Estimation Method for Exchange Capacity of Mixed Bed Using Monitoring Minicolumns

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The methods of estimation of the exchange capacity of mixed bed demineralizer used in nuclear power plants were studied for the purpose of protection against contamination of condensed water with leaked sea water flowing as a coolant in the heat exchanger. It was identified by numerical calculations and experimental works that the performance of mixed bed could be represented by the model for a system of single sort of ion exchange resin and single solute.

The intraparticle diffusivities and ion exchange equilibrium constants for the monitoring minicolumns can be obtained experimentally with the breakthrough curves for different packed height and the equilibrium constant for 1 m packed height can be known by extrapolation. The constants for 1 m packed height are substituted to the theoretical approximate formula which has been already recognized as a solution for the transient behavior of the adsorption system of a single solute, then the breakthrough time for actually working column of 1 m packed height can be calculated. For the rough estimation of degree of degradation for the deteriorated resin, a simple prediction method was presented in which the relations between the initial concentrations of the effluent from the minicolumns and the packed heights were applied.

KEYWORDS: breakthrough curve, ion exchange capacity, mixed bed, numerical calculation, nuclear power plants, demineralization, ion exchange, water chemistry

1. INTRODUCTION

This research has a purpose of providing the methods to estimate the capacity of the mixed bed demineralizer working in the nuclear power plants. The mixed bed is used to demineralize the condensed water being cooled by sea water. The roles of mixed bed are to remove colloidal metal compound originated from structural materials and to protect mixing in condensed water with leaked sea water from the heat exchanger. Because the capacity of ion exchange resin in mixed bed decreases with recurring use, the remained capacity of mixed bed must be always checked for the safety operation of power plant.

The packed height of working mixed bed is about 1 m. Hitherto the checking method was to measure the breakthrough time for testing column of 1 m packed height in which the sample of used resins were packed. The processing time of measurement is about 150 h. It is too long to serve as a checking method and to avoid the radiation exposure of the worker. But the short monitoring column gives too rough estimation to be used for safety operation because the suitable calculation method has not been found.

We have developed the method that the capacity of mixed bed can be estimated by the combined procedure of the measurements of short processing time using minicolumns which contain small quantity of resin samples and the theoretical calculations.

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The mathematical solution for the transient behavior of a system of single solute and one sort of ion exchange resin has been already established (1)~(13), but the report for the transient behavior of mixed bed is not available.

II. SIMPLIFICATION OF THEORETICAL TREATMENTS FOR SYSTEM OF MIXED BED AND MULTICOMPONENT

It is necessary to simplify the model of the system of mixture to solve the problem by means of mathematics for the transient behavior of ion exchange column. As this work has a purpose of estimation of the breakthrough curve for leaked sea water, it is sufficient to know the behavior of NaCl solution through the mixed bed. The ion exchange reactions between NaCl solution and ion exchange resins and neutralization in the solution are represented as follows:

\[ R-SO_3H + NaCl = R-SO_3Na + HCl, \]
\[ R=NOH + NaCl = R=NCI + NaOH, \]
\[ HCl + NaOH = NaCl + H_2O. \]

The neutralization reaction of HCl and NaOH in solution is rapid as compared with ion exchange in the resin particles in which the diffusion should be the rate determining step. Then the neutralization reaction in solution is concerned only with stoichiometric coefficient. As the binary diffusions are proceeding simultaneously in different resin particles in the mixed bed, there are too much variables to solve the problem mathematically.

We supposed a simplified model in which micro beds of cation and anion exchange resin e.g. laminated beds are arranged in a column as illustrated in Fig. 1(b). It is considered that in the simplified model the equilibrium constants are equal to those of Eq. (1) or (2) for respectively cation and anion exchange resin, but each micro bed could be treated as an independent bed. The flow of solute in the mixed bed is presented in Fig. 1(a). If the simplified model illustrated in Fig. 1(b) were applied to the mixed bed in place of the actual model (a) (Fig. 1), the solution for the adsorption system of single solute could be employed to calculate the breakthrough curve for mixed bed. The system of the major ion in the effluent at early period of breakthrough will be preferred as a system to be calculated on the purpose of this work.

