to cell geometry and time is found by integration of Equations 3 and 4 using Schumann's method. These equations may be simplified by the substitution of

$$k_{1} = \frac{\tau \Lambda \Delta E}{D_{B}^{2} F} + \frac{2\tau R T \Lambda}{D_{B}^{2} F^{2}}$$
(8)

$$k_{2} = \frac{2\tau RT\Lambda}{D_{\alpha} D_{\beta} F^{2}}$$
(9)

to give

$$\partial c^{\beta}/\partial t + u \partial c^{\beta}/\partial x = -k_1(c^{\beta} - S)$$
 (10)

$$\frac{\partial S}{\partial t} = k_2 (C^\beta - S) \tag{11}$$

where

$$S = \frac{D_{\alpha}}{D_{\beta}} \frac{k_2}{k_1} C^{\alpha}$$

For a complete solution of these equations, the following boundary conditions must be satisfied. At x = 0

 $u = V_x$

$$C^{\beta} = C_{o}$$
 for all time
 $S = S_{o}$ at $t = 0$ (12)

and, from Equation 11,

- ..

$$S = C_0 - (C_0 - S_0) e^{-K_2 t}$$
(13)

When x is less than the length of the electrode, the concentrations at the farthest point reached by solution are, i.e. at x = ut,

$$S \doteq S_0 \tag{14}$$

$$C^{\beta} = S_{0} + (C_{0} - S_{0})e^{-k_{1}t}$$
(15)

Equation 15 is found by considering the infinitesimal volume at the leading edge of the solution. Because the concentration in this volume is independent of x, Equation 10 becomes, for the leading edge of the solution,

$$\partial C^{\beta} / \partial t = -k_1 (C^{\beta} - S_0)$$
 (16)

Integration of this equation leads to Equation 15.

Equations 10 and 11 are reduced to the simpler forms

$$\partial c^{\beta} / \partial y = S - c^{\beta}$$
 (17)

$$\partial S/\partial z = C^{\beta} - S$$
 (18)

by the introduction of two new independent variables

$$y = k_1 x / u \tag{19}$$

$$z = k_2(t - x/u)$$
 (20)

Equations 10 and 11 are further simplified by introducing two new dependent variables U and V, where

$$S = C_0(U - V)e^{-y-z}$$
 (21)

$$C^{\beta} = C_{o}(U + V)e^{-y-z}$$
(22)

Substituting these values into Equations 17 and 18, the new equations are

$$\frac{\partial z}{\partial u} - \frac{\partial z}{\partial v} = u + v \tag{53}$$

$$\frac{\partial \Lambda}{\partial \Pi} + \frac{\partial \Lambda}{\partial \Lambda} = \Pi - \Lambda$$
 (54)

By further differentiation

$$\frac{\partial^2 V}{\partial y \partial z} = V \tag{25}$$

Combining Equations 21 and 22 with the boundary conditions discussed above, the boundary conditions for U and V are, at y = 0

$$U = e^{Z} - (1 - S_{o}/C_{o})/2$$
(26)

$$V = (1 - S_0/C_0)/2$$
(27)

at z = 0

.

$$U = (1 - S_0/C_0)/2 + (S_0/C_0)e^y$$
(28)

$$V = (1 - S_0/C_0)/2$$
(29)

To solve Equation 25 subject to the boundary conditions given by Equations 27 and 29, let

$$\phi^2 = -4yz \tag{30}$$

Equation 25 reduces to

$$\frac{\mathrm{d}^2 \mathrm{V}}{\mathrm{d}\phi^2} + \frac{1}{\phi} \frac{\mathrm{d}\mathrm{V}}{\mathrm{d}\phi} + \mathrm{V} = 0 \tag{31}$$

which is a form of Bessel's equation, of which a well-known solution is

$$V = AJ_{o}(\phi)$$
(32)

where A is a constant and $J_o(\phi)$ is a Bessel function of the

first kind of order zero.

The boundary conditions are satisfied if $A = (1 - S_0/C_0)/2$; therefore, the solution is

$$V = (1/2)(1 - S_0/C_0)J_0(\phi)$$
(33)

or

$$V = (1/2)(1 - S_0/C_0)M_0(yz)$$

where $M_o(yz)$ is defined as

$$M_{o}(yz) = J_{o}(2i\sqrt{yz}) = \sum_{m=0}^{\infty} \frac{(yz)^{m}}{(m!)^{2}}$$
(34)

Having obtained a relationship for V, a relationship for U satisfying Equations 23 and 24 and the given boundary conditions must be found. Equation 23 can be integrated as an ordinary linear differential equation to yield

$$U = V + 2e^{z} \int e^{-z} V dz + f(y)e^{z}$$
(35)

where f(y) is a function of y. Successive partial integration gives

$$2e^{Z} \int e^{-Z} V dz = -2(V + \frac{\partial V}{\partial z} + \frac{\partial^{2} V}{\partial z^{2}} + \dots)$$
$$= -(1 - S_{o}/C_{o}) \sum_{m=0}^{\infty} y^{m} M_{m}(yz) \qquad (36)$$

where

_ -

$$M_{\rm m}(yz) = \frac{d^{\rm m}M_{\rm o}(yz)}{d(yz)^{\rm m}}$$
(37)

Therefore, Equation 35 becomes

$$U = (1/2)(1 - S_0/C_0) M_0(yz) + f(y)e^{Z}$$

-(1 - S_0/C_0) $\sum_{m=0}^{\infty} y^m M_m(yz)$ (38)

Consideration of the boundary conditions when z = 0 and noting that

$$\sum_{m=0}^{\infty} \dot{y}^{m} M_{m}(yz) = e^{y} (for z = 0)$$

 $f(y) = e^y$ and Equation 38 becomes

$$U = (1/2)(1 - S_{o}/C_{o})M_{o}(yz) + e^{y+z}$$

-(1 - S_{o}/C_{o}) $\sum_{m=0}^{\infty} y^{m}M_{m}(yz)$ (39)

Although this relationship satisfies the boundary conditions, it still must be shown that it also is consistent with Equation 24.

Using Equations 35 and 36, U can be expressed as

$$\Omega = \Lambda + e_{\lambda+z} - 5(\Lambda + \frac{9z}{9\Lambda} + \frac{9z_5}{9_5\Lambda} + \cdots)$$

Therefore,

$$\frac{\partial U}{\partial y} = \frac{\partial V}{\partial y} + e^{y+z} - 2\left(\frac{\partial V}{\partial y} + \frac{\partial^2 V}{\partial y\partial z} + \frac{\partial^3 V}{\partial y\partial z^2} + \dots\right)$$

$$= e^{y+z} - \frac{\partial V}{\partial y} - 2\left(V + \frac{\partial V}{\partial z} + \frac{\partial^2 V}{\partial z^2} + \dots\right)$$
(40)

since $\frac{\partial^2 V}{\partial y \partial z} = V$. These relationships for U and $\partial U / \partial y$ satisfy Equation 24.

The equation for the concentration as a function of cell geometry and time is found by substituting the values of U and V into equation 22 and using the relationship given by Schumann (25)

$$\sum_{m=0}^{\infty} (y^{m} + z^{m}) M_{n}(yz) = e^{y+z} + M_{0}(yz)$$
(41)

yields

$$C^{\beta}/C_{o} = (1 - S_{o}/C_{o})e^{-y-z} \sum_{m=0}^{\infty} z^{m}M_{m}(yz) + S_{o}/C_{o}$$
 (42)

Putting $M_{M}(yz)$ in the form of an infinite series, Equation 42 becomes

$$\frac{c^{\beta}}{c_{o}} = \left[1 - \frac{S_{o}}{c_{o}}\right]e^{-y-z} \sum_{m=0}^{\infty} \frac{z^{m}}{m!} \sum_{j=0}^{m} \frac{y^{j}}{j!} + \frac{S_{o}}{c_{o}}$$
(43)

which gives the ratio of the concentration to the feed solution concentration in terms of the dimensionless distance, y, from cell entrance to the point of interest and dimensionless time, z. Examination of the limiting cases shows that the behavior of the equation corresponds to the observed behavior in the demineralization cell. As y approaches zero, where the concentration is C_0 , the equation reduces to $C^{\beta}/C_0 = 1$. At large values of z, which correspond to electrode saturation, $C^{\beta}/C_0 = 1$ for any given y value.

