RELATIVE PARTICLE AND FILM DIFFUSION CONTROL
IN COUNTERCURRENT COLUMNAR ION EXCHANGE
FOR THE SYSTEM (Cu$^{++}$-Na$^+_2$)SO$_4^-$ - DOWEX 50W-X8

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This book contains numerous pages with the original printing being skewed differently from the top of the page to the bottom.
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NOMENCLATURE

\( A_{0,1,2,3} \) - coefficients corresponding to a power series fit of equilibrium data for a (\( \text{Cu}^{++}-\text{Na}^{+} \)) \( \text{SO}_4^{2-} \) - Dowex 50W-X8 system.

\( A_I \) - coefficient for the \( I^{th} \) difference equation of the resin diffusion equation.

\( B_{1,2,3,4} \) - coefficients corresponding to a power series fit of equilibrium data for a (\( \text{Cu}^{++}-\text{Na}^{+} \)) \( \text{SO}_4^{2-} \) - Dowex 50W-X8 system.

\( B_I \) - coefficient for the \( I^{th} \) difference equation of the resin diffusion equation.

\( C_{1,2} \) - constants contained in the \( \text{Cu}^{++} \) variation equation for the bulk solution phase.

\( C_{\text{Cu}} \) - concentration of \( \text{Cu}^{++} \) in the resin, moles/cm\(^3\).

\( C_I \) - coefficient for the \( I^{th} \) difference equation of the resin diffusion equation.

\( C_0 \) - total equivalent in liquid per liter of solution.

\( D_I \) - coefficient for the \( I^{th} \) difference equation of the resin diffusion equation.

\( D_{\text{Cu}}, D_{\text{Na}} \) - self diffusivity of \( \text{Cu}^{++} \) and \( \text{Na}^{+} \) ions in the film, cm\(^2\)/sec.

\( D_{\text{Cu}}, D_{\text{Na}} \) - self diffusivity of \( \text{Cu}^{++} \) and \( \text{Na}^{+} \) ions in the resin phase, cm\(^2\)/sec.

\( D_{\text{Cu-Na}} \) - interdiffusion coefficient in the resin, cm\(^2\)/sec.

\( D_P \) - resin particle diameter, cm.

\( D(\alpha, \beta) \) - interdiffusion coefficient in the resin at discrete position \( \beta \) and time \( \alpha \).

\( K_F \) - mass transfer coefficient in film, \( \frac{\text{meq}}{\text{cm}^2 \cdot \text{sec}} \).

\( l \) - length, cm.

\( L \) - length of the contacting section, cm.

\( N \) - number of discrete position points.

\( N_{\text{Cu}} \) - number of moles of \( \text{Cu}^{++} \) in the resin per unit time per unit area, moles/cm\(^2\)\cdot sec.
$N_{Re}$ - Reynold's number, $D_R V_L/\nu$.

$N_{Sc}$ - Schmidt number, $\mu/\rho D^F$.

$N_{Sh}$ - Sherwood number, $K_F D_p / D_{Cu-Na}^F$.

PPG - number of particles per gram of resin.

$Q$ - total resin capacity, meq/gm dry resin.

$r$ - radial direction, cm.

$R$ - radius of the resin particle, cm.

$V_L$ - flow rate of the bulk or solution phase, cm/sec.

$V_R$ - flow rate of the resin phase, cm/sec.

$W^R_{Cu}, W^F_{Cu}$ - instantaneous mass transfer rate per particle in the resin and film respectively, meq/sec.

$W^R_{Cu,G}, W^F_{Cu,G}$ - instantaneous mass transfer rate per gm of resin in the resin and film respectively, meq/sec/gm.

$W^C_{Cu,G}$ - instantaneous mass transfer rate per gm of resin calculated from the combined control model, meq/gm·sec.

$X_1, X_2$ - equivalent fraction of $Cu^{++}$ in the bulk solution at the inlet and outlet of the contacting section respectively.

$X_B$ - equivalent fraction of $Cu^{++}$ in the bulk or solution phase.

$X_{Cu}, X_{Na}$ - equivalent fraction of $Cu^{++}$ and $Na^+$ in the liquid film respectively.

$X_s$ - equivalent fraction of $Cu^{++}$ in the film at the resin surface.

$Y_1, Y_2$ - equivalent fraction of $Cu^{++}$ in the resin phase at the inlet and outlet of the contacting section respectively.

$Y_{Cu}, Y_{Na}$ - equivalent fraction of $Cu^{++}$ and $Na^+$ in the resin respectively.

$Y_s$ - equivalent fraction of $Cu^{++}$ in the resin at the resin surface.

$\bar{Y}_{Cu}$ - average equivalent fraction of $Cu^{++}$ in the resin.

$Y(\alpha, \beta)$ - equivalent fraction of $Cu^{++}$ at the discrete radial position $\beta$ and resin time $\alpha$.

$Y(I)$ - equivalent fraction of $Cu^{++}$ at discrete radial position $I$ and resin time $\alpha$. 
YY(I) - equivalent fraction of Cu\(^{++}\) at discrete radial position I
and resin time \(\alpha + \Delta\alpha\).

\(Z_{Cu}, Z_{Na}\) - valence of Cu\(^{++}\) and Na\(^{+}\) ions respectively, eq./mole.

\(\alpha\) - dimensionless resin time and distance, \(t/\tau = l/L\).

\(\beta\) - dimensionless radial direction, \(r/R\).

\(\Delta r\) - thickness of a spherical shell, cm.

\(\Delta X\) - difference between outlet and inlet Cu\(^{++}\) equivalent fractions
in the bulk phase.

\(\Delta\alpha\) - dimensionless time increment.

\(\Delta\beta\) - dimensionless position increment.

\(\varepsilon\) - void fraction in packed bed, \(cm^3/cm^3\).

\(\mu\) - solution viscosity, gm/cm sec.

\(\rho\) - solution density gm/cm\(^3\).

\(\rho_{R}, \rho_{R}\) - gm dry resin per ml of wet resin.

\(\tau\) - resin resident time, \(L/V_{R}\), sec.
1.0 INTRODUCTION

In a continuous counter-current ion exchange column, the solution is in continuous counter-current contact with the resin phase. Mass transfer takes place, exchanging ions from the solution phase with different ions in the resin phase. Due to this mass transfer process, the solution and resin phase compositions change continuously as they pass through the length of the column.

Assuming the transport of ions within the resin phase occurs by a process of ionic diffusion, the well understood mathematical relations governing this process can be applied to determine if the transport within the resin phase governs the kinetics of the column. If indeed the resin phase does control the mass transport, then mathematical relationships describing the ion exchange column kinetics may be applied to an analytical design model for the continuous counter-current ion exchange column.

Similarly, the liquid film can be assumed to control the mass transport process and the column kinetics described on this basis.

This work examines the continuous counter-current ion exchange column data of Olsen and Meyer (1, 2, 3) to determine under what conditions of solution concentration (cupric-sodium sulfate) and resin particle size (Dowex 50W-X8) the column kinetics are controlled by mass transport in the resin or the solution phase.

In undertaking this study, an expression for the change in the solution phase Cu$^{++}$ composition along the length of the column was obtained from the experimental data of Olsen and Meyer. Using this time dependent expression, the transfer of Cu$^{++}$ ions from the solution phase* into the resin was

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*Implied although not specifically stated is the simultaneous transfer of the other counter ion, Na$^+$, from the resin phase into the solution phase.
assumed (4) to 1) controlled completely by ionic diffusion in the resin phase, 2) controlled completely by mass transport through a liquid layer adhering to the particle surface (the so-called "film"), and 3) controlled by the resistance of both the liquid film and resin particle phases (combination of 1) and 2)). Mass transfer rates and concentration profiles obtained, based on assumptions 1), 2) and 3) above, are compared to determine which of the two phases offered the major mass transfer resistance.
2.0 DESCRIPTION OF APPARATUS

Column operating data used in this study were obtained from the earlier work performed by Olsen and Meyer. These workers constructed, operated and evaluated a counter-current, liquid-solids contactor for continuous ion exchange operations (1, 2, 3).

The continuous counter-current ion exchange system consists of two columns; one for the sorption of Cu\(^{++}\) from the feed solution and the other for the regeneration of the resin (conversion back to Na\(^+\) form). Each column includes a resin reservoir, resin valve, active sorption section, dead section, rinsing section and a bottom chamber (Figure 1(a) and 1(b)).

The resin is moved down and through the column by a pulsing device. As the bellows of the pulser expands (Figure 2), an increase in volume in the column takes place, which causes the resin valve to open and allows resin from the reservoir to be drawn down into the active section of the column. As the bellows collapse, the volume of the system decreases and closes the resin valve. The process solution entering the bottom of the active section and moving upward is then permitted to leave the column through an outlet in the resin valve. During this positive part of the cycle, the pulse causes the resin bed to divide at the bottom of the column and a quantity of resin is ejected through the resin outlet line (bottom section of the columns) to the resin reservoir of the other column. The feed solution is metered into the active sorption section continuously.

The rate at which resin leaves column one is controlled by a resin metering device located at the top of column two. The resin return line from column one serves as the input to the meter. The resin meter consists of 3 porous cylindrical baskets (1/2 in. diameter, 1 in. in length). The
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Fig. 1a. Continuous countercurrent ion exchange contactor of Meyer and Olsen.
THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE. THIS IS AS RECEIVED FROM CUSTOMER.
Fig. 1b. Schematic drawing of the continuous countercurrent ion exchange contactor of Olsen and Meyer (1,2,3).
baskets are held between two polyethylene rotating disks which in turn are held between two stationary plates. As the disk rotates, a basket picks up resin from the resin return line through a hole in the upper plate. It rotates 180°, where the resin is then released through a hole in the lower stationary plate into the reservoir of column two. The setting and control of the resin flow rate is controlled by adjusting the angular velocity of the meter. The meter is driven by a variable speed motor.

To control the resin height in column two, a photo cell-electric pinch cock device is employed. By keeping the resin level in column two constant this device will keep the resin flow rates in the two columns equal on a time average basis.
3.0 EXPERIMENTAL DATA

In the experimental work of Olsen and Meyer, CuSO$_4$ solutions were used as the feed for the continuous counter-current ion exchange column previously described, while Na$_2$SO$_4$ solutions were used as the eluent (resin regeneration). Dowex 50W-X8 (20 to 50 mesh size) was the ion exchange resin used. Dowex 50W-X8 is a strong cation exchange resin made by nuclear sulfonation of styrene-divinylbenzene beads (5). It is commercially available in the form of spherical particles of various diameters.

Figure 3 shows the continuous counter-current ion exchange system as considered here and the experimental or operational data needed for this study. Table 1 lists the experimental data used in this study.
Fig. 3. Operational data for the continuous counter-current contactor.
Table 1. Experimental Data of Olsen and Meyer (1, 2, 3) for a Continuous Countercurrent Ion Exchange Contactor

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Soln. Normality</th>
<th>$V_R$ Resin Flow Rate cm/sec</th>
<th>$V_L$ Soln Flow Rate cm/sec</th>
<th>L Column Height cm</th>
<th>$X_1$ Soln Ph. Eq. Fract.</th>
<th>$Y_1$ Resin Ph. Eq. Fract.</th>
<th>$X_2$ Soln Ph. Eq. Fract.</th>
<th>$Y_2$ Resin Ph. Eq. Fract.</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.2</td>
<td>1.00</td>
<td>4.0</td>
<td>18.9</td>
<td>123.5</td>
<td>0.995</td>
<td>0.980</td>
<td>0.230</td>
<td>0.235</td>
</tr>
<tr>
<td>14.2</td>
<td>1.00</td>
<td>4.0</td>
<td>18.9</td>
<td>62.6</td>
<td>0.975</td>
<td>0.948</td>
<td>0.305</td>
<td>0.239</td>
</tr>
<tr>
<td>15.2</td>
<td>1.00</td>
<td>3.0</td>
<td>14.0</td>
<td>62.6</td>
<td>1.000</td>
<td>0.956</td>
<td>0.255</td>
<td>0.203</td>
</tr>
<tr>
<td>16.2</td>
<td>0.50</td>
<td>4.0</td>
<td>37.5</td>
<td>62.6</td>
<td>0.984</td>
<td>0.961</td>
<td>0.357</td>
<td>0.383</td>
</tr>
<tr>
<td>17.2</td>
<td>0.50</td>
<td>4.0</td>
<td>37.5</td>
<td>32.4</td>
<td>0.990</td>
<td>0.931</td>
<td>0.515</td>
<td>0.478</td>
</tr>
<tr>
<td>20.2</td>
<td>0.20</td>
<td>4.0</td>
<td>96.4</td>
<td>32.4</td>
<td>0.952</td>
<td>0.946</td>
<td>0.404</td>
<td>0.358</td>
</tr>
<tr>
<td>21.2</td>
<td>0.20</td>
<td>2.0</td>
<td>48.5</td>
<td>32.4</td>
<td>0.954</td>
<td>0.976</td>
<td>0.136</td>
<td>0.224</td>
</tr>
<tr>
<td>22.2</td>
<td>1.00</td>
<td>4.0</td>
<td>18.7</td>
<td>32.4</td>
<td>0.968</td>
<td>0.876</td>
<td>0.455</td>
<td>0.343</td>
</tr>
<tr>
<td>23.2</td>
<td>1.00</td>
<td>4.0</td>
<td>9.4</td>
<td>32.4</td>
<td>0.962</td>
<td>0.946</td>
<td>0.355</td>
<td>0.314</td>
</tr>
</tbody>
</table>
4.0 VARIATION OF Cu$^{++}$ CONCENTRATION IN SOLUTION PHASE

The variation of the Cu$^{++}$ concentration in the solution or bulk phase, $X_B$, may be expressed by a relation which reflects the resin flow rate and the column (contact) length. This concentration is expected to be inversely proportional to the resin flow rate, $V_R$, and directly proportional to the column length $L$. Correlation of the experimental data of Olsen (3) and Olsen and Meyer (1, 2) showed that $X_B$ can be expressed as

$$X_B = X_2 + C_1 \left( \frac{L}{V_R} \right) C_2$$  \hspace{1cm} (1)

where $C_1$, $C_2$ = constants determined by the operating conditions of the column. Noting that

$$\tau = \frac{L}{V_R}$$  \hspace{1cm} (2)

where $\tau$ = time the resin spends in the column, sec., Eq. (1) becomes

$$X_B = X_2 + C_1 (\alpha \tau) C_2$$  \hspace{1cm} (3)

where $\alpha$ = the dimensionless resin time, $t/\tau$.

Analyzing the data ($X_1$, $X_2$, $Y_2$, $\tau$) of Olsen (3) and Olsen and Meyer (1, 2) by a least squares procedure, the constants ($C_1$, $C_2$) were evaluated. Table 2 lists these for total solution normalities of 1.0, 0.50 and 0.20 (Cu$^{++}$/Na$^+$, SO$_4^{2-}$) respectively.
Table 2. Values of $C_1$, $C_2$ for the $X_B$ Expression
Describing the Cu$^{++}$ Concentration Variation
In the Bulk Solution Phase.

<table>
<thead>
<tr>
<th>Total Solution Normality</th>
<th>$C_1^+$</th>
<th>$C_2^+$</th>
<th>Average % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.034</td>
<td>0.427</td>
<td>4.6</td>
</tr>
<tr>
<td>0.50</td>
<td>0.077</td>
<td>0.310</td>
<td>3.6</td>
</tr>
<tr>
<td>0.20</td>
<td>0.015</td>
<td>0.578</td>
<td>0.0*</td>
</tr>
</tbody>
</table>

*C$_1$, C$_2$ were solved by simultaneous solution of Eq. 3 for the 0.2 N solution.