There is no apriori reason to expect that these two different models will give quite similar breakthrough curves. It is also impossible by means of experimental work to certify that the similar breakthrough curves could be obtained for both of model (a) and model (b). The assumption of the model (b) has a purpose of applying the theoretical
formula derived for the more simple system to the system of mixed bed. The conception that the analytical solution for the adsorption system of a single solute could be applied to the calculation of the breakthrough curve for mixed bed, was introduced by the following arguments (1)~(5). Hereinafter referred to as AER for anion exchange resin and CER for cation exchange resin.

(1) It is explicit that the numerical calculations give the similar results for both of the model (a) and the model (b), because the quite identical calculation procedures should be used for both of two models.

(2) The breakthrough curves obtained by the numerical calculations coincide with the experimental results. (Figs. 6 and 7)

(3) The model (b) may be assumed as a combined bed of column of AER and column of CER.

(4) If the equivalent ratio of CER/AER is larger than 1.0, the solution in the column contains HCl, and small quantity of OH\textsuperscript{-} ions. Then the column of AER can be assumed approximately as a system of single solute of Cl\textsuperscript{-} ion. On the contrary two kinds of ion concentration of H\textsuperscript{+} ion and Na\textsuperscript{+} ion must be taken into account for the column of CER in the model (b).

(5) In the case that equivalent ratio of CER/AER in the mixed bed is larger than 1.0 an analytical solution for the adsorption system of single solute of Cl\textsuperscript{-} ion could be applied to the column of AER in the model (b). But the analytical solution cannot be applied to the column of CER in the model (b). If the breakthrough curve of Na\textsuperscript{+} ion for the column of CER in the model (b) is calculated as a system of single solute of Na\textsuperscript{+} ion, the error is increased as the packed height become larger as shown in Fig. 2.

The numerical techniques used for the solution of the hyperbolic partial differential equation representing the transient behavior of a column of ion exchange are stated as follows.

If the mixed bed is packed with $V_A$ m\textsuperscript{3} of AER and $V_C$ m\textsuperscript{3} of CER, the equations of conservation for each independent bed are respectively given by\textsuperscript{(2)(12)}

\begin{align}
\nu \left( \frac{\partial C_A}{\partial z} \right) + \frac{\partial C_A}{\partial t} &= - \frac{\partial q_A}{\partial t} \left( \frac{V_A}{V_A + V_C} \right) / m, \\
\nu \left( \frac{\partial C_C}{\partial z} \right) + \frac{\partial C_C}{\partial t} &= - \frac{\partial q_C}{\partial t} \left( \frac{V_C}{V_A + V_C} \right) / m.
\end{align}

By the change of variables $x = z/m\nu$, $\theta = t - z/v$, these equations are respectively written as

\begin{align}
\frac{\partial C_A}{\partial x} &= - \left( \frac{V_A}{V_A + V_C} \right) \frac{\partial q_A}{\partial \theta}, \\
\frac{\partial C_C}{\partial x} &= - \left( \frac{V_C}{V_A + V_C} \right) \frac{\partial q_C}{\partial \theta}.
\end{align}

The concentration distribution of adsorbate in the particle of AER is given by

\begin{equation}
\frac{\partial q_A}{\partial \theta} = \frac{D_a}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_A}{\partial r} \right)
\end{equation}

and for CER

\begin{equation}
\frac{\partial q_C}{\partial \theta} = \frac{D_c}{r^2} \cdot \frac{\partial}{\partial r} \left( r^2 \frac{\partial q_C}{\partial r} \right).
\end{equation}
The initial and boundary conditions are

\[ \begin{align*}
\theta &= 0, \quad 0 \leq r \leq R_A, \quad q_A(r, x, 0) = 0 \\
0 \leq r \leq R_C, \quad q_C(r, x, 0) = 0, \\
\theta &= 0, \quad r = 0, \quad \frac{\partial q_A}{\partial r} = 0 \\
\frac{\partial q_C}{\partial r} &= 0 \\
r &= R_A, \quad \left. \frac{\partial q_A}{\partial r} \right|_{r=R_A} = \frac{k_{fA}}{D_A} (C_A - C_{SA}) \\
r &= R_C, \quad \left. \frac{\partial q_C}{\partial r} \right|_{r=R_C} = \frac{k_{fC}}{D_C} (C_C - C_{SC}).
\end{align*} \]  

The equilibrium relations are

\[ \begin{align*}
q_{SA} &= \alpha_A C_{SA} \beta_A, \\
q_{SC} &= \alpha_C C_{SC} \beta_C.
\end{align*} \]  

These non-linear expressions for equilibrium are used only in the numerical calculations and not used in analytical solution which is expressed in error function as stated in later section.