One other interesting limiting case is the one where z goes to zero. Looking at the individual terms of the summation given in Equation 43

$$C^{\beta}/C_{o} = (1 - S_{o}/C_{o})e^{-y-z}[1 + z(1 + y) + z^{2}(1 + y + y^{2}) + ...] + S_{o}/C_{o}$$

As z goes to zero, this equation becomes

$$c^{\beta}/c_{o}|_{z=0} = (1 - S_{o}/c_{o})e^{-y} + S_{o}/c_{o}$$
 (44)
Experimental difficulties limit the usefulness of this equa-
tion; however, it can be used in determining the S_o/C_o value
needed to fit the data with a particular y value.

CHAPTER III

EXPERIMENTAL PROCEDURE AND TREATMENT OF DATA

A. Experimental Procedure

The procedures and equipment used in this work are modifications of those used by other investigators to study the desalination behavior of porous carbon electrodes (1-4). The demineralization cell described in Chapter II, the DC-7 cell, was originally developed to study the salt removal capacities of carbon electrodes. For this work the cell is operated with solution pumped continuously through the cell from bottom to top, where the conductivity and pH are measured and recorded. On applying a potential of the proper polarity, the electrodes adsorb salt until their capacity is reached, at which time the conductivity measured at the cell outlet is that of the feed solution. Regeneration is accomplished by reversing the polarity. The time during which the cell is under a demineralization potential is termed a demineralization phase. The regeneration phase is similarly defined. A demineralization cycle consists of two phases, one regeneration and one demineralization.

The experimental data used to test Equation 43 consist of the curves, called effluent curves, obtained by

plotting the effluent concentration from the demineralization cell versus time for experiments performed in the following manner: The cell is cycled several times, and at the end of a regeneration phase the power supply is removed and the cell left on open circuit with solution flowing through it. The potential difference between the electrical connections of the cell is measured periodically until the potential showed no change on two consecutive days, at which time it is considered to be near equilibrium. The potential determined just prior to emptying the cell will be called hereafter the final potential. The cell is then emptied and the specific conductivity of the effluent, the pH of the effluent and the current are recorded as a function of time for the demineralization The instant that solution reaches the bottom of the phase. electrode is taken as zero time. These experiments differ from those run by previous investigators in two ways; previously, the cell was not emptied prior to measuring the demineralization phase and the equilibration procedure described above was not used in earlier work. The cell is emptied initially in these experiments because the mathematical description of the cell is simpler under this condition. The equilibration procedure is used to insure reproducibility.

At the end of a regeneration phase the potential between the electrodes in the cell is equal in magnitude and opposite in sign to the potential applied during the regeneration phase. Because this potential decays exponentially

on open circuit, its magnitude is uncertain at the start of the demineralization phase. The open circuit equilibration described above insures a reproducible initial potential. An experiment was performed in which the open circuit equilibration step was omitted so that a comparison with the equilibrated experiments could be made. All potential measurements for these experiments were made with a recording potentiometer which is described in Appendix A.

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A schematic diagram of the experimental arrangement is given in Figure 2. Solution is pumped into the cell at the bottom and emerges at the top, where it flows through a conductivity cell and then through the pH electrode holder. All conductivity and pH measurements referred to later in the discussion were made at the points shown in Figure 2. The conductivity cell is connected to a bridge which gives a d.c. potential output proportional to the conductivity. This potential is then recorded on a recording potentiometer. The conductivity measuring system is calibrated in place with sodium chloride solutions of known concentration. Calibration data for the system are given in Appendix B. The pH electrodes are connected through an impedence matching device to a recording potentiometer. The pH measuring system is calibrated with commercially available buffer solutions.

The conductivity and pH data obtained are used to calculate the total salt concentration. In the absence of a pH effect, the concentration can be obtained directly from the calibration of the conductivity bridge; however, the pH



Figure 2. Diagram of Experimental Apparatus

of the effluent changes somewhat during the demineralization phase, and this must be taken into account when calculating the concentration. See Section C for a discussion of the pH corrections.

The travel time, x/u, through the cell is determined from the current-time record. Since current does not flow until solution reaches the bottom of the electrodes and falls off exponentially when solution passes the top of the electrode, the value of x/u can be determined from the time difference of these two phenomena on the current-time record. The concentration of interest is the concentration at the top of the electrodes, and because the concentration is measured outside the demineralization cell, there is a time lag in the conductivity-time record. This lag is corrected for by taking the time when the solution first reaches the conductivity cell as zero for the corrected time, (t - x/u).

B. Treatment of Data

The experimental data are plotted as C^{β}/C_{0} versus log (t - x/u). Because of the direct proportionality between z and (t - x/u), the semilog plots permit comparison of the experimentally determined effluent curves to plots of C^{β}/C_{0} versus log z given by Equation 43 without knowing the value of the constant relating z and (t - x/u). The constants k_{1} and k_{2} cannot be calculated directly, since the expressions for these constants (see Equation 8) contain quantities, such as ΔE , D_{β} , and D_{α} , which cannot be determined at present with

sufficient accuracy to calculate meaningful values of k_1 and Since k_1 and k_2 cannot be calculated directly, and, k2. therefore, the experimental data cannot be tested against the theory directly, the data are tested by a fitting technique in which the plot of C^{β}/C_{0} versus log (t - x/u) is visually compared with plots of C^{β}/C_{o} versus log z for various values of y and S_0/C_0 . The plots of C^{β}/C_0 versus log z are calculated for a range of z values from Equation 43 using a high speed computer. A computer program for the calculation of such values is given in Appendix C. Once a library of theoretical plots of C^{β}/C_{o} versus log z is built up, it is simple to determine the ability of the theory to fit an experimental curve from a small number of comparisons and a knowledge of the manner in which the shape of the theoretical curves change with changes in y and S_0/C_0 . Figures 3 and 4 show plots of C^{β}/C_{o} versus log z from the theory. The first shows how the mid-point slope of the curve increases as y increases, and the second shows the decrease of the mid-point slope as S_0/C_0 increases. Increasing y decreases the concentration ratio at z=0, while increasing S_0/C_0 increases this ratio, the limits of change being to zero in the first case and S_0/C_0 in the second.

C. pH Corrections

The concentration of the effluent from the demineralization cell is determined from conductivity measurements. Because the conductivity is a function of the number and type of ions present, the meaning of a concentration determined



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Figure 4. C^{β}/C_{o} versus log z from Theory for Various Values of S_{o}/C_{o} . y = 3.0.

from a conductivity measurement must be carefully defined. Solutions above pH 7 will contain Na⁺, Cl⁻, and OH⁻; those below pH 7 will contain Na⁺, H⁺, and Cl⁻. The concentration of interest is the total positive or negative ion concentration in each case. In the case of high pH, the concentration of interest is, therefore, the Na⁺ concentration. This is determined from the following equation

$$L \times 10^3 = \sum_{i} \Lambda_i C_i$$
 (45)

where

L = specific conductivity

 Λ_1 = equivalent conductivity of ith ion

 $C_1 = \text{concentration of ith ion}$

Upon application of the electroneutrality principle and rearrangement, one obtains

$$C_{Na^{+}} = \frac{L \times 10^{3} - C_{OH^{-}}(\Lambda_{OH^{-}} - \Lambda_{Cl^{-}})}{\Lambda_{Na^{+}} + \Lambda_{Cl^{-}}}$$
(46)

