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# A THEORETICAL STUDY OF MULTICOMPONENT RADIAL FLOW CHROMATOGRAPHY

TINGYUE GU, GOW-JEN TSAI and GEORGE T. TSAO†
School of Chemical Engineering and Laboratory of Renewable Resources Engineering, A. A. Potter Engineering Center, Purdue University, West Lafayette, IN 47907, U.S.A.

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**Abstract**—A theoretical study of radial flow chromatography was carried out based on a general nonlinear multicomponent rate model which considers radial dispersion, external mass transfer, intraparticle diffusion, and nonlinear multicomponent isotherms. Radial dispersion and mass transfer coefficients were treated as variables which are dependent on the radial coordinate of the radial flow column. The model was solved numerically by using the finite element method and the orthogonal collocation method for the discretization of partial differential equations and Gear's stiff method for the solution of the resulting ordinary differential equation system. Computer simulations were carried out for various multicomponent chromatographic operations. Dispersion and mass transfer effects were investigated. The question of whether radial dispersion and mass transfer coefficients should be treated as variables was discussed. The difference between inward flow and outward flow in radial flow chromatography and the comparison between conventional axial flow chromatography and radial flow chromatography were studied. Langmuir isotherms were used in this work.

## INTRODUCTION

Chromatography has long been established as an effective means of separation. It is becoming more and more popular in this age of rapid development of biotechnology. The demand for efficient preparative and large-scale liquid chromatographic separation processes is ever increasing. Radial flow chromatography (RFC), since its introduction in the commercial market in the mid 1980s (McCormick, 1988), has proved to be a promising alternative to the conventional axial flow chromatography (AFC). Compared to AFC, the RFC geometry (Fig. 1) provides a relatively large flow area and short flow path. These factors enable a larger volumetric flow rate and shorter shift time in liquid chromatographic separations. If soft gels or affinity matrix materials are used as separation media, the low pressure drop of RFC helps prevent bed compression (Saxena *et al.*, 1987; Ernst, 1987). A full range of sizes from 50 ml to 200 l in bed volume of RFC columns both prepacked and unpacked can be obtained from commercial companies. Separation of various biological products has been reported (Chen and Hou, 1985; Saxena *et al.*, 1987; Saxena and Weil, 1987; Huang *et al.*, 1988; Plaigin *et al.*, 1989; Lee *et al.*, 1990). An experimental case study of the comparison of RFC and AFC was carried out by Saxena and Weil (1987) for the separation of ascites using QAE cellulose packings. They reported that by using a higher flow rate, the separation time for RFC was one-fourth of that needed for a longer AFC column with the same bed volume. It was claimed that by using RFC instead of AFC, separation productivity can be improved quite significantly (McCormick, 1988). RFC is especially suitable for affinity chromatography in which solutes are usually strongly retained. This permits the use of high flow rate and short flow path for fast treatment of a large volume of samples. RFC is advantageous for separation processes in which the effluent from the column is being recycled and the adsorbate will not be lost in the effluent stream (Liapis, 1989), such as in the case of *in situ* separation during fermentation (Yang *et al.*, 1989).

Radial flow packed-bed reactors have been used for a variety of industrial applications such as ammonia and methanol syntheses, catalytic reforming, and vapor phase desulfurization (Balakotaiah and Luss, 1981; Strauss and Budde, 1978). It is worthwhile pointing out that unlike the radial flow reactor RFC is used primarily for liquid phase chromatographic separation. There are quite a few papers that are related to the theoretical and experimental studies of radial

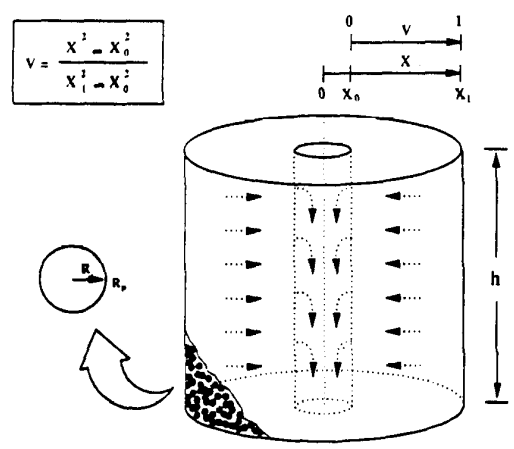


Fig. 1. Structure of a radial flow column.

†Author to whom correspondence should be addressed.

flow reactors. A brief review was given by Hlavacek and Votruba (1977). More recent papers include Strauss and Budde (1978), Balakotaiah and Luss (1981), Chang *et al.* (1983), Lopez de Ramos and Pironti (1987) and Tharakan and Chau (1987). The study of RFC may provide some useful information for the understanding of mass transfer processes in radial flow reactors.

Because of the special flow geometry in RFC some complications may arise in mathematical modeling. Since the linear flow velocity ($v$) in the RFC column changes constantly along the radial coordinate of the column (Fig. 1), unlike in most cases of AFC, the radial dispersion and external mass transfer coefficients are no longer constants. This important feature was rarely considered in mathematical modelings of RFC in past literature. Extensive theoretical studies have been reported for single component ideal RFC, which neglects radial dispersion, intraparticle diffusion, and external mass transfer resistance. In such studies local equilibrium and linear isotherm were often assumed. The earliest theoretical treatment of RFC was done by Lapidus and Amundson (1950). A similar study was carried out by Rachinskii (1968). Later Inchin and Rachinskii (1973) included bulk fluid phase molecular diffusion in their modeling. Lee *et al.* (1988) proposed a unified approach for moments in chromatography, both AFC and RFC. They used several single component rate models for the comparison of statistical moments for RFC and AFC. Their models included radial dispersion, intraparticle diffusion, and external mass transfer effects. Kalinichev and Zolotarev (1977) also carried out an analytical study on moments for single component RFC in which they treated the radial dispersion coefficient as a variable.

A rate model for nonlinear single component RFC was solved numerically by Lee (1989) by using the finite difference method and the orthogonal collocation method. His model considered radial dispersion, intraparticle diffusion, external mass transfer, and nonlinear isotherms. His model used averaged radial dispersion and mass transfer coefficients instead of treating them as variables. A nonlinear model of this kind of complexity has no analytical solution and must be solved numerically.