The average concentration in the resin particles are given by

\[ \begin{align*}
q_A^* &= \frac{3}{R_A^2} \int_0^{R_A} q_A r^2 \, dr, \\
q_C^* &= \frac{3}{R_C^2} \int_0^{R_C} q_C r^2 \, dr.
\end{align*} \]  

Finite-difference representations for above partial derivatives are described with no dimensional parameters. No dimensional parameters are denoted that

\[ \begin{align*}
A &= D_A \theta / R_A, \quad B = D_C \theta / R_C, \\
\xi_A &= r / R_A, \quad \xi_C = r / R_C, \\
u_A &= C_A / C_{0A}, \quad u_C = C_C / C_{0C}, \\
Q_A &= (q_A / q_{0A}) \xi_A, \quad Q_C = (q_C / q_{0C}) \xi_C, \\
Q_A^* &= (q_A^* / q_{0A}^*), \quad Q_C^* = (q_C^* / q_{0C}^*).
\end{align*} \]

Let the height of the bed denoted by a vector \( z_i = (z_1, z_2, \ldots, z_i, \ldots, z_p) \), the time parameter by \( \tau_j = (\tau_1, \tau_2, \ldots, \tau_j, \ldots) \), and the spacing on domain in resin particle by \( \xi_k = (\xi_1, \xi_2, \ldots, \xi_k, \ldots, \xi_N) \).

Then at the surface of resin particles, concentration of adsorbate can be written for AER

\[ \xi_A = 1 \]

\[ Q_A(i, j, N+1) = Q_A(i, j, N-1) + 2 \Delta \xi_A [H_{KA}(u_A(i, j) - H_0 A) Q_A(i, j, N)]^\beta_A + Q_A(i, j, N) \]

where \( H_{KA} = \frac{k_{fA} R_A C_{0A}}{D_A q_{0A}}, \quad H_0 A = \frac{1}{C_{0A}} (\frac{q_{0A}}{\alpha_A})^{1/\beta_A} \)

for CER

\[ \xi_C = 1 \]

\[ Q_C(i, j, N+1) = Q_C(i, j, N-1) + 2 \Delta \xi_C [H_{KC}(u_C(i, j) - H_0 C) Q_C(i, j, N)]^\beta_C + Q_C(i, j, N) \]

where \( H_{KC} = \frac{k_{fC} R_C C_{0C}}{D_C q_{0C}}, \quad H_0 C = \frac{1}{C_{0C}} (\frac{q_{0C}}{\alpha_C})^{1/\beta_C} \)

inner concentration of adsorbate on the particles of AER

\[ \xi_A < 1 \]

\[ Q_A(i, j, k+1) = Q_A(i, j, k) + (\Delta \xi_A)^2 [Q_A(i, j, k-1) - 2 Q_A(i, j, k) + Q_A(i, j, k+1)] \]  

\[ -55 - \]
for CER

\[ \xi_c < 1 \]

\[ Q_c(i, j+1, k) = Q_c(i, j, k) + (\delta c_c / \delta \xi_c) \{ Q_c(i, j, k-1) - 2Q_c(i, j, k) + Q_c(i, j, k+1) \} \]  \hspace{1cm} (23)

at the center of resin particle

\[ \xi_A = 0 \]

\[ Q_A(i, j+1, 0) = 0, \]  \hspace{1cm} (24)

\[ \xi_c = 0 \]

\[ Q_c(i, j+1, 0) = 0. \]  \hspace{1cm} (25)

