Modeling Chemically Active Liquid Membranes in Tubular Inorganic Supports

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A numerical model is presented to evaluate the dynamic behavior of mass transfer in the shell-and-tube-type membrane modules for metal ion removal from aqueous streams. The analysis that considers the effects of axial-flow velocity on the radial pressure difference across the membrane wall permits the specification of this operating parameter to avoid expression of impregnated carrier from the membranes and to prevent membrane wall rupture. The model accounts for effects of boundary layer mass-transfer and kinetic rate resistances at the interfaces on membrane flux. The performance of different size membrane modules was estimated for two operating modes of a shell-and-tube-type module: one for the flow of feed solution inside the membrane tube and strip solution flow in the annular region and the other for the flow of strip solution inside the membrane tube and feed solution flow in the annular region of the module. A case system evaluated is copper ion extraction from acidic solutions using 2-hydroxy-5-nonylacetophenone oxime impregnated in α-alumina/silica ceramic membranes. The performance of shell-and-tube-type membrane modules depends on the sizes and operating methods. In these calculations, the operation condition of no-pressure difference across the membrane was imposed on the design. This condition is achieved by adjusting the ratio of the flow velocities of the feed and strip solutions within the inside and annular regions of the modules.

Introduction

Supported liquid membranes are recognized as a promising technology for the separation or purification of toxic or valuable metal ions from aqueous streams, since they combine the processes of extraction, stripping, and regeneration into a single stage (Danesi et al., 1983; Noble and Way, 1987; Noble, 1987; Tanigaki et al., 1988; Marchese et al., 1989; Sugiura et al., 1989; Teramoto et al., 1989; Drioli et al., 1989; Chaudry et al., 1990; Juang, 1993). In this process, the forward extraction reaction occurs on the feed side and the reverse stripping reaction occurs on the receiving side. In the pores of the membrane, the chelated molecules are transported to the receiving side and regenerated ion-exchange molecules diffuse in the opposite direction to renew the process.

Review of supported liquid membrane applications are presented elsewhere (Way et al., 1982; Schultz, 1983; Danesi, 1984; Noble et al., 1989). The relevant advantages of supported liquid membranes over conventional separation technology (such as solvent extraction) include uphill transport against concentration gradients, high feed/strip volume ratios, and use of small amounts of extractants (Kim and Stoeve, 1989). Despite promising performance, few processes using supported membrane technology have been commercialized for large-scale hydrometallurgical extraction (Noble and Way, 1987). The main disadvantages exhibited by the polymeric membranes being used are: sensitivity to temperature, pH and many chemical environments (Noble, 1987), plasticizer effects (Sugiura, 1990), and loss of mechanical stability in modular operation (Teramoto and Tanimoto, 1983). These needs suggest the use of ceramic substrates which have potential to overcome the above difficulties. They exhibit reliability and long life, neither creep nor deformation occurs during cooling, and high permeabilities can be achieved.

Ceramic supported membranes filled with organic chelation acid show promise as the basis for inorganic membrane separator units for copper ion separations from dilute aque-

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ous streams (Yi and Tavlarides, 1992). The performance of such membranes in disk geometry was evaluated experimentally. However, the planar geometry of these membranes have a limited contact surface area per unit contactor volume when compared to tubular membrane modules. For practical purpose, the shell–and–tube-type modules can be used to increase the surface/volume ratio.

Analyses of the shell–and–tube-type membrane modules are important for optimal operation, scale-up and control purposes. Numerous theoretical and experimental studies have been published in the literature for the hollow-fiber modules treating feed and membrane phases for prediction of mass-transfer performance (Colton et al., 1971; Cooney et al., 1974; Noble, 1983; D'elia et al., 1986; Noble and Danesi, 1987; Kim and Stroeve, 1988, 1989; Dahuron and Cussler, 1988; Kang et al., 1990). Mass transfer in membrane devices often is limited by solute transport through the membranes. The additions of mobile carrier species and chemically active compounds can increase the membrane flux and selectivity (Bungay et al., 1986; Stroeve and Kim, 1987). Recently, liquid membranes containing mobile complexing agents have been widely studied (Sengupta et al., 1988; Kim and Stroeve, 1989) for solute extraction using tubular membrane modules.

Theoretical analyses of the transport phenomena for tubular module application have been reported for the limiting cases of fast chemical reaction at the interfaces or of negligible concentration at the strip solution (Cox and Flett, 1983; Chapman, 1987; Kim and Stroeve, 1988, 1989). However, experimental results show that the aqueous film diffusion process and interfacial chemical reactions at both sides of the feed and strip solutions simultaneously control the performance of supported liquid membranes for metal chelation based separations (Yi and Tavlarides, 1992; Juang, 1993).

Furthermore, in order to reduce mass-transfer resistance at the outside wall of the tubular membranes and to neglect the effect of the strip concentration change with the reaction progress along the tubular axial distance, the average velocity (or volumetric flow rate) of the strip solution is assumed to be very large compared with the feed solution flow (Colton et al., 1974; Kim and Stroeve, 1989). For this operation, however, the pressure difference across the membrane can be large enough to rupture thin membranes or express the impregnated chemical compounds from the pores. Eventually, the membrane life time decreases significantly by membrane destruction.

Also, when the strip solution concentration is not constant, whether differences are large or negligibly small, the concentration fields in the feed, membrane, and strip solutions are coupled through mutual boundary conditions at the interfaces and the problem should be treated as a coupled boundary problem.