Rhee *et al.* (1970) discussed the extension of their multicomponent chromatography theory for ideal AFC with Langmuir isotherms, which is a parallel treatise to the interference theory developed by Helfferich and Klein (1970), to RFC. Apart from this, no other detailed theoretical treatment of nonlinear multicomponent RFC is available in the literature.

With the development of powerful computers and efficient numerical methods, more complicated treatment of multicomponent RFC becomes possible. A general model for multicomponent RFC may provide some very valuable information. In this work we propose a numerical approach to the solution of a general rate model for multicomponent RFC. The model was solved by using the finite element and orthogonal collocation methods. The solution of the model enabled us to address several important issues concerning the characteristics and performance of RFC and its differences from AFC. The question of whether one should treat dispersion and mass transfer coefficients as variables was also discussed.

## A GENERAL RATE MODEL FOR NONLINEAR MULTICOMPONENT RFC

Consider a fixed bed with cylindrical radial flow geometry (Fig. 1) which is filled with uniform spherical porous solid adsorbents. Suppose the process is isothermal and there is no concentration gradient in the axial direction of the column. Although it can be a problem in some real cases, the possible maldistribution of flow streams is ignored in this theoretical study. Also, local equilibrium is assumed for each component between the pore surface and the liquid phase in the macropores in particles. Based on these basic assumptions, the following governing equations for component $i$ in the bulk fluid and particle phases via mass balances in the two phases can be formulated:

$$-\frac{1}{X}\frac{\partial}{\partial X}\left(D_{bi}X\frac{\partial C_{bi}}{\partial X}\right) \pm v\frac{\partial C_{bi}}{\partial X} + \frac{\partial C_{bi}}{\partial t} + \frac{3k_i(1-\epsilon_b)}{\epsilon_b R_p}(C_{bi} - C_{pi,R=R_p}) = 0 \quad (1)$$

$$\frac{\partial}{\partial t}[(1-\epsilon_p)C^s_{pi} + \epsilon_p C_{pi}] - \epsilon_p D_{pi}\left[\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_{pi}}{\partial R}\right)\right] = 0 \quad (2)$$

where in eq. (1) $+v$ is for outward flow and $-v$ for inward flow. Note that in eq. (1), $D_{bi}$ and $k_i$ are variables which are dependent on $v$.

The initial and boundary conditions are

$$t = 0,\ C_{bi} = C_{bi}(0, X)\ C_{pi} = C_{pi}(0, R, X) \quad (3, 4)$$

$$R = 0.\ \frac{\partial C_{pi}}{\partial R} = 0;\ R = R_p,$$

$$\frac{\partial C_{pi}}{\partial R} = \frac{k_i}{\epsilon_p D_{pi}}(C_{bi} - C_{pi,R=R_p}). \quad (5, 6)$$

For outward flow

$$X = X_0,\ \frac{\partial C_{bi}}{\partial X} = \frac{v}{D_{bi}}(C_{bi} - C_{fi}(t))\ X = X_1,\ \frac{\partial C_{bi}}{\partial X} = 0 \quad (7a, 8a)$$

and for inward flow

$$X = X_1,\ \frac{\partial C_{bi}}{\partial X} = \frac{v}{D_{bi}}(C_{bi} - C_{fi}(t))\ X = X_0,\ \frac{\partial C_{bi}}{\partial X} = 0. \quad (7b, 8b)$$

These equations can be expressed in the following

dimensionless forms:

$$-\frac{\partial}{\partial V}\left(\frac{\alpha}{Pe_i}\frac{\partial c_{bi}}{\partial V}\right) \pm \frac{\partial c_{bi}}{\partial V} + \frac{\partial c_{bi}}{\partial \tau} + \xi_i(c_{bi} - c_{pi,r=1}) = 0 \tag{9}$$

$$\frac{\partial}{\partial \tau}[(1-\epsilon_p)c^s_{pi} + \epsilon_p c_{pi}] - \eta_i\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{pi}}{\partial r}\right)\right] = 0 \tag{10}$$

where for the bulk phase equation (9), the local volume averaging method (Slattery, 1981; Lee, 1989) was used for its nondimensionalization. In eq. (9), the radial flow Peclet number is defined as $Pe_i = v(X_1 - X_0)/D_{bi}$. The introduction of the radial flow Peclet number and the use of the local volume averaging method in the transformation streamlined the analogy and comparison between the RFC model and the AFC model (Gu *et al.*, 1990a), which is of great interest to us.

Initial conditions:

$$\tau = 0,\ c_{bi} = c_{bi}(0, V),\ c_{pi} = c_{pi}(0, r, V) \tag{11, 12}$$

Boundary conditions for outward flow:

$$V = 0,\ \frac{\partial c_{bi}}{\partial V} = \frac{Pe_i}{\alpha}[c_{bi} - C_{fi}(\tau)/C_{0i}] \tag{13}$$

For frontal adsorption, $C_{fi}(\tau)/C_{0i} = 1$

For elution, $C_{fi}(\tau)/C_{0i} = \begin{cases} 1 & 0 \leqslant \tau \leqslant \tau_{\text{imp}} \\ 0 & \text{otherwise} \end{cases}$

After the sample has been introduced:
(in the form of frontal adsorption)

if component $i$ is displaced,

$$C_{fi}(\tau)/C_{0i} = 0$$

if component $i$ is a displacer,

$$C_{fi}(\tau)/C_{0i} = 1$$

$$V = 1,\ \frac{\partial c_{bi}}{\partial V} = 0 \tag{14}$$

$$r = 0,\ \frac{\partial c_{pi}}{\partial r} = 0\ \ r = 1,\ \frac{\partial c_{pi}}{\partial r} = Bi_i(c_{bi} - c_{pi,r=1}). \tag{15, 16}$$

For inward flow we only need to swap $V = 0$ in eq. (13) with $V = 1$ in eq. (14).

The general solution strategy for the coupled partial differential equation (PDE) system [eqs (9) and (10)] is summarized in Fig. 2. A similar approach was used in the corresponding AFC model (Gu *et al.*, 1990a), which has been used in a study of interference effects in multicomponent chromatography (Gu *et al.*, 1990b). Compared to AFC, the solution for RFC seems to be more complicated due to variations in some physical properties of the system, as we have already mentioned. The finite element method is apparently an ideal approach for this kind of system.