†C$_1$, C$_2$ determined for 20-50 mesh Dowex 50W-X8 as delivered.
5.0 THEORY

5.1 Fundamentals

In simple terms ion exchange resin (6) is a three dimensioned cross-linked network of hydrocarbon chains which carry fixed ionic groups. The electric charge of these fixed ionic groups (for example $-\text{SO}_3^-$, $-\text{COO}^-$ and $-\text{NH}_3^+$) is balanced by mobile oppositely charged counter ions. These counter ions are free to diffuse within the resin structure.

The term ion exchange as used here is defined as the reversible exchange of ions (counter ions) between the resin structure and a liquid solution phase; it is assumed there is no substantial change in the structure of the resin accompanying the exchange of one ion for another (5). For example, consider a bed of spherical ion exchange particles of uniform size saturated with the counter ion $A^+$ in a solution of electrolyte (BY) where $B^+$ is a second counter ion. As equilibrium is approached, $A^+$ diffuses out of the particles into the solution while ions $B^+$ simultaneously diffuse from the solution into the particles. This interdiffusion (4) of counter ions is called ion exchange and in equation form may be expressed as

$$AR + B^+ \leftrightarrow BR + A^+$$

where $R^-$ = the ion exchange resin.

Ion exchange as a consequence of the electroneutrality requirement is a stoichiometric process. As counter ion $A^+$ diffuses out of the particle (due to a concentration gradient) an electronic surplus charge of the opposite sign will arise within the particle. This charge will attract the other counter ion $B^+$. Thus $B^+$ is taken up by the resin to maintain a quasi-steady state condition of neutrality. Hence the fluxes of counter ions in terms of chemical equivalents must be equal in magnitude although in opposite directions.
While fluxes of counter ions are equal in magnitude, their mobilities may be quite different. If the mobility is different, a diffusion potential (4) is created by the faster ion. The charge created will reduce the mobility of the faster ion while accelerating the diffusion of the slower ion; thus the fluxes of the two counter ions will tend to become equal. The fluxes of the two counter ions are thus electrically coupled and it is this important fact that differentiates ion exchange from a simple diffusion problem where the driving force is simply a concentration gradient.

Because of electrolyte (BY) sorption and desorption (which accompanies ion exchange) the co-ion content of the ion exchange resin may be changed leading to slight deviations from the stoichiometric behavior just described. Co-ions are mobile ions with charges of the same sign as the framework or fixed ionic group (in the above example, $Y^-$ is a co-ion). Usually the co-ion concentration within the resin particle is small (4) so that deviations from the stoichiometric requirement can be neglected.

The rate controlling step for ion exchange is the interdiffusion of counter ions. The transfer of counter ions by diffusion takes place in both the solution and the resin phases. The process of transferring an ion from the solution and into the resin particle can be described in terms of transport (4) of the ion through 1) the bulk solution, 2) a liquid film which adheres to the resin particle and 3) the resin particle (Figure 4).

Because of good mixing, concentration differences through the bulk solution are assumed small and thus transport of the ions through the bulk phase is considered rapid and not rate controlling. The rate controlling step must then involve transport of counter ions through the liquid film and/or the resin particle.
Fig. 4. Transfer of Cu^{++} through the solution and resin particle.
This study was directed to determine the controlling step for the transfer of Cu\(^{++}\) from an upwardly flowing bulk solution (cupric-sodium sulfate) into a downward flowing resin phase (Dowex 50W-X8).

5.2 Particle Diffusion Control

To study particle diffusion control of the overall ion exchange process, it is first assumed that the major mass transfer resistance is in the resin particle while the resistance due to the presence of the liquid film is neglected. Other necessary assumptions (4, 6, 7) are as follows:

1. a quasi-homogeneous phase exists in the resin particle,
2. the concentration of fixed ionic groups and individual diffusion coefficients are assumed to be constant,
3. the presence of co-ions, variation of selectivity coefficients, changes in swelling and swelling pressure are neglected,
4. gradients of activity coefficients are neglected,
5. the surface of the resin particle is in equilibrium with the bulk liquid concentration as the particle falls through the column,
6. the bulk liquid concentration may be expressed by Eq. (3).

First consider a spherical resin particle (with Na\(^+\) counter ions) of radius R which comes into contact with a bulk solution concentration of Cu\(^{++}\); the Cu\(^{++}\) concentration is changing with time. Following the standard procedure (8) of writing a mass balance (with no production) on Cu\(^{++}\) transport through a spherical shell of thickness \(\Delta r\), in the radial direction (neglecting polar and azimuthal dependence due to symmetry), and taking

\[
\lim_{\Delta r \to 0} \frac{\Delta r}{\Delta r} = 0
\]
the following expression for the Cu\textsuperscript{++} transfer is obtained

$$\frac{-1}{r^2} \frac{\partial}{\partial r} (r^2 N_{Cu}) = \frac{\partial C_{Cu}}{\partial t}$$

(5)

where $N_{Cu} =$ number of moles of Cu\textsuperscript{++} per unit time per unit area, moles/cm\textsuperscript{2} · sec,

$C_{Cu} =$ concentration of Cu\textsuperscript{++} in moles per unit volume, moles/cm\textsuperscript{3},

$t =$ time, sec,

$r =$ radial distance from the center of the resin particle, cm.

Assuming that the mass transport is purely diffusional, neglecting the bulk flow term and introducing Fick's first law,

$$N_{Cu} = -D_{Cu-Na}^R (r) \frac{\partial C_{Cu}}{\partial r}$$

(6)

where the diffusivity $D_{Cu-Na}^R$ is a function of $r$. Substituting Eq. (6) into Eq. (5) the following relation is obtained:

$$\frac{\partial C_{Cu}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 D_{Cu-Na}^R (r) \frac{\partial C_{Cu}}{\partial r}].$$

(7)

Dividing both sides of Eq. (7) by $Z_{Cu}/Q_{R}$ and placing Eq. (7) in dimensionless form the following equation is obtained

$$\frac{\partial Y_{Cu}}{\partial \alpha} = \frac{r}{R^2 \beta^2} \frac{\partial}{\partial \beta} [D_{Cu-Na}^R (\beta) \beta^2 \frac{\partial Y_{Cu}}{\partial \beta}]$$

(8)

where $Y_{Cu} =$ equivalent fraction of Cu in the resin,

$\alpha = \ell/L = t/\tau$,

$\beta = r/R$.

The dimensionless time, $\alpha$, is the time the resin spends in the column (resin time).
The boundary and initial conditions governing Eq. (8) are:

\[
\begin{align*}
\alpha & \leq 0 & Y &= Y_2 & 0 & \leq \beta & \leq 1 \\
\alpha & > 0 & Y_s &= f_e(X_B)^* & \beta &= 1 \\
\alpha & > 0 & \frac{\partial Y}{\partial \alpha} &= 0 & \beta &= 0
\end{align*}
\]  

where \(Y_2\) = initial concentration of \(Cu^{++}\) in the resin particle,

\(Y_s\) = the surface concentration in equilibrium with the bulk liquid concentration \(X_B\).

The interdiffusion coefficient as derived by Helfferich (4) can be expressed by the following relation:

\[
D_{Cu-Na}^R = D_{Cu}^R D_{Na}^R \left[ \frac{Z_{Cu}^2 Y_{Cu}^2 + Z_{Na}^2 Y_{Na}^2}{Z_{Cu}^2 Y_{Cu}^2 D_{Cu}^R + Z_{Na}^2 Y_{Na}^2 D_{Na}^R} \right] 
\]  

\(D_{Cu-Na}^R\) is a function of \(Y\), Eq. (8) is a nonlinear differential equation. Solutions of Eq. (8) were obtained numerically using finite difference approximations to express the derivatives.

Another necessary quantity is the mass transfer rate into the resin particle \(W_{Cu}^R\), which can be expressed as

\[
W_{Cu}^R = 4\pi R Q_{\theta} D_{Cu-Na}^R \frac{\partial Y}{\partial \beta} \bigg|_{\beta=1} 
\]

where \(W_{Cu}^R\) is expressed in milliequivalents per unit time. Eq. (11) is obtained by applying Eq. (6) at the outer surface \((\beta=1)\) of the resin particle.

Concentration profiles and mass transfer rates for sorption of \(Cu^{++}\) on the resin as a function of resin time \(\alpha\) were determined from the numerical solution of Eq. (8).

\(^*\) \(f_e(X_B)\) expresses the equilibrium relationship at the resin particle surface, refer to Section 6.1.1, Eq. (27).
5.3 Liquid Film Control

In film control, the major resistance to mass transfer is assumed to be in the liquid film region surrounding the particle. Mass transfer resistance due to the resin particle is neglected, i.e., the concentration gradient in the resin particle is flat.

The liquid film (9, 10) is assumed thin enough that the curvature and accumulation of ions within the film are negligible (at steady state). Again, as in particle diffusion control, the liquid bulk concentration is expressed by Eq. (3).

The governing equation for the transfer of Cu$^{++}$ through the liquid film is given by the standard expression (11) for mass transport from a surface to a moving fluid as follows:

$$W^F_{Cu} = 4\pi R^2 K_F (X_B - X_S)$$  \hspace{1cm} (12)

where $W^F_{Cu}$ = instantaneous mass transfer rate through the film, meq/sec,

$K_F$ = mass transfer coefficient, meq/cm$^2$ \cdot sec

$X_S$ = concentration of Cu$^{++}$ in the film in equilibrium with Cu$^{++}$ in the resin particle,

$X_B$ = bulk concentration and assumed to be the concentration of Cu$^{++}$ at the outer film surface.

The mass transfer coefficient, $K_F$, is known. It (8, 11) is related to the Reynolds number ($N_{Re}$), Schmidt number ($N_{Sc}$) and was obtained in this study from correlations with the Sherwood number ($N_{Sh}$).

The liquid film diffusion coefficient $D^F_{Cu-Na}$ is given by Smith and Dranoff (9) as:
\[
D_{Cu-Na}^F = \frac{2 D_{Cu}^F}{2 + X_{Cu} \left( \frac{D_{Cu}^F}{D_{Na}^F} - 1 \right)}
\]

where \( D_{Cu}^F, D_{Na}^F \) = self diffusivities of \( Cu^{++}, Na^+ \) respectively.

\( X_{Cu} \) = equivalent fraction of \( Cu^{++} \) in the film.

In order to determine \( X_s \) (\( X_s \) is in equilibrium with \( \bar{Y}_{Cu} \)), the average concentration of \( Cu^{++} \) in the resin particle (\( \bar{Y}_{Cu} \)) is required. This quantity can be obtained from the relation

\[
\bar{Y}_{Cu} = \frac{\int_0^t W_{Cu,G}^F(t) \, dt}{Q}
\]

where \( W_{Cu,G}^F \) = the instantaneous mass transfer rate per gram of resin,

\( Q \) = resin capacity (milliequivalents per gm of resin).

The numerator of Eq. (14) is the amount of \( Cu^{++} \) transferred through the film into the resin particle from time zero to a particular resin time, \( t \). \( W_{Cu,G}^F \) is obtained by multiplying \( W_{Cu}^F \) by the number of resin particles per gram of resin. Since \( X_s \) and \( X_B \) are functions of resin time (\( X_s, X_B \) vary as the resin flows down the column), \( W_{Cu,G}^F \) is a function of resin time. Dividing the numerator by \( Q \), the resin ionic capacity, gives the average equivalent fraction of \( Cu^{++} \) in the resin.

Table 3 presents literature values of the \( N_{Sh} \) determined for experimental conditions similar to those used in this work. The values of \( N_{Sh} \) determined by Sunkoori and Kaparthi and also Frantz were questionable since the experimental data were taken at fluidizing velocities with no correction for void space. These values were not considered in the calculations made here but were included in Table 3 for completeness.
Table 3. Values of $N_{Sh}$ from Various Correlations in the Literature Approximating Experimental Conditions of this Study

<table>
<thead>
<tr>
<th>Author</th>
<th>Correlation</th>
<th>$N_{Sh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunkoori &amp; Kaparthi (12)</td>
<td>$N_{Sh} = 0.0039 + 2.1 N_{Re}^{2.1}$</td>
<td>0.14</td>
</tr>
<tr>
<td>Frantz (13)</td>
<td>$N_{Sh} = 0.016 N_{Re}^{1.3} N_{Sc}^{.67}$</td>
<td>0.50</td>
</tr>
<tr>
<td>Pfeffer &amp; Happel (14)</td>
<td>$N_{Sh} = 3.4 N_{Re}^{1/3} N_{Sc}^{1/3}$</td>
<td>78</td>
</tr>
<tr>
<td>Moison &amp; Ohern (15)</td>
<td>$N_{Sh} = 0.7 N_{Re}^{1/3} N_{Sc}^{1/3}$</td>
<td>54</td>
</tr>
<tr>
<td>Wilson &amp; Geankoplis (16)</td>
<td>$N_{Sh} = \frac{1.09}{\varepsilon} N_{Re}^{1/3} N_{Sc}$</td>
<td>67</td>
</tr>
<tr>
<td>Carberry (17)</td>
<td>$N_{Sh} = (.49) N_{Re}^{1/3} N_{Sc}^{1/3}$</td>
<td>37</td>
</tr>
<tr>
<td>Helfferich (4)</td>
<td>$N_{Sh} = 2.0 + 0.37 N_{Re}^{.6} N_{Sc}^{1/3}$</td>
<td>10.6</td>
</tr>
</tbody>
</table>
Table 3 shows a wide spread in the values of $N_{Sh}$ for relevant experimental conditions. Thus selection of an appropriate value of $N_{Sh}$ is necessary; a conservative value of 14 was selected. This choice was based on a decision to place bias on the film resistance purposely, i.e., to place as much emphasis on resistance in the liquid film as was consistent with the literature information. Since $K_F$ is directly related to $N_{Sh}$, selection of a low value of $N_{Sh}$ would produce a low value of $K_F$ and thus a relatively high resistance due to the liquid film.

Olsen and Meyer (1, 2, 3) observed that the resin phase apparently controlled the transfer of Cu$^{++}$ for total solution (Cu$^{++}$/Na$_2^+$, SO$_4^{--}$) normalities of 1.0 and 0.50. To verify this observation as part of this analytical study, it was decided to give a bias to liquid film resistance and then under the conditions favoring liquid film control compare the relative resistance of the liquid film and the resin particle. If the equations developed here for the ion exchange kinetics indeed show that the resin phase controls the mass transfer process in spite of the bias given the liquid film, one would have confidence in this conclusion. The same confidence would not be possible if a less conservative value of $N_{Sh}$ were used.

5.4 Combined Resin Particle and Liquid Film Control

After looking at the separate situations of resin particle and liquid film control of the continuous ion exchange process, the combined control of the mass transport by the two effects is considered. The assumptions made with respect to the separate control mechanisms also apply here.

In this case, however, one equation cannot be written to describe the entire diffusion process through the liquid film and into the resin particle, but rather a series of equations (which must be solved numerically) were
written. The solution of this series of equations is a trial and error procedure since the concentration at the surface of the particle is not independently known.

The solution of the combined resistance problem begins with consideration of the diffusion of Cu$^{++}$ from the bulk solution into the resin particle (the other counter ion Na$^+$ is diffusing in the opposite direction). Again, the concentration of Cu$^{++}$ in the bulk solution (varying as the resin particle moves down the column) is expressed by Eq. (3).

Transport of Cu$^{++}$ through the liquid film is described by Eqs. (12) and (13). The concentration at the interface is expressed by the equilibrium relationship. This relationship is available as a power series determined from a least square analysis of the experimental equilibrium data of Olsen (3).

Eqs. (8), (10) and the boundary condition at the center of the resin particle describe the diffusion of Cu$^{++}$ in the resin particle. The mass transfer rate of Cu$^{++}$ into the pellet is given by Eq. (11).