In this study, numerical calculations are performed to estimate the performance of shell–and–tube-type membrane modules prepared for metal ion removal from aqueous streams, and to predict the operating conditions for four possible operation modes. The first operation mode (mode 1) is that feed solution flows inside the membrane tube and strip solution flows in the annular region in the shell–and–tube-type module. The second operation mode (mode 2) is that strip solution flows inside the membrane tube and feed solution flows in the annular region in the module. Also, extraction performances of two different size tubular modules (modules A and B) are estimated for each different operating modes.

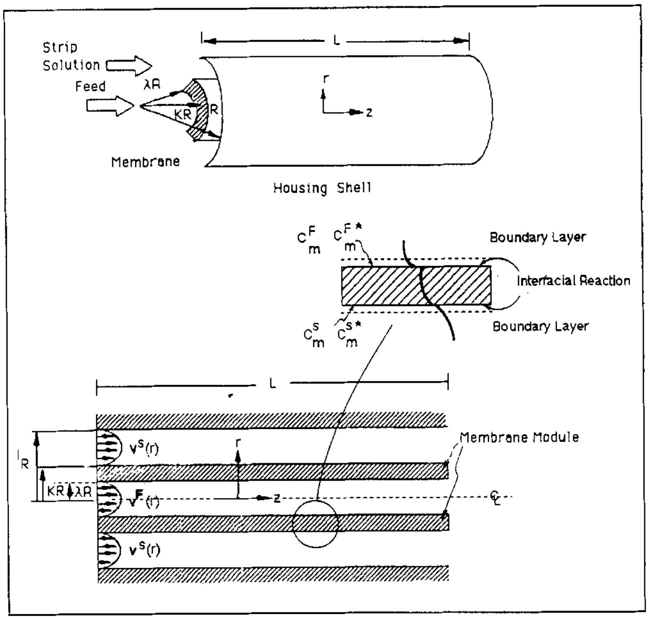

Figure 1. Shell–and–tube-type tubular module for operation mode 1.

In these calculations, the operation condition of no-pressure difference across the membrane is imposed, since no-pressure difference across the membrane in the shell–and–tube-type module is an important operating factor to prevent thin membrane ruptures and expression of impregnated materials from the pores. This condition is achieved by the ratio adjustment of the average flow velocities of the feed and strip solutions flowing within the inside and annular regions of the tubular membrane modules.

Theoretical Background

The membrane system for a shell–and–tube-type module geometry is shown in Figure 1 for mode 1, for which the feed solution flows inside the membrane tube and the strip solution flows in the annular region in the shell–and–tube-type membrane module. Assuming fully developed laminar flow, the Newtonian fluids of the feed and strip solution streams contact the reactive membrane part. The active chelation agent is constrained within the pores of the porous membrane by capillary forces (Noble and Way, 1987; Prasad and Sirkar, 1988; Yi and Tavlarides, 1992). As fluids flow along the reactive section of the membrane, metal ions diffuse through the boundary layer and react with the chelation acid at the interface between the aqueous and organic membrane phase. The chelated complexes formed by the reaction diffuse through the membrane phase, and the stripping reaction occurs at the interface on the other side of the membrane. Stripped metal ions diffuse through the boundary layer to the strip bulk solution. This series of metal ion transport paths are shown in Figure 2.

As depicted in Figure 1, the mass conservation equation for metal-containing species and the associated boundary

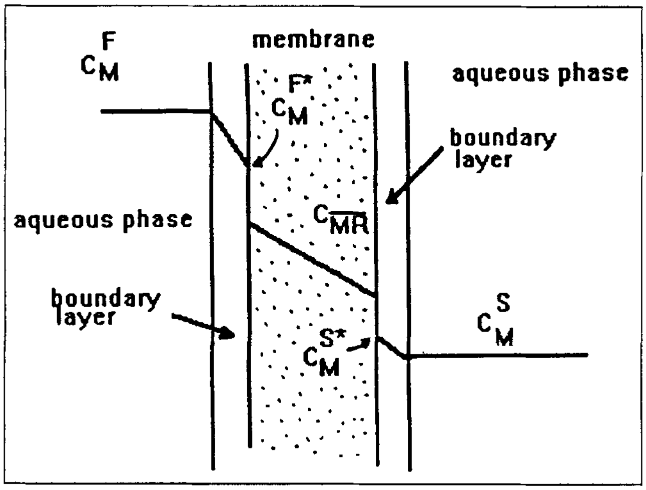

Figure 2. Metal ion extraction using supported liquid membrane.