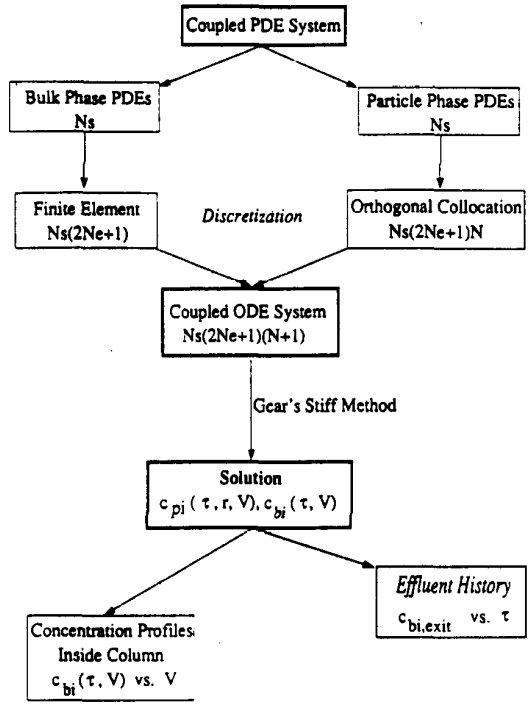


Fig. 2. Solution strategy.

## NUMERICAL SOLUTION

Equations (9) and (10) are transformed to a set of ODEs by the finite element method and the orthogonal collocation (OC) method (Villadsen and Michelsen, 1978; Finlayson, 1980), respectively. Using the Galerkin approximation (Reddy, 1984), eq. (9) becomes

$$[\mathbf{DB}_i][\mathbf{c}'_{bi}] + [\mathbf{AKB}_i][\mathbf{c}_{bi}] = [\mathbf{PB}_i] + [\mathbf{AFB}_i] \tag{17}$$

where

$$(\mathbf{DB}_i)^e_{m,n} = \int \phi_m \phi_n \, \mathrm{d}V \tag{18}$$

$$(\mathbf{AKB}_i)^e_{m,n} = \int\left[\frac{\alpha}{Pe_i}\frac{\partial \phi_m}{\partial V}\frac{\partial \phi_n}{\partial V} \pm \phi_m\frac{\partial \phi_n}{\partial V} + \xi_i \phi_m \phi_n\right]\mathrm{d}V \tag{19}$$

$$(\mathbf{AFB}_i)^e_m = \int \xi_i \phi_m c_{pi,r=1}\, \mathrm{d}V \tag{20}$$

in which $m, n = 1, 2, 3$, and the superscript $e$ indicates finite element matrices and vectors evaluated over each individual element before global assembly. In eq. (19) we take $+\phi_m$ for outward flow and $-\phi_m$ for inward flow. The natural boundary condition $(\mathbf{PB}_i) = -c_{bi} + C_{fi}(\tau)/C_{0i}$ is applied to $[\mathbf{AFB}_i]$ and $[\mathbf{AFB}_i]$ at $V = 0$ for outward flow or $(\mathbf{PB}_i) = c_{bi} - C_{fi}(\tau)/C_{0i}$ at $V = 1$ for inward flow. $(\mathbf{PB}_i) = 0$ elsewhere. Note that in eq. (19) $\alpha$ is a function of $V$.

The particle phase equation can be discretized with $N$ interior collocation points. The ODE system resulting from the numerical discretization can then be

solved using Gear's stiff method. The procedure is the same as that reported for AFC (Gu *et al.*, 1990a).

In this numerical procedure $D_{bi}$ and $k_i$ values are treated as variables which are dependent on the variations of $v$ along the radial coordinate $V$. Meanwhile, intraparticle diffusivities ($D_{pi}$) are regarded as independent of the variations of $v$. Dispersion is caused by molecular diffusion and turbulent mixing or eddy diffusion (Ruthven, 1984). A simple linear approximation for a single component system may be represented by (Ruthven, 1984; Jonsson, 1987)

$$D_b = \gamma_1 D_m + \gamma_2 (2R_p) v \tag{21}$$

where $\gamma_1$ and $\gamma_2$ are constants which normally have values of about 0.7 and 0.5, respectively. The molecular diffusion ($\gamma_1 D_m$) of a liquid is negligible compared to eddy diffusion, even at low Reynolds numbers (Ruthven, 1984). Thus in eq. (21) the second term, eddy diffusivity, is the dominant term in liquid chromatography, especially when the flow velocity is not low, which is the case for RFC. Then we have $D_b \propto v$. This relationship has been acknowledged by some researchers (Weber and Carr, 1989; Lee, 1989). In this work, for simplicity, we neglect the mixing effects in diffusional and film mass transfer coefficients ($D_{bi}$, $D_{pi}$ and $k_i$) for multicomponent systems. Thus $D_{bi} \propto v$, and $Pe_i = v(X_1 - X_0)/D_{bi}$ = constant for each component. We also assume $k_i \propto v^{1/3}$, which is in agreement with the two different experimental correlations reported by Pfeffer and Happel (1964), Wilson and Geankoplis (1966), and Ruthven (1984) for liquid systems at low Reynolds ($Re = 2R_p v\rho/\mu$) numbers, which is the case for liquid chromatography (Kaizuma *et al.*, 1970; Horvath and Lin, 1976). The relationship $k_i \propto v^{1/3}$ was also indicated by Horvath and Lin (1976).

Since $k_i \propto v^{1/3}$ and

$$v \propto \frac{1}{X} \propto \frac{1}{\sqrt{V + V_0}}, \tag{22}$$

we have

$$Bi_i \propto k_i \propto (1/X)^{1/3} \propto (V + V_0)^{-1/6}. \tag{23}$$

If $Bi_{i,V=1}$ (i.e., $Bi_{i,X=X_1}$) values are given as input values, then

$$Bi_{i,V} = \left[\frac{1 + V_0}{V + V_0}\right]^{1/6} Bi_{i,V=1}. \tag{24}$$

For $\xi_i$ at any $V$ position we have

$$\xi_{i,V} = \frac{3\eta_i(1 - \epsilon_b) Bi_{i,V}}{\epsilon_b} = \frac{3\eta_i(1 - \epsilon_b)}{\epsilon_b} \times \left[\frac{1 + V_0}{V + V_0}\right]^{1/6} Bi_{i,V=1}. \tag{25}$$

Equation (25) is used for the evaluation of eq. (19). In eq. (19), due to the special geometry of radial flow chromatography, we have two space coordinate ($V$) dependent variables, $\alpha$ and $\xi_i$. The finite element integral in eq. (19) is evaluated for each local element and $\alpha$, $\xi_i$ can be dealt with routinely without any trouble, since in this work finite element integrals are evaluated using four-point Gauss–Legendre quadratures (Reddy, 1984). The ability to deal with variable physical properties with ease is one of the well-known advantages of the finite element method. Accuracy is another notable advantage of the method. The accommodation of variable $Bi_i$ in eq. (22) for the particle phase is also very easy. Since particle phase equations must be solved at each finite element node (with given nodal position, $V$) in the function subroutine, $Bi_{i,V}$ values can be readily obtained from eq. (24).