The mass transfer rate across the film (Eq. 12) must equal the mass transferred into the particle (Eq. (11)). Using Eqs. (11) and (12) a method is available to determine $X_s$. By assuming a value of $X_s$, then calculating $W^F_{Cu}$ and $W^R_{Cu}$ and comparing their values, a trial and error value of $X_s$ is determined.

A computer code was written which combined the codes for the particle and film control with a trial and error routine for $X_s$. The concentration profiles for the resin particle ($Y_{Cu}$) and the liquid film ($X_s, X_b$) were calculated along with the instantaneous mass transfer rates as a function of column residence time ($\tau$).
6.0 NUMERICAL PROCEDURE

6.1 Solution for the Resin Particle Control Model

The governing equation for the resin phase control problem, Eq. (8), is a nonlinear parabolic equation. This type of equation lends itself to a numerical solution using the finite difference approximation. Eq. (8) was replaced by a difference equation and the continuous region in which the solution is desired was replaced by a set of discrete points (14).

The resultant difference equation may be solved for 1) an explicit method (18) and/or 2) an implicit method (18). The explicit method was the simplest to program and was used initially (19) but when using this method, to insure reasonable accuracy and at the same time observe the stability condition, the execution time had to be large (in excess of one hour of IBM 360/50 computation time) to solve the problem by the explicit method.

Since it involves simultaneous solution of difference equations, the implicit method is a more complicated problem to program. This method does not have as restrictive stability criteria as the explicit method and thus permitted the use of a larger time increment. Using the large time increment, the IBM 360/50 execution time for the implicit problem was only 20 minutes and achieved the same accuracy requirement. Since the particle control model at total solution normalities (Cu$^{++}$/Na$^+$, $SO_4^{2-}$) of 1.0, 0.50 and 0.20 N was also treated by the explicit method, the implicit method solutions provided a check on the explicit results and then the implicit technique was used for all remaining calculations.
6.1.1 The Explicit Method

The partial derivatives in Eq. (8) were approximated by the following relations:

\[ \frac{\partial^2 Y}{\partial \alpha \partial \beta} = \frac{Y(\alpha + \Delta \alpha, \beta) - Y(\alpha, \beta)}{\Delta \alpha} \]  \hspace{1cm} (15)

\[ \frac{\partial^2 Y}{\partial \beta^2} = \frac{Y(\alpha, \beta + \Delta \beta) - Y(\alpha, \beta - \Delta \beta)}{2\Delta \beta} \]  \hspace{1cm} (16)

\[ \frac{\partial^2 D_{\text{Cu}-\text{Na}}}{\partial \beta^2} = \frac{D(\alpha, \beta + \Delta \beta) - D(\alpha, \beta - \Delta \beta)}{2\Delta \beta} \]  \hspace{1cm} (17)

\[ \frac{\partial^4 Y}{\partial \alpha \partial \beta^2} = \frac{Y(\alpha, \beta + \Delta \beta) - 2Y(\alpha, \beta) + Y(\alpha, \beta - \Delta \beta)}{\Delta \beta^2} \]  \hspace{1cm} (18)

where

\[ Y(\alpha, \beta) = \text{equivalent fraction at time } \alpha \text{ and position } \beta. \]

\[ \Delta \alpha, \Delta \beta = \text{dimensionless time and radius increments.} \]

\[ Y(\alpha + \Delta \alpha, \beta) = \text{equivalent fraction at the next time step } \alpha + \Delta \alpha \]

\[ \text{and position } \beta. \]

The dimensionless radius (position) increment is given by:

\[ \Delta \beta = 1/N \]  \hspace{1cm} (19)

where \( N \) = number of discrete position points.

Substituting Eqs. (15), (16), (17), and (18) for the partial derivatives in Eq. (8) and after some rearrangement, the following difference expression is obtained:

\[ Y(\alpha + \Delta \alpha, \beta) = Y(\alpha, \beta) + h_1 [Y(\alpha, \beta + \Delta \beta) - 2Y(\alpha, \beta) + Y(\alpha, \beta - \Delta \beta)] \]

\[ + h_2 [Y(\alpha, \beta + \Delta \beta) - Y(\alpha, \beta - \Delta \beta)] \]

\[ + h_3 [D(\alpha, \beta + \Delta \beta) - D(\alpha, \beta - \Delta \beta)] \cdot [Y(\alpha, \beta + \Delta \beta) - Y(\alpha, \beta - \Delta \beta)] \]  \hspace{1cm} (20)

where

\[ D(\alpha, \beta) = \frac{D_{\text{Cu}} [Y(\alpha, \beta) + 1.0]}{3.0 - 2.0 Y(\alpha, \beta)} \]  \hspace{1cm} (21)
\[ h_1 = \frac{D(\alpha, \beta) \tau \Delta \alpha}{K^2 \Delta \beta^2} \]  
(22)

\[ h_2 = \frac{D(\alpha, \beta) \tau \Delta \alpha}{K^2 \beta \Delta \beta} \]  
(23)

\[ h_3 = \frac{\tau \Delta \alpha}{4K^2 \Delta \beta^2} \]  
(24)

At the center (\( \beta = 0 \)) Eq. (20) is not defined because of the 1/\( \beta \) term in \( h_2 \). Applying L'Hospital's rule to Eq. (8) and recalling that

\[ \lim_{\beta \to 0} \frac{3Y}{3\beta} = \frac{3^2 Y}{3\beta^2} \]  
(25)

and then replacing the partial derivatives with the appropriate difference equations, Eq. (20) for the center boundary condition becomes

\[ Y(\alpha + \Delta \alpha, 0) = Y(\alpha, 0) + 6h_1 [Y(\alpha, \Delta \beta) - Y(\alpha, 0)] \]  
(26)

At the outer boundary (\( \beta = 1 \)), the Cu\(^{++} \) resin concentration is assumed to be in equilibrium with the bulk Cu\(^{++} \) concentration and is expressed by the following relation:

\[ Y(\alpha + \Delta \alpha, 1) = B_1 X_B + B_2 X_B^2 + B_3 X_B^3 + B_4 X_B^4 \]  
(27)

where \( B_1, B_2, B_3, B_4 \) = constants determined from a least squares set of experimental equilibrium data obtained by Olsen.

The initial condition (\( \alpha = 0, 0 \leq \beta \leq 1 \)) is given by

\[ Y(0, 0 \leq \beta \leq 1) = Y_2 \]  
(28)

where \( Y_2 \) is the initial concentration of Cu\(^{++} \) in the resin.

The stability condition for Eq. (20) was taken from Helfferich (5) and presented by Courant (20) as
\[
\frac{D(\alpha, \beta) \Delta \alpha}{R^2 \Delta \beta} \leq 0.4
\]

(29)

The explicit method involves a line-by-line calculation. The unknown \( Y \) at the \( \alpha + \Delta \alpha \) step is calculated explicitly from the \( Y \)'s on the \( \alpha \) step. To start, the initial condition and boundary conditions are used to calculate \( Y \) for the first time step at all positions of \( \beta \). Once the entire row of \( Y(1, \beta)'s \) are known, then the \( Y(2, \beta)'s \) can be calculated using Eq. (20), the known boundary values (Eqs. 26 and 27) and the \( Y(1, \beta)'s \). The calculation procedure continues through the time domain \( (0 \leq \tau \leq 1) \).

With the determination of the concentration in the resin particle at discrete positions, the instantaneous mass transfer rate per gram can then be calculated at each time step by the relation

\[
W_{Cu,G}^R = 4\pi R (PPG) \rho R D(\alpha, \beta) \frac{[Y(\alpha, 1) - Y(\alpha, 1 - \Delta \beta)]}{\Delta \beta}
\]

(30)

where \( PPG \) is the number of particles per gram which is determined from the resin properties.

To obtain the best compromise between accuracy and computer time, the following procedure was used. The position increment \( \Delta \beta \) was set and \( \Delta \alpha \) was varied according to the stability condition, Eq. (29), until there was less than 1% difference in the values of \( Y \) between two different \( \Delta \alpha \)'s. Using this procedure, the numerical solution was broken into four different time increments for four time regions of \( \tau \), which are as follows:

<table>
<thead>
<tr>
<th>( \Delta \alpha )</th>
<th>( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000025</td>
<td>0 ( \rightarrow ) 0.064</td>
</tr>
<tr>
<td>0.00005</td>
<td>0.064 ( \rightarrow ) 0.128</td>
</tr>
<tr>
<td>0.00001</td>
<td>0.128 ( \rightarrow ) 0.256</td>
</tr>
<tr>
<td>0.00005</td>
<td>0.256 ( \rightarrow ) 1.000</td>
</tr>
</tbody>
</table>
6.1.2 The Implicit Method

A larger time increment may be used for the implicit method since $\Delta \alpha$ is not restricted by stability criteria (or convergence) but only by the allowable truncation error \((18)\). To use this method, the partial derivatives of Eq. \((8)\) were approximated with difference equations which were an average of the $\alpha + \Delta \alpha$ and $\alpha$ rows instead of the $\alpha$ row alone as in the explicit approach. Figure 5 shows the implicit subscript notation used. The radius is divided into $N$ increments of $\Delta \beta$ length with $N + 1$ discrete positions. Also note that:

$$\beta = (I-1) \Delta \beta \quad I = 1, 2, ..., N+1$$

\[ (31) \]

where

$$\left\{ \begin{array}{c} I = 1, \beta = 0 \\ I = N+1, \beta = 1 \end{array} \right. \]

The following partial derivatives were expressed by the following approximate difference equations:

$$\frac{\partial^2 Y_{Cu}}{\partial \beta^2} = \frac{YY(I+1) - 2YY(I) + YY(I-1) + Y(I+1) - 2Y(I) + Y(I-1)}{2\Delta \beta^2}$$

\[ (32) \]

$$\frac{\partial Y_{Cu}}{\partial \beta} = \frac{1}{2} \left( \frac{YY(I+1) - YY(I-1)}{2\Delta \beta} \right) + \frac{Y(I+1) - Y(I-1)}{2\Delta \beta}$$

\[ (33) \]

$$\frac{\partial D_{Cu-Na}}{\partial \beta} = \frac{D(I+1) - D(I-1)}{2\Delta \beta}$$

\[ (34) \]

Substituting Eqs. \((32)\), \((33)\) and \((34)\) into Eq. \((8)\) and after some rearrangement, Eq. \((8)\) becomes:

$$C_Y YY(I-1) + A_Y YY(I) + B_Y YY(I+1) = D_Y$$

\[ (35) \]
Fig. 5. Mesh spacing and subscript notation for the implicit method.
where

\[ C_I = \frac{\tau \Delta \alpha}{2R^2 \Delta \beta^2} \left[ \frac{D(I+1) - 4D(I) - D(I-1)}{4} + D(I) \frac{\Delta \beta}{\beta} \right] \]  
\[ (36) \]

\[ A_I = 1 + \frac{\tau \Delta \alpha}{R^2 \Delta \beta} D(I) \]  
\[ (37) \]

\[ B_I = \frac{-\tau \Delta \alpha}{2R^2 \Delta \beta^2} \left[ \frac{D(I+1) + 4D(I) - D(I-1)}{4} + \frac{D(I) \Delta \beta}{\beta} \right] \]  
\[ (38) \]

\[ D_I = Y(I) + \frac{\tau \Delta \alpha}{2R^2 \Delta \beta^2} \left[ D(I) [Y(I+1) - 2Y(I) + Y(I-1)] \right. \]
\[ + \left. \frac{D(I+1) - D(I-1)}{4} [Y(I+1) - Y(I-1)] \right] \]
\[ + \frac{\Delta \beta}{\beta} D(I) [Y(I+1) - Y(I-1)] \]  
\[ (39) \]

At \( \beta = 0 \), again applying L'Hospital's rule to Eq. (8) and substituting in the appropriate difference approximations, Eq. (39) becomes:

\[ A_1 YY(1) + B_1 YY(2) = D_1 \]  
\[ (40) \]

where

\[ A_1 = 1 + 3 \frac{\tau \Delta \alpha}{R^2 \Delta \beta^2} D(1) \]  
\[ (41) \]

\[ B_1 = \frac{-3 \tau \Delta \alpha}{R^2 \Delta \beta^2} D(1) \]  
\[ (42) \]

\[ D_1 = Y(1) + \frac{3 \tau \Delta \alpha}{R^2 \Delta \beta^2} [Y(2) - Y(1)] \]  
\[ (43) \]

For the outer boundary \( \beta = 1 \) (\( I = N+1 \)), \( YY(N+1) \) is known from the equilibrium relationship, Eq. (27), and Eq. (35) becomes:

\[ A_N YY(N) + C_N YY(N-1) = D_N \]  
\[ (44) \]

where

\[ D_N = D_N - B_N YY(N+1) \]  
\[ (44) \]

and \( A_N, C_N \) are given by Eqs. (37) and (36) respectively.
The initial condition \((\tau = 0)\) is expressed by:

\[
Y(1 \leq I \leq N) = Y_2.
\]  

(46)

Applying the difference equations, Eqs. (35), (40) and (44) at each point on the \(\alpha\) row, a set of \(N\) simultaneous equations is obtained:

\[
A_1 YY(1) + B_1 YY(2) = D_1
\]

\[
C_I YY(I-1) + A_I YY(I) + B_I YY(I+1) = D_I \quad I = 2, 3, \ldots, N-1
\]  

(47)

\[
C_N YY(N-1) + A_N YY(N) = D_N.
\]

Since the \(YY(I)'s\) are unknown, the above set of equations must be solved simultaneously to obtain them. Upon obtaining the values of \(YY(I)'s\), the solution advances to the \(\alpha + \Delta \alpha\) row, replaces the values of \(Y(I)'s\) from the \(\alpha\) row with the values of the \(YY(I)'s\), and using the boundary conditions, again solves the above set of equations. Calculations continue by proceeding up the time domain \((0 \leq \tau \leq 1)\).

To solve the set of equations, Eq. (47), the method of Thomas (18) is used (Appendix B). Once the concentration profile is determined for a value of \(\alpha\), the instantaneous mass transfer rate per gram is calculated from Eq. (30).

6.2 Solution for the Film Control Model

Calculation of \(X_s\), \(X_B\) and the instantaneous mass transfer rate per gram of resin consisted of the following procedure:

(1) Given \(Y_2\), \(X_2\) at \(\tau = 0\), \(X_s\) was calculated from the equilibrium relationship \((Y = Y_2)\)

\[
X_s = A_0 + A_1 Y^1 + A_2 Y^2 + A_3 Y^3
\]  

(48)

where \(A_0, A_1, A_2, A_3\) = constants determined by a least squares analysis of equilibrium data obtained by Olsen.
(2) Add $\Delta \alpha$ to $\tau$.

(3) Calculate $X_B^p$ from Eq. (3).

(4) Calculate $D_{Cu-Na}^F$ at $X_s$, $X_B$ and average $D_{Cu-Na}^F$.

(5) The mass transfer coefficient $K_p$, is calculated from $N_{Sh}$ where:

$$N_{Sh} = \frac{K_p D_p}{C_o D_{Cu-Na}} \quad (49)$$

and

$$K_F = \frac{N_{Sh} C_o D_{Cu-Na}}{D_p} \quad (50)$$

(6) The mass transfer rate per gram of resin is calculated from:

$$w_{Cu,G}^F = K_F (PPG) (4\pi R^2) (X_B - X_s) \quad (51)$$

where PPG = number of particles per gram of resin.

(7) The average resin composition $\bar{Y}$ is then determined by Eq. (14).

(8) From $\bar{Y}$, a new $X_s$ is calculated from Eq. (48); then steps 2-7 are repeated until the desired time ($0 \leq \tau \leq 1$) is attained.

