Comparison of Simulated Ion Exchange Performance of a Fixed Annular Bed for Outwards and Inwards Flow

Y. Tsaur and *D. C. Shallcross

Department of Chemical Engineering, University of Melbourne, Melbourne, Victoria 3010

(Manuscript submitted May 11, 2007; accepted July 2, 2007)

Abstract

Simulations are performed using a model developed to predict ion exchange performance in radial flow. The model which has been validated previously by experiments predicts the performance in a wedge-shaped annular bed. The injected solution flows radially between a port at the bed's axis and the bed's outer periphery. Flow is either outwards away from the bed's axis or inwards towards the axis. It is found that under identical operating conditions, the radial ion exchange process studied is significantly more efficient when the flow is outwards rather than inwards.

Key words: ion exchange, radial flow

1 Introduction

A model has been developed to simulate ion exchange performance within a fixed, annular ion exchange bed [1-3]. The model considers radial dispersion to be a linear function of the solution velocity, and assumes that instantaneous pointwise equilibrium exists throughout the bed between the exchanging ions in the solution and the exchanger phases. Experiments to validate the model were conducted using a horizontal wedge-shaped annular ion exchange bed having 30° of arc and containing commercially-available strong acid cation exchange resin. The injected solution flows radially from the inlet located at the bed's axis to the outlet located at the bed's periphery. The predictions of this model have been validated by experiments for both the exhaustion and regeneration cycles of the Na⁺-H⁺ and Ca²⁺-H⁺ cation binary systems. It is found that the predicted performances of the bed and the experimental observations are in close agreement [1,2].

While the experiments used to validate the authors' radial ion exchange model were conducted with the solution flowing outwards away from the bed's axis, the same model is equally applicable for inwards flow. In such a case the solution is injected into the exchanger bed uniformly across the bed's outer periphery and flows towards the outlet located at the bed's axis.

This paper compares the simulated ion exchange performances in a wedge-shaped annular bed operating with the solution flowing either outwards or inwards. The simulations are performed with all other conditions identical. The simulation results permit direct comparisons of the bed's operating efficiencies to be made between operations in either of the two different flow modes.
2 Ion Exchange Performance Model

The model for simulating ion exchange performance in radial flow is developed based upon the equilibrium theory, i.e., the models assume that instantaneous pointwise ion exchange equilibrium between the solution and resin phases exists throughout the fixed bed. The model takes account of non-idealities of ion exchange behaviour in both phases and also dispersion effects in the flow direction. The development of this model is described in more detail elsewhere [1,2]. Only the key points are presented here.

Based upon a material balance written over an infinitesimally thin annular element of the radial ion exchange bed, equation (1) may be derived [1,2]. The simultaneous solution of this equation along with the equilibrium relationship between the two phases allows the compositions with respect to the exchanging ions of both phases to be predicted as a function of time and space.

\[
\frac{\partial x}{\partial t} + \frac{Q_T}{\varepsilon C_0} \left[ \frac{\pi (R_O^2 - R_I^2) H}{12} \right] \frac{\partial y}{\partial t} = \frac{1}{Pe_R} \frac{\partial^2 x}{\partial r^2} + \left( \frac{1}{Pe_R} \right) \frac{1}{r \partial r} \frac{\partial x}{\partial r} + \frac{1}{Pe_R D_{LR}} \frac{\partial D_{LR}}{\partial R} \frac{\partial x}{\partial r} \tag{1}
\]

In the equation \( x \) and \( y \) are mole fractions of the exchanging ions in the solution and the resin phase, respectively; \( t \) is the dimensionless time; \( r \) is the dimensionless radial distance from the bed's axis; \( Pe_R \) and \( D_{LR} \) are the Péclet number and dispersion coefficient, both being functions of the radial distance within the bed; \( Q_T \) is the bed's exchange capacity; \( \varepsilon \) is the bed's porosity; \( H \) is the bed's thickness; \( R_I \) and \( R_O \) are the two radii of the bed, assuming that \( R_I < R_O \) and the bed is wedge-shaped with an arc of 30\(^\circ\); and \( C_0 \) is the concentration of the injection solution.