It is very helpful to study the effects of treating $D_{bi}$ and $k_i$ as variables compared to treating them as constants, as is the case in most of the existing papers in the literature. There are two easy ways to take averaged $D_{bi}$ and $k_i$ values for the modeling. In both cases $Pe_i = v(X_1 - X_0)/D_{bi}$ will no longer be constant. In all the radial flow cases in this work we assumed that in the input data for simulation $Bi_{i,V=1}$ values are given.

Below we will discuss how to modify the algorithm to accommodate cases using the averaged $D_{bi}$ and $k_i$ values in order to make comparisons.

(1) *Using* v *value at* V = 0.5 *for calculations of average* $D_{bi}$ *and* $k_i$

$$\frac{\alpha}{\overline{Pe}_i} = \frac{\alpha}{\dfrac{v(X_1 - X_0)}{\bar{D}_{bi}}} = \frac{\alpha}{\dfrac{v(X_1 - X_0)}{D_{bi}} \dfrac{D_{bi}}{\bar{D}_{bi}}} = \frac{\alpha}{Pe_i} \frac{\bar{D}_{bi}}{D_{bi}}. \tag{26}$$

Since $D_{bi} \propto v$, from eq. (22) it is easy to obtain

$$\frac{\alpha}{\overline{Pe}_i} = \frac{\alpha}{Pe_i} \sqrt{\frac{V + V_0}{0.5 + V_0}}. \tag{27}$$

Equation (24) gives

$$\overline{Bi}_i = Bi_{i,V=0.5} = \left[\frac{1 + V_0}{0.5 + V_0}\right]^{1/6} Bi_{i,V=1}. \tag{28}$$

(2) *Using* v *value at* $X = (X_1 + X_0)/2$ *for calculations of the average of* $D_{bi}$ *and* $k_i$

$$\frac{\alpha}{\overline{Pe}_i} = \frac{\alpha}{Pe_i} \frac{\bar{D}_{bi}}{D_{bi}} = \frac{\alpha}{Pe_i} \frac{X}{(X_1 + X_0)/2} = \frac{\alpha}{Pe_i} \frac{\sqrt{V + V_0}}{(\sqrt{1 + V_0} + \sqrt{V_0})/2}. \tag{29}$$

For $Bi_i$ we have

$$\frac{Bi_{i,(X_1 + X_0)/2}}{Bi_{i,X_1}} = \left[\frac{X_1}{(X_1 + X_0)/2}\right]^{1/3} = \left[\frac{\sqrt{1 + V_0}}{(\sqrt{1 + V_0} + \sqrt{V_0})/2}\right]^{1/3} \tag{30}$$

Table 1. Parameter values used for simulation†

| Figure | Physical parameters | | | | | | Numerical parameters | |
|---|---|---|---|---|---|---|---|---|
| | Species | $Pe_{Li}$ | $\eta_i$ | $Bi_i$ | $a_i$ | $b_i \times C_{0i}$ | $Ne$ | $N$ |
| 3 | 1 | 30 | 8 | 10 | 4 | 5 × 0.2 | 8 | 2 |
| | 2 | 30 | 8 | 10 | 8 | 10 × 0.2 | | |
| 4 | 1 | 25 | 10 | 3 | 4 | 5 × 0.1 | 4 | 2 |
| | 2 | 25 | 10 | 3 | 8 | 10 × 0.3 | | |
| 5 | 1 | 50 | 15 | 12 | 1 | 2 × 0.2 | 6 | 2 |
| | 2 | 65 | 20 | 8 | 10 | 20 × 0.2 | | |
| 6 | 1 | 30 | 10 | 20 | 5 | 5 × 0.2 | 6 | 2 |
| | 2 | 30 | 10 | 20 | 6 | 6 × 0.8 | | |

†In all runs, $\epsilon_p = 0.4$ and $\epsilon_b = 0.4$, and $V_0 = 0.04$ or otherwise as specified. For elution cases, sample size is $\tau_{imp} = 0.2$. The ODE solver's (IMSL's IVPAG subroutine) tolerance is tol = $10^{-5}$. Double precision is used in the Fortran code. CPU times on SUN 4/280 for some typical multicomponent cases (solid lines): Fig. 3, 4.65 min; Fig. 4, 0.9 min; Fig. 5, 4.0 min; Fig. 6, 5.4 min.

which gives

$$\overline{Bi}_i = Bi_{i,(X_i - X_0)/2} = \left[\frac{\sqrt{1+V_0}}{(\sqrt{1+V_0}+\sqrt{V_0})/2}\right]^{1.3} Bi_{i,V=1}. \quad (31)$$

If we use the averages of $D_{bi}$ and $k_i$ instead of treating them as variable dependents of $v$, we only need to use $\alpha/\overline{Pe}_i$ in eq. (27) or eq. (29) to replace $\alpha/Pe_i$ in eq. (19), and use $\overline{Bi}_i$ replace $Bi_i$ in eq. (23). $Bi_i$ should also be used for calculations of $\xi_i$.

All the simulations in this work were carried out on a SUN 4/280 computer. Parameter values used in simulations are listed in Table 1, or mentioned during discussions.

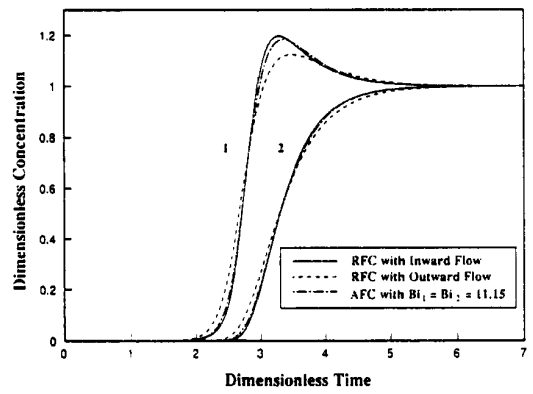


Fig. 3. Comparison of inward and outward flow RFC and AFC in frontal adsorption.