6.3 Solution for the Combined Film and Resin Particle Control Model

The mass transfer rate and concentration profiles for both the liquid film and resin particle are determined when both film and particle resistances are present. To do this, a trial and error, finite difference, numerical method was designed. This method involved combining the numerical solutions for the film and resin particle-diffusion control problems; Figure 6 shows the relationships and equations used.

The trial and error routine for $X_s$ requires setting the value of $X_s$ equal to $X_B$, then calculating the concentration profile in the resin particle as well as a value for $K_F$. A new value of $X_s$ ($X_s^{New}$) is calculated from
Fig. 6. Equations for numerical solution of combined control model.
\[ X_{s}^{\text{New}} = X_{B} - \frac{D_{\text{Cu-Na}}^R Q \rho r \frac{\partial Y}{\partial R}}{K_{FR}} \bigg| \beta = 1 \] (52)

(Eq. (52) is obtained by equating the mass transfer rate in the film, Eq. (12), and in the particle, Eq. (11), and solving for \( X_{s} \).) The new value of the resin surface concentration, \( X_{s}^{\text{New}} \), is then compared to \( X_{s} \). If the values of \( X_{s} \) don't agree, the difference between the values of \( X_{s} \) and \( X_{s}^{\text{New}} \) is halved, and added to, or subtracted from \( X_{s} \) (depending on the sign of the difference). The calculation procedure is repeated until the difference between the old and new \( X_{s} \) values is reduced to less than 0.1% of \( X_{s}^{\text{New}} \). This procedure is repeated for each time interval.
7.0 RESULTS AND DISCUSSION

7.1 General

Starting with an expression for the variation of Cu$^{++}$ in the solution phase, Eq. (3), the transfer of Cu$^{++}$ from the upwardly flowing bulk solution (cupric sulfate-sodium sulfate) into the downward flowing resin is assumed to be 1) controlled completely by ionic diffusion within the resin phase, 2) controlled completely by transport through a liquid film existing between the bulk solution and resin particle and adhering to the resin particle and 3) controlled by the combined effect of 1) and 2) acting simultaneously on the mass transfer process.

Expressions are provided to describe the kinetic relations appropriate to cases 1), 2) and 3). The expressions are solved numerically to obtain Cu$^{++}$ concentration profiles and mass transfer rates within the resin particle and liquid film from each model (resin particle, film and combined resin particle-film control models).

By comparison of the concentration profiles and mass transfer rates calculated from each model, the controlling phase is determined. The smaller mass transfer rate or steeper slope of the Cu$^{++}$ profile of one phase when compared to the other indicates the greater resistance to transfer of Cu$^{++}$. The greater resistance identifies the controlling phase.

Resin phase and liquid film control of Cu$^{++}$ transfer is studied for cupric-sodium sulfate solutions of 1.0, 0.50 and 0.20 N. Using the 0.50 N (Cu$^{++}$/Na$_2^+$, SO$_4^{--}$) solution case, resin particle and film control is also studied for resin particle diameters of 0.030, 0.058 and 0.082 cm. For each particle diameter, the feed solution Reynolds number is held constant.
7.2 Effect of Solution Concentration

Tables 4, 5 and 6 show the instantaneous mass transfer rates per gram of resin calculated from the resin particle, liquid film and combined resin particle-film control models at total solution normalities ($\text{Cu}^{++}/\text{Na}_2^+, \text{SO}_4^-$) of 1.0, 0.50 and 0.20. The instantaneous mass transfer rates per gram of resin are given for varying resin times (or equivalent column length). The resin particle diameter is 0.058 cm.

For the 1.0 N total solution, concentrated case, the resin phase controls the transfer of $\text{Cu}^{++}$ throughout the column. Mass transfer rates for the resin phase are three to four times smaller than for the liquid film. Initially, as the resin first comes into contact with the solution phase, the liquid film does contribute to the overall resistance (film and resin particle phases). This observation is established by comparing the difference between the rates for the resin particle control and the combined resin-film control model at small resin times. After admission of the resin to the column, the resin particle control and combined resin-film control mass transfer rates approach each other. This indicates that the resin phase became the predominant resistance and thus controls the mass transfer process.

The resin phase also controls the mass transfer of $\text{Cu}^{++}$ for the 0.5 N ($\text{Cu}^{++}/\text{Na}_2^+, \text{SO}_4^-$) solution. The film resistance, however, is a more important factor at early resin times in the column than noted in the 1.0 N solution study. This observation is based on the smaller difference between the mass transfer rates for the film and resin phase control models at early resin times than that noted for the 1.0 N case.

For the 0.2 N ($\text{Cu}^{++}/\text{Na}_2^+, \text{SO}_4^-$) solution, a cross over point is noted; the film controls the mass transfer process for a short time after an
Table 4. Instantaneous Mass Transfer Rates per Gram of Resin from the Film, Resin and Combined Control Models for the 1.0 N Total Solution Concentration (Cu$^{2+}$/Na$^+$, SO$_4^{2-}$).

<table>
<thead>
<tr>
<th>TIME, $\alpha$ ($\tau = 939$ sec)</th>
<th>$W_{Cu,G}^F$ Meq/gm·sec $\times 10^{-2}$</th>
<th>$W_{Cu,G}^R$ Meq/gm·sec $\times 10^{-2}$</th>
<th>$W_{Cu,G}^C$ Meq/gm·sec $\times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.089</td>
<td>0.492</td>
<td>0.391</td>
</tr>
<tr>
<td>0.04</td>
<td>1.137</td>
<td>0.378</td>
<td>0.337</td>
</tr>
<tr>
<td>0.06</td>
<td>1.120</td>
<td>0.321</td>
<td>0.302</td>
</tr>
<tr>
<td>0.08</td>
<td>1.075</td>
<td>0.283</td>
<td>0.275</td>
</tr>
<tr>
<td>0.10</td>
<td>1.020</td>
<td>0.254</td>
<td>0.253</td>
</tr>
<tr>
<td>0.20</td>
<td>0.687</td>
<td>0.165</td>
<td>0.178</td>
</tr>
<tr>
<td>0.30</td>
<td>0.436</td>
<td>0.110</td>
<td>0.127</td>
</tr>
<tr>
<td>0.40</td>
<td>0.283</td>
<td>0.073</td>
<td>0.088</td>
</tr>
<tr>
<td>0.50</td>
<td>0.199</td>
<td>0.051</td>
<td>0.061</td>
</tr>
<tr>
<td>0.60</td>
<td>0.152</td>
<td>0.038</td>
<td>0.044</td>
</tr>
<tr>
<td>0.70</td>
<td>0.125</td>
<td>0.031</td>
<td>0.034</td>
</tr>
<tr>
<td>0.80</td>
<td>0.108</td>
<td>0.026</td>
<td>0.028</td>
</tr>
<tr>
<td>0.90</td>
<td>0.095</td>
<td>0.023</td>
<td>0.024</td>
</tr>
<tr>
<td>1.00</td>
<td>0.086</td>
<td>0.020</td>
<td>0.021</td>
</tr>
</tbody>
</table>
Table 5. Instantaneous Mass Transfer Rates per Gram of Resin from the Film, Resin and Combined Control Models for the 0.5 N Total Solution Concentration (Cu$^{+2}$/Na$_2$, SO$_4^{2-}$).

<table>
<thead>
<tr>
<th>Time, $\alpha$ ($\tau = 939$ sec)</th>
<th>$W_{Cu,G}^F$</th>
<th>$W_{Cu,G}^R$</th>
<th>$W_{Cu,G}^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Meq/sec•gm $10^{+2}$</td>
<td>Meq/sec•gm $10^{+2}$</td>
<td>Meq/sec•gm $10^{+2}$</td>
</tr>
<tr>
<td>0.02</td>
<td>0.607</td>
<td>0.414</td>
<td>0.297</td>
</tr>
<tr>
<td>0.04</td>
<td>0.666</td>
<td>0.311</td>
<td>0.267</td>
</tr>
<tr>
<td>0.06</td>
<td>0.693</td>
<td>0.260</td>
<td>0.244</td>
</tr>
<tr>
<td>0.08</td>
<td>0.703</td>
<td>0.227</td>
<td>0.225</td>
</tr>
<tr>
<td>0.10</td>
<td>0.701</td>
<td>0.202</td>
<td>0.208</td>
</tr>
<tr>
<td>0.20</td>
<td>0.600</td>
<td>0.126</td>
<td>0.146</td>
</tr>
<tr>
<td>0.30</td>
<td>0.447</td>
<td>0.083</td>
<td>0.103</td>
</tr>
<tr>
<td>0.40</td>
<td>0.315</td>
<td>0.057</td>
<td>0.072</td>
</tr>
<tr>
<td>0.50</td>
<td>0.223</td>
<td>0.043</td>
<td>0.052</td>
</tr>
<tr>
<td>0.60</td>
<td>0.165</td>
<td>0.035</td>
<td>0.040</td>
</tr>
<tr>
<td>0.70</td>
<td>0.129</td>
<td>0.031</td>
<td>0.034</td>
</tr>
<tr>
<td>0.80</td>
<td>0.108</td>
<td>0.028</td>
<td>0.030</td>
</tr>
<tr>
<td>1.00</td>
<td>0.084</td>
<td>0.024</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Table 6. Instantaneous Mass Transfer Rates per Gram of Resin from the Film, Resin and Combined Control Models for the 0.20 N Total Solution Concentration (Cu^{2+}/Na^+, SO_4^2-).

<table>
<thead>
<tr>
<th>Time, $\alpha$</th>
<th>$W_{Cu,G}^F$ Meq/gm·sec $\times 10^2$</th>
<th>$W_{Cu,G}^R$ Meq/gm·sec $\times 10^2$</th>
<th>$W_{Cu,G}^C$ Meq/gm·sec $\times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau = 486$ sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.419</td>
<td>0.915</td>
<td>0.338</td>
</tr>
<tr>
<td>0.04</td>
<td>0.448</td>
<td>0.627</td>
<td>0.328</td>
</tr>
<tr>
<td>0.06</td>
<td>0.470</td>
<td>0.502</td>
<td>0.317</td>
</tr>
<tr>
<td>0.08</td>
<td>0.488</td>
<td>0.424</td>
<td>0.309</td>
</tr>
<tr>
<td>0.10</td>
<td>0.504</td>
<td>0.369</td>
<td>0.302</td>
</tr>
<tr>
<td>0.20</td>
<td>0.555</td>
<td>0.219</td>
<td>0.275</td>
</tr>
<tr>
<td>0.30</td>
<td>0.579</td>
<td>0.152</td>
<td>0.241</td>
</tr>
<tr>
<td>0.40</td>
<td>0.586</td>
<td>0.118</td>
<td>0.191</td>
</tr>
<tr>
<td>0.50</td>
<td>0.580</td>
<td>0.102</td>
<td>0.142</td>
</tr>
<tr>
<td>0.60</td>
<td>0.562</td>
<td>0.095</td>
<td>0.113</td>
</tr>
<tr>
<td>0.70</td>
<td>0.533</td>
<td>0.091</td>
<td>0.100</td>
</tr>
<tr>
<td>0.80</td>
<td>0.492 SATURATION</td>
<td></td>
<td>0.094</td>
</tr>
<tr>
<td>0.90</td>
<td>0.439</td>
<td>&quot;&quot;</td>
<td>0.089 SATURATION</td>
</tr>
<tr>
<td>1.00</td>
<td>0.378</td>
<td>&quot;&quot;</td>
<td>SATURATION</td>
</tr>
</tbody>
</table>
increment of resin starts down the column. The initial film resistance is finally overcome for \( r \geq 0.10 \) but the film still contributes significant resistance to the overall mass transfer process. This observation is based on the difference between the instantaneous mass transfer rates for the three different control models at increasing values of \( r \).

The effect of the resin particle phase and liquid film on the control of the mass transfer process is also studied based on the comparison of concentration profiles in the resin particle and adhering liquid film. Figure 7 shows Cu\(^{++}\) concentration profiles within a resin particle calculated from (1) the resin particle control model and (2) the combined resin-film control model where the Cu\(^{++}\) concentration through the film was also calculated. Figure 7 compares these two phase control model concentration profiles for total solution normalities of 1.0, 0.50 and 0.20 N respectively.

Profiles calculated from the resin phase control model show the Cu\(^{++}\) diffusion within the resin particle in the absence of film resistance while the combined resin-film control model profiles show the Cu\(^{++}\) concentration within the particle with the film resistance present.

Comparison of the Cu\(^{++}\) profiles calculated from the two control models at corresponding resin times and total solution normalities show the effect of the film in reducing the Cu\(^{++}\) mass transfer rate. The effect of the film is greatest for the 0.20 N solution and decreased with increasing solution normality.

To study film and/or resin phase control using Cu\(^{++}\) concentration profiles, profiles in the film and corresponding resin particle calculated from the combined model (Figure 7) must be examined. The greater the slope of the Cu\(^{++}\) profile in the resin particle or liquid film at the film-resin particle interface, the greater is the resistance to the mass transfer in that phase.
Fig. 7 CONCENTRATION PROFILES FOR TOTAL SOLUTION CONCENTRATIONS OF 1.0, 0.50, 0.20 N AT VARIOUS RESIN TIMES CALCULATED FROM THE RESIN AND COMBINED CONTROL MODELS.
(the greater resistance being the controlling phase). This comparison must be made at corresponding resin times.

In making this type of comparison for the three total solution concentrations (Cu$^{2+}$/Na$_2$, Sf$^-$), it is observed that resin particle control is favored as the total solution concentration increased while film control is favored as the total solution concentration decreased.

Figure 8 shows $X_B$, $X_S$ (film resistance) and $X_S$ (film and resin particle resistance) as a function of time or equivalent column distance for the three solution concentrations. The surface concentration, $X_S$, is determined separately from the film model, $X_S$ (film resistance), which assumes no resin phase resistance and from the combined resin-film control model, $X_S$ (film and resin particle resistance), which considers both the effects of resin phase and liquid film resistance. For each model $X_B$ would be the same.

The most important information obtained from the film Cu$^{2+}$ concentration profiles is the increasing difference between $X_B$ and $X_S$ (film and resin particle resistance) as the solution concentration decreased. This shows that the film resistance becomes greater as the total solution normality decreases; the greatest relative film resistance occurring in the 0.20 solution case. This observation is not as apparent from the previous comparisons of resin Cu$^{2+}$ concentration profiles and instantaneous mass transfer rates per gram of resin.

The difference between $X_B$ and $X_S$ (film resistance) is greatest for the 0.2 N solution, but the shape of the $X_S$ (film resistance) curve is also different from the 0.5 and 1.0 N solution $X_S$ (film resistance) curves. These differences, although primarily caused by the greater liquid film resistance, are in part due to the equilibrium relation between the particle and solution phase Cu$^{2+}$ concentration at the particle-film interface. Fig. (9) shows
Fig. 8 CALCULATED CONCENTRATION OF Cu$^{2+}$ FOR THE BULK PHASE AND RESIN PARTICLE FILM INTERFACE FOR TOTAL SOLUTION CONCENTRATIONS OF 1.0, 0.50 and 0.20 N.
Fig. 9. Equilibria of cupric ion and sodium ion between aqueous sulfate solutions and Dowex 50W-X8 (taken from Ref. (3)).
the equilibrium curves for the resin phase and solution phase $\text{Cu}^{++}$ equivalent fractions at total ($\text{Cu}^{++}/\text{Na}^+, \text{SO}_4^-$) solution normalities of 1.0, 0.5 and 0.2 on Dowex 50W-X8 obtained from Olsen (3). For the 0.2 N solution, the equilibrium $\text{Cu}^{++}$ concentration in the resin phase approaches saturation (at the corresponding solution phase $\text{Cu}^{++}$ concentration) much faster than either the 0.5 or 1.0 N solutions. Because of the shape of the curve, $\tilde{Y}$ determined from the liquid film control model, Eq. (14), results in a much smaller equilibrium value of $X_5$ (film resistance, Eq. (48)), for the 0.2 N solution than for either the 0.5 and 1.0 N solutions.