In the above equation dimensionless time and radial distance are defined by:

\[
t = \frac{\tau F_L}{2 \pi R_O H R_O} \quad \text{and} \quad r = \frac{R}{R_O} \tag{2a & 2b}
\]

where, \( R \) is the radial distance from the bed's axis; \( t \) is the time and \( F_L \) is the volumetric flow rate of the injected solution. Several assumptions are implicit in equation (1): the resin bed is homogeneous with constant porosity; the resin bed has finite inner and outer radii and a constant thickness; the resin bed is fixed and does not move; both fluid and resin beads compressibilities are negligible and gravity effects are neglected; fluid flows at a rate constant with time and under isothermal conditions; the solution is injected at a rate uniform across the inlet of the bed and fluid is produced from the outlet of the resin bed at a rate uniform around the entire circumference of the bed; molecular diffusion is negligible; dispersion occurs only in the flow direction and is isotropic for the same radius; the dispersion coefficient is independent of the chemical concentration but is a function of the radial distance.

For a binary ion exchange, A cations in the solution exchange onto the ion exchange resin and B cations on the resin exchange into the solution:

\[
b A^a + a B^b \rightarrow b A^a + a B^b \tag{3}
\]

where \( a \) and \( b \) are the valencies of the ionic species A and B, respectively, and the underline indicates that the particular ion is on the resin rather than in the solution phase.

Initially the resin bed is in the B-form (i.e. all the exchanger sites of the resin are occupied by B cations), and the solution within the pores of the resin bed contains B cations only initially. Then, the initial conditions are:

\[
x = 0 \quad \text{at} \quad t = 0 \quad \text{for} \quad r_O \geq r \geq r_I \\
y = 0 \quad \text{at} \quad t = 0 \quad \text{for} \quad r_O \geq r \geq r_I \tag{4}
\]

In the above and following equations \( r_I \) and \( r_O \) are the dimensionless radii of the bed's inner and outer boundaries respectively. At some time, \( t = 0 \), a solution containing A cations is injected into the resin bed. The solution is injected at a constant rate, and uniform across the inlet of the bed. The concentration of A cations in the injected solution is step-increased and thereafter remains constant. At the same time a solution is produced from the
outlet of the bed at a rate uniform around the entire circumference of the bed. For the experimentally-practical resin bed with a limited inner and outer radii, the solution concentration gradient of A cations at the bed outlet is assumed to be constant. The boundary conditions for the outwards flow then are:

\[ x = 1 \quad \text{at} \quad r = r_l \quad \text{for} \quad t > 0 \]

\[ \frac{\partial^2 x}{\partial r^2} = 0 \quad \text{at} \quad r = r_o \quad \text{for} \quad t > 0 \tag{5} \]

and the boundary conditions for the inwards flow are:

\[ x = 1 \quad \text{at} \quad r = r_o \quad \text{for} \quad t > 0 \]

\[ -\frac{2}{r^2} \frac{\partial x}{\partial r} = 0 \quad \text{at} \quad r = r_l \quad \text{for} \quad t > 0 \tag{6} \]

Equation (1) is numerically solved using finite difference techniques. The improved ion exchange equilibrium model of Mehablia et al. [4-6] is incorporated to calculate the equilibrium concentrations of both the solution and resin phases [1]. Non-idealities in both phases are considered by applying the Pitzer model [7,8] and the Wilson model [9] to calculate the activity coefficients in the solution and resin phases respectively. Limited availability of free ions for ion exchange by ion pairs formation in the electrolytes solution is also taken into account [10,11]. The thermodynamic equilibrium constant is calculated independently using the approach of Argersinger et al. [12]. Argersinger et al. thermodynamic equilibrium constant for the binary cation exchange presented in equation (3) then is:

\[ K_{AB}^{T} = \left( \frac{y_A^b}{y_B^a} \right) \left( \frac{C_B^a}{C_A^b} \right) \left( \frac{y_B^a}{y_B^a} \right) \left( \frac{y_A^b}{y_B^a} \right) = K_{AB}^{a} \left( \frac{y_A^b}{y_B^a} \right) \tag{7} \]

where \( y_i \) is the equilibrium mole fraction of cations \( i \) in the resin phase; \( C_i \) is the equilibrium molality of cations \( i \) in the solution phase; and \( y_B^a \) and \( y_B^a \) are activity coefficients of cations \( i \) in the solution and resin phases, respectively; and \( K_{AB}^{a} \) is the experimentally-accessible equilibrium quotient. The thermodynamic equilibrium constant of Argersinger et al. is calculated from the equilibrium quotient:

\[ \ln K_{AB}^{T} = \frac{1}{0} \ln K_{AB}^{a} d y_{i,a} \tag{8} \]

where, \( y_{i,a} \) is the equivalent ionic fraction of A ions in the resin phase. The thermodynamic equilibrium constant and the Wilson binary interaction parameters which the equilibrium model requires, are determined independently by experiments.