## RESULTS AND DISCUSSION

The model is capable of taking any mathematically stable nonlinear multicomponent isotherms. Two types of multicomponent isotherms are the most popular. One is the stoichiometric isotherm with constant separation factors which is often used for ion-exchange systems (Helfferich and Klein, 1970). The other is the multicomponent Langmuir isotherm which is used in this work. The multicomponent Langmuir isotherm is expressed as follows:

$$C^s_{pi} = \frac{a_i C_{pi}}{1 + \sum_{j=1}^{Ns} b_j C_{pj}},$$

$$\text{i.e.,} \quad c^s_{pi} = \frac{a_i c_{pi}}{1 + \sum_{j=1}^{Ns} (b_j C_{0j}) c_{pj}} \quad \text{(dimensionless)} \quad (32)$$

in which $a_i$ can also be expressed as $b_i C_i^\infty$. Note that $(b_i C_{0j})$ for each component may be treated as a dimensionless group. Thermodynamic consistency requires that the saturation capacities $(C_i^\infty)$ for all the components be the same.

(1) *Simulations of different chromatographic operations*

Figure 3 shows the simulated breakthrough curves for two components in inward and outward flow RFC. The parameter values for the simulation are listed in Table 1. The corresponding breakthrough curves in AFC are shown for comparison in Fig. 3. They were obtained by using the same dimensionless parameters and isotherms in the RFC case, except that $Bi_1 = Bi_2 = 11.15$ were used. These two $Bi$ values for AFC are the ones its corresponding RFC possesses at $V = 0.5$. Figure 3 clearly shows that in RFC, inward flow provides sharper concentration profiles than outward flow. This is in agreement with the results obtained by Lee (1989) for single component RFC. For a comparison similar to that shown in Fig. 3, the simulated effluent history for a step change displacement process is presented in Fig. 4. In this case the column was presaturated with component 1. Component 2 was introduced via a step change as a displacer to displace the adsorbed molecules of component 1. Again, inward flow RFC offers sharper concentration profiles, which are favorable for separa-

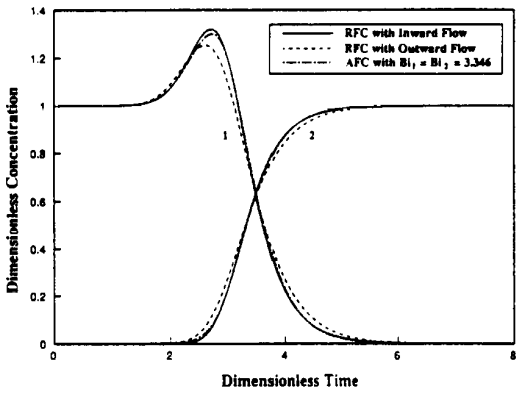


Fig. 4. Comparison of inward and outward flow RFC and AFC in displacement.

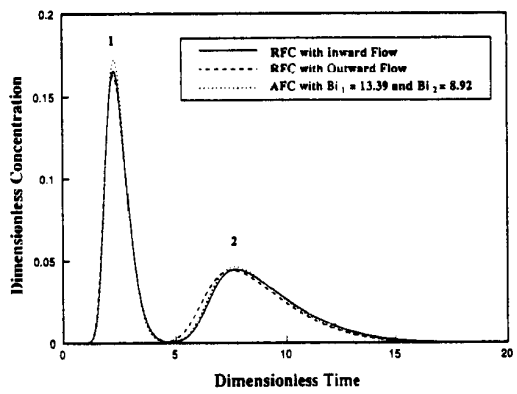


Fig. 5. Comparison of inward and outward flow RFC and AFC in elution.

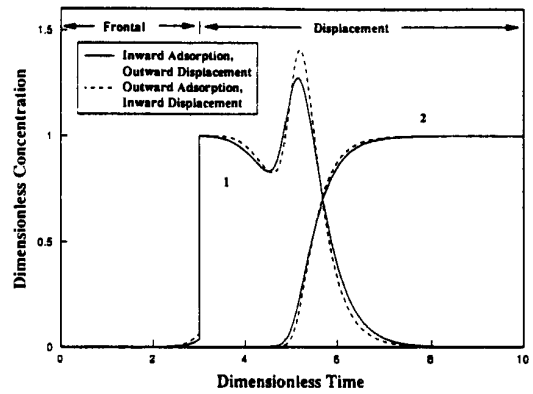


Fig. 6. Effect of RFC flow direction in reverse flow displacement.

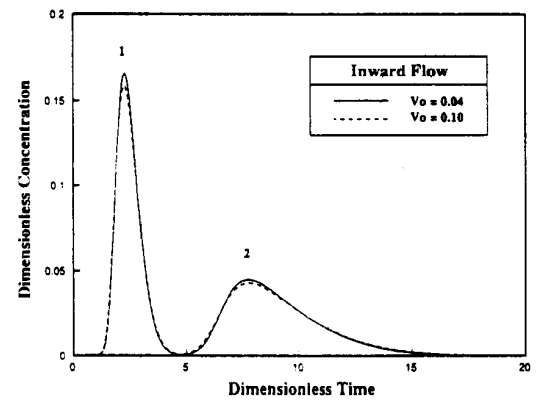


Fig. 7. Effect of $V_0$ on elution in inward flow RFC.

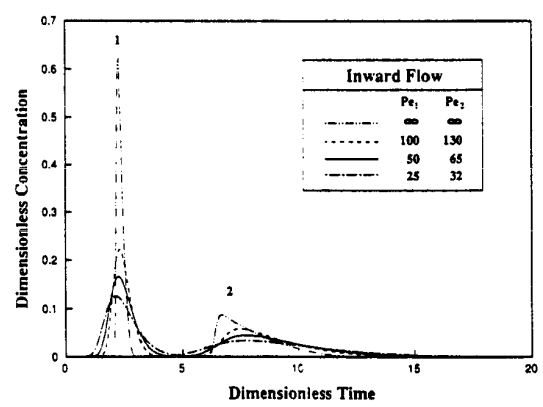


Fig. 8. Effect of $Pe_i$ on elution in inward flow RFC.

tion. The same conclusion also holds for the two component elution case shown in Fig. 5.