The effect of film control is seen to be most important as the resin enters the column and just comes into contact with the solution phase, this effect increasing in importance as the solution concentration decreases. The resin phase, however, is found to be more important for longer column residence times, $\tau$, and as the solution concentration increases. These results are in substantial agreement with the statement of Helfferich (4) that "every ion exchange is film controlled during an initial, if extremely short, period and the tendency toward particle diffusion control increases as the exchange progresses."

Helfferich (4) also states that for low (dilute) solution concentrations, film control predominates over resin phase control. From the three solution concentrations studied here, comparison of results show the tendency toward increasing film control of the mass transport as total solution concentration decreases.

For the 0.5 N and 1.0 N solutions ($\text{Cu}^{++}/\text{Na}^+, \text{SO}_4^-$), the resin phase is observed essentially to control the mass transfer process. These same results were experimentally observed by Olsen and Meyer (1, 2, 3) using their continuous countercurrent ion exchange contactor.
7.3 Effect of Particle Size

The effect of particle size on resin particle and film phase control is studied for a 0.50 N (Cu\textsuperscript{2+}/Na\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-}) solution. The particle diameters selected corresponded to the upper, mean and lower particle diameters of the 20 to 50 mesh size range of the Dowex 50W-X8 resin used in the experimental studies. The Reynolds number is held constant for these three calculations and, thus, permits the use of a constant Sherwood number.

Tables 7, 8 and 9 compare the instantaneous mass transfer rates per gram for particle diameters of 0.030, 0.058 and 0.082 cm respectively. For each particle diameter the instantaneous mass transfer rates per gram of resin are calculated from the three control models.

The resin phase controls the transfer of Cu\textsuperscript{2+} throughout the column for the smaller particle size (0.30 cm). For the mean particle size (0.058 cm), film resistance is present initially as the resin started down the column but the resin phase essentially controls the Cu\textsuperscript{2+} transfer throughout the column. These observations are based on the large differences between \( W_{Cu,G}^F \) and \( W_{Cu,G}^R \), while the differences between \( W_{Cu,G}^R \) and \( W_{Cu,G}^C \) are small at corresponding resin times (\( \alpha \)).

For the largest particle size studied, the film and resin phase contributes about the same amount of control initially. As the resin continued down the column, the resin phase exhibits increasing control of the mass transfer process. This may be clearly observed by comparison of \( W_{Cu,G}^F \), \( W_{Cu,G}^R \) and \( W_{Cu,G}^C \).

Figure 10 also shows the effect of particle size on resin particle and liquid film control. Concentration profiles for Cu\textsuperscript{2+} are again calculated from 1) the resin phase control model which neglects effects of both resistance of the film and 2) the combined resin-film control model which
Table 7. Instantaneous Mass Transfer Rates per Gram of Resin from the Film, Resin and Combined Phase Control Models for 0.030 cm Particle Diameter.

<table>
<thead>
<tr>
<th>Time, $\tau$</th>
<th>$W_{Cu,G}^F$</th>
<th>$W_{Cu,G}^R$</th>
<th>$W_{Cu,G}^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau = 939$ sec</td>
<td>$10^{-2}$</td>
<td>$10^{-2}$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>0.02</td>
<td>1.911</td>
<td>0.627</td>
<td>0.617</td>
</tr>
<tr>
<td>0.04</td>
<td>1.735</td>
<td>0.415</td>
<td>0.456</td>
</tr>
<tr>
<td>0.06</td>
<td>1.466</td>
<td>0.300</td>
<td>0.353</td>
</tr>
<tr>
<td>0.08</td>
<td>1.192</td>
<td>0.222</td>
<td>0.275</td>
</tr>
<tr>
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<td>0.950</td>
<td>0.169</td>
<td>0.215</td>
</tr>
<tr>
<td>0.20</td>
<td>0.347</td>
<td>0.075</td>
<td>0.084</td>
</tr>
<tr>
<td>0.30</td>
<td>0.209</td>
<td>0.053</td>
<td>0.055</td>
</tr>
<tr>
<td>0.40</td>
<td>0.160</td>
<td>0.042</td>
<td>0.044</td>
</tr>
<tr>
<td>0.50</td>
<td>0.133</td>
<td>0.036</td>
<td>0.037</td>
</tr>
<tr>
<td>0.60</td>
<td>0.115</td>
<td>0.032</td>
<td>0.032</td>
</tr>
<tr>
<td>0.70</td>
<td>0.101</td>
<td>0.029</td>
<td>0.029</td>
</tr>
<tr>
<td>0.80</td>
<td>0.091</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>0.90</td>
<td>0.083</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>1.00</td>
<td>0.076</td>
<td>0.023</td>
<td>0.024</td>
</tr>
</tbody>
</table>
Table 8. Instantaneous Mass Transfer Rates per Gram of Resin from the Film Resin and Combined Phase Control Models for 0.058 cm Particle Diameter.

<table>
<thead>
<tr>
<th>Time, $\alpha$ ($\tau = 939$ sec)</th>
<th>$W_{Cu,G}^F$ Meq/sec·gm $\times 10^{+2}$</th>
<th>$W_{Cu,G}^R$ Meq/sec·gm $\times 10^{+2}$</th>
<th>$W_{Cu,G}^C$ Meq/sec·gm $\times 10^{+2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.607</td>
<td>0.414</td>
<td>0.297</td>
</tr>
<tr>
<td>0.04</td>
<td>0.666</td>
<td>0.311</td>
<td>0.267</td>
</tr>
<tr>
<td>0.06</td>
<td>0.693</td>
<td>0.260</td>
<td>0.244</td>
</tr>
<tr>
<td>0.08</td>
<td>0.703</td>
<td>0.227</td>
<td>0.225</td>
</tr>
<tr>
<td>0.10</td>
<td>0.701</td>
<td>0.202</td>
<td>0.208</td>
</tr>
<tr>
<td>0.20</td>
<td>0.600</td>
<td>0.126</td>
<td>0.146</td>
</tr>
<tr>
<td>0.30</td>
<td>0.447</td>
<td>0.083</td>
<td>0.103</td>
</tr>
<tr>
<td>0.40</td>
<td>0.315</td>
<td>0.057</td>
<td>0.072</td>
</tr>
<tr>
<td>0.50</td>
<td>0.223</td>
<td>0.043</td>
<td>0.052</td>
</tr>
<tr>
<td>0.60</td>
<td>0.165</td>
<td>0.035</td>
<td>0.040</td>
</tr>
<tr>
<td>0.70</td>
<td>0.129</td>
<td>0.031</td>
<td>0.034</td>
</tr>
<tr>
<td>0.80</td>
<td>0.108</td>
<td>0.028</td>
<td>0.030</td>
</tr>
<tr>
<td>0.90</td>
<td>0.094</td>
<td>0.026</td>
<td>0.027</td>
</tr>
<tr>
<td>1.00</td>
<td>0.084</td>
<td>0.024</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Table 9. Instantaneous Mass Transfer Rates per Gram of Resin from the Film, Resin and Combined Phase Control Models for 0.082 cm Particle Diameter.

<table>
<thead>
<tr>
<th>Time, ( \alpha ) ( \tau = 939 \text{ sec} )</th>
<th>( \frac{W_{Cu,G}^F}{\text{Meq/gm\cdotsec}} \times 10^{+2} )</th>
<th>( \frac{W_{Cu,G}^R}{\text{Meq/gm\cdotsec}} \times 10^{+2} )</th>
<th>( \frac{W_{Cu,G}^C}{\text{Meq/gm\cdotsec}} \times 10^{+2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.313</td>
<td>0.323</td>
<td>0.181</td>
</tr>
<tr>
<td>0.04</td>
<td>0.354</td>
<td>0.245</td>
<td>0.175</td>
</tr>
<tr>
<td>0.06</td>
<td>0.381</td>
<td>0.210</td>
<td>0.168</td>
</tr>
<tr>
<td>0.08</td>
<td>0.399</td>
<td>0.187</td>
<td>0.162</td>
</tr>
<tr>
<td>0.10</td>
<td>0.412</td>
<td>0.171</td>
<td>0.154</td>
</tr>
<tr>
<td>0.20</td>
<td>0.433</td>
<td>0.123</td>
<td>0.127</td>
</tr>
<tr>
<td>0.30</td>
<td>0.412</td>
<td>0.096</td>
<td>0.106</td>
</tr>
<tr>
<td>0.40</td>
<td>0.371</td>
<td>0.076</td>
<td>0.089</td>
</tr>
<tr>
<td>0.50</td>
<td>0.320</td>
<td>0.061</td>
<td>0.074</td>
</tr>
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<td>0.60</td>
<td>0.268</td>
<td>0.049</td>
<td>0.061</td>
</tr>
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<td>0.70</td>
<td>0.220</td>
<td>0.040</td>
<td>0.051</td>
</tr>
<tr>
<td>0.80</td>
<td>0.181</td>
<td>0.034</td>
<td>0.042</td>
</tr>
<tr>
<td>0.90</td>
<td>0.148</td>
<td>0.030</td>
<td>0.036</td>
</tr>
<tr>
<td>1.00</td>
<td>0.123</td>
<td>0.027</td>
<td>0.031</td>
</tr>
</tbody>
</table>
Fig. 10 CONCENTRATION PROFILES FOR TOTAL SOLUTION CONCENTRATION OF 0.50N AND RESIN PARTICLE DIAMETERS OF 0.030, 0.058 and 0.082 cm. AT VARIOUS RESIN TIMES CALCULATED FROM THE RESIN AND COMBINED CONTROL MODELS.
considers effects of both resistances. Profiles calculated from the two models are given for the three particle diameters at a total solution normality (Cu\(^+\)/Na\(_2\)^+ \text{SO}_4^-\) of 0.50.

The Cu\(^+\) profile in the film and also in the resin particle calculated from the combined model, examined at corresponding resin times, show that the slope of the film and resin particle profile at the resin-film interface becomes larger (steeper) as the particle diameter increases. This result indicates that as the particle size increases, the liquid film resistance to mass transfer also increases. Similarly, the resistance of the resin phase is observed to increase as the particle size increases.

Comparison of the Cu\(^+\) profiles calculated from the resin phase control model show more dramatically the effect of increased resin resistance as the particle size increases. This model neglects the presence of the film and assumes only resin particle resistance to mass transfer. One can easily observe the increased resistance to mass transfer as the particle size increases.

As the particle diameter increases, both film and resin phase control are favored. These results are for a constant $N_{Re}$ (thus the same $N_{Sh}$ was used for each particle diameter).

A change in solution velocity ($N_{Re}$ varying) was not studied here but its effect on film and resin particle control can be noted by examining one of the correlations for $N_{Sh}$ given in Table 3, e.g., the correlation obtained by Pfeffer and Happel,

$$N_{Sh} = \frac{K_F D_p}{C_0 D_{Cu-Na}} = 3.14 \left( \frac{D_p V \rho}{\mu} \right)^{1/3} \left( \frac{\mu}{\rho D_{Cu-Na}} \right)^{1/3}.$$
Since $K_F$ is directly related to $N_{Re}$, as the solution velocity increases, $K_F$ increases, thus producing a decrease in the film resistance and film control. Therefore a high solution velocity will tend to favor resin phase control (low film resistance) while a low solution velocity would favor film control (high film resistance).

7.4 Perturbation of the Cu$^{++}$ Solution Concentration

The expression for the variation Cu$^{++}$ concentration in the solution phase through the column is given by Eq. (3). The constants $C_1$ and $C_2$ are obtained by a least squares analysis of the experimental data of Olsen and Meyer. For the 1.0 N total solution concentration (Cu$^{++}$/Na$_2^+$, SO$_4^{2-}$), the average error for this fit is 4.6%. The average error being defined as:

$$\text{average error} = \frac{\Delta X(\text{experimental}) - \Delta X(\text{calculated})}{\text{number of experimental points}} \times 100$$ (53)

where $\Delta X = X_2 - X_1$.

To test the sensitivity of the film and resin phase control model to an error in Eq. (3), the equation is perturbed to produce $X_B$ values at 95% and 105% of those produced with the Eq. (3) constants listed earlier. The perturbed equations are:

$$X_B = X_2 + .95 \times C_1 \times (\alpha \tau)$$ (54)

$$X_B = X_2 + 1.05 \times C_1 \times (\alpha \tau)$$ (55)

Using the combined control model for the 1.0 N total solution (Cu$^{++}$/Na$_2^+$, SO$_4^{2-}$) case and a particle diameter of 0.058 cm, Eq. (3) was replaced by Eqs. (54) and (55) respectively and calculations made. Table 10 shows the instantaneous mass transfer rates per gram of resin calculated from these three equations.
Table 10. Comparison of Instantaneous Mass Transfer Rates per Gram of Resin by Perturbation of the Cu^{++} Concentration in the Bulk Phase.

<table>
<thead>
<tr>
<th>Time, ( \alpha ) (( \tau = 939 ) sec)</th>
<th>( W_{Cu,G}^C ) (Eq. 3) Meq/gm\cdot sec X 10^{+2}</th>
<th>( W_{Cu,G}^C ) (Eq. 54) Meq/gm\cdot sec X 10^{+2}</th>
<th>( W_{Cu,G}^C ) (Eq. 55) Meq/gm\cdot sec X 10^{+2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.478</td>
<td>0.458</td>
<td>0.497</td>
</tr>
<tr>
<td>0.04</td>
<td>0.374</td>
<td>0.358</td>
<td>0.390</td>
</tr>
<tr>
<td>0.06</td>
<td>0.320</td>
<td>0.306</td>
<td>0.334</td>
</tr>
<tr>
<td>0.08</td>
<td>0.284</td>
<td>0.272</td>
<td>0.297</td>
</tr>
<tr>
<td>0.10</td>
<td>0.257</td>
<td>0.245</td>
<td>0.268</td>
</tr>
<tr>
<td>0.20</td>
<td>0.169</td>
<td>0.162</td>
<td>0.176</td>
</tr>
<tr>
<td>0.30</td>
<td>0.115</td>
<td>0.111</td>
<td>0.118</td>
</tr>
<tr>
<td>0.40</td>
<td>0.077</td>
<td>0.076</td>
<td>0.078</td>
</tr>
<tr>
<td>0.50</td>
<td>0.054</td>
<td>0.052</td>
<td>0.054</td>
</tr>
<tr>
<td>0.60</td>
<td>0.041</td>
<td>0.040</td>
<td>0.040</td>
</tr>
<tr>
<td>0.70</td>
<td>0.033</td>
<td>0.033</td>
<td>0.033</td>
</tr>
<tr>
<td>0.80</td>
<td>0.028</td>
<td>0.028</td>
<td>0.027</td>
</tr>
<tr>
<td>0.90</td>
<td>0.024</td>
<td>0.024</td>
<td>0.023</td>
</tr>
<tr>
<td>1.00</td>
<td>0.021</td>
<td>0.021</td>
<td>0.021</td>
</tr>
</tbody>
</table>
The perturbed instantaneous mass transfer rates are between 4-6% below in the case of Eq. (54) and 4-6% above in the case of Eq. (55) the results obtained with the unperturbed instantaneous mass transfer rates for early resin times ($\alpha < 0.5$). Thus the combined model was only sensitive to an error in the Cu$^{+\text{+}}$ variation at early resin times, but not so sensitive as to alter the general observations made to this point. It would take a much larger error in Eq. (3) than $\pm \text{5\%}$ to alter the general trend of obtained results.
8.0 CONCLUSIONS

In studying the mass transfer process (counter-diffusion of Cu$^{++}$ and Na$^+$ ions), the resistance offered by both the liquid film (Cu$^{++}$/Na$_2^+$, S0$_4^-$) adhering to the resin particle and the resin particle phase (Dowex 50WX-8) must be considered. For the solution concentration ranges studied (0.20, 0.50 and 1.0 total solution normality), both resistances were present for at least some portion of the total resin time. Except for a very short time immediately after the resin entered the column the resin phase controls the mass transfer process for the 1.0 and 0.50 total solution normality cases studied. For this short time period, the resistance from the liquid film is present but the larger resistance is still due to the resin phase. Liquid film controls the mass transfer for the 0.2 N total solution concentration initially as an increment of resin entered the column but for resin times greater than ($\alpha > 0.1$) this short time period resin particle control predominates over film control.