Equations (6) and (7) can be respectively written as

\[ u_A(i+1, j) = (\delta x / \delta \xi_A) \{ H_{VA}(Q_A(i+1, j-1) - Q_A(i, j)) \} + u_A(i, j), \]  \hspace{1cm} (26)

\[ u_c(i+1, j) = (\delta x / \delta \xi_c) \{ H_{VC}(Q_c(i+1, j-1) - Q_c(i, j)) \} + u_c(i, j), \]  \hspace{1cm} (27)

where

\[ H_{VA} = \frac{q_{0A}D_A}{C_{0A}R_A^2} \left( \frac{V_A}{V_A + V_C} \right), \quad H_{VC} = \frac{q_{0C}D_C}{C_{0C}R_C^2} \left( \frac{V_C}{V_A + V_C} \right). \]

The concentration distributions of adsorbates in the adsorbent particles are calculated by Eqs. (20)~(25), and \( q_A^* \) and \( q_C^* \) can be obtained as the mean values of them. The equations of conservation Eqs. (4) and (5) are calculated by Eqs. (26) and (27).

The breakthrough curves for packed height of 0.01, 0.03, 0.06, 0.1, 0.5 and 1 m of column of AER and column of CER in the model (b) were numerically calculated and shown in Fig. 2(a), (b). The calculations were carried out with the values of \( k_{fA} = 3.12 \)
The breakthrough curves in Fig. 2 were obtained by Eq. (20) to Eq. (27) for Cl\(^{-}\) ion and Na\(^{+}\) ion in the effluent. The full lines are the breakthrough curves of Cl\(^{-}\) ion for the columns of AER which assumed as a system of single solute Cl\(^{-}\) ion and the broken lines and the dot-dash-lines are the breakthrough curve of Na\(^{+}\) ion for the columns of CER which are the systems of two sort of solutes of H\(^{+}\) and Na\(^{+}\). The broken lines show the results obtained by the assumption that the columns of CER would be the system of one sort of solute of Na\(^{+}\) ion. The dot-dash-lines are taken into account of two sort of concentrations of H\(^{+}\) ion and Na\(^{+}\) ion. The longer the packed height the larger the difference between the two profiles, as shown in Fig. 2. The effluent from the 1 m packed height contains only Cl\(^{-}\) ion at the early period of breakthrough. In each calculations the ratio \(V_c/V_A\) is 1.77 which is a value for actually working mixed bed in nuclear power plants. Since the solution in such a mixed bed contains HCl, the value of OH\(^{-}\)/(OH\(^{-}\)+Cl\(^{-}\)) is negligible small compared with Cl\(^{-}\)/(OH\(^{-}\)+Cl\(^{-}\)).

Then it is considered that the breakthrough curve of Cl\(^{-}\) ion for mixed bed can be presented with the model for the system of a single sort of solute Cl\(^{-}\) ion and a single sort of AER. Therefore the theoretical solution for the adsorption system of single solute which has been already developed\(^{(19)-(18)}\), can be applied to estimate the breakthrough curve of Cl\(^{-}\) ion for mixed bed. The approximate solution for the system is presented in the form

\[
u_A = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{3\alpha \theta / 2 - \rho x}{\sqrt{\rho x / 5}} \right) \right]. \tag{28}
\]

This expression, originally developed by Rosen\(^{(2)}\) for an adsorption system of single solute, has been recognized as a useful expression with following restriction. The restrictions for Eq. (28), accurate to 1%, are

\[
\gamma x = 3D_A K_A z / (mv R_A^3) \geq 50. \tag{29}
\]

The values of \(\gamma x\) for minicolumns of 0.01, 0.03, 0.06 m and actually working column of 1 m are presented in Table 1. As seen in Table 1, Eq. (28) cannot be applied to the monitoring minicolumns, while is useful for 1 m packed height.

<table>
<thead>
<tr>
<th>(x(m))</th>
<th>0.01</th>
<th>0.03</th>
<th>0.06</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma x)</td>
<td>4.40</td>
<td>5.29</td>
<td>7.05</td>
<td>58.7</td>
</tr>
</tbody>
</table>

Then we chose the method that \(D_A\) and \(K_A\) were obtained by the breakthrough curves for minicolumns of different packed height and \(K_A\) for 1 m packed height was extrapolated with these values. The relations between \(\partial u_A/\partial \theta\) and \(D_A, K_A\) in the monitoring minicolumns were derived by dimension analysis as follows.