Multistage operations can also be simulated using our code. Figure 6 shows the effluent history of a reverse flow displacement process, in which the displacer (Component 2) was introduced with a reversed flow direction after an incomplete period of frontal adsorption of Component 1, which lasted $\tau = 3$. Such a reverse flow displacement operation is actually very common in industrial AFC practice (Ruthven, 1984) aimed at improving process efficiency and reducing column clogging. It has been used in the elution stage of affinity chromatography by Chase (1985). In Fig. 6, the combination of outward flow adosprtion and inward flow displacement gives better results, since its process time is slightly shorter.

(2) *Effect of* $V_0$

$V_0$ represents the ratio of the central cavity volume of an RFC column to the bed volume. The effect of its value on the elution process is shown in Fig. 8, in which we fixed the RFC column's $X_1$ and $h$ while changing the $X_0$ value. In Fig. 7, the solid lines are the same as those in Fig. 5. The way we increased $V_0$ values from 0.04 to 0.1 requires that the $Pe_i$ values for $V_0 = 0.1$ be reduced to 86.88% of those for the $V_0 = 0.04$ case, and for $\eta_i$ values the percentage is 94.54%. These two percentage values can easily be obtained by checking the changes in $(X_1 - X_0)$ and $V_b$ and their relationship with $Pe_i$ and $\eta_i$. Figure 7 shows that the peak heights are reduced and so is the

peak resolution when $V_0$ is increased from 0.04 to 0.1. This has the same effect as reducing column length in AFC.

(3) *Effects of* $Pe_i$, $\eta_i$ *and* $Bi_i$ *on elution*

Figures 8–10 clearly show that the increase of $Pe_i$, $\eta_i$, or $Bi_i$ values increases the peak heights and the peak resolution. In these three figures the solid line curves are the same as those in Fig. 5. In Fig. 8, the $Pe_1 = Pe_2 = \infty$ case is plotted in order to show the errors that one may encounter if radial dispersion is neglected. In the case shown in Fig. 8 such errors are quite large. Figure 9 also indicates that the peaks are sharper if film mass transfer coefficients for the two components are larger since the dimensionless parameter $\eta_i$ is proportional to $k_i$. Figure 11 shows that the resolution of the elution peaks is decreased if the intraparticle diffusion coefficients are reduced, as reflected in the dimensionless parameters $\eta_i$ and $Bi_i$.

(4) *Effect of treating* $D_{bi}$ *and* $k_i$ *as variables*

The two component frontal adsorption system shown in Fig. 3 was chosen as a case study. Figure 12 shows three sets of inward flow breakthrough curves obtained from using the variable $D_{bi}$ and $k_i$ average values evaluated at $V = 0.5$, or $(X_1 + X_0)/2$, respectively. These three sets of curves show some differences in the sharpness and height of the "roll-up" peak. The corresponding outward flow case is given in Fig. 13. In Figs 12 and 13, it is obvious that there are some differences among the three sets of curves in each figure caused by the way $D_{bi}$ and $k_i$ were treated. The average $D_{bi}$ and $k_i$ evaluated at $(X_1 + X_0)/2$ are higher than those evaluated at $V = 0.5$ since $(X_1 + X_0)/2$ is closer to the center of the radial flow

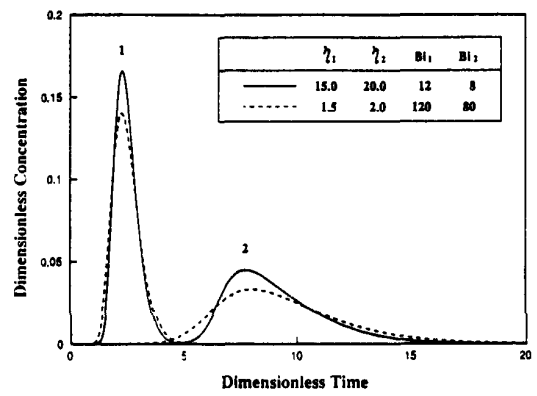


Fig. 11. Effect of $D_{pi}$ on elution in inward flow RFC.

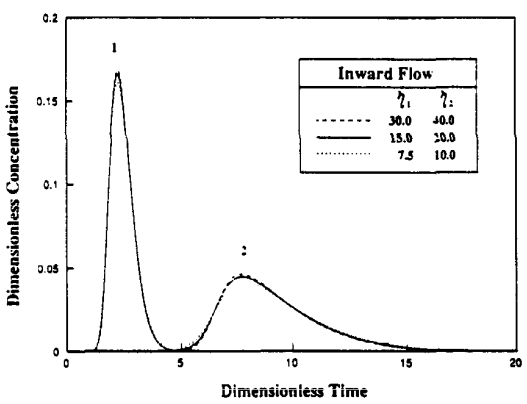


Fig. 9. Effect on $\eta_i$ on elution in inward flow RFC.

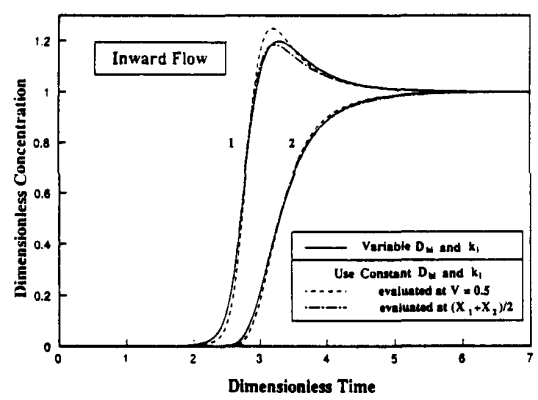


Fig. 12. Effect of treating $D_{bi}$ and $k_i$ as variables in inward flow RFC.

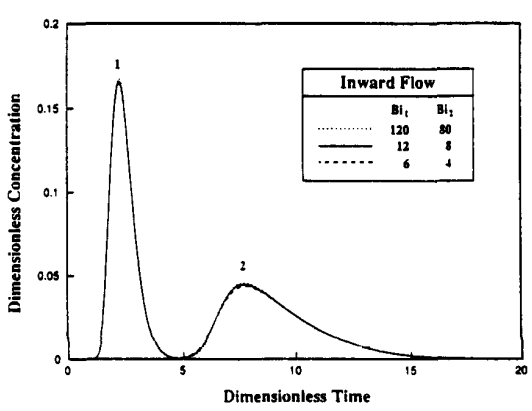


Fig. 10. Effect of $Bi_i$ on elution in inward flow RFC.