The dispersion coefficient in equation (1) is determined by history matching the model predictions to the experimental data obtained independently by tracer experiments using the wedge-shaped resin bed. The model for dispersion within the porous resin bed is obtained by considering that the resin bed is chemically inert with respect to the tracer solution. The model equation is:

\[ \frac{\partial x}{\partial t} = \frac{1}{Pe_R} \frac{\partial^2 x}{\partial r^2} + \left( \frac{1}{Pe_R} - 1 \right) \frac{1}{r} \frac{\partial x}{\partial r} + \frac{1}{Pe_R D_{LR}} \frac{\partial D_{LR}}{\partial r} \frac{\partial x}{\partial r} \tag{9} \]

For radial flow in the wedge-shaped resin bed the dispersion coefficient is found to be a linear function of pore velocity [13].

Given the thermodynamic equilibrium constant, the Wilson binary interaction parameters of a binary ion exchange system, and corresponding dispersion coefficients, equation (1) allows ion exchange performances in the wedge-shaped resin bed to be simulated. With only the boundary conditions differing, the model may be used to predict the breakthrough curves for ion exchange operation in either of the two flow modes.
3 Operating Conditions Used For Simulations

The simulations are performed within the range of operating conditions used to validate the model by experiments. Of the two systems used to validate the model the Ca\(^{2+}\)-H\(^+\) binary system is chosen as the system for this present study, because compared with the Na\(^+\)-H\(^+\) binary system, the resin displays a higher degree of selectivity for one cation over the other. The simulated wedge-shaped bed has inner and outer radii of 24.0 mm and 280.0 mm respectively, and a thickness of 12.46 mm. It subtends an angle of 30.0\(^\circ\) at its axis. Based upon experimental data these dimensions give the simulated bed a cation exchange capacity of 500 meq. The porosities of the bed in the H and Ca-forms are 0.310 and 0.330 respectively. The two sets of simulation are performed under identical operating conditions with only the direction flow of the solution differing.

Dispersion within the porous bed is assumed to be a function of the solution's pore velocity irrespective of the flow direction. Since the pore velocity changes not only with radial position but also with changes in the bed's porosity, dispersion will change as the radial distance away from the central axis changes and as the resin progressively changes form between the Ca-form and the H-form. The dispersion coefficient is assumed to be a linear function of pore velocity [1]:

\[
D_{LR} = \lambda U_{RP}
\]  

(10)

\(D_{LR}\) is the dispersion coefficient for radial flow, \(\lambda\) is the dispersion length, and \(U_{RP}\) is the pore velocity in the wedge-shaped resin bed.

4 Comparisons Between Inwards And Outwards Flow Predictions

Table 1 summarises the conditions and results of the sixteen simulations performed. The simulations were performed for both the exhaustion and regeneration cycles, at a range of different solution flow rates, concentrations and under both modes of flow. Capacity at break through refers to the number of exchange sites expressed in milliequivalents occupied by the displacing cation (Ca\(^{2+}\) for the exhaustion cycle and H\(^+\) for the regeneration cycle) when the mole fraction of displacing cations in the effluent rises to 0.050.

Table 1 : Simulations of the ion exchange performance in the wedge-shaped resin bed.

<table>
<thead>
<tr>
<th>cycle</th>
<th>resin bed form</th>
<th>injection solution</th>
<th>solution concentration [ N ]</th>
<th>flow rate [ ml/h ]</th>
<th>capacity at breakthrough [ meq ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>inwards</td>
</tr>
<tr>
<td>exhaustion</td>
<td>H</td>
<td>CaCl(_2)</td>
<td>0.50</td>
<td>400</td>
<td>451.9</td>
</tr>
<tr>
<td>exhaustion</td>
<td>H</td>
<td>CaCl(_2)</td>
<td>0.50</td>
<td>800</td>
<td>440.0</td>
</tr>
<tr>
<td>exhaustion</td>
<td>H</td>
<td>CaCl(_2)</td>
<td>0.50</td>
<td>1200</td>
<td>431.8</td>
</tr>
<tr>
<td>exhaustion</td>
<td>H</td>
<td>CaCl(_2)</td>
<td>1.0</td>
<td>400</td>
<td>467.8</td>
</tr>
<tr>
<td>regeneration</td>
<td>Ca</td>
<td>HCl</td>
<td>0.50</td>
<td>400</td>
<td>238.5</td>
</tr>
<tr>
<td>regeneration</td>
<td>Ca</td>
<td>HCl</td>
<td>0.50</td>
<td>800</td>
<td>223.7</td>
</tr>
<tr>
<td>regeneration</td>
<td>Ca</td>
<td>HCl</td>
<td>0.50</td>
<td>1200</td>
<td>205.8</td>
</tr>
<tr>
<td>regeneration</td>
<td>Ca</td>
<td>HCl</td>
<td>1.0</td>
<td>400</td>
<td>309.4</td>
</tr>
</tbody>
</table>
The exhaustion cycle refers to the case when the H\(^+\) ions initially on the resin are displaced by the more preferred Ca\(^{2+}\) ions. Because the resin prefers the Ca\(^{2+}\) ions, the equivalent ionic fraction of the Ca\(^{2+}\) ions on the resin will always be higher than the corresponding values in the solution. The regeneration cycle refers to the case when the Ca\(^{2+}\) ions are initially on the resin and are displaced by the less preferred H\(^+\) ions in solution. Because H\(^+\) ions are the less preferred ions break through of the H\(^+\) ions in the effluent during regeneration takes place much earlier than Ca\(^{2+}\) ion break through during exhaustion. Resin selectivity therefore greatly affects the break through capacity of an ion exchange process.