No dimension groups contain the following terms

\[
\partial u_A/\partial \theta, D_A, K_A, R_A, k_{fA}, V_A/(V_A+V_C), \theta, z, v\text{ and }m.
\]

No dimensional equation is represented as

\[
f \left( K_A, V_A/(V_A+V_C), m, k_{fA}/v, R_A^3/D_A(\partial u_A/\partial \theta), D_A\theta / R_A^3, D_A x/(R_A^3 v) \right) = 0.
\] \tag{30}

The gradients at the points on the breakthrough curve for the monitoring column have a profile as shown in Fig. 3.
As an arbitrary function satisfying the dimensional relations we chose the exponential function \( F \exp \left\{ -(A\theta - B)^2 \right\} \) whose derivatives will give the similar profile like that shown in Fig. 3.

The following relation can be assumed to be satisfied by Eq. (30)

\[
\frac{\partial u_A}{\partial \theta} = F \exp \left\{ -3.75 \frac{D_A}{R_A x} (\theta - K_A x)^2 \right\}, \tag{31}
\]

where

\[
F = F' \frac{D_A k_{LA}}{R_A^2 v} \left( \frac{V_A}{V_A + V_C} \right).
\]

If the values of \( \frac{\partial u_A}{\partial \theta} \) would be obtained by breakthrough curves for monitoring minicolumns, the values of \( D_A \) and \( K_A \) could be known.

### III. Apparatus and Procedure

The experimental apparatus are shown in Fig. 4. The monitoring minicolumns are packed with ion exchange resin in uniform and the bed must not hold air bubbles in it and not be fluidized at the top of the bed by feed flow.

![Fig. 4 Schematic diagram of experimental apparatus](image)

As the ion exchange resin in the bed repeats swelling and shrinking in the ion exchange cycle, the cavity is easy to be made under the perforated plate. The column is furnished with the magnetic devices inside and outside of the cylinder for the purpose of controlling the packed condition as shown in Fig. 5. The upper perforated plate is attached to the supporter which hold the top surface of the bed in a horizontal position and is furnished with inner magnet. The upper perforated plate can be moved vertically by the outside magnet to remove the cavity in the bed. The conditions of beds were checked by the conductivity of the beds which were measured between entrance and exit perforated plate being furnished with platinum mesh.

The packed heights of monitoring minicolumns were 0.01, 0.03 and 0.06 m. These different packed heights are necessary to obtain \( K_A \) for 1 m packed height by extrapolation. The column of 1 m packed height is provided to identify the applicability of the method developed in this research.

The ion exchange resin was regenerated with \( \text{H}_2\text{SO}_4 \) or \( \text{NaOH} \) and washed with pure water of 5 MΩ before packing them in the monitoring column, and washed moreover
with pure water of 18 MΩ flowing in the monitoring column.

The specific conductivity of effluent was measured by flow cell of Balsbaugh and Na\(^+\) concentration were measured by Na\(^+\) ion meter and Cl\(^-\) concentration were calculated using these values.

The radius of ion exchange resin, the concentration and the flow rate of feed and the conditions of regeneration of resin used in the experimental work are presented on Table 2.

The all measurement were carried out at room temperature (293~298 K).

**IV. RESULTS AND DISCUSSION**

As the required concentration of the effluent for the mixed bed demineralizer in the generator plant is considerably low such as 1.47 x 10\(^{-4}\) mol/m\(^3\), it is occasionally found that the concentration of effluent from the demineralizer exceeds the required value at the beginning of breakthrough for the degraded resin. In this case the problem is not for estimation of the breakthrough time. Then we added a method of determination of degree of degradation for the exhausted resin to the principal work of prediction method of breakthrough time for specified effluent concentration.

The comparisons between the theoretical values for numerical calculations by Eqs. (20)~(27) and the experimental values for breakthrough curves for the column of 0.03 m and 1 m packed height are shown respectively in Fig. 6(a) and (b). As the profiles in the figures show good agreement between each of them, it is considered that there are no serious problems associated with the modeling and the computations.

The basic soundness of the simplified model has been already described in the former chapter. If \(D_A\) and \(K_A\) for 1 m packed height could be obtained, Eq. (28) would be applied to calculate the breakthrough curve for the column of 1 m packed height.