conditions can be given as:
feed phase $(0 \geq r \geq \lambda R)$

$$\frac{\partial C_M^F}{\partial t} + v^F(r)\frac{\partial C_M^F}{\partial z} = \frac{D_M}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_M^F}{\partial r}\right) \tag{1}$$

membrane phase $(\lambda R \leq r \leq \kappa R)$

$$\frac{\partial C_{\overline{MR}}}{\partial t} = \frac{D_{\overline{MR}}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\overline{MR}}}{\partial r}\right) \tag{2}$$

strip phase $(\kappa R \leq r \leq R)$

$$\frac{\partial C_M^S}{\partial t} + v^S(r)\frac{\partial C_M^S}{\partial z} = \frac{D_M}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_M^S}{\partial r}\right) \tag{3}$$

with the boundary conditions

for $0 \leq z \leq L$

$$\left.\frac{\partial C_M^F}{\partial r}\right|_{r=0} = 0 \tag{4}$$

$$-D_M\left.\frac{\partial C_M^F}{\partial r}\right|_{r=\lambda R} = k_M^F(C_M^F - C_M^{F*}) \tag{5}$$

$$-D_{\overline{MR}}\left.\frac{\partial C_{\overline{MR}}}{\partial r}\right|_{r=\lambda R} = R^F \tag{6}$$

$$-D_{\overline{MR}}\left.\frac{\partial C_{\overline{MR}}}{\partial r}\right|_{r=\kappa R} = R^S \tag{7}$$

$$-D_M\left.\frac{\partial C_M^S}{\partial r}\right|_{r=\kappa R} = k_M^S(C_M^{S*} - C_M^S) \tag{8}$$

$$\left.\frac{\partial C_M^S}{\partial r}\right|_{r=R} = 0 \tag{9}$$

for $z = 0$ and $t \geq 0$

$$C_M^F = C_M^{F0} \quad C_{\overline{MR}} = C_T^0 \quad C_M^S = C_M^{S0} \tag{10}$$

initial conditions at $t = 0$

$$C_M^F = C_{M0}^{F0} \quad C_{\overline{MR}} = C_{\overline{MR}0}^0 \quad C_M^S = C_{M0}^{S0} \tag{11}$$

where C_M^i is the metal ion concentration in the bulk solution, and C_M^{i*} is the interfacial concentration at the i-side, i = Feed or Strip. $C_{\overline{MR}}$ is the metal complex concentration in the membrane. D_M and $D_{\overline{MR}}$ are the diffusion coefficients of the metal ion and metal complex in the membrane phase, respectively. k_M^i is the mass-transfer coefficient at the boundary layer of i-side, i = Feed or Strip. R^F and R^S denote the interfacial reaction expression at the feed and strip side, respectively. In the above equations, axial diffusion is assumed to be negligible compared to axial convection in the feed and strip solution streams. This assumption is valid when the Peclet number is greater than 100 (Schneider, 1957). In Eqs. 1 and 3, $v^i(r)$ ($i = F$ or S) is the flow velocity expression, and λR and κR are the inside and the outside radii of the tubular membrane, respectively. R is the inner radius of the membrane housing shell. Equation 4 implies that the system is symmetric for cylindrical geometry, while Eq. 9 indicates no flux occurs through the housing wall. Equations 5 and 8 imply that the metal ion flux from the feed solution is dependent upon the mass-transfer rate through the boundary layer. The latter is approximated by the film theory and is proportional to the concentration difference between bulk feed (C_M^F, C_M^S) and at the interfaces (C_M^{F*}, C_M^{S*}). Equations 6 and 7 indicate that the metal complex flux through the membrane at the interface is dependent upon the interfacial reaction kinetics, which are a function of interfacial concentrations of the metal and the chelated metal complex, as in Eqs. 14 and 15. Equations 5–8 imply that the fluxes through the boundary layer and the interfacial reaction rates play a role in controlling metal ion transport through the supported liquid membrane system.

The interfacial reaction expressions R^F and R^S can be derived theoretically and were described in the work by Yi and Tavlarides (1992). Briefly, the following stoichiometric expression is assumed to describe the overall extraction process which occurs on either side of the membrane/solution interface:

$$M^{2+} + 2\overline{HR} \leftrightarrow \overline{MR}_2 + 2H^+ \tag{12}$$

where M^{2+} and $\overline{HR}$ represent the metal ion species and the chelation acid, respectively. A kinetic model for the interfacial reaction was derived based on a series of five elementary reactions at the interface in a similar fashion as Lee and Tavlarides (1986). The lumped expression for the interfacial reaction R^i can be written as:

$$R^i = k'_{+i} C_M^{i*} \frac{C_{\overline{HR}}^{i*}}{C_H^{i*}} - k'_{-i} C_{\overline{MR}}^{i*} \frac{C_H^{i*}}{C_{\overline{HR}}^{i*}} \tag{13}$$

where C_j^{i*}, i = feed or strip solution, denote the interfacial concentrations of species j at the i-side. Kinetic expressions of this form have been reported for copper ion extraction rates in similar systems (Kojima and Miyauchi, 1981; Komasawa and Otake, 1983; Tallarico et al., 1989). When the reaction takes place at high concentrations of chelation acid as compared to the metal ion concentration, and the pH is maintained constant and/or the hydrogen ion concentrations are large compared with the metal ion or metal complex concentrations, the approximations yield interfacial reaction rates of the form of first-order reversible reactions as:

$$R^F = k_{+F} C_M^{F*} - k_{-F} C_{\overline{MR}}^{F*} \qquad \text{at } r = \lambda R \tag{14}$$

and

$$R^S = k_{-S} C_{\overline{MR}}^{S*} - k_{+S} C_M^{S*} \qquad \text{at } r = \kappa R \tag{15}$$

where k_{+i} and k_{-i} are the interfacial rate coefficients at the i side, i = Feed or Strip, respectively.