The specific conductivity is experimentally determined, the C_{OH} - is obtained from the pH and the equivalent conductivity values are obtained from the literature (28, 29). In the case of low pH values, the concentration of interest is Cl⁻ concentration. A treatment similar to the one above yields

$$C_{C1^{-}} = \frac{L \times 10^{3} - C_{H^{+}}(\Lambda_{H^{+}} - \Lambda_{Na^{+}})}{\Lambda_{Na^{+}} + \Lambda_{C1^{-}}}$$
(47)

CHAPTER IV

DISCUSSION OF RESULTS

A test of the theory is the ability of Equation 43 to fit the concentration-time curves of the effluent for demineralization experiments. The experiments used to test the theoretical equations were performed under four different operating conditions:

Condition I	<pre>- applied potential = .6v, rate = 50ml/hr, feed solu .03N NaCl</pre>	flow tion =
Condition II	- applied potential = .6v, rate = 100ml/hr, feed sol 03N NaCl	flow ution =
Condition II	<pre>- applied potential = .6v, rate = 50ml/hr, feed solu .01N NaCl</pre>	flow tion =
Condition IV	<pre>- applied potential = .9v, rate = 50ml/hr, feed solu .03N NaCl</pre>	flow tion =

Two separate experiments were performed under each condition for each type of electrode pair tested. Two types of electrode pairs were tested, S.K. versus Ag,AgCl and S.K. versus N:G(2:1), 5% PEI (electrode types described in the Glossary). The first pair was tested under all conditions, and the second pair under Conditions I and III only. These experiments permit testing of the theoretical equation under a range of experimental conditions, as well as subsequent comparisons of the faraday efficiency of the process for the various electrode pairs and operating conditions. One additional experiment was performed under Condition I, but without the equilibration procedure described in the previous chapter, in order to show the necessity for this procedure.

Experimental data for S.K. electrodes versus Ag, AgCl electrodes are compared with the best-fitting theoretical curves in Figures 5-13, the experimental data treated as described in Chapter III. The original concentration data are given in Tables 1-9, along with the pH and corrected concentrations. Calibration data for the relationship between potential and concentration are located in Appendix B. Other pertinent data are summarized in Table 10. Figures 5, 6, and 7 and Tables 1, 2, and 3 show data obtained under Condition I; Figures 8 and 9 and Tables 4 and 5 show data obtained under Condition II; Figures 10 and 11 and Tables 6 and 7 show data obtained under Condition III; and Figures 12 and 13 and Tables 8 and 9 show data obtained under Condition IV. These figures amply demonstrate that the theoretical equation is capable of fitting the data obtained under the several operating conditions. In all but three cases (Figures 5, 12 and 13) the chosen theoretical curves fit the data quite well. The first of the three was made under Condition I; however, the cell was not allowed to equilibrate on open circuit after regeneration, but was emptied while under a regeneration potential (S.K. .6v positive with respect to Ag,AgC1). This

TABLE 1

EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1185 (NE)^{a,b}

Condition I (.6v, 50ml/hr, .03N NaCl)

Time(min)	Potential(mv)	C ^β (equiv∕l)	C ^β ∕C₀
$\begin{array}{c} 22.5\\ 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 37.5\\ 40.0\\ 42.5\\ 45.0\\ 50.0\\ 55.0\\ 60.0\\ 70.0\\ 80.0\\ 90.0\\ 100.0\\ 120.0\\ 140.0\\ 160.0\\ 180.0\\ 200.0\\ \end{array}$	1.31 1.40 1.52 1.68 1.84 2.00 2.18 2.37 2.55 2.659 3.26 3.26 3.26 3.26 3.26 3.26 3.26 3.26	. 00883 . 00947 . 01031 . 01144 . 01257 . 01370 . 01497 . 01631 . 01730 . 01828 . 01998 . 02131 . 02237 . 02399 . 02498 . 02562 . 02611 . 02682 . 02724 . 02759 . 02780 . 02808 . 02830	.312 .335 .364 .404 .444 .484 .529 .576 .611 .646 .706 .753 .790 .8483 .9053 .923 .948 .963 .975 .982 .992 1.000

^aNo pH data obtained for this experiment.

 $^{b}NE = no$ equilibration.
EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1185A^a

	······		
Time(min)	Potential(mv)	C ^β (equiv∕l)	c ^β /c _o
$\begin{array}{c} 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 37.5\\ 40.0\\ 45.0\\ 50.0\\ 55.0\\ 60.0\\ 70.0\\ 80.0\\ 90.0\\ 100.0\\ 100.0\\ 120.0\\ 130.0\\ \infty\end{array}$	1.60 1.72 1.86 1.99 2.15 2.28 2.41 2.82 2.97 3.26 2.97 3.26 2.97 3.26 3.54 3.554 3.554 3.558 3.558 3.60	.01355 .01465 .01585 .01705 .01840 .01970 .02070 .02260 .02435 .02570 .02680 .02815 .02920 .02980 .03085 .03105 .03120 .03135	. 432 . 467 . 507 . 544 . 584 . 628 . 659 . 721 . 776 . 817 . 855 . 898 . 931 . 951 . 971 . 983 . 989 . 995 1. 000

Condition I (.6v, 50ml/hr, .03N NaCl)

^aNo pH data were taken for this experiment.

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1185B

Condition I (.6v, 50ml/hr, .03N NaCl)

Time(min)	Potential(mv)	C ^B (equiv/l) ^a	C ^β ∕C₀	рН
22.5 25.0 27.5 30.0 32.5 35.0 37.5 40.0 45.0 50.0^{-} 55.0 60.0 70.0 80.0 90.0 100.0 100.0 100.0 120.0 130.0 ∞	1.78 1.89 2.01 2.15 2.30 2.45 2.79 2.58 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.79 2.15 2.35 2.99 3.15 3.35 3.45 4.00 2.02 3.45 3.99 3.90 2.02 3.99 3.99 3.90 3.90 3.90 3.90 3.90 3.90	. 01242 . 01321 . 01407 . 01507 . 01615 . 01723 . 01816 . 01931 . 02111 . 02254 . 02362 . 02441 . 02578 . 02693 . 02765 . 02815 . 02836 . 02851 . 02858 . 02865	.434 .4361 .49260 .556037 .6677382 .55663777882 .5990520 .999990 .999990 .999990 .999990 .999990 .999990 .99990 .99990 .99990 .99990 .99990	6-7777777788888888888888888888888888888

^aNo pH corrections were necessary for these data.

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1179A

Condition II (.6v,	l00ml/hr,	.03N	NaCl)
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Time(min)	Potential(mv)	C ^β (equiv/l) ^a	c ^β ∕c₀	рH
$ \begin{array}{c} 14.0\\ 15.0\\ 17.5\\ 20.0\\ 22.5\\ 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 40.0\\ 45.0\\ 50.0\\ 55.0\\ 60.0\\ 70.0\\ 80.0\\ 90.0\\ 100.0\\ 110.0\\ 120.0\\ 130.0\\ \infty\end{array} $	2.62 2.64 2.74 2.94 3.01 3.10 3.19 3.28 3.37 3.50 3.63 3.90 3.999 4.10 4.12 4.13 4.15 4.17 4.18	. 01845 . 01859 . 01931 . 02003 . 02075 . 02125 . 02190 . 02255 . 02319 . 02384 . 02477 . 02571 . 02635 . 02700 . 02765 . 02829 . 02908 . 02923 . 02908 . 02923 . 02930 . 02944 . 02959 . 02966	.622 .627 .651 .675 .700 .716 .738 .760 .782 .804 .835 .867 .888 .910 .932 .958 .988 .9953 .988 .988 .988 .988 .988 .988 .998 .99	66666666899999999999999999999999999999

^aNo pH corrections were necessary for these data.