The effect of increasing particle size at a fixed Reynolds number is to increase the magnitude of both the resin phase and film resistance. For particle diameters of 0.030 and 0.058 cm, the resin phase contributes the major control of the mass transfer process throughout the column. For the largest particle size, 0.082 cm, both the liquid film and resin phase contributes resistance to the transfer of Cu$^{++}$ but again the resin phase offers the larger resistance.
9.0 SUGGESTIONS FOR FURTHER STUDY

The basis for this work was the assumption that the relation

$$X_B = X_2 + C_1(\alpha t)^{C_2}$$

adequately expresses the variation of Cu$^{++}$ concentration in the solution phase throughout the length of the ion exchange column. This equation says nothing about the radial variation in the Cu$^{++}$ concentration. Additional work is required to (1) better establish this relation (or obtain an alternative correlation) and (2) determine if the radial variation in the Cu$^{++}$ concentration is an important column variable and thus should be included in the expression for $X_B$.

In this work, resin particle size effects on the resin particle and liquid film control of the mass transfer process at constant Reynolds number were calculated. It would be worthwhile to examine the same effect as a function of Reynolds number.

The trend toward liquid film control as the solution concentration (Cu$^{++}$/Na$^{+}$, SO$_4^{2-}$) decreases has been established by the computational procedure used. Experimental studies at lower solution phase concentrations should be completed to verify this trend. It would be interesting to determine if the liquid film will completely control the mass transfer process for very low solution concentrations.

An exact value of $K_F$ was not needed in the computations made here since only relative mass transfer rates were needed to examine resin particle or liquid film control of the mass transfer process. To extend this work into column design, well established values of $K_F$ as a function of column variables will be needed. To obtain this information, detailed experimental measurements should be made on an actual continuous countercurrent ion exchange system.
10.0 ACKNOWLEDGEMENTS

First, the author wants to extend his sincere appreciation to Dr. W. Meyer for his guidance and many thoughtful suggestions for this investigation.

Secondly, a special thanks to Dr.'s J. O. Mingle and J. C. Matthews for their helpful suggestions with the numerical procedure used in this study.

Thirdly, financial help from the National Defense Education Act and the Atomic Energy Commission (obtained through the Department of Nuclear Engineering) was greatly appreciated.
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APPENDIX A

Resin and Solution Phase Properties

A-1 Resin Properties

Properties of Dowex 50W - X8, the resin phase, are presented here. Dowex 50W - X8 is available commercially in the form of spherical beads, 20 to 50 mesh size Na+ or H+ form (5). The mean particle diameter was calculated as the arithmetic mean between the diameter of 20 to 50 mesh particles.

<table>
<thead>
<tr>
<th>TABLE A-1. Resin Properties of Dowex 50W-X8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry exchange capacity, in H⁺ form</td>
</tr>
<tr>
<td>Dry exchange capacity, in H⁺ form</td>
</tr>
<tr>
<td>Wet density, ρ</td>
</tr>
<tr>
<td>Porosity (3), X</td>
</tr>
<tr>
<td>Mean particle diameter</td>
</tr>
</tbody>
</table>
A-2 Self Diffusivities of Cu\(^{++}\), Na\(^{+}\)

The self diffusivity of Na\(^{+}\), \(D_{Na}^R\), was taken as 6 times \(D_{Cu}^R\) as reported by Rao (21) is

\[ D_{Na}^R = 1.60 \times 10^{-6} \text{ cm}^2/\text{sec}, \]

thus

\[ D_{Cu}^R = 2.67 \times 10^{-7} \text{ cm}^2/\text{sec}. \]

The self diffusivity in the solution phase for Na\(^{+}\) (22) and Cu\(^{++}\) (23) are given in Table A-2.

<table>
<thead>
<tr>
<th>Material</th>
<th>(D^F \times 10^{-5} \text{ cm}^2/\text{sec})</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na_2SO_4)</td>
<td>.77</td>
<td>1.0N, 20°C</td>
</tr>
<tr>
<td></td>
<td>.71</td>
<td>0.5N, 20°C</td>
</tr>
<tr>
<td></td>
<td>.93</td>
<td>0.2N, 20°C</td>
</tr>
<tr>
<td>(CuSO_4)</td>
<td>.32</td>
<td>1.0N, 20°C</td>
</tr>
<tr>
<td></td>
<td>.38</td>
<td>0.5N, 20°C</td>
</tr>
<tr>
<td></td>
<td>.45</td>
<td>0.2N, 20°C</td>
</tr>
</tbody>
</table>

A-3 Correlation of Equilibrium Data for \((Cu^{++}/Na^{+}, SO_4^{2-})\) on Dowex 50W-X8

A power series was used to correlate equilibrium data of \((Cu^{++}/Na^{+},\) 
\(SO_4^{2-}\)) on Dowex 50W-X8 obtained by Olsen. Table A3 shows the coefficients 
and standard deviations of these correlations.
TABLE A-3 Power Series Correlation of \((\text{Cu}^{2+}/\text{Na}_2^+, \text{SO}_4^{2-})\) on Dowex 50W-X8

Equilibrium Data.

\[ X = B_0 + B_1 Y + B_2 Y^2 + B_3 Y^3 \ldots \]

<table>
<thead>
<tr>
<th>( C_O = 1.0 \text{ N} )</th>
<th>( C_O = 0.5 \text{ N} )</th>
<th>( C_O = 0.2 \text{ N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_0 = 0.0 )</td>
<td>( B_0 = 0.0 )</td>
<td>( B_0 = -0.088 )</td>
</tr>
<tr>
<td>( B_1 = 0.9217 )</td>
<td>( B_1 = 0.4480 )</td>
<td>( B_1 = 1.401 )</td>
</tr>
<tr>
<td>( B_2 = -0.2245 )</td>
<td>( B_2 = 0.1705 )</td>
<td>( B_2 = -6.8901 )</td>
</tr>
<tr>
<td>( B_3 = 0.2838 )</td>
<td>( B_3 = 0.3395 )</td>
<td>( B_3 = 18.343 )</td>
</tr>
<tr>
<td>( B_4 = 0.0 )</td>
<td>( B_4 = 0.0 )</td>
<td>( B_4 = -20.847 )</td>
</tr>
<tr>
<td>( B_5 = 0.0 )</td>
<td>( B_5 = 0.0 )</td>
<td>( B_5 = 9.7648 )</td>
</tr>
<tr>
<td>( B_6 = 0.0 )</td>
<td>( B_6 = 0.0 )</td>
<td>( B_6 = -0.6951 )</td>
</tr>
<tr>
<td>St. Dev = 0.011</td>
<td>St. Dev = 0.021</td>
<td>St. Dev = .0037</td>
</tr>
</tbody>
</table>

\[ Y = A_0 + A_1 X + A_2 X^2 + A_3 X^3 \ldots \]

<table>
<thead>
<tr>
<th>( C_O = 1.0 \text{ N} )</th>
<th>( C_O = 0.5 \text{ N} )</th>
<th>( C_O = 0.2 \text{ N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 = 0.0189 )</td>
<td>( A_0 = 0.0489 )</td>
<td>( A_0 = 0.0424 )</td>
</tr>
<tr>
<td>( A_1 = 0.9945 )</td>
<td>( A_1 = 1.7558 )</td>
<td>( A_1 = 5.4754 )</td>
</tr>
<tr>
<td>( A_2 = 0.3856 )</td>
<td>( A_2 = -1.245 )</td>
<td>( A_2 = -28.888 )</td>
</tr>
<tr>
<td>( A_3 = -0.4001 )</td>
<td>( A_3 = 0.4457 )</td>
<td>( A_3 = 95.691 )</td>
</tr>
<tr>
<td>( A_4 = 0.0 )</td>
<td>( A_4 = 0.0 )</td>
<td>( A_4 = -166.62 )</td>
</tr>
<tr>
<td>( A_5 = 0.0 )</td>
<td>( A_5 = 0.0 )</td>
<td>( A_5 = 141.59 )</td>
</tr>
<tr>
<td>( A_6 = 0.0 )</td>
<td>( A_6 = 0.0 )</td>
<td>( A_6 = -46.298 )</td>
</tr>
<tr>
<td>St. Dev = 0.0081</td>
<td>St. Dev. = 0.0236</td>
<td>St. Dev. = 0.0023</td>
</tr>
</tbody>
</table>

A-4 Number of Resin Particles per Gram

The various codes used calculated instantaneous mass transfer rates on a basis of a single pellet \((W_{Cu}^{F,R,C})\). For comparison purposes, the mass transfer rates were placed on a per gram of resin basis \((w_{Cu,G}^{R,R,C})\) by multiplying \(W_{Cu}^{F,R,C}\) by the number of pellets per gram of resin (PPG). The procedure for calculating PPG is as follows (for \(D_p = 0.058 \text{ cm}\):
(1) Volume of one pellet
\[ V = \frac{4}{3} \pi r^3 = \left(\frac{4}{3}\right) (\pi)(0.029)^3 = 1.022 \times 10^{-3} \ \text{cm}^3 \text{per pellet} \]

(2) Density of the resin in gm/cm\(^3\) of wt resin
\[ \frac{\text{gm}}{\text{cm}^3} = \frac{1.315 \ \text{gm/cm}^3 \text{Wet resin bed}}{(1 - 0.38)} = \left(\frac{2.11 \ \text{gm}}{\text{cm}^3} \right) \]

(3) Number of pellets per gram is
\[ \text{PPG} = \frac{1 \ \text{cm}^3}{2.11 \ \text{gms}} \times \frac{1 \ \text{pellet}}{1.022 \times 10^{-3} \ \text{cm}^3} = 4633 \ \text{pellets/gm} \]

In a similar manner, PPG for 0.030 and 0.082 cm particle diameters is
\[ \text{PPG}(D_p = 0.030 \ \text{cm}) = 3.352 \times 10^4 \ \text{pellets/gm}, \]
\[ \text{PPG}(D_p = 0.082 \ \text{cm}) = 1.641 \times 10^3 \ \text{pellets/gm}. \]
APPENDIX B

Solution of Difference Equations by the Thomas Method (18)

First we want to consider a system of \( N \) simultaneous equations

\[
A_1 YY(1) + B_1 YY(2) = D_1
\]

\[
C_1 YY(I - 1) + A_1 YY(I) + B_1 YY(I + 1) = D_I \quad I = 2, 3, \ldots, N-1 \quad (B-1)
\]

\[
C_N YY(N - 1) + A_N YY(N) = D_N
\]

where \( A, B, C, D \) = known scalar values,

\( YY \)'s = unknown values.

Equation (B-1) in matrix notation becomes

\[
\begin{bmatrix}
A_1 & B_1 \\
C_2 & A_2 & B_2 \\
\vdots & \vdots & \ddots & B_{N-1} \\
C_N & A_N
\end{bmatrix}
\begin{bmatrix}
YY(1) \\
YY(2) \\
\vdots \\
YY(N)
\end{bmatrix}
=
\begin{bmatrix}
D_1 \\
D_2 \\
\vdots \\
D_N
\end{bmatrix} \quad (B-2)
\]

The unknowns \( YY \) are eliminated by proceeding from the top and letting

\[
W_1 = A_1
\]

\[
W_I = A_I - C_I Q_{I-1} \quad I = 2, 3, \ldots, N
\]

where

\[
Q_{I-1} = B_{I-1}/W_{I-1}
\]

and

\[
G_1 = D_1/W_1
\]

\[
G_I = \frac{D_I - C_I G_{I-1}}{W_I} \quad I = 2, 3, \ldots, N
\]

The above thus transforms Eq. (B-1) to

\[
YY(N) = G(N)
\]

\[
YY(I) = G(I) - Q(I) X (I + 1) \quad (B-3)
\]

where \( J = 1, 2, 3, \ldots, N-1 \).

To summarize, \( W, Z, \) and \( G \) are calculated in order of increasing \( I \), then

Eq. (B-3) is used to calculate \( YY \) in order of decreasing \( I \). Flow sheet

is included in Appendix D.
APPENDIX C

Flow Sheet and Fortran Listing for Liquid Film Control Model Solution

Fig. C-1. Flow sheet.
Fig. C-1. Flow sheet (continued).
C******************************************************************************FORTRAN LISTING******************************************************************************
C
C****THIS PROGRAM EXAMINES LIQUID FILM CONTROL FOR ION EXCHANGE IN A
C CONTINUOUS COUNTERCURRENT ION EXCHANGE SYSTEM OF (CU/NA2,SO4)
C ON DOWEX 50W-XB
C
C******************************************************************************LISTING OF PARAMETERS******************************************************************************
C
C A,B ARE CONSTANTS FOR THE CU SOLUTION PHASE VARIATION EQ.
C CT IS THE TOTAL SOLUTION CONCENTRATION, I.E., 1.0N
C DA,DB ARE SELF DIFFUSIVITIES OF CU,NA IN THE LIQUID FILM
C DELT IS THE DIMENSIONLESS TIME INCREMENT
C DP IS THE RESIN PARTICLE DIAMETER
C E,G,H ARE CONSTANTS FOR THE EQUILIBRIUM EQ.
C PMAX IS THE NUMBER OF TIME STEPS BEFORE PRINTOUT
C PPG IS THE NUMBER OF PELLETS PER GRAM OF RESIN
C Q IS THE RESIN CAPACITY
C T IS DIMENSIONLESS TIME
C TAU IS THE MAXIMUM RESIDENT TIME
C TMAX IS THE MAXIMUM RESIDENT TIME DESIRED FOR CALCULATIONS
C X2,Y2 ARE INITIAL EQUIVALENT FRACTIONS OF CU IN SOLUTION AND RESIN
C XB,XS ARE THE CONCENTRATION OF BULK PHASE AND AND FILM-RESIN INTERFACE
C Y IS THE AVERAGE CU CONCENTRATION IN THE RESIN
C
C******************************************************************************GO KSU WILDCATS******************************************************************************
C
99 FORMAT(5F13.6)
100 FORMAT(5E12.4)
105 FORMAT(2E12.4)
110 FORMAT(1H0,F10.6,9E12.5)
115 FORMAT(1H6,E12.5)
199 FORMAT(1HL1,5F13.6)
117 FORMAT(1H6,5X,1HT,11X,2HXS,9X,2HXB,9X,5HAVE Y,3X,12HWAP(MEQ/SGM),
11X,11HDFBS(CCM/S),1X,11HDFBB(CCM/S),1X,10HDFB(CCM/S),2X,9HAK(CCM/S)
2),3X,11HTMT(MEQ/GM))
C
READ INPUT DATA
3 READ(1,99) T,DELT,TAU,PMAX,TMAX
C
CHECK VALUE OF TMAX FOR PROGRAM TERMINATION
C LAST DATA CARD MUST HAVE A ZERO VALUE OF TMAX FOR PROGRAM
C TERMINATION
IF(TMAX .LT.0.) GO TO 51
READ(1,100) CT,A,B,X2,Y2
READ(1,100) TMT,E,G,H
READ(1,100) RE,DP,Q,PPG
READ(1,105) DA,DB
READ(1,100) Y
C
C CHECK VALUES OF INPUT DATA
WRITE(3,199) T,DELT,T,TAU,PMA{T,MXX
WRITE(3,115)A,B,X2,Y2,Y
WRITE(3,115) RE,DP,Q,PPG
WRITE(3,115) TMT,E,G,H,DA,DB
WRITE(3,117)
C
C INITIALLY XB=X2
XB=X2
AREA=(3.1415*DP*DP*PPG)
C
C SET INITIAL VALUES FOR THE PRINTOUT COUNTER
COUNT3=1.0
APRINT=0.0
5 CONTINUE
C
C ADVANCE ONE TIME INCREMENT, ADD TO THE RESIN TIME
T=T+DELT
C
C CALCULATE SURFACE CONCENTRATION
XS=E*Y + G*Y*Y + H*Y*Y*Y
C
C CALCULATE BULK PHASE CONCENTRATION
XB=X2 + A*(T*TAU)**B
C
C CALCULATE FILM DIFFUSIVITIES AND TAKE AN AVERAGE
DFBS=(2.0*DA)/(2.0 + (DA/DB - 1.0)*XS)
DFBB=(2.0*DA)/(2.0 + (DA/DB - 1.0)*XB)
DFB=(DFBS + DFBB)/2.0
C
C CALCULATE MASS TRANSFER COEFFICIENT
AK=(60.0*DFB*CT)/DP
C
C CALCULATE MASS TRANSFER RATE PER GRAM OF RESIN
WAP=AK*AREA*(XB - XS)
C
C CALCULATE AVERAGE CONCENTRATION OF Cu IN THE RESIN PHASE
ATMT=WAP*DELT*TAU
TMT=TMT + ATMT
Y= Y2 + TMT/Q
C
C CHECK TO SEE IF PRINTOUT IS DESIRED AT THIS TIME
C IF NOT, CONTINUE, ADVANCE ONE TIME STEP
IF(APRINT)15,10,10
10 WRITE(3,110)T,XS,XB,Y,WAP,DFBS,DFBB,DFB,AK,TMT
15 CONTINUE
IF(IT - TMAX)20,20,50
20 COUNT3=COUNT3 + 1.0
IF(COUNT3 - PMA{T,MXX35,40,40}
35  APRINT=-5.0
   GO TO 5
40  APRINT=5.0
    COUNT3=0.0
    GO TO 5
50  CONTINUE
    GO TO 3
51  CONTINUE
    STOP
    END
APPENDIX D
Flow Sheet and Fortran Listing for Resin Particle Control Model Solution