The fluid velocity expressions for fluids flowing inside the tube ($v^F(r)$) and in annular region [$v^S(r)$] in the tubular module in Eqs. 1 and 3 can be written for Newtonian fluids as (Bird et al., 1960):

$$v^F(r) = \frac{(P_0^F - P_L^F)}{4\mu L} \lambda^2 R^2 \left\{ 1 - \frac{1}{\lambda^2} \left(\frac{r}{R} \right)^2 \right\} \tag{16}$$

$$v^S(r) = \frac{(P_0^S - P_L^S)}{4\mu L} R^2 \left\{ 1 - \left(\frac{r}{R} \right)^2 + \frac{1-\kappa^2}{\ln(1/\kappa)} \ln\left(\frac{r}{R} \right) \right\} \tag{17}$$

and the average velocities $\bar{v}^F$ and $\bar{v}^S$ are given as:

$$\bar{v}^F = \frac{(P_0^F - P_L^F)}{8\mu L} \lambda^2 R^2 \tag{18}$$

$$\bar{v}^S = \frac{(P_0^S - P_L^S)}{8\mu L} R^2 \left\{ 1 + \kappa^2 - \frac{1-\kappa^2}{\ln(1/\kappa)} \right\} \tag{19}$$

Here the (P_0^i, P_L^i) terms $i = F$ or S represent fluid pressure drops along the axial distance (L) of the tube, and μ is the viscosity.

The major operational problem is to prevent the expression of the supported chelation liquid from the membrane pores. Thus, it is necessary to maintain near zero pressure difference across the membrane along the axial position of the tube at any position z. It was noted in Eqs. 16 and 17 that the fluid velocities of the inside and annular region of the shell-and-tube-type of modules are related to the pressure drop between the inlet (P_0^F, P_0^S) and the outlet axial positions (P_L^F, P_L^S). The pressure profiles along the length of the flowing fluid at the position z ($0 < z < L$) can be obtained as:

$$P_0^F - P_z^F = \frac{8\mu \cdot z}{\lambda^2 R^2} \bar{v}^F \tag{20}$$

$$P_0^S - P_z^S = \frac{8\mu \cdot z}{R^2} \bar{v}^s \left\{ 1 + \kappa^2 - \frac{1-\kappa^2}{\ln(1/\kappa)} \right\}^{-1} \tag{21}$$

Assuming the inlet pressures of fluids P_0^F and P_0^S are the same, the pressures at position z can have the same values by adjusting the average flow velocities at a given position along the tubular module. The ratio of the average velocity for the $P_z^F = P_z^S$ can be given as:

$$\frac{\bar{v}^F}{\bar{v}^S} = \frac{\lambda^2}{\left\{ 1 + \kappa^2 - \dfrac{1-\kappa^2}{\ln(1/\kappa)} \right\}} \tag{22}$$

Equation 22 implies that when the flow rates are maintained at this ratio, there is no pressure difference across the membrane. This operating condition is important for the prevention and minimization of the expression of impregnating compounds from the pores.

For ease of solution and analysis, it is convenient to use dimensionless forms of Eqs. 1–3. Using Eqs. 14–17 and 22, these are written as:

$$\frac{\partial f}{\partial \tau} + 2\left(1 - \frac{x^2}{\lambda^2}\right) \frac{\partial f}{\partial y} = \frac{\epsilon s^2}{x} \frac{\partial}{\partial x}\left(x \frac{\partial f}{\partial x} \right) \qquad \text{for } 0 \le x \le \lambda \tag{23}$$

$$\frac{\partial g}{\partial \tau} = \frac{s^2}{x} \frac{\partial}{\partial x}\left(x \frac{\partial g}{\partial x} \right) \qquad \text{for } \lambda \le x \le \kappa \tag{24}$$

$$\frac{\partial u}{\partial \tau} + \frac{2}{\lambda^2}(1 - x^2 + d \ln x) \frac{\partial u}{\partial y} = \frac{\epsilon s^2}{x} \frac{\partial}{\partial x}\left(x \frac{\partial u}{\partial x} \right) \qquad \text{for } \kappa \le x \le 1 \tag{25}$$

with the boundary conditions

for $0 \le x \le 1$

$$\left. \frac{\partial f}{\partial x} \right|_{x=0} = 0 \tag{26}$$

$$\left. \frac{\partial f}{\partial x} \right|_{x=\lambda} = B_F^F (g - f) \tag{27}$$

$$\left. \frac{\partial g}{\partial x} \right|_{x=\lambda} = B_g^F (g - f) \tag{28}$$

$$\left. \frac{\partial g}{\partial x} \right|_{x=\kappa} = B_g^S (u - g) \tag{29}$$

$$\left. \frac{\partial u}{\partial x} \right|_{x=\kappa} = B_F^S (u - g) \tag{30}$$

$$\left. \frac{\partial u}{\partial x} \right|_{x=1} = 0 \tag{31}$$

$$\text{at} \quad y = 0, \quad f = F, \quad g = G, \quad u = U \tag{32}$$

$$\text{at} \quad \tau = 0, \quad f = f_0, \quad u = u_0, \quad g = g_0 \tag{33}$$

where

$$B_F^i = \frac{R}{D_M}\Delta^i \quad B_g^i = \frac{RK^i}{D_{\overline{MR}}}\Delta^i \quad \Delta^i = \left(\frac{1}{k_M^i} + \frac{1}{k_{+1}}\right)^{-1}$$

$$K^i = k_{-i}/k_{+i} \quad (i = F \text{ or } S)$$

with dimensionless groups

$$f = C_M^F/K^F C_T^0, \quad u = C_M^S/K^S C_T^0, \quad g = C_{\overline{MR}}/C_T^0,$$

$$\tau = D_{\overline{MR}}\frac{t}{s^2R^2}, \quad x = r/R, \quad \epsilon = D_M/D_{\overline{MR}}, s^2 = (\kappa - \lambda)^2,$$

$$d = \frac{1-\kappa^2}{\ln(1/\kappa)},$$

where C_T^0 is the initial metal chelating agent concentration in the membrane. This dimensionless axial distance down the tubular module y can be given as $y = (z/\bar{v}^F)/(s^2R^2/D_{\overline{MR}}) =$ residence time of feed solution in the membrane module/diffusion time in the membrane phase.