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TABLE	5
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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1179B

Condition II	(.6v, 100ml/	hr, .03N NaCl)
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Time(min)	Potential(mv)	$C^{\beta}(equiv/1)^{a}$	C ^β ∕C₀	рН
$ \begin{array}{c} 15.0\\ 17.5\\ 20.0\\ 22.5\\ 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 40.0\\ 45.0\\ 55.0\\ 60.0\\ 70.0\\ 80.0\\ 90.0\\ 100.0\\ 100.0\\ 120.0\\ \end{array} $	2.70 2.886 2.896 3.1344 3.1344 3.135 3.1344 3.135 2.22 2.22 3.1344 3.135 2.29 3.136 0.136 0.126 2.22 2.25 3.136 2.22 2.22 3.136 2.22 2.22 3.136 2.22 2.22 3.136 3.137 3.137 3.136 2.22 2.22 3.136 3.137 3.137 3.137 3.136 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.14766 3.	.01883 .01955 .02001 .02069 .02138 .02230 .02314 .02412 .02484 .02602 .02687 .02763 .02890 .02913 .02936 .02968 .02968 .02978 .02994	.629 .658 .66914 .7145 .77706 .8369 .973 .93515 .9781 .9955 .99515 .9951 .9951 .9991 .9991 .9951 .9991 .9991 .9995 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9905 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005 .9005.9005	6-77 6-7777777778888279137 6677777888889999

^aNo pH corrections were necessary for these data.

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1187A^a

Condition III (.6v, 50ml/hr, .01N NaCl)

Time(min)	Potential(mv)	C ^β (equiv/l)	C ^β ∕C₀
$\begin{array}{c} 20.0\\ 22.5\\ 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 37.5\\ 40.0\\ 45.0\\ 50.0\\ 55.0\\ 60.0\\ 55.0\\ 60.0\\ 65.0\\ 70.0\\ 80.0\\ 90.0\\ 100.0\\ 110.0\\ 120.0\\ 130.0\\ 140.0\\ 150.0\\ 170.0\\ 190.0\\ 210.0\\ 230.0\\ \infty\end{array}$.67 .69 .73 .79 .85 .90 .97 1.02 1.09 1.20 1.30 1.42 1.53 01 2.25 80 1.12 2.58 10 1.356 98 0.3 .99 1.17 4.24	00149 00154 00163 00178 00221 00221 00233 00250 00276 00300 00329 00367 00403 00444 00521 00600 00732 00732 00732 00782 00866 00897 00943 00943 00996 00996 01005	.148 .153 .162 .177 .191 .203 .220 .232 .249 .275 .299 .327 .365 .401 .442 .518 .597 .664 .728 .778 .824 .862 .893 .938 .967 .983 .991 1.000

^aNo pH data were obtained for this experiment.

EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1187B

Condition III (.6v, 50ml/hr, .01N NaCl)

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Time(min)	Potential(mv)	C ^β (equiv/l) ^a	C ^β ∕C₀	pH
$\begin{array}{c} 22.5\\ 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 37.5\\ 40.0\\ 45.0\\ 50.0\\ 55.0\\ 60.0\\ 55.0\\ 60.0\\ 55.0\\ 60.0\\ 55.0\\ 90.0\\ 100.0\\ 100.0\\ 100.0\\ 100.0\\ 100.0\\ 140.0\\ 160.0\\ 180.0\\ 200.0\\ 240.0\\ 240.0\\ 260.0\\ \infty\end{array}$.90 .94 1.008 1.153 1.231 1.350 1.5538 1.5538 1.5538 1.5538 1.557 1.577 1.557 1.557 1.577 1.557 1.557 1.577 1.557 1.5777 1.5777 1.5777 1.5777 1.5777 1.5777 1.5777 1.57777 1.57777 1.57777 1.577777 1.57777777777	00202 00212 00246 00262 00282 00301 00313 00347 00347 00347 00347 00348 00414 00445 00445 00522 00558 00592 00558 00592 006628 00662 00727 00780 00823 00883 00919 00946 00992 00992 00996	221246880148067840415936730966660 .22224688014826936730996666 .28282829999999999999999999999999999999	6-7777777778850245678999999900000 100.00000000000000000000000

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^aNo pH corrections were necessary for these data.

EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1189A

Condition IV (.9v, 50ml/hr, .03N NaCl

Time(min)	Potential(mv)	$C^{\beta}(\text{equiv/l})^{a}$	c ^β ∕c₀ ^ª	рН
25.0 27.5 30.0 32.5 35.0 37.5 40.0 42.5 45.0 55.0 55.0 55.0 55.0 55.0 55.0 55	1.32 1.41 1.50 1.60 1.69 1.78 1.97 2.22 2.31 1.97 2.22 2.35 1.23 2.22 2.35 3.35 3.35 3.35 3.35 3.35 3	00888 00958 01020 01090 01147 01206 01277 01332 01407 01483 01558 01690 01816 01927 02017 02105 02172 02274 02274 02522 02575 02606 02654 02737	.325789147774197444704125551203578990 .55566677779368889924120350 .999900 .001	$\begin{array}{c} 6.7\\ 6.8\\ 7.4\\ 9.8\\ 10.4\\ 10.66\\ 10.9\\ 10.0\\ 10.0\\ 10.0\\ 10.0\\ 11.1\\ 11.2\\ 23333\\ 11.3\\ 1$

^aCorrected for pH.

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7AG1-1189B

Condition IV (.9v, 50ml/hr, .03N NaCl)

	Potential(mv)	C ^β (equiv/l) ^a	C ^β ∕C₀	рН
$\begin{array}{c} 25.0\\ 27.5\\ 30.0\\ 32.5\\ 35.0\\ 37.5\\ 40.0\\ 42.5\\ 45.0\\ 47.5\\ 50.0\\ 55.0\\ 65.0\\ 70.0\\ 75.0\\ 80.0\\ 90.0\\ 100.0\\ 110.0\\ 120.0\\ 140.0\\ 160.0\\ 140.0\\ 160.0\\ 200.0\\ 240.0\\ 280.0\\ \end{array}$	$\begin{array}{c} 1.46\\ 1.53\\ 1.64\\ 1.75\\ 1.89\\ 2.10\\ 2.29\\ 2.38\\ 7.66\\ 4.02\\ 2.29\\ 2.38\\ 7.66\\ 4.02\\ 2.29\\ 2.38\\ 7.66\\ 4.09\\ 5.99\\$	00993 01043 01120 01188 01266 01339 01418 01488 01545 01611 01675 01811 01930 02030 02116 02201 02263 02263 02355 02418 02483 02533 02604 02662 02712 02712 02761 02832	.351 .368 .3999 .44705 .556919 .556919 .5566919 .5566919 .566777792479 .88879999 .9956599 .99900 .99900 .99900	7.0 7.9 9.8 10.1 10.3 10.4 10.5 10.6 10.6 10.6 10.6 10.6 10.6 10.7 10.8 10.8 10.9 11.0 11.1 11.1 11.1 11.2 11.2 11.2

^aCorrected for pH effect.

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Figure 5. Experimental Data for Run No. 7AG1-1185NE Compared with the Theoretical Curve for y = 2.3, $k_1 = 2.04 \times 10^{-3}$, $k_2 = 1.37 \times 10^{-3}$, and $S_0/C_0 = .14$. Operating Condition - .6v, 50ml/hr, .03N NaC1.



Figure 6. Experimental Data for Run No. 7AG1-1185A (Points) Compared with the Theoretical Curve for y = 1.8, $k_1 = 1.62 \times 10^{-3}$, $k_2 = 1.35 \times 10^{-3}$, and $S_0/C_0 = .15$. Operating Condition - .6v, 50ml/hr, .03N NaCl



Figure 7. Experimental Data for Run No. 7AG1-1185B (Points) Compared with the Theoretical Curve for y = 2.0, $k_1 = 1.71 \times 10^{-3}$, $k_2 = 1.4 \times 10^{-3}$, and $S_0/C_0 = .24$. Operating Condition - .6v, 50ml/hr, .03N NaCl.