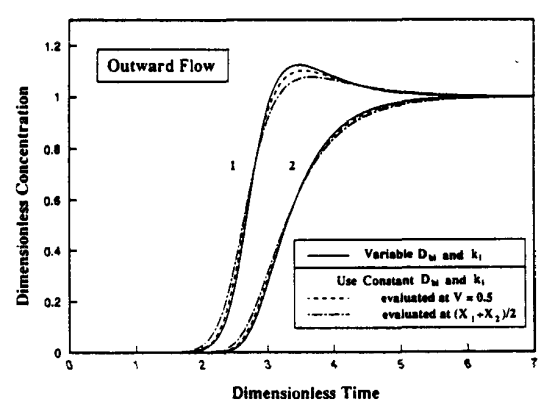


Fig. 13. Effect of treating $D_{bi}$ and $k_i$ as variables in outward flow RFC.

column than $V = 0.5$, and $v$ is higher at $(X_1 + X_0)/2$. Higher $D_{bi}$ values give lower $\overline{Pe_i}$ values and the concentration profiles tend to be more diffused, while higher $k_i$ values give higher $Bi_i$ values and the concentration profiles tend to be sharper. Between these two compromising factors, the $D_{bi}$ factor is more dominant than the $k_i$ factor, since the dependence of $k_i$ on the coordinate $X$ or $V$ is much weaker.

It is well known in mass transfer studies that both Peclet and Biot numbers show some asymptotic behavior. When $Pe_i$ values become larger, the system becomes less sensitive to the changes in $Pe_i$ values. When $Bi_i$ values are in the range above 1, the higher the $Bi_i$ values the less sensitive the system to the increase of $Bi_i$ values. If $Bi_i$ values are sufficiently large, the external interface mass transfer resistances become negligible. These arguments are very helpful in determining the parameter ranges in which the treatment of $D_{bi}$ and $k_i$ as variables become important. Generally speaking, when the $Pe_i$ values are large, the errors caused by using averaged $D_{bi}$ values are small. If $Bi_i$ values are not close to 1, then the treatment of $k_i$ values as variables will have little effect. In most cases such averaging treatment causes some error, but this is not terribly severe. If an averaging treatment is necessary, such as in some analytical treatments in which simplification may be essential, one should not be inhibited to do so. A good averaging method obviously can reduce error. It is difficult to provide exact general rules for averaging $D_{bi}$ and $k_i$ values, since the system is quite complex. From Figs 12 and 13, and other extensive simulations, including different RFC operation and different flow directions, we found that the averaging point should be at an $X$ position farther away from $X_0$ than $(X_1 + X_0)/2$. $V = 0.5$ sometimes proves to be too close to $X_1$ as an averaging point, while at other times it becomes too far away, but generally speaking it is a better choice than $(X_1 + X_0)/2$. For numerical solutions it is desirable to treat $D_{bi}$ and $k_i$ as variable, since it is not only possible but also quite convenient if a suitable numerical procedure, such as the one presented in this work, is used.

(5) *Comparison of RFC and AFC*

If the radial dispersion term in eq. (9) is nelgected, and $k_i$ values are treated as constants independent of the variation of $v$, i.e., $\xi_i$ and $Bi_i$ are treated as constants, then the RFC's dimensionless PDE system [eqs (9) and (10)] become the same as the corresponding AFC's dimensionless PDE system presented by Gu *et al.* (1990a). Inward and outward flow difference will also disappear. This can be easily verified by using a coordinate transformation with $V^* = 1 - V$. This conclusion is, of course, valid for more simplified cases, such as the ideal RFC which neglects radial dispersion, external film mass transfer, and intraparticle diffusion. Rhee *et al.* (1970) pointed out that system equations for ideal radial flow chromatography can be transformed to the system equations for ideal AFC with Langmuir isotherms. A similar conclusion was also reached by Rice (1982) and Huang *et al.* (1988).

We have already shown the effects of radial dispersion on elution in Fig. 9. It is often very important to account for radial dispersion in the modeling of RFC. The $\alpha$ values in the radial dispersion term [eq. (9)] are in the neighborhood of 1. For $V_0 = 0.04$, we have $0.328 \leqslant \alpha \leqslant 1.672$. Comparing the definition of radial flow Peclet number in RFC with the axial flow Peclet number in AFC, it is reasonable to say that their ratio is close to $(X_1 - X_0)/L$. Obviously, Peclet numbers for radial flow in RFC are much smaller than those for axial flow in AFC. A ratio between 1:20 and 1:5 should not be uncommon. Furthermore, radial flow chromatography is designed primarily for preparative and production scale separation, thus Peclet numbers for radial flow tend to be even smaller. A typical value may often be below 100. This is in agreement with the estimation by Tharakan and Chau (1987) in their study of a radial flow bio-reactor for mammalian cell culture. In AFC Peclet numbers often reach hundreds or higher and neglecting axial dispersion (i.e. assuming Peclet numbers equal to infinity) often does not give large errors. For RFC, one may not be able to make such assumptions without risking substantial errors. Thus, one should be very cautious when assuming negligible radial dispersion in RFC. As we have discussed already, in RFC, radial dispersion coefficients are inversely proportional to the radial coordinate $R$. This is actually a very important identity of RFC arising from its special flow geometry, which also differentiates RFC from AFC in terms of dimensionless mathematical expressions. Neglecting radial dispersion in RFC means that its identity in mathematical modeling is partially lost.

As we have already seen in Figs 3–5, if we set the corresponding dimensionless parameters and isotherm expressions the same for both RFC and AFC, their difference in simulated effluent histories are similar. In order to have similar dimensionless constants for an AFC and an RFC, the AFC column should be a short one. Note that the dimensionless parameter $V_0$ is unique in RFC, and for the corresponding AFC we need to pick the $Bi_i$ values from the variable $Bi_i$ values of RFC. Because of this kind of close analogy, one may make use of some data obtained from a short AFC column for reference in RFC. This also helps in transforming an existing AFC set-up to RFC. It is also obvious that many studies for AFC, such as multicomponent interference, can be qualitatively applied to RFC.