The dimensionless length, as defined here, is dependent upon the axial distance z and the average flow velocity $\bar{v}^F$.

The dimensionless mixing cup concentrations of the feed $\hat{f}$ and the strip solution $\hat{u}$, which define the average concentration of a flowing system, are more useful than the local concentrations, and these are given as:

$$\hat{f} = \frac{\int_0^\lambda v^F(x) f x dx}{\int_0^\lambda v^F(x) x dx} = \frac{4}{\lambda^2}\int_0^\lambda f\left(1 - \frac{x^2}{\lambda^2}\right) x dx \tag{34}$$

$$\hat{u} = \frac{\int_\kappa^1 v^s(x) u x dx}{\int_\kappa^1 v^S(x) x dx} = \frac{4}{\int_\kappa^1 v^S(x) x dx}\int_\kappa^1 u(1 - x^2 + d\ln\kappa) x dx \tag{35}$$

To investigate the performance of tubular membrane modules, the feed and strip concentration changes with selected parameter values for various operation modes were evaluated. The average concentrations of feed and strip solutions can be nondimensionalized based on the feed concentration at the inlet as $\hat{X} = \hat{f}/F =$ mixing cup concentration of the feed at the outlet/feed concentration at the inlet and $\hat{Y} = (\hat{u}/F)(K^S/K^F) =$ mixing cup concentration of the strip solution at the outlet/feed concentration at the inlet.

By similar procedures, the governing equations can be derived for the mode 2, in which strip solution flows inside the membrane tube and feed solution flows in the annular region in the module.

Results and Discussion

In this study, tubular modules of α-alumina/silica ceramic membranes were selected as a model, since the performance of such membranes in disk geometry was evaluated experimentally (Yi and Tavlarides, 1992). The dimensions of the tubular membrane prepared is 0.6 cm ID, 0.75 cm OD, and 25 cm long. The case system studied is copper ion extraction from acidic solution employing 2-hydroxy-5-nonylacetophenone oxime impregnated in the tubular membranes.

Table 1. Dimensions of Two Modules Studied

	Module A	Module B
R	1.0 cm	1.5 cm
λ	0.6	0.4
κ	0.75	0.5

The performance of shell-and-tube-type modules for this system is calculated for four different operational modes, two different size units operated at two sets of operation conditions. The two different sizes of membrane modules are designated as module A and module B. Module A is designed such that the cross-sectional flow areas of the inside tube and annular region are nearly equal. Module B is designed such that the average flow velocities inside the membrane tube and in the annular region are nearly equal in order to approach the no-pressure difference operation condition across the membrane. Table 1 lists the dimensions of modules A and B, which were designed and prepared in our laboratory for experimental studies.

The two modules will be considered for two sets of operating conditions. In operation mode 1, the feed solution flows inside the membrane tube and the strip solution flows in the annular region. In operation mode 2, the channels in which the stream flows are reversed from mode 1.

Since the chelation agent in the membrane reacts selectively with the metal ion, the membrane module can selectively extract metal ions present in the aqueous stream. However, it is important to prevent the expression of the chemically active compounds impregnated in the membrane for stable and long-term operation. This stability can be achieved by the prevention or minimization of the pressure difference across the membrane and/or by the chemical modification/treatment of the membrane surfaces before or after impregnation. The latter approach is beyond the scope of this study. The results presented in the following section are for the operation modes in which there is no pressure difference across the membrane.

As described in the previous section, the pressure difference across the membrane can be prevented or minimized by adjusting the ratio of flow rate in the inside tube to the value in the annular region of the shell-and-tube-type module. Figure 3a displays this relationship determined in Eq. 22 for the two different modules. The average flow velocity ratios are 8.628 and 0.953 for modules A and B respectively. For these operational conditions, the pressures of the fluid streams inside and outside tubular membrane are the same.