The breakthrough curves for new resin mixture of IRA400T and IR120B and new
resin mixture of IRA900 and Amb. 200C are illustrated respectively in Fig. 7(A) and (B).

New resin means the product which has never been used in the demineralizing cycle. Those for resin mixture of IRA900 and Amb. 200C being used in 3 yr and for resin mixture of IRA900 and Amb.200C being used in 5 yr are illustrated respectively in Fig. 8(A) and (B). In each figures of Figs. 7 and 8, (a) shows measured conductivity of the effluent, (b) shows Na+ concentration of the effluent and (c) shows concentration of Cl- calculated from (a) and (b). The DA and KA for minicolumns are obtained by the breakthrough curves of (c) in Figs. 7 and 8.

Let \( \frac{\partial u_A}{\partial \theta} \) for the breakthrough curves be denoted by \( u_1, u_2, u_3 \) corresponding to \( \theta_1, \theta_2, \theta_3 \). The \( K_A \) and \( D_A \) can be obtained by substituting \( u_1, u_2, u_3 \) and \( \theta_1, \theta_2, \theta_3 \) to Eq. (31), there results

\[
K_A = \frac{G}{(2x)},
\]

\[
D_A = \ln \left( \frac{u'_1 / u'_2}{u'_2 / u_1} \right) + \gamma (\theta_2 - \theta_1) \left\{ (\theta_3 + \theta_1) / G - 1 \right\},
\]

where

\[
G = \frac{(\theta_1 - \theta_2) \ln(u'_1 / u'_2) - (\theta_2 - \theta_3) \ln(u'_3 / u'_2)}{\ln(u'_1 / u'_2) - (\theta_3 - \theta_1) \ln(u'_3 / u'_2)}.
\]

The values of \( D_A \) and \( K_A \) are presented on Table 3.

The \( D_A \) is substantially not varied with the packed height because it is intraparticle
coefficient. Nevertheless the value of $D_A$ varies slightly with the concentration of the solution as shown in Fig. 9.

The value of $K_A$ is naturally varied with the packed height because the extent of ion exchange in column is varied with packed height. The relations between $K_A$ and $z$ can be obtained by Eq. (32) and presented in Fig. 10. The value of $K_A$ is almost constant for the column over 1 m packed height. This is a reasonable relationship because the packed height of 1 m of demineralizer has been decided empirically to realize that the extent of ion exchange should be zero on the resin near the exit at the beginning of breakthrough. It is interesting that the values of $K_A$ for the resin used in power plants in 3 to 5 yr are almost equal to those for the new resin, not-withstanding $D_A$ considerably decrease.

The breakthrough time for 1 m packed height can be calculated for specified concentration of effluent using the Eq. (28) substituted with the value of $D_A$ (obtained from Fig. 9) and $K_A$ (obtained from Fig. 10). The examples of comparisons of the estimated values using minicolumns and the measured values for the column of 1 m packed height are pre-

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Fig. 7 (A),(B) Breakthrough curves for mixed bed packed with new resin of IRA400T and IR120B, and IRA900 and Amb. 200C

$\nu=0.034$ m/s, $C_0=0.171$ mol/m$^3$
The estimated values have about 6\% error to measured values. The estimated values by numerical calculations are also presented on Table 4 together with the estimated values by error function and the actually measured values. It seems that the accuracies of both estimation methods are almost equal. Since the storage and computational time requirement for solving such large systems for reverse operation to require the breakthrough time using numerical calculation or analytical exact solution may be completely impractical, the applicability of approximate solution is important for the practical work.

The more simple method can be used for rough
estimation of the capacity of ion exchange resin being used as demineralizer in long period. This prediction method is useful for the determination of the remained capacity of the degraded resin when used as a demineralizer of 1 m packed height, but the breakthrough time for any effluent concentration cannot be estimated.