The difference between RFC and AFC may arise from the differences in the dimensionless parameters, especially $Pe_i$ and $\eta_i$. In reality, $Pe_i$ and $\eta_i$ values for RFC columns are usually several times smaller than in a longer AFC column. Notice that $\eta_i$ values are proportional to the "dead volume time" of the bed and this time value for RFC is often several times smaller than in AFC due to the shorter flow path in

RFC. Figures 9 and 10 show that both $Pe_i$ and $\eta_i$ values are very important to the sharpness of the concentration profiles and peak resolutions. The higher the $Pe_i$ and $\eta_i$ values the better resolution. Thus, generally speaking, RFC provides lower resolution than does AFC. This is why RFC is not intended for analytical pruposes. The effect arising from the difference of $Bi_i$ values in RFC and AFC is not discussed here because of some uncertainties. $Bi_i$ values for RFC can be either higher or lower than those in AFC depending on value ranges of $v$ in RFC and AFC. RFC usually has higher volumetric flow rate, but it does not necessarily have larger linear flow velocities since its cross-sectional flow area is much larger than AFC.

The most important advantage of RFC over AFC with a longer column is, as we have already mentioned, that in RFC the cross-sectional area perpendicular to the flow direction is very large and the flow path is relatively short. These two factors help reduce pressure drop in the bed and permit a much higher flow rate, and thus promote productivity.

## CONCLUSIONS

A general nonlinear multicomponent rate model for RFC was developed. Radial dispersion and mass transfer coefficients were treated as variables in the model. The model was solved numerically by using the finite element and orthogonal collocation methods for the discretizations of bulk fluid and particle phase PDEs, respectively. Gear's stiff method was used to solve the resulting ODE system. Various chromatographic operations were simulated. The diffusional and mass transfer effects on the RFC elution process were studied. It was found that for simple chromatographic operations inward flow is generally better than outward flow in RFC, since inward flow generally provides sharper concentration profiles. The treatment of radial dispersion and mass transfer coefficients by using averaged values instead of treating them as variables causes some error and such error may be reduced by properly taking the averages. In numerical calculations, treating the radial dispersion and mass transfer coefficients as variables adds very little complexity if the finite element method is used for the discretization of the bulk phase governing equation. It is found that, unlike in AFC, dispersion in the flow direction is often very important in RFC. The dynamic RFC behavior is similar to that of AFC with a shorter column, which has low $Pe_i$ and $\eta_i$ in nondimensional analysis values. The theoretical treatment of RFC with comparison to AFC provides some useful information and it is helpful for the scale-up of RFC, either from a smaller scale RFC or from AFC to RFC. This work also serves as an example of how to deal with fixed bed problems involving variable physical properties. Such problems are actually quite common in chemical engineering.

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## NOTATION

$a_i$, $b_i$ constants in Langmuir isotherm for component $i$

$Bi_i$ Biot number of mass transfer for component $i$ $(k_i R_p (\epsilon_p D_{pi}))$

$\bar{Bi}_i$ averaged $Bi_i$

$C_{bi}$ bulk fluid phase concentration of component $i$

$C_{fi}$ feed concentration profile of component $i$, a time-dependent variable

$C_{0i}$ concentration used for nondimensionalization for component $i$ $(\max\{C_{fi}(t)\})$

$c_{bi}$ $= C_{bi}/C_{0i}$

$C_{pi}$ concentration of component $i$ in the fluid phase within particle

$c_{pi}$ $= C_{pi}/C_{0i}$

$C^s_{pi}$ concentration of component $i$ in the solid phase of the particle (based on the unit volume of particle solid, excluding pores)

$c^s_{pi}$ $= C^s_{pi}/C_{0i}$

$C^\infty_i$ adsorption saturation limit for component $i$. Same value for all components in this work

$D_{bi}$ radial dispersion coefficient of component $i$

$\bar{D}_{bi}$ averaged $D_{bi}$

$D_{pi}$ effective diffusivity of component $i$

$h$ axial bed length of the radial flow column

$k_i$ film mass transfer coefficient of component $i$

$L$ column length in axial flow chromatography

$N$ number of interior collocation points

$Ne$ number of quadratic elements

$Ns$ number of components

$Pe_i$ Peclet number for radial flow in bulk fluid phase for component $i$ $\left(\dfrac{v(X_1 - X_0)}{D_{bi}}\right)$

$Q$ volumetric flow rate of the mobile phase

$X$ radial coordinate for the radial flow column

$X_1$ outer radius of the radial flow column

$X_0$ inner radius of the radial flow column

$R$ radial coordinate for particles

$R_p$ particle radius

$r$ dimensionless radial coordinate for particle $(R/R_p)$

$t$ time

$v$ interstitial velocity $\left(\dfrac{Q}{2\pi h X \epsilon_b}\right)$

$V_b$ bed volume $(\pi h(X_1^2 - X_0^2))$

$V_0$ dimensionless constant $\left(\dfrac{\pi h X_0^2}{V_b} \text{ or } \dfrac{X_0^2}{X_1^2 - X_0^2}\right)$

$V$ dimensionless volumetric coordinate $\left(\dfrac{\pi h(X^2 - X_0^2)}{V_b} \text{ or } \dfrac{X^2 - X_0^2}{X_1^2 - X_0^2},\ V \in [0, 1]\right)$

*Greek letters*

$\alpha$ $= 2\sqrt{V - V_0}(\sqrt{1 + V_0} - \sqrt{V_0})$

$\epsilon_b$ bed void volume fraction

$\epsilon_p$ particle porosity

$\eta_i$ dimensionless constant for component $i\left(\frac{\epsilon_p D_{pi}}{R_p^2}\frac{V_b\epsilon_b}{Q}\right)$

$\xi_i$ dimensionless constant for component $i\left(3Bi_i\eta_i(1-\epsilon_b)/\epsilon_b \text{ or } \frac{3k_i(1-\epsilon_b)V_b}{R_pQ}\right)$

$\tau$ dimensionless time $(tQ/(V_b\epsilon_b))$

$\tau_{imp}$ dimensionless time duration for a rectangular sample input

$\phi$ Lagrangian interpolation function

$\rho$ liquid density

$\mu$ liquid viscosity

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