For reactor operation, the average volumetric flow rate is more useful and easy to measure and control. The volumetric flow rate ratio of the stream flowing inside the tube ($\overline{Q}_F$) to the stream flowing in the annular region ($\overline{Q}_S$) in the shell-and-tube-type of tubular module can be written as:

$$\frac{\overline{Q}_F}{\overline{Q}_S} = \left(\frac{\bar{v}^F}{\bar{v}^S}\right)\left(\frac{\lambda^2}{(1-\kappa^2)}\right) \tag{36}$$

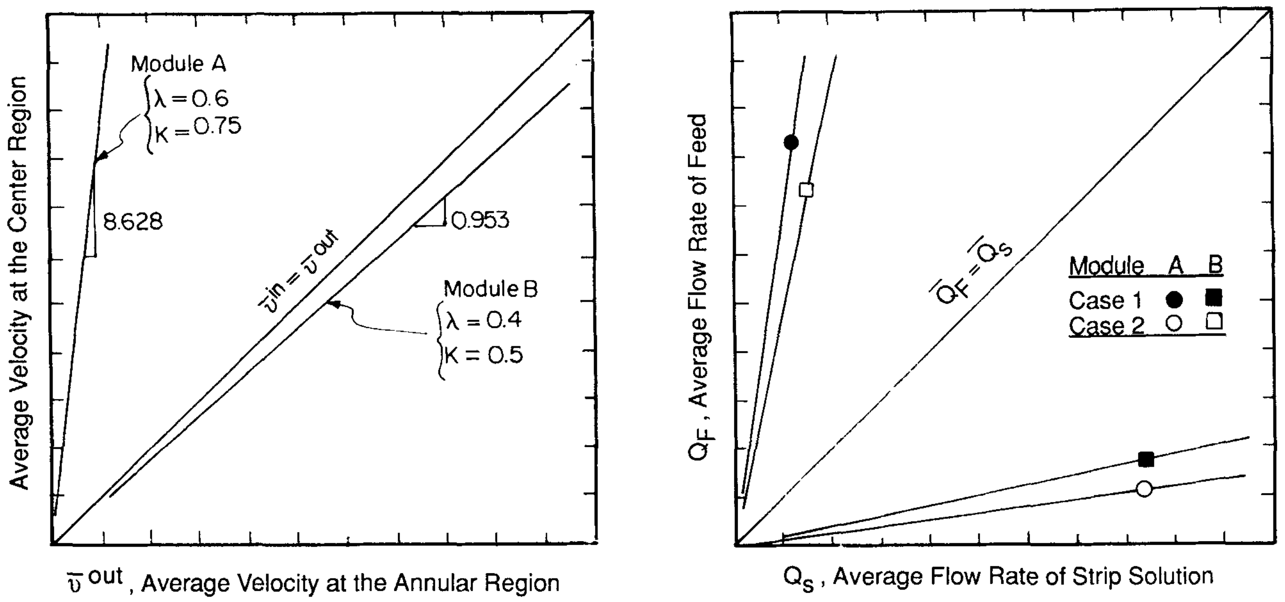

Figure 3. Relationship between average velocities (*a*) and average volumetric flow rates (*b*) at the center region and in the annular regions for no-pressure difference across the membrane.

Figure 3b shows calculated volumetric flow rates of feed solution ($\overline{Q}_F$) and strip solution ($\overline{Q}_S$) for the operating conditions of no-pressure difference across the membrane for the two different size modules for two different operation modes.

The case system studied for the performance evaluations is copper ion extraction from acidic solutions employing 2-hydroxy-5-nonylacetophenone oxime (Henkel) impregnated in α-alumina/silica ceramic membranes (Coors Ceramic Co.). The structure of the membranes used in the study is a symmetric material with uniform porosity of 41.7% and average pore size of 49–55 μm. The conditions employed were copper sulfate feed solution of 0.03 gmol/L, feed solution pH of 3, strip solution of 1.5 gmol/L sulfuric acid, and impregnation solution concentration of 3.2 gmol/L. Under these experimental conditions, the physical and chemical parameters of diffusivities ($D_M = 5\times10^{-6}$ cm^2/s and $D_{\overline{MR}} = 2.3\times10^{-7}$ cm^2/s), kinetic coefficients ($k_{+F} = 7.3\times10^{-4}$ cm/s, $k_{-F} = 7.1\times10^{-6}$ cm/s, $k_{+S} = 6.9\times10^{-8}$ cm/s and $k_{-S} = 3.6\times10^{-6}$ cm/s), and equilibrium coefficients ($K^F = 9.7\times10^{-3}$ and $K^S = 52.2$) reported earlier (Yi and Tavlarides, 1992) are used here.

To solve the coupled partial differential Eqs. 23–25 with the boundary conditions Eqs. 26–32, a finite difference method was used in the x and y directions, and a set of ordinary differential equations at each grid point of x and y were obtained. These differential equations were solved using the EPISODE routine (Byrne and Hindmarch, 1976), where the tolerance was set to 10^{-5}.

The parameter ranges employed in these calculations were defined based on the values determined experimentally earlier (Yi and Tavlarides, 1992). We approximate the parameter values for this calculation as $D_M/D_{\overline{MR}} = 10$, $K^F = 10^{-2}$ and $K^s = 10^2$. The computer programs yielded values for the concentrations as a function of x and y and other parameters. For steady-state performance analysis, the partial difference method was used in the x direction, and after obtaining a set of ordinary differential equations, the EPISODE routine (Byrne and Hindmarch, 1976) was also employed for the solution of these differential equations. The tolerance was set to 10^{-5}.

In this study, the "feed stream" term is used to express solution stream which contains metal ion species to be extracted. Thus, as the feed stream flows through the membrane module, the metal ions are extracted from the feed solution and transferred to the strip solution. Thus, the metal ion concentration of the feed stream decreases as the extraction reaction progresses along the axial distance of tubular membrane module.