Figure 8. Experimental Data for Run No. 7AG1-1179A (Points) Compared with the Theoretical Curve for y = 1.95, $k_1 = 3.25 \times 10^{-3}$, $k_2 = 1.30 \times 10^{-3}$, and $S_0/C_0 = .497$. Operating Condition - .6v, 100ml/hr, .03N NaC1.



Figure 9. Experimental Data for Run No. 7AG1-1179B (Points) Compared with the Theoretical Curve for y = 3.00, $k_1 = 4.63 \times 10^{-3}$, $k_2 = 2.10 \times 10^{-3}$, and $S_0/C_0 = .56$. Operating Condition - .6v, 100ml/hr, .03N NaCl.



Figure 10. Experimental Data for Run No. 7AG1-1187A (Points) Compared with the Theoretical Curve for y = 5.40, $k_1 = 6.55 \times 10^{-3}$, $k_2 = 1.14 \times 10^{-3}$, and $S_0/C_0 = .132$. Operating Condition - .6v, 50ml/hr, .01N NaC1.



Figure 11. Experimental Data for Run No. 7AG1-1187B (Points) Compared with the Theoretical Curve for y = 4.2, $k_1 = 4.83 \times 10^{-3}$, $k_2 = .98 \times 10^{-3}$, and $S_0/C_0 = .156$. Operating Condition - .6v, 50ml/hr, .01N NaCl.

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Figure 12. Experimental Data for Run No. 7AG1-1189A (Points) Compared with the Theoretical Curve for y = 1.65, $k_1 = 1.45 \times 10^{-3}$, $k_2 = .69 \times 10^{-3}$, and $S_0/C_0 = .07$. Operating Condition - .9v, 50ml/hr, .03N NaCl.



Figure 13. Experimental Data for Run No. 7AG1-1189B (Points) Compared with the Theoretical Curve for y = 1.50, $k_1 = 1.31 \times 10^{-3}$, $k_2 = .67 \times 10^{-3}$, and $S_0/C_0 = .06$. Operating Condition = .9v, 50ml/hr, .03N NaCl.

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SUMMARY OF EXPERIMENTAL DATA FOR EXPERIMENTS WITH S.K. VERSUS Ag, AgC1 ELECTRODES

Run No.	Operating Condition	Final Potential(v)	Cell ^b Volume(ml)	Flow Rate (ml/hr)	x/u (min)
7AG1-1185 -1185 -1185 -1179 -1179 -1187 -1187 -1187 -1189 -1189	A I B I NE I A II B III A III B III A IV B IV	.132 .163 .155 .163 .208 .226 .140 .132	14.8 15.6 15.0 16.9 18.2 11.1 11.7 15.1 15.2	48.0 48.0 101.5 101.0 48.5 48.5 47.7 47.9	18.5 19.5 18.8 10.0 10.8 13.8 14.5 19.0 19.1

^aNo equilibration, cell emptied while under .6v regeneration potential.

^bVolume determined from the travel time, x/u, and the flow rate.

means that the cell itself had a .6v potential difference between the cell contacts at the beginning of the experiment and this potential is of such a sign as to cause demineralization if the electrodes were shorted together, a phenomena observed by previous investigators (4). Evidently, the theory will not completely account for the effluent curve for the demineralization phase in such an experiment. The other two experiments were performed under Condition IV (Figures 12 and 13). The curves are fitted visually, consequently the constants obtained are not necessarily those corresponding to the optimum fit. Condition IV involves the use of an applied potential of .9v, whereas all other

conditions involved applied potentials of .6v. Larger pH changes were observed during these experiments, and these changes necessitated pH corrections in the effluent concentration. The possibility that the difficulty in fitting these experiments might involve the pH correction was investigated, because these were the only runs in which a pH correction was required. The accuracy of the pH measuring apparatus is ± 0.1 pH, which could lead to an error of more than 20% in the OH- concentration. Since the pH in these experiments varied from near pH 7.0 to above 11.0, the largest pH corrections occur near the end of the experiment, where the value of Co is established. The uncertainty in Co causes the values of C/Co near the beginning of the experiment to be the most affected, because the concentration values in this range are not changed much by the pH correction, while those near C_0 are changed in almost the same amount as Co. However, the error in the pH measurement is not of sufficient magnitude to account for the difficulty in fitting these experiments.

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The cause of the difficulties in fitting these experiments is obscure; however, it should be noted that the faraday efficiency for them, as will be discussed later, is lower than for experiments performed under the other conditions, and the applied potential (.9v) is approaching the gassing potential. From these observations it seems reasonable to assume that some reactions are occurring which do not occur

at lower potentials, and these reactions cause concentration changes not accounted for by the theory.

The constants k_1 , k_2 , and S_0/C_0 , as found from comparing the experimental data with the best-fitting theoretical curve, are shown in Table 11. The values of D_B given in the same table are calculated from the measured cell volumes (Table 10) using the geometrical area of the electrode face, 77.4 cm². The distance D_{β} varies due to differences in electrode and space thickness. The expression for k_1 is multiplied by D_{β}^{2} to remove its direct dependence on cell geometry, and values of this product are also reported in Table 11. This quantity serves as a check on the consistency of duplicate runs. On this basis the duplicate runs are seen to be consistent with the exception of Condition II. The constant, k_1 , will also vary with the value of the ΔE constant appearing in the expression for k_1 (Equation 8). In the case of Runs 7AG1-1179A and B (Condition II), the difference in $D_B^2 k_1$ for the two runs could be explained on the basis of errors in D_{β} and differences in ΔE , since the $D_{\beta}^2k_1$ difference can vary from .11 cm^2/sec to .04 cm^2/sec , assuming changes of only .02 cm in $\rm D_{\rm g}.$ The values of all constants fall within physically possible limits, and, therefore, do not conflict with the model.

Experimental data for N:G(2:1), 5% PEI electrodes versus S.K. electrodes are compared with the best-fitting

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FITTING CONSTANTS FOR EXPERIMENTS WITH S.K. VS. Ag, AgC1 ELECTRODES

Run No.	Operating Condition	у	k ₁ (sec ⁻¹)x10 ³	k ₂ (sec ⁻¹)x10 ³	S _o /C _o	D _β (cm)	D _B 2xk2x10 ³ (cm ² /sec)
7AG1-1185A -1185B -1185NE -1179A -1179B -1187A -1187B -1189A -1189B	I I II III III IV IV	1.80 2.00 2.30 1.95 3.00 5.40 4.20 1.65 1.50	1.62 1.71 2.04 3.25 4.63 6.55 4.83 1.45 1.31	1.35 1.40 1.37 1.30 2.10 1.41 .98 .69 .67	.150 .240 .140 .497 .560 .132 .156 .070 .060	.19 .20 .19 .22 .24 .14 .15 .20 .20	.06 .07 .08 .15 .26 .13 .11 .06 .04

theoretical curves in Figures 14-17. The original concentration data are given in Tables 12-15, along with the pH data and corrected concentrations. Table 16 summarizes other pertinent experimental data. Figures 14 and 15 and Tables 12 and 13 show data obtained under Condition I; Figures 16 and 17 and Tables 14 and 15 show data obtained under Condition III. No experiments were carried out under the other conditions for this electrode pair. Run Number 7GG1-1191 is the only run for this series in which the concentration of the effluent had to be corrected for pH. In all cases the chosen theoretical curves fit the data quite well.

The constants k_1 , k_2 , and S_0/C_0 , as found from compar_ng the experimental data with the best-fitting theoretical curve, are reported in Table 17. Here again, the values of the constants fall within limits which do not conflict with the model.

A check on the consistency of the model was attempted by comparing values of ΔE and D^{α} as calculated from k_1 and k_2 and their expressions as predicted by the model. This attempt proved to be inconclusive because of the strong dependence of ΔE and D^{α} on the value of D^{β} . Variations within the experimental error of D^{β} yielded widely different values of ΔE and D^{α} .