Fig. D-1. Flow sheet.
Fig. D-1. Flow sheet (continued).
Fig. D-1. Flow sheet (continued).
Fig. D-2. Flow sheet of Thomas Method.
C*****************************************************************************************FORTRAN LISTING*******************************************************************************************
C
C***THIS PROGRAM EXAMINES RESIN PARTICLE CONTROL FOR ION EXCHANGE
C    IN A CONTINUOUS COUNTERCURRENT ION EXCHANGE SYSTEM OF
C    (CU/NA2,SO4) ON DOWEX 50WX-8
C
C***SOLUTION OF THE DIFFUSION EQUATIONS INVOLVES THE SIMULTANEOUS
C    SOLUTION OF DIFFERENCE EQUATIONS USING THE METHOD OF THOMAS
C
C*****************************************************************************************LISTING OF PARAMETERS*******************************************************************************************
C
C AE,BE ARE THE CONSTANTS FOR THE CU VARIATION IN THE BULK PHASE
C AMAX IS THE NUMBER OF TIME STEPS BEFORE PRINTOUT
C C1,C2,C3,C4 ARE THE CONSTANTS FOR THE EQUILIBRIUM EQ.
C DA,DB ARE SELF DIFFUSIVITIES OF CU,NA IN THE LIQUID FILM
C DB IS THE DIMENSIONLESS RADIAL POSITION INCREMENT
C DT IS THE DIMENSIONLESS TIME INCREMENT
C N IS THE NUMBER OF POSITION POINTS
C PPG IS THE NUMBER OF PELLETS PER GRAM OF RESIN
C QH0 IS THE RESIN CAPACITY
C R IS THE RADIUS OF THE RESIN PARTICLE
C T IS DIMENSIONLESS TIME
C TAU IS THE MAXIMUM RESIDENT TIME
C TMAX IS THE MAXIMUM RESIDENT TIME DESIRED FOR CALCULATIONS
C X2 IS THE CU CONCENTRATION IN THE BULK PHASE AT TIME = 0
C Y IS THE EQUIVALENT FRACTION OF CU IN THE RESIN AT TIME T
C YIN IS THE INITIAL CONCENTRATION OF CU IN THE RESIN PARTICLE
C YY IS THE EQUIVALENT FRACTION OF CU IN THE RESIN AT TIME T + DT
C
C*****************************************************************************************GO KSU WILDCATS*******************************************************************************************
C
DIMENSION YY(51),Y(51),DX(51),DX1(51)
DIMENSION A(51),B(51),C(51),D(51)

C 'READ IN NECESSARY CONSTANTS OR PARAMETERS
16 READ(1,100) DT,DB,T,TAU,N
C
C PROGRAM TERMINATES IF N IS 0 OR NEGATIVE, LAST CARD MUST HAVE A 0
C OR NEGATIVE VALUE OF N FOR PROGRAM TO TERMINATE
IF(N)17,17,15
15 READ(1,101) DA,R,QH0,PPG
READ(1,100) YIN,X2,CT
READ(1,101)C1,C2,C3,C4,C5,C6,C7
READ(1,100)AE,BE
READ(1,100)TMAX,AMAX
100 FORMAT(4F10.6,15)
101 FORMAT(4E12.5)

C CHECK INPUT LISTING
WRITE(3,200)
200 FORMAT(1H1,15X,'INPUT LISTING')
   WRITE(3,210)DT,DB,T
210 FORMAT(1H,'TIME INCREMENT=',F10.4,2X,'POSITION INCREMENT=',F6.3,2X,'INITIAL TIME=',F10.6)
   WRITE(3,219)TAU,N
219 FORMAT(1H,'TOTAL RESIDENT TIME=',F10.6,2X,'NO. OF POSITIONS=',I5)
   WRITE(3,212)DA,R,QRH0,PPG
212 FORMAT(1H0,'CU SELF DIFFUSIVITY=',E12.5,2X,'PARTICLE RADIUS=',F6.4,2X,'RESIN CAPACITY=',F10.6,2X,'NUMBER OF PELLETS PER GRAM=',E12.5,2X)
   WRITE(3,214)YIN,X2
214 FORMAT(1H0,27HINITIAL RESIN EQ. FRACTION=',F10.6,2X,28HFINAL SOLUTION EQ. FRACTION=',F10.6)
   WRITE(3,215)
215 FORMAT(1H0,10X,'EQUILIBRIUM CONSTANTS')
   WRITE(3,216)C1,C2,C3,C4,C5,C6,C7
216 FORMAT(1H,'E12.5')
   WRITE(3,217)AE,BE
217 FORMAT(1H0,38HCONSTANTS FOR THE FREUNDLICH EQUATION=',2F10.6)
   WRITE(3,218)TMAX,AMAX
218 FORMAT(1H0,22HMAXIMUM RESIDENT TIME=',F10.6,2X,18HPRINTOUT INTERVAL 1=',F10.6)
   C
   C SKIP TO A NEW PAGE
   WRITE(3,300)
300 FORMAT(1H1)
   WRITE(3,301)CT
301 FORMAT(1H,'25X,'FEED SOLUTION NORMALITY=',F10.6)
   C
   C SET INITIAL COUNTER VALUE
   APRINT=0.0
   C
   C SET UP INITIAL PARTICLE CONCENTRATION PROFILE
   DO 10 I=1,N
     Y(I)=YIN
   10 CONTINUE
   C
   C START COUNTER
   9 APRINT=APRINT + 1.0
   C
   C CALCULATE INITIAL PARTICLE DIFFUSIVITIES
   DO 11 I=1,N
     DX(I)=(3.*DA*(1. + Y(I)))/(3. - 2.*Y(I))
   11 CONTINUE
   C
   C SET THE COLUMN TIME OR EQUILIVANT COLUMN DISTANCE
   T=T + DT
   C
   C CALCULATE LIQUID PHASE SURFACE CONCENTRATION FROM THE
   C CU VARIATION IN BULK PHASE EQ.
   XS=X2 + AE*(T*TAU)**BE
C
C CALCULATE RESIN PHASE SURFACE CONCENTRATION FROM THE
C EQUILIBRIUM EQUATION
    YY(N)=C1+ C2*X5 +C3*X5*X5 + C4*X5*X5*X5*X5 + C5*X5*X5*X5*X5*X5 + C6*X5*
    1*X5*X5*X5*X5*X5 + C7*X5*X5*X5*X5*X5*X5*X5*X5*X5
C
C CALCULATE CONCENTRATION PROFILE USING THE IMPLICIT METHOD
C SINCE THE DIFFUSIVITIES ARE NOT KNOWN AT THE NEW CONCENTRATIONS,
C IT WILL ALSO BE NECESSARY TO ITERATE OVER YY UNTIL THE
C DIFFERENCE BETWEEN PREVIOUS DX'S AND NEW DX'S IS SMALL
C SET UP THE COEFFICIENT MATRIX FOR THE THOMAS METHOD SOLUTION
N1=N-1
    AA=(TAU*DT)/(2.*R*R*DB*DB)
C SET COUNTER FOR THE DIFFUSIVITY ITERATION
J=0
C POSITION AT THE CENTER
32 A(I)=1. +AA*X5**DX(I)
    B(I)=-AA*X5**DX(I)
    D(I)= Y(I) +(AA*X5**DX(I)*(Y(2)-Y(I)))
C REMAINING POSITIONS
    DO 12 I=2,N1
    BX=(I-1)*DB
    C(I)=AA*(-DX(I) + (DX(I+1)-DX(I-1))/4.0) +(DB*DX(I))/(BX)
    A(I)=AA*2.*DX(I)+ 1.0
    B(I)=(0.-AA*(DX(I) + (DX(I+1)-DX(I-1))/4.0) +(DX(I)*DB)/(BX))
    D(I)=Y(I) + AA*(DX(I)*(Y(I+1)-2.*Y(I) +Y(I-1)) +((DX(I+1)-DX(I-1))
    1/(4.*)))*(Y(I+1)-Y(I-1)) +(DB*DX(I)*(Y(I+1)-Y(I-1)))/(BX))
     IF(I-N1)12,41,41
    12 CONTINUE
    41 D(N1)=D(N1)-YY(N)*B(N1)
    CALL TOMAS(A,B,C,D,YY,N)
C
C ITERATE OVER YY TO FIND CORRECT DX-S
    DO 13 I=1,N
    DX(I)=(3.*DA*(1. + YY(I)))/(3. - 2.*YY(I))
    13 CONTINUE
C
C COMPARE DX WITH DX1
    DO 20 I=1,N
    XI=(DX1(I)-DX(I))/(DX1(I))
    IF(ABS(XI).GE. .1E-03) GO TO 30
    20 CONTINUE
    GO TO 31
    30 J=J+1
    DO 21 I=1,N
    DX(I)=DX1(I)
    21 CONTINUE
    GO TO 32
    31 CONTINUE
C CHECK TO SEE IF PRINTOUT IS DESIRED AT THIS TIME, IF SO
C ALSO CALCULATE THE INSTANTANEOUS MASS TRANSFER RATE PER GRAM
   IF(APRINT=AMAX)4,5,5
      5 CONTINUE
C
C CALCULATE THE INSTANTANEOUS MASS TRANSFER RATE PER GRAM
   XMASST=PG*12.565*R*DX(N)*QRHO*(1.0*YY(N)-4.0*YY(N-1)+YY(N-2))/(21.0*DB)
   WRITE(3,220)T,XMASST,J
220 FORMAT(1H0,5HTIME=,F10.6,3X,23HMIST MASS TRANSFER RATE=,F10.6,3X,11
   1HITERATIONS=,I5)
   WRITE(3,222)
222 FORMAT(1H0,21X,'EQUIVALENT FRACTION COMPOSITION')
   WRITE(3,224)(YY(I),I=1,N)
224 FORMAT(1H ,7F10.6)
   WRITE(3,225)
225 FORMAT(1H0,24X,'DIFFUSION COEFFICIENTS')
   WRITE(3,226)(DX(I),I=1,N)
226 FORMAT(1H ,7E10.4)
   APRINT=0.0
   AP CONTINUE
C
C CHECK TO SEE IF DESIRED RESIDENT TIME IS EXCEEDED
   IF(T-TMAX)7,7,8
      7 CONTINUE
C
C THE NEW VALUES NOW BECOME THE PREVIOUS VALUES FOR THE NEXT
C TIME STEP
   DO 14 I=1,N
      Y(I)=YY(I)
   14 CONTINUE
C
C TRANSFER TO STATEMENT 9 AND DETERMINE THE CONCENTRATION
C PROFILE FOR THE NEXT TIME STEP
   GO TO 9
   8 CONTINUE
C
C READ NEW SET OF DATA
   GO TO 16
17 CONTINUE
C
C STOP
C
C SUBROUTINE TOMAS(A,B,C,D,X1,N)
C
C OBTAIN THE UNKNOWN CONCENTRATION USING THOMAS-S METHOD
C DIMENSION A(51),B(51),D(21),C(51),X1(51)
C DIMENSION W(51),G(51)
C
C EVALUATION OF THE COEFFICIENTS IN ORDER OF INCREASING R
C N1=N-1
N2=N1-1
W(1)=A(1)
G(1)=D(1)/W(1)
DO 10 I=2,N1
   W(I)=A(I)-C(I)*(B(I-1)/W(I-1))
   G(I)=(D(I)-C(I)*G(I-1))/W(I)
10 CONTINUE
C
C CONCENTRATION IS CALCULATED IN ORDER OF DECREASING R
   X1(N1)=G(N1)
   DO 11 I=1,N2
      J=N1-I
      X1(J)=G(J)-X1(J+1)*(B(J)/W(J))
11 CONTINUE
RETURN
END
APPENDIX E

Flow Sheet and Fortran Listing for Combined Resin-Film Control Model Solution

Fig. E-1. Flow sheet.
Fig. E-1. Flow sheet (continued).

Calc. $X_B$

$X_S = X_B = .01$

250

CALL

Tomas($A_1$, $B_1$, $C_1$, $D_1$, $YY$, $N$)

Implicit Method

3? 