Figure 4 displays the unsteady-state performance for the module A with operation mode 1. This figure plots the concentration changes of the feed stream at the outlet of the tubular modules against the dimensionless operation time of material processing through the module. The concentrations represent the outlet mixing cup concentration for a given length of membrane module, since no flux occurs after the operating times beyond the residence time of the fluids in a given length of membrane module and flow velocity. Figure 4 compares the performances for three possible relative values of mass-transfer and reaction kinetic parameters; mass transfer is the rate-determining step (RDS), the interfacial reaction is the RDS, or these two mechanisms are competitive. When the interfacial reaction is the RDS, the best membrane performance in comparison to the other cases studied is observed. Unsteady-state performances were obtained for other operation modes and modular unit configurations. Although the results are not presented here, similar trends were observed that the feed mixing cup concentrations decrease and the strip mixing cup concentrations increase.

Since the common mode of operation is steady state, it is useful to investigate the membrane performance and concentration changes for the steady-state operation. Figure 5 shows the feed and strip solution concentration changes with the

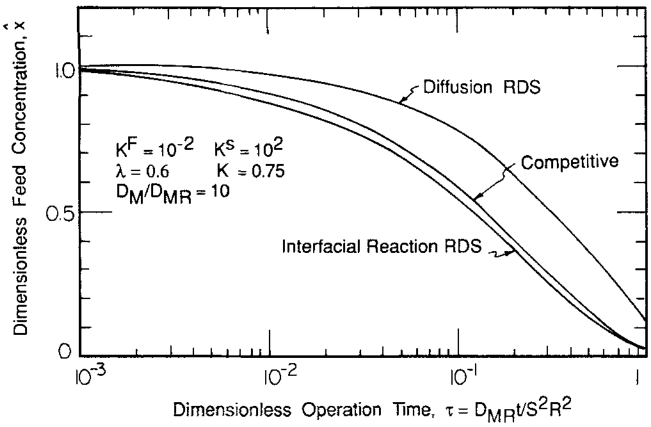

Figure 4. Dimensionless feed concentration vs. dimensionless operating time for operation mode 1 using module A.

dimensionless length for module A with operation mode 1 for the steady-state operation. The three possible operation cases shown are the diffusion step is the RDS, the interfacial reaction is the RDS, or these two steps are competitive. For all three cases, the feed concentrations decrease and the strip concentrations increase. When the interfacial reaction is the RDS, the performance is the best. Also, uphill transport occurs when the value of the dimensionless length is larger than about 0.1, as shown in Figure 5. Based on these calculations, when the dimensionless length is 10^{-2} and the average volumetric flow rate is 11.3 cm^3/min, the feed concentration decreases to about 75% of the inlet concentration. For this performance, the tubular membrane length required is about 1.6 m (for a tubular membrane module with an ID of 12 mm and an OD of 15 mm which is prepared for experimental studies).

Figure 6 represents the feed concentration changes for the module A with operation mode 2. This figure plots the performances for the three rate determining steps. For all three cases, the feed concentrations decrease. The changes of strip concentrations however are very small, since the volumetric flow rate of the strip solution is 7.2 times greater than that of the feed solution described in Figure 3b. This result suggests that the strip solution should be operated in a recycle mode or tube bundle type membrane modules (multiple tubular membranes installed in one housing shell) should be used, as a practical method of module A operation with mode 2. Also, the membrane performance is the best when the interfacial reaction is the RDS.

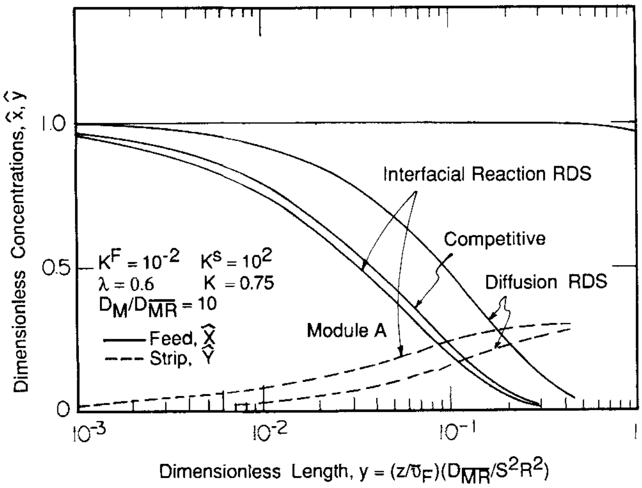

Figure 5. Dimensionless feed and strip concentrations vs. dimensionless length for operation mode 1 using module A.

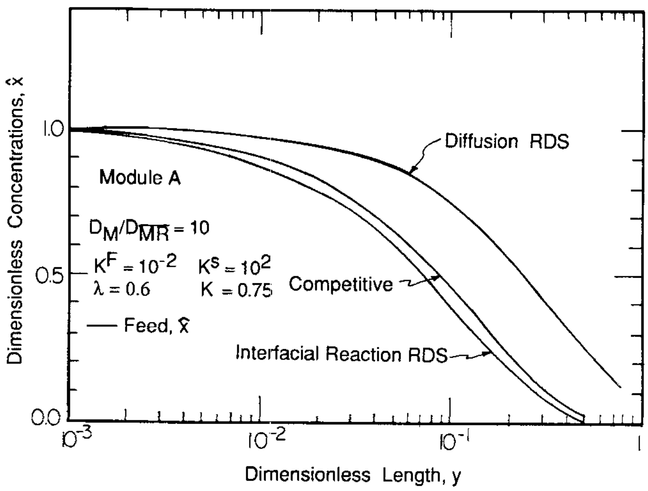

Figure 6. Dimensionless feed concentration vs. dimensionless length for operation mode 2 using module A.