The relation between \( \frac{C}{C_0} \) and \( z \) at \( \theta = 0 \) can be derived from Eq. (6) and Eq. (34) in which the rate of ion exchange is given in terms of surface concentration \( q_{SA}^* \).

\[
\frac{\partial q_{SA}^*}{\partial \theta} = \frac{3k_{fA}^*}{R_A}(C_A - q_{SA}/K_A). \tag{34}
\]

The solution can be written in the form

\[
u_A(x, 0) = \exp[-3k_{fA}^*x/R_A(V_A/(V_A + V_C))]. \tag{35}
\]

The relations between \( C/C_0 \) and \( z \) at \( \theta = 0 \) can be derived from the following equations:

### Table 3: Experimental values of \( K_A \) and \( D_A \) for monitoring minicolumns

<table>
<thead>
<tr>
<th></th>
<th>( C_0 ) (mol/m³)</th>
<th>( v ) (m/s)</th>
<th>( z ) (m)</th>
<th>( K_A \times 10^{11} ) (m²/s)</th>
</tr>
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<tbody>
<tr>
<td><strong>New resin</strong></td>
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<tr>
<td>(IRA400T and IR120B)</td>
<td>0.171</td>
<td>0.034</td>
<td>0.01</td>
<td>5568</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>2226</td>
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<td></td>
<td>0.06</td>
<td>1146</td>
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<td>0.089</td>
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<td>0.01</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.06</td>
<td>2005</td>
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<td></td>
<td>0.017</td>
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<td></td>
<td>0.03</td>
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<td>0.06</td>
<td>13900</td>
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<tr>
<td>(IRA900 and Amb. 200C)</td>
<td>0.171</td>
<td>0.034</td>
<td>0.01</td>
<td>4333</td>
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<td></td>
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for the mixed bed concerning two sorts of new resin and two sorts of used resin are shown in Fig. 11. For the resin used 5 yr, it is seen that the concentration $C/C_0$ of the effluent at beginning of breakthrough from the column of 1 m packed height exceed already the specified value of $C/C_0=0.01$ as shown in Fig. 11. Then this resin must not be used for the demineralizer. For the new resins, $C/C_0$ at beginning of breakthrough from similar column are far below the specified value 0.01. Then it is easy to be determined that these resin are useful for demineralizer but precise data for breakthrough will be given by the principal estimation method applying error function.

V. CONCLUSION

The breakthrough time at a specified concentration for the mixed bed of 1 m packed height can be estimated using the monitoring columns of few cm packed height. The estimation method is based on the conception that the model for the system of the single solute and single sort of resin could be used to calculate the breakthrough curve for mixed bed instead of the model for the system of mixed resin and multicomponent of ion.

The adaptability of the conception assuming simplified model was identified by the numerical calculations and experiments. The diffusivity in the ion exchange resin particle and equilibrium constant can be obtained experimentally using minicolumns. The diffusivity is not varied with packed height but varied with concentration of solution. The equilibrium constant is inversely proportional to the packed height and approach to a constant value over 1 m packed height.

The estimated values by the theoretical approximate solution substituted with the diffusivity and equilibrium constant which were obtained from minicolumns have about 6% error to the measured values for the mixed bed of 1 m packed height.
The degree of degradation for the exhausted resin can be roughly estimated by another simple method using the initial concentration of the effluent for monitoring minicolumns.

**[NOMENCLATURE]**

- **C**: Concentration in solution (mol/m³)
- **C_s**: Concentration on ion exchange resin surface (mol/m²)
- **C₀**: Concentration of feed (mol/m³)
- **D**: Diffusion coefficient in ion exchange resin (m²/s)
- **F**: Coefficient
- **K**: Equilibrium constant
- **k_f**: Liquid film coefficient (m/s)
- **m**: Void volume per unit volume of ion exchange resin
- **Q= (q/q₀)ξ**: Average of concentration in ion exchange resin (mol/m³)
- **Q₀**: Equilibrium concentration in ion exchange resin with **C₀** (mol/m³)
- **q**: Internal concentration in ion exchange resin (mol/m³)
- **q_s = q(R, x, θ)**

- **R**: Radius of spherical ion exchange resin (m)
- **r**: Radius distance from center of ion exchange resin (m)
- **t**: Time (s)
- **V**: Amount of ion exchange resin (m³)
- **v**: Linear flow velocity (m/s)
- **z**: Height of packed bed (m)
- **α**: Coefficient ((mol/m³)⁻¹⁻β)
- **β**: Coefficient

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**REFERENCES**


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