Calc. remaining $A_1$

Calc. $A_1$, $B_1$, $D_1$

$J = 0$

251

$X_S = X_SN$

20

Calc. YY($N$)

$N1 = N - 1$

C

D
Fig. E-1. Flow sheet (continued).
**Fig. E-1. Flow sheet (continued).**
FIG. E-1. Flow sheet (continued).
C******************************************************************
C
C****THIS PROGRAM EXAMINES THE COMBINED RESISTANCES OF THE LIQUID FILM
C AND RESIN PARTICLE PHASE ON THE CONTROL OF ION EXCHANGE IN A
C CONTINUOUS COUNTERCURRENT ION EXCHANGE SYSTEM OF (CU/NA2,SO4)
C ON DOWEX 50W-X8
C****SOLUTION OF THE DIFFUSION EQUATIONS INVOLVES THE SIMULTANEOUS
C SOLUTION OF DIFFERENCE EQUATIONS USING THE METHOD OF THOMAS
C
C****A TRIAL AND ERROR PROCEDURE IS ALSO INVOLVED TO DETERMINE
C THE CONCENTRATION OF CU AT THE RESIN PARTICLE- LIQUID FILM
C INTERFACE
C
C******************************************************************
C
C AE,BE ARE THE CONSTANTS FOR THE CU VARIATION IN THE BULK PHASE
C AMAX IS THE NUMBER OF TIME STEPS BEFORE PRINTOUT
C CI,C2,C3,C4,C5,C6,C7 ARE THE CONSTANTS FOR THE EQUIL. EQ.
C CT IS THE TOTAL SOLUTION CONCENTRATION(CU/NA2,SO4)
C DA,DB ARE SELF DIFFUSIVITIES OF CU,NA IN THE LIQUID FILM
C DB IS THE DIMENSIONLESS RADIAL POSITION INCREMENT
C DT IS THE DIMENSIONLESS TIME INCREMENT
C DI,DJ ARE THE SELF DIFFUSIVITIES OF CU,NA IN THE BULK PHASE
C N IS THE NUMBER OF POSITION POINTS
C PPG IS THE NUMBER OF PELLETS PER GRAM OF RESIN
C QRHO IS THE RESIN CAPACITY
C R IS THE RADIUS OF THE RESIN PARTICLE
C T IS DIMENSIONLESS TIME
C TAU IS THE MAXIMUM RESIDENT TIME
C Tmax IS THE MAXIMUM RESIDENT TIME DESIRED FOR CALCULATIONS
C X2 IS THE CU CONCENTRATION IN THE BULK PHASE AT TIME = 0
C YIN IS THE INITIAL CONCENTRATION OF CU IN THE RESIN PARTICLE
C Y IS THE EQUIVALENT FRACTION OF CU IN THE RESIN AT TIME T
C YY IS THE EQUIVALENT FRACTION OF CU IN THE RESIN AT TIME T + DT
C
C******************************************************************
C
C DIMENSION YY(51),Y(51),DX(51),DX1(51)
C DIMENSION A(51),B(51),C(51),D(51)
C
C READ IN NECESSARY CONSTANTS OR PARAMETERS
C 16 READ(1,100) DT,DB,T,TAU,N
C
C PROGRAM TERMINATES IF N IS O OR NEGATIVE, LAST CARD MUST HAVE A 0
C OR NEGATIVE VALUE OF N FOR PROGRAM TO TERMINATE
C 15 READ(1,101) DA,R,QRHO,PPG
C READ(1,100) YIN,X2,CT
C READ(1,101)C1,C2,C3,C4,C5,C6,C7
C READ(1,100)AE,Be
C
C******************************************************************
C
C
READ(1,101)D1,D2
READ(1,100)TMAX,AQMAX
100 FORMAT(4F10.6,15)
101 FORMAT(4E12.5)
C
C CHECK INPUT LISTING
WRITE(3,200)
200 FORMAT(1H1,28X,'INPUT LISTING')
WRITE(3,210)DT, DB, T
210 FORMAT(1H0,'TIME INCREMENT=', F10.4, 2X,'POSITION INCREMENT=', F6.3, 2X,'INITIAL TIME=', F10.6)
WRITE(3,219)TAU,N
219 FORMAT(1H0,'TOTAL RESIDENT TIME=', F10.6, 2X,'NO. OF POSITIONS=', I5)
WRITE(3,212)DA,R,CRHO,PPG
212 FORMAT(1H0,'CU SELF DIFFUSIVITY=', E12.5, 2X,'PARTICLE RADIUS=', F6.4, 2X,'RESIN CAPACITY=', F10.6, 2X,'NUMBER OF PELLETS PER GRAM=', E12.5, 2X)
WRITE(3,214)YIN,X2
214 FORMAT(1H0, 27H INITIAL RESIN EQ. FRACTION=', F10.6, 2X, 28H FINAL SOLUTION EQ. FRACTION=', F10.6)
WRITE(3,215)
215 FORMAT(1H0, 10X,'EQUILIBRIUM CONSTANTS')
WRITE(3,216)C1,C2,C3,C4,C5,C6,C7
216 FORMAT(1H1,4E12.5)
WRITE(3,217)AE,BE
217 FORMAT(1H0,37H CONSTANTS FOR THE FREUNDLICH EQUATION=', 2F10.6)
WRITE(3,230)D1,D2,CT
230 FORMAT(1H0,'FILM-MOLECULAR DIFFUSIVITIES=', 2E12.5, 5X,'SOLUTION CONCENTRATION (NORMALITY)=', F10.6)
WRITE(3,218)TMAX,AMAX
218 FORMAT(1H0, 22H MAXIMUM RESIDENT TIME=', F10.6, 2X, 18H PRINTOUT INTERVAL 1=', F10.6)
C
C SKIP TO A NEW PAGE
WRITE(3,300)
300 FORMAT(1H1)
WRITE(3,301)CT
301 FORMAT(1H1,25X,'FEED SOLUTION NORMALITY=', F10.6)
C
C SET INITIAL COUNTER VALUE
APRINT=0.0
MF=6.0
C
C SET UP INITIAL PARTICLE CONCENTRATION PROFILE
DO 10 I=1,N
Y(I)=YIN
10 CONTINUE
C
C START COUNTER
9 APRINT=APRINT + 1.0
C CALCULATE INITIAL PARTICLE DIFFUSIVITIES
  DO 11 I=1,N
  DX(I)=(3.*DA*(1. + Y(I)))/(3. - 2.*Y(I))
11 CONTINUE
C
C SET THE COLUMN TIME OR EQUIVALENT COLUMN DISTANCE
  T=T + DT
C
C CALCULATE LIQUID PHASE SURFACE CONCENTRATION FROM THE
C CU VARIATION IN BULK PHASE EQ.
  XB=X2 + AE*(T*TAU)**BE
C
C MAKE AN INITIAL GUESS OF THE LIQUID PHASE SURFACE CONCENTRATION
IF(MF)250,251,251
  250 XS=XB-.1
  GO TO 20
  251 CONTINUE
XS=XS
L=0
20 CONTINUE
C
C CALCULATE RESIN PHASE SURFACE CONCENTRATION FROM THE
C EQUILIBRIUM EQUATION
  YY(N)=C1+ C2*XS +C3*XS*XS + C4*XS*XS*XS + C5*XS*XS*XS*XS + C6*XS*
  1XS*XS*XS*XS + C7*XS*XS*XS*XS + C8*XS*XS*XS*XS + C9*XS*XS*XS*XS
C
C CALCULATE CONCENTRATION PROFILE USING THE IMPLICIT METHOD
C SINCE THE DIFFUSIVITIES ARE NOT KNOWN AT THE NEW CONCENTRATIONS,
C IT WILL ALSO BE NECESSARY TO ITERATE OVER YY UNTIL THE
C DIFFERENCE BETWEEN PREVIOUS DX'S AND NEW DX'S IS SMALL
C SET UP THE COEFFICIENT MATRIX FOR THE THOMAS METHOD SOLUTION
  N1=N-1
  AA=(TAU*DT)/(2.*R*R*DB*DB)
C
C SET COUNTER FOR THE DIFFUSIVITY ITERATION
  J=0
C
C POSITION AT THE CENTER
32 A(1)=1. +AA*6.*DX(1))
  B(I)=-AA*6.*DX(I)
  D(I)= Y(I) +((AA*6.*DX(1)*(Y(2)-Y(1)))
C
C REMAINING POSITIONS
  DO 12 I=2,N1
    BX=(I-1)*DB
    C(I)=AA*(1.-DX(I)+ (DX(I+1)-DX(I-1))/(4.0) +(DB*DX(I))/(BX))
    A(I)=AA*2.*DX(I)+ 1.0
    B(I)=0.*AA*(DX(I) +DX(I+1)-DX(I-1))/(4.0) + (DX(I)*DB)/(BX))
    D(I)=Y(I) + AA*(DX(I)*(Y(I+1)+2.*Y(I) +Y(I-1)) +((DX(I+1)-DX(I-1))
    1/(4.0))*(Y(I+1)-Y(I-1)) +(DB*DX(I)*(Y(I+1)-Y(I-1)))/(BX))
    IF(I-N1)12,41,41
12 CONTINUE
41 D(N1)=D(N1)-YY(N)*B(N1)
   CALL TOMAS(A,B,C,D,YY,N)
C
C ITERATE OVER YY TO FIND CORRECT DX-S
   DO 13 I=1,N
      DX1(I)=(3.*DA*(1. + YY(I)))/(3. - 2.*YY(I))
13 CONTINUE
C
C COMPARE DX WITH DX1
   DO 22 I=1,N
      XI=(DX1(I)-DX(I))/(DX1(I))
      IF(ABS(XI).GE. .1E-03) GO TO 30
22 CONTINUE
   GO TO 31
30 J=J+1
   DO 21 I=1,N
      DX(I)=DX1(I)
21 CONTINUE
   GO TO 32
31 CONTINUE
C
C CALCULATE FILM DIFFUSIVITIES
   DFBS=(2.0*D1)/(2.0 +(D1/D2-1.0)*XS)
   DFBB=(2.0*D1)/(2.0+(D1/D2-1.0)*XB)
   DAB=(DFBS+DFBB)/2.0
C
C CALCULATE MASS TRANSFER COEFFICIENT THROUGH THE FILM
   RK=(60.0*DAB*CT)/(2.0*R)
C
C CALCULATE A NEW SURFACE CONCENTRATION FROM EQUATING THE INST.
C TRANSFER RATES FOR THE PARTICLE AND FILM MODELS AT THE
C PARTICLE SURFACE
   DER2=(3.0*YY(N)-4.0*YY(N-1) + YY(N-2))/(2.0*DB)
   XSN=XB - QRHO*DX1(N)*DER2/(R*RK)
C
C ROUTINE FOR TRIAL AND ERROR SOLUTION FOR XS
C CALCULATE DIFFERENCE BETWEEN NEW AND PREVIOUS VALUE OF XS
   .DELX=XS-XSN
C
C CHECK SIGN, AND TRANSFER TO CORRESPONDING LOCATION
   IF(DELX)304,340,305
C
C ONCE THIS IS DONE, CHECK TO SEE IF THE ERROR CRITERIA HAS BEEN
C MET, IF NOT, HALVE THE DIFFERENCE ADD OR SUBTRACT TO THE
C PREVIOUS VALUE OF XS, TRANSFER TO BEGINNING AND CALCULATE A
C A NEW XS
304 TEST=ABS(DELX/XS)
   IF(TEST .LT. .9E-04) GO TO 340
   XS=XS-DELX/2.
   L=L+1
   GO TO 20
305 TEST=ABS(DELX/XS)
   IF (TEST .LT. .9E-04) GO TO 340
   XS=XS - DELX/2.0
   L=L+1
   GO TO 20
340 CONTINUE
   MF=-5.0
C
C CHECK TO SEE IF PRINTOUT IS DESIRED AT THIS TIME, IF SO
C ALSO CALCULATE THE INSTANTANEOUS MASS TRANSFER RATE AND AN ERROR
C TERM FOR XS
   IF (APRINT-AMAX)4,5,5
   5 CONTINUE
C
C CALCULATE THE INSTANTANEOUS MASS TRANSFER RATE
   XMASST=RK*12.5656*R*R*PPG*(XB-XS)
C
C CHECK ERROR TERM FOR XS FROM TRIAL AND ERROR ROUTINE
   TEST=(XS-XSN)/XS
   WRITE(3,220) T
   220 FORMAT(1HO,34X,'TIME=',F10.6)
   WRITE(3,227)XMASST, J, L
   227 FORMAT(1HO,'INST MASS TRANSFER RATE=',F10.6,5X,'NO OF ITERATIONS D
   IVER D AND XS=',I5,5X,I5)
   WRITE(3,228)TEST,XS,XB
   228 FORMAT(1HO,'ERROR IN XS=',E12.5,17X,'XS=',F10.6,17X,'XB=',F10.6)
   WRITE(3,222)
   222 FORMAT(1HO,27X,'EQUIVALENT FRACTION COMPOSITION')
   WRITE(3,224)(YY(I), I=1,N)
   224 FORMAT(1H ,7F12.6)
   WRITE(3,225)
   225 FORMAT(1HO,31X,'DIFFUSION COEFFICIENTS')
   WRITE(3,226)(DX1(I), I=1,N)
   226 FORMAT(1H ,7E12.6)
   APRINT=0.0
   4 CONTINUE
C
C CHECK TO SEE IF DESIRED RESIDENT TIME IS EXCEEDED
   IF (IT-TMAX)7,7,8
   7 CONTINUE
C
C THE NEW VALUES NOW BECOME THE PREVIOUS VALUES FOR THE NEXT
C TIME STEP
   DO 14 I=1,N
   Y(I)=YY(I)
   14 CONTINUE
C
C TRANSFER TO STATEMENT 9 AND DETERMINE THE CONCENTRATION
C PROFILE FOR THE NEXT TIME STEP
   GO TO 9
8 CONTINUE
C
C READ NEW SET OF DATA
GO TO 16
17 CONTINUE
STOP
END
SUBROUTINE TOMAS(A,B,C,D,X1,N)
C
C OBTAIN THE UNKNOWN CONCENTRATION USING THOMAS-S METHOD
DIMENSION A(51),B(51),D(21),C(51),X1(51)
DIMENSION W(51),G(51)
C
C EVALUATION OF THE COEFFICIENTS IN ORDER OF INCREASING R
N1=N-1
N2=N1-1
W(1)=A(1)
G(1)=D(1)/W(1)
DO 10 I=2,N1
W(I)=A(I)-C(I)*(B(I-1)/W(I-1))
G(I)=(D(I)-C(I)*G(I-1))/W(I)
10 CONTINUE
C
C CONCENTRATION IS CALCULATED IN ORDER OF DECREASING R
X1(N1)=G(N1)
DO 11 I=1,N2
J=N1-I
X1(J)=G(J)-X1(J+1)*(B(J)/W(J))
11 CONTINUE
RETURN
END
RELATIVE PARTICLE AND FILM DIFFUSION CONTROL

IN COUNTERCURRENT COLUMNAR ION EXCHANGE

FOR THE SYSTEM (Cu^{++}-Na^{+})SO_{4}^{=} - DOWEX 50W-X8

by

LAWRENCE F. DREAL

B.S., The University of Nebraska, 1967

AN ABSTRACT OF A MASTER'S THESIS

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MASTER OF SCIENCE

Department of Nuclear Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1971
ABSTRACT

Both resin particle and solution phase* resistance to the inter-
diffusion of counter ions, Cu\(^{++}\) and Na\(^{+}\) must be considered for the ion
exchange system (Cu\(^{++}\)/Na\(_2\)\(^{+}\), SO\(_4\)\(^{-}\)) – Dowex 50W-X8 (Na\(^{+}\) form) during
continuous countercurrent columnar ion exchange. At total solution
normalities of 1.0 and 0.50, the resin particle phase was found to control
the mass transfer process (Cu\(^{++}\) diffusing into the resin, Na\(^{+}\) into the
solution) throughout the length of the column.

For a total solution concentration of 0.20 N, both the liquid film
and resin particle phases exhibited resistance to the mass transfer pro-
cess. The liquid film dominated the control of the mass transfer initially
(\(\tau<0.1\)) but as the resin continued down the column, the resin phase offered
the larger resistance to mass transfer although it did not completely
control.

Similar studies for resin particle diameters of 0.30, 0.051 and 0.082
cm at a total solution normality of 0.50 showed that at constant Reynold's
number both the resin and liquid film resistances were increased as the
resin particle diameter increased. At diameters of 0.030 and 0.058 cm,
the resin phase was found to control the mass transfer process. Both the
liquid film and resin phases contributed significant resistance for a
particle diameter of 0.082 cm. No one phase was found to completely
control the transfer process through the column, but the resin phase
exhibited the largest resistance.

* Solution phase resistance is described in terms of resistance of a
liquid film adhering to the resin particle.