The final potential of the demineralization cell after equilibration should be related to the amount of salt on the

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7GG1-1188A^a

Ťime(min)	Potential(mv)	C ^β (equiv/l)	c ^β /c _o
25.0 28.0 30.5 33.0 35.5 38.0 45.5 55.5 55.5 55.5 65.5 55.5 55.5 50.5 70.5 70.5 80.5 90.5 110.5 120.5 140.5	3.03 3.16 3.28 3.39 3.498 3.5681 3.681 3.921 4.0821 4.170 4.2258 4.229 4.229 4.322 4.332 4.332	02096 02188 02272 02343 02421 02484 02555 02646 02724 02787 02837 02865 02900 02921 02928 02957 02978 02992 03006 03013	.696 .726 .754 .778 .804 .824 .824 .904 .925 .942 .951 .962 .969 .972 .981 .988 .991 .993 .998 1.000

Condition I (.6v, 50ml/hr, .03N NaCl)

^aNo pH data were obtained for this experiment.

EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7GG1-1188B

······································				
Time(min)	Potential(mv)	C ^β (equiv∕l)	C ^β ∕C₀	рН
22.5 25.0 27.5 30.0 32.5 35.0 37.5 40.0 45.0 50.0 55.0 60.0 70.0 80.0 90.0 100.0 120.0 ∞	2.99 3.121 3.234 3.556 5.567 3.99 5.170 1.1200 1.1200	. 02111 . 02190 . 02269 . 02334 . 02420 . 02484 . 02543 . 02585 . 02648 . 02700 . 02765 . 02822 . 02887 . 02923 . 02959 . 02980 . 02987 . 03009	.702 .728 .754 .776 .804 .826 .847 .866 .893 .919 .938 .919 .938 .959 .971 .983 .990 .993 1.000	20998777998777766555

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Condition I (.6v, 50ml/hr, .03N NaCl)

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EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7GG1-1190^a

Condition III (.6v, 50ml/hr, .01N NaCl)

Time(min)	Potential(mv)	C ^β (equiv∕l)	c ^β ∕c₀
22.5 25.0 27.5 32.5 35.0 370.5 42.0 55.0 55.0 55.0 55.0 55.0 55.0 55.0 5	1.60 1.68 1.79 1.90 2.02 2.15 2.27 2.40 2.55 2.20 2.20 2.20 2.55 2.20 2.20 2.55 2.20 2.55 2.20 2.55 2.20 2.55 2.20 2.55 2.20 2.55 2.55	00376 00396 00422 00448 00480 00509 00571 00600 00631 00688 00734 00778 00815 00845 00845 00871 00892 00923 00947 00962 00984 00991	379 400 426 452 484 514 576 605 637 694 741 785 822 853 879 900 931 956 971 982 993 1000

 $^{\rm a}{\rm pH}$ remained between pH 5 and pH 6 throughout the experiment.

EFFLUENT CONCENTRATION VS. TIME, RUN NUMBER 7GG1-1191

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Time(min)	Potential(mv)	C ^β (equiv/l) ^a	c ^β ∕c₀	рH		
22.5 25.0 27.5 30.0 32.5 35.0 37.5 40.0 45.0 50.0 55.0 60.0 70.0 80.0 90.0 100.0 120.0 140.0 160.0	1.57 1.74 1.90 2.07 2.22 2.38 2.54 2.67 2.91 3.10 3.27 3.41 3.63 3.92 4.01 4.13 4.17 4.21 4.23	. 00365 . 00404 . 00438 . 00475 . 00509 . 00548 . 00584 . 00616 . 00675 . 00718 . 00759 . 00718 . 00759 . 00791 . 00846 . 00886 . 00915 . 00937 . 00966 . 00977 . 00986 . 00990	.367 .441 .4712 .5589 .6823 .55820 .68235 .5688 .776952 .688924 .99538 .99999 .99998 .9998	4.8 4.4 4.2 4.2 4.1 4.1 4.1 4.1 4.0 4.0 4.0 4.0 4.0 4.0 4.0		
00	4.24	.00993	1.000	4.0		

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Condition III (.6v, 50ml/hr, .01N NaCl)

^aCorrected for pH.



Figure 14. Experimental Data for Run No. 7GG1-1188A (Points) Compared with the Theoretical Curve for y = 1.245, $k_1 = 1.31x10^{-3}$, $k_2 = 1.24x10^{-3}$, and $S_0/C_0 = .38$. Operating Condition - .6v, 50ml/hr, .03N NaCl.



Figure 15. Experimental Data for Run No. 7GG1-1188B (Points) Compared with the Theoretical Curve for y = 1.4, $k_1 = 1.50 \times 10^{-3}$, $k_2 = 1.28 \times 10^{-3}$, and $S_0/C_0 = .49$. Operating Condition - .6v, 50ml/hr, .03N NaCl.

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Figure 16. Experimental Data for Run No. 7GG1-1190 (Points) Compared with the Theoretical Curve for y = 3.4, $k_1 = 3.70 \times 10^{-3}$, $k_2 = 1.63 \times 10^{-3}$, and $S_0/C_0 = .27$. Operating Condition - .6v, 50ml/hr, .01N NaCl.



Figure 17. Experimental Data for Run No. 7GG1-1191 (Points) Compared with the Theoretical Curve for y = 2.00, $k_1 = 2.22x10^{-3}$, $k_2 = 1.15x10^{-3}$, and $S_0/C_0 = .135$. Operating Condition - .6v, 50ml/hr, .01N NaCl.

SUMMARY OF EXPERIMENTAL DATA FOR EXPERIMENTS WITH S.K. VS. N:G(2:1), 5% PEI ELECTRODES

Run No.	Operating Condition	Final ^a Potential (v)	Cell ^b Volume (ml)	Flow Rate (ml/hr)	x/u (min)
7GG1-1188A	I	0130	13.5	50.8	15.9
-1188B	I	+.0125	13.1	50.9	15.5
-1190	III	+.0242	12.9	50.4	15.3
-1191	III	+.0444	12.1	48.2	15.0

^aPotential difference taken as potential S.K. with respect to anion-responsive electrode.

^bCell volume determined from flow rate and travel time.

TABLE 17

FITTING CONSTANTS FOR EXPERIMENTS WITH S.K. VS. N:G(2:1), 5% PEI ELECTRODES

Run No.	Operating Condition	g n y	k ₁ x10 ³ (sec-1)	k2x10 ³ (sec-1)	So/Co	D _β (cm)	$\frac{D_{\beta}^{2}k_{1}x10^{3}}{(cm^{2}/sec)}$
7GG1-1188A	I	1.245	1.31	1.24	.380	.17	.04
-1188B	I	1.40	1.50	1.28	.490	.17	.04
-1190	III	3.40	3.70	1.63	.270	.17	.09
-1191	III	2.00	2.22	1.15	.135	.16	.05

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on the electrodes.

The measured final potentials are compared with the values of S_0/C_0 obtained by fitting a theoretical curve to the experimental data in Table 18.

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Run No.	Operating Condition	Final Potential(v)	So/Co
7AG1-1185A -1185A -1179A -1179B -1187A -1187B -1187B -1189A -1189B	I I II III III IV IV	+.132 +.163 +.155 +.163 +.208 +.226 +.140 +.132	.150 .240 .497 .560 .132 .156 .070 .060
7GG1-1188A -1188B -1190 -1191	I I III III	0130 +.0125 +.0242 +.0444	.380 .490 .270 .135

COMPARISON OF FINAL POTENTIALS WITH So/Co

For duplicate runs, i.e. runs under duplicate conditions with the same electrodes, the higher potentials correspond to higher values of S_0/C_0 . In the case where two duplicate electrodes were run under the same conditions, the correspondence was not found (Runs 7GG1-1190 and -1191, Table 18).

CHAPTER V

FARADAY EFFICIENCY

The demineralization theory has an important application in the calculation of the faraday efficiency. The discussion which follows clarifies the necessity for using the theory.