A number of important trends are apparent from the predicted break through capacities presented in Table 1:

- The break through capacities for both the exhaustion and regeneration cycles for outwards and inwards flow decrease with increasing flow rate. This decreasing trend is more significant when the flow is inwards rather than outwards.
- The break through capacities for both the exhaustion and regeneration cycles for outwards and inwards flow increase with increasing concentration. This increase is least significant for the exhaustion cycle with inwards flow and most significant for regeneration under outwards flow.
- The break through capacities for the exhaustion cycle are always significantly higher than for the corresponding regeneration cycle conducted under similar process conditions. This is because during regeneration of the resin, the more preferred Ca\(^{2+}\) ions already occupy sites on the resin.
- Higher fractions of the bed's sites are occupied by the displacing cations at break through for the outwards flow cases than for the corresponding cases for inwards flow.

While the predicted break through capacities presented in Table 1 allow the above important trends to be identified care must be taken in making use of the exact calculated values for the capacities. The simulations performed, and hence the break through capacities calculated are all strongly dependent on the nature of the relationship between the solution pore velocity and the dispersion coefficient. As noted above, based upon experimental investigations reported more fully elsewhere [1,2] dispersion is assumed to be a linear function of pore velocity as described by equation (10).

Figure 1: Simulated break through curves for the Ca-H binary system. (a) exhaustion (b) regeneration.

Figure 1 compares the four break through curves predicted for the exhaustion process with an injection flow rate of 400 ml/h. While the leading edge of the concentration front is relatively sharp for all four simulations, the
trailing edge is less well defined. Dispersion causes the trailing edge to spread out. This effect is greatest for outwards flow at the higher concentration, and least for inwards flow at the lower concentration. The four corresponding breakthrough curves for the regeneration process are presented in Figure 2. If any concentration trend can be discerned it is that the trailing edge of the concentration front tends to be slightly more spread out at the lower concentration for both modes of flow. This is contrary to what is observed for the exhaustion process.

5 Concluding Remarks

The ion exchange selectivity displayed by the resin greatly affects both the breakthrough capacity and the sharpness of the breakthrough curves for both the exhaustion and regeneration cycles. Increasing solution concentration has a noticeable effect on the breakthrough for the exhaustion cycle but can significantly delay the breakthrough for regeneration. This in turn increases the regeneration breakthrough capacity. For both the exhaustion and regeneration cycles the increased breakthrough capacities observed when the solution concentration increases are greater for outwards flow than when the solution flows radially inwards.

When taken together with the results of an earlier simulation study reported by the authors [3] the simulations of the present study suggest that under identical operating conditions, outwards flow radial ion exchange is more efficient that inwards flow, which in turn is more efficient than the more conventional linear ion exchange process. It should be stressed however that the relative efficiencies of the three processes may vary if the physical properties of the resin bed, viz. porosity and dispersion, vary significantly.

Other factors not considered here might suggest that the inwards flow radial process might be the most appropriate choice for a particular application. For example, if a fixed bed radial exchanger is to be used to treat a solution with a relatively high concentration of suspended solids then operating the exchanger bed in the inwards flow mode would probably be the better choice. In inwards flow the solution enters the exchanger bed through its outer periphery. With a greater area perpendicular to flow at the inlet, the filter cake that would build up would be distributed over a greater area than would be the case for outwards flow where the cake would build up in the immediately vicinity of the bed's much smaller inner face. Thus, a radial bed with the solution flowing inwards would operate for a longer period of time before the formation of the filter cake would cause the process to fail.

References