The faraday efficiency at a given time is defined as the ratio of the number of equivalents of salt removed to the number of equivalents of charge passed from the beginning of the phase to the given time. The equivalents of charge are evaluated by graphical integration of the area under the current-time curve. A similar integration of the concentration-time curve would lead to the equivalents of salt removed, except that at a given time an appreciable volume of solution from which salt has been removed remains inside the To evaluate the amount of salt removed from this solucell. tion requires that the concentration be known at various points inside the cell. Equation 43 provides a means of calculating these concentrations once k_1 and k_2 are known, and these are determined by the procedure described previously. A computer program and equation are given in Appendix C for calculating the average concentration inside the cell.

The faraday efficiency as a function of time for S.K.

electrodes versus Ag,AgCl electrodes under operating conditions I-IV are compared in Figures 18 and 19. In all experiments except those performed under Condition IV (7AGl-1189A and B, Figure 19) there is no significant difference between the various operating conditions. The Condition IV experiments show lower efficiencies as would be expected if the higher applied potential used in these experiments was causing reactions other than those resulting in salt removal.

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Efficiencies for N:G(2:1), 5% PEI electrodes paired with S.K. electrodes are shown as a function of time in Figure 20. These experiments were performed under Condition I and Condition III, and there appears to be no significant difference in the efficiencies under the two conditions. The efficiencies for these pairs of carbon electrodes are slightly smaller than efficiencies for the S.K., Ag,AgCl electrode pairs mentioned above, although they all level off between 65 and 90%. The lower efficiencies are not surprising, considering the mixed responsiveness of the N:G(2:1), 5% PEI electrodes which have cation responsive character, as well as anion responsive character.

The faraday efficiency is seen to be low initially and to level off to a relatively constant value. These low initial efficiencies are due to the fact that the actual demineralization process involves some removal of salt within the electrode pores not balanced immediately by migration from β , and this is not accounted for in the model.






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ure 20. Faraday Efficiency as a Function of Time. O - 7GG1-1188A, □ - 7GG1-1188B, ∇ - 7GG1-1190, O- 7GG1-1191

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Experiments with both S.K. versus Ag,AgCl electrodes and S.K. versus N:G(2:1), 5% PEI demonstrate the high faraday efficiency for this demineralization process.

CHAPTER VI

CONCLUSIONS

The concentration changes occurring in the demineralization can be explained by choosing a relatively simple model to represent the more complex carbon electrode system composing the demineralization cell. A model consisting of solution compartments separated by permselective membranes was chosen in this research, the electrodes being represented by compartments of fixed volume. From this model an equation was arrived at which fits the concentration-time curve for the effluent from the demineralization cell. This equation contains three parameters which in principle can be calculated from the model, but which involve quantities which are difficult to measure. Because of the difficulty in calculating the fitting parameters, a technique was found in which these parameters were evaluated from comparison of experimental to theoretical curves.

The theoretical equation was tested against experiments performed under a variety of operating conditions, involving flow rates, feed solution concentration, and applied potential. It was shown that for both S.K. electrodes versus Ag,AgCl electrodes and S.K. electrodes versus N:G(2:1), 5% PEI (an anion responsive carbon electrode), the theoretical

equation was successful in fitting the concentration-time curves. Experimental data obtained under the highest applied potentials were not fitted to the same precision, but nevertheless, were successfully treated.

The theory has been applied to the calculation of the faraday efficiency of the process. The efficiencies thus calculated permit a comparison of the various operating conditions and electrode combinations. For the electrode pair, S.K. versus Ag,AgCl, the efficiencies for all operating conditions were above 90% except in the case of the highest applied potential for which the efficiency was 70-75%. The electrode pair, S.K. versus N:G(2:1), 5% PEI, demonstrated efficiencies of 65-90% which are surprisingly high, considering the mixed responsiveness of the N:G(2:1), 5% PEI electrode.

APPENDIX A

EQUIPMENT

The demineralization apparatus can be divided into three groups according to function: the demineralization cell, the operating and controlling equipment, and the measuring equipment.

Demineralization Cell

A brief description of the cell will suffice, since a complete description has been recorded elsewhere (3, 30). The demineralization cell consists of a pair of end-plates for support and electrical connection to the electrodes, the electrodes, separators for spacing the electrodes and a pair of Lucite plates, which are bolted around the end-plates for support. Cells of this type are described and pictured by Stevens (30). The end-plates are made from sheet graphite which is impregnated with a high-melting wax, Pyseal, to prevent solution leakage. The electrodes are prepared by depositing carbon or carbon-graphite mixtures on a fiber backing material from a slurry. Procedures for preparing electrodes are described by Tucker (4). The electrodes are held against the end-plates by separators made of plastic netting, and spacing between the electrodes is maintained by means of gaskets cut from sheet polyethylene. Electrical connection to the electrodes is made by direct fitting of

brass machine screws into threaded holes in the end-plates. The solution inlet and outlet parts are also fitted directly into the end-plates.

Operating Equipment

The solution is circulated through the demineralization cells by means of Beckman Solution Metering pumps. Power is supplied to the cells by Kepco solid-state DC power supplies which are operated at a constant potential.

Measuring Equipment

The demineralization cells are contained in an air bath maintained at $25.0 \pm 0.2^{\circ}$ C, which is necessary for accurate, reproducible conductivity measurements on the cell effluent. Conductivity measurements are made with an Industiral Instruments RA-4 Solu Meter. The RA-4 Solu Meter gives a potential output which is proportional to the conductivity. This potential is recorded on one channel of a Westronics Model D 11A dual channel recorder. The other channel is used in conjunction with a Westronics Model SSVA-1 input module to record the electrical current flowing through the cell. The conductance cells are made of glass tubing and contain spirals of platinum wire platinized in the usual manner.

The pH of the cell effluent can be continuously recorded by means of electrodes inserted into the solution stream and connected through a Sargent pH Recording Adapter to a potentiometric recorder.

APPENDIX B

CALIBRATION OF CONDUCTIVITY METER

Concentrations determinations on the effluent from the demineralization cell are made by measuring the conductivity and converting it to concentration. The conductivity meter used gives a d.c. potential output which is proportional to the conductivity, and this potential is recorded with a recording potentiometer. Using solutions of known concentration, the potential scale of the recorder was calibrated directly in concentration units. Data are given below from which calibration curves were plotted.

The specific conductivity of a solution can be determined from the recorded potential by first finding the corresponding concentration from the calibration and then using the empirical equation given by MacInnes (31) for sodium chloride

 $L \times 10^3 = (126.45C + 95.79C^2 - 65.29C^3)(1 - 2273C^{1/3}) - 59.78C^{3/2}$

CALIBRATION I

Experiment: 7AG1-1185A Conductivity Cell: LC-5e

NaCl Conc.	(equiv/l)	Potential (mv)
·		
	•	

.0020

NaCl Conc. (equiv/l)	Potential (mv)
.0050	.61
.0071	.84
.0100	1.20
.0150	1.78
.0200	2.33
.0305	3.48
.0401	4.56
CALIB	RATION II
Experiments: 7AG1-118	B5NE, 7GG1-1188A
Conductivity Cell: LC	C-5e
Least Squares Data: s	slope = 141.8 mv-1/equiv,
intercept = .06 m	nv
NaCl Conc. (equiv/l)	Potential (mv)
.00208	.32
.00686	1.02
.00998	1.49
.01479	2.19
.02000	2.91
.02506	3.62
.03000	4.30
.03498	5.00
CALIBR	ATION III
Experiment: 7AG1-118	7A
Conductivity Cell: Lo	C-13
Least Squares Data:	slope = 416.8 mv-1/equiv,
intercept = .05	mv
NaCl Conc. (equiv/l)	Potential (mv)
.00208	.90
.00686	2.93
.00998	4.22
.01479	6.20

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CALIBRATION I--Continued

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CALIBRATION IV

Experiments: 7AG1-1179A, 7AG1-1185B, 7GG1-1188B Conductivity Cell: LC-5e Least Squares Data: slope = 139.2 mv-1/equiv, intercept = .05 mv

NaCl Conc. (equiv/l)	Potential (mv)
.00208	.32
.00686	1.00
.00998	1.43
.01479	2.14
.02000	2.87
.02506	3.56
.03000	4.21
.03498	4.90

CALIBRATION V

Experiment: 7AG1-1187B Conductivity Cell: LC-13 Least Squares Data: slope = 415.6 mv-1/equiv, intercept = .06 mv

NaCl Conc. (equiv/l)	Potential (mv)	
.00208 .00686 .00998 .01479 .02000	.88 2.92 4.24 6.27 8.31	

CALIBRATION VI

Experiments: 7GG1-1190, 7GG1-1191 Conductivity Cell: LC-13 Least Squares Data: slope = 410.5 mv-1/equiv, intercept = .05 mv

.00208

.88

CALIBRATION VI--Continued

NaCl Conc. (equiv/l)	Potential (mv)
.00686	2.87
.00998	4.18
.01479	6.17
.02000	8.22
CALIBRA	TION VII
Experiments: 7AG1-1179	9B, 7AG1-1189A, 7AG1-1189B
Conductivity Cell: LC	-5e
Least Squares Data: si	lope = 139.0 mv-1/equiv,
intercept = .08 m	v
NaCl Conc. (equiv/l)	Potential (mv)
.00208	.40
.00686	1.00
.00998	1.45
.01479	2.15
.02000	2.87
.02506	3.57
.03000	4.25
.03498	4.94

APPENDIX C

COMPUTER PROGRAMS

The FORTRAN language computer programs listed below were written so that the IBM 1410 computer could be utilized in this research. Without the aid of the IBM 1410 these calculations would be extremely laborious. Program I is written to calculate values of C^{β}/C_{0} for a series of z values from the equation

$$\frac{C^{\beta}}{C_{o}} = 1 - \frac{S_{o}}{C_{o}} e^{-y-z} \sum_{m=0}^{\infty} \frac{z^{m}}{m!} \sum_{j=0}^{m} \frac{y^{j}}{j!} + \frac{S_{o}}{C_{o}}$$

Values of y and S_0/C_0 are read into the computer and for each y, S_0/C_0 combination twenty-five values of C^{β}/C_0 are calculated for a range of z values from .2 to 12.5.

Program II is written to calculate the average value of the function

$$F = C_0 e^{(k_2/k_1-1)y_e - k_2 t} \sum_{m=0}^{\infty} \frac{(t - y/k_1)^m}{m!} \sum_{j=0}^m \frac{y^j}{j!}$$

Multiplying this function by $(1 - S_0/C_0)$ and adding S_0 (from $C_0(S_0/C_0)$) yields the average concentration in the demineralization cell at time t. The average value is arrived at by integration of this function over y using Simpson's Rule and dividing the resulting integral by the maximum value of y.

The information read into the computer includes y, k_1 , k_2 , C_0 , t, and the number of divisions to be used in the Simpson's Rule integration. The output is the average value of function and the time.

PROGRAM I

	DIMENSION A(5)
	READ 97,(A(I),I=1,5)
97	FORMAT(5F10.4)
1	READ 99,Y
99	FORMAT (F8.2)
	IF(Y)101,101,2
2	ҮҮ=-Ү
	EPY=EXPF(YY)
	DO 10 K=1,25
	J=2
	Z=K
	IF(K-15)16,16,17
16	Z=Z*.2
	GO TO 18
17	Z=Z-12.5
18	ZZ=-Z
	EPZ=EXPF(ZZ)
	M=O
	TERM=1.0
	SUM=0.0

PROGRAM I--Continued

11 MM=M+l

IF(J-2)31,32,31

32 TER=1.0

,

HOLD=1.0

SL=0.0

DO 20 L=1,MM

TER=TER*HOLD

SL=SL+TER

TES=TER/SL

IF(TES-.1E-6)21,21,22

21 J=3

GO TO 31

22 XL=L

HOLD=Y/XL

- 20 CONTINUE
- 31 SUM=SUM+TERM*SL

TEST=(TERM*SL)/SUM

IF(TEST-.1E-3)41,41,42

42 M=M+1

XM⊨M

TERM=(TERM*Z)/XM

GO TO 11

CCO=EPY*EPZ*SUM 41

PROGRAM I--Continued

98	FORMAT(49X,F8.2,5X,F8.2,5X,F12.5,fX,I4)
	DO 30 II=1,5
	$CK=CCO^{*}(1A(II))+A(II)$
	PRINT 96,CK,A(II) -
96	FORMAT(49x,3HCK=,E15.8,5X,F10.4)
30	CONTINUE
10	CONTINUE
	GO TO 1
101	STOP
	END
	PROGRAM II
	DIMENSIONEKY(51), TYK(51), F(3)
2	READ99,Y,XK1,XK2,C0,NN
99	FORMAT(F10.3,2E15.8,F10.6,I4)
	IF(Y)101,101,1
1	XMULT=XK2/XK1-1.0
	XNN=NN
	XY=Y/XNN
	XX=0.0
	EKY(1)=1.0
	DO10N=1,NN
	XX=XX+XY
	XKY=XX*XMULT
	NX=N+1

PROGRAM II--Continued

	-
	EKY(NX) = EXPF(XKY)
10	CONTINUE
6	READ98,T
98	FORMAT(F10.0)
	IF(T)2,2,3
3	ХКТ= (- ХК2) *Т
	EKT=EXPF(XKT)
	LJ=2
	F(1)=CO
	YX=0.0
	TYK(1) = T
	DO20I=1,NN
	II=I+l
	YX=YX+XY
	TYK(II)=T-YX/XK1
20	CONTINUE
	XD=0.0
	PRINT96,T
96	FORMAT(60X, 2HT=, F10.0)
	SUMS=0.0
	DO30K=1,NN
	XD=XD+XY
	J K =2
	KK=K+1

FACT=CO*EXT*EKY(KK)

PROGRAM II--Continued

SUM=1.0

TERM=1.0

M=O

13 M=M+1

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XM=M

TERM=TERM*XK2*TYK(KK)/XM

IF(JK-2)11,39,11

39 TER=1.0

SJ=0.0

MM=M+1

DO4OJ=1,MM

SJ=SJ+TER

TESTJ=TER/SJ

IF(TESTJ-.1E-4)38,38,12

38 JK=JK+1

GO TO 11

12 XJ=J TER=(TER*XD)/XJ

40 CONTINUE

11 HOLD=TERM*SJ

SUM=SUM+HOLD

CHECK=HOLD/SUM

TEST=ABSF(CHECK)

IF(TEST-.1E-4)14,14,13

14 IF(LJ-2)21,21,22

PROGRAM II--Continued

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21 F(LJ)=FACT*SUM LJ=LJ+1 GO TO 30 F(LJ)=FACT*SUM 22 $SIMP=XY/3.0^{*}(F(1)+4.0^{*}F(2)+F(3))$ SUMS=SUMS+SIMP F(1)=F(LJ)LJ=2 30 CONTINUE AVGC=SUMS/Y PRINT97,AVGC FORMAT(59X,E15.8) 97 GOTOG 101 STOP END

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GLOSSARY

DC-7

Effluent Curves

N:G(2:1), 5% PEI

Demineralization cell type 7 developed at the University of Oklahoma

Plots of the concentration ratio, C^β/C_o versus time for the solution flowing out of the demineralization cell

A standard anion responsive carbon electrode developed at the University of Oklahoma. A mixture of the charcoal, Norit A, to Dixon's Airspun 200-10 graphite in the ratio two parts charcoal to one part graphite containing PEI in the amount of 5% of the carbon-graphite weight.

PEI

S.K.

Polyethylene imine

Standard cation electrode developed at the University of Oklahoma. It consists of mixed acid treated N:G(2:1) which has been deposited from a water slurry of the N:G(2:1), tannic acid, and ammonium hydroxide, on a fibrous backing material.