In most cases studied on mass transfer in tubular module devices, the governing equation (mass conservation equation) for the feed solution stream flowing within a tube is solved with the equilibrium relationship at the interface (Colton et al., 1974; Kim and Stroeve, 1988, 1989). The strip solution concentration is usually assumed to be constant along the tubular axial position (Colton et al., 1974; Kim and Stroeve, 1989, 1990). Under these conditions, it is difficult to explicitly examine the effect of the diffusion coefficient of the solute in the membrane phase (copper complex in this study) on the performance of the tubular module of a separation device.

However, it is important to investigate the effect of the diffusion coefficient ratio of the solute in the aqueous phase (copper ion in this study) to that in the membrane phase (copper complex in this study) on the tubular module performance for design purposes. The diffusion coefficient of chelated molecules in the membrane is smaller than the diffusion coefficient of free copper ion in the aqueous phase, since the molecular weight of the complexed compound in the membrane is much larger than that of copper ion in the aqueous solution and the pore fluid could have a relatively high viscosity. Further, the effective diffusivity of complex in the pores is related to the structure of the membrane. Experimental results indicate that the diffusivity of copper ion in an acidic solution is approximately one order of magnitude larger than that of the copper complex in the membrane (Yi and Tavlarides, 1992).

In this study, the unequal diffusivities of these two components were considered. The models described in Eqs. 23–32 allow one to analyze this effect on the shell-and-tube-type membrane performance by treating the feed, strip, and mem-

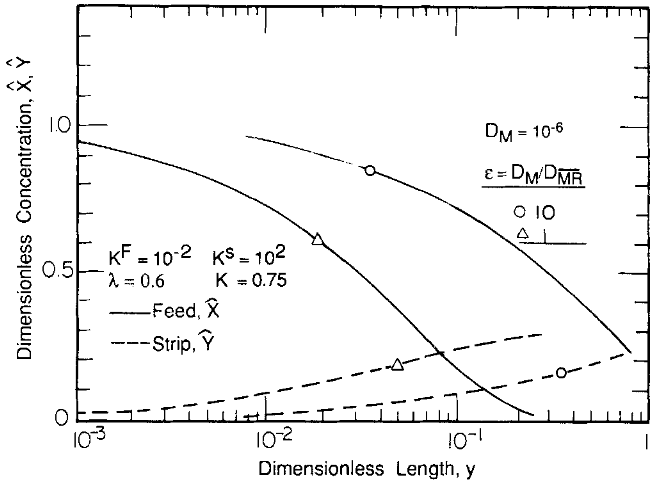

Figure 7. Effect of diffusion coefficient of copper complex in the membrane on the module performance.

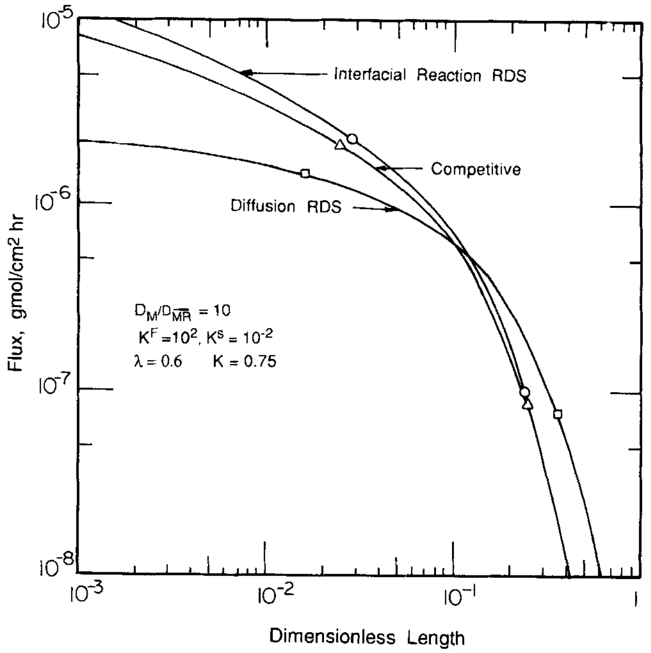

Figure 8. Flux changes with dimensionless length.

brane phases simultaneously as controlling factors. Figure 7 shows the concentration changes of the feed and strip solutions at steady-state operation for two different diffusion coefficient ratios of copper in the aqueous phase to copper complex in the membrane. This figure shows that when the diffusivity ratio ($\epsilon = D_M/D_{\overline{MR}}$) is one, the calculated separation performance is overestimated. This figure also shows the importance of large diffusivity values for the copper complex in the membrane phase on membrane module performance. For example, when a tubular module is designed, the solute diffusivity in the membrane should be as large as possible. Large porosity, low molecular weight of chelation acid and low viscosity of pore fluid are desirable.

For practical use of shell–and–tube-type modules, the relationship between flux and membrane length is important. Since feed concentration decreases and strip concentration increases as the extraction reaction progresses along the axial distance, the flux decreases abruptly at a certain length of tubular membrane module. Beyond this length, fluxes become very small. When the flux is lower than a certain value, the effectiveness of the membrane module is relatively low. Figure 8 shows the flux changes with dimensionless length for module A with operation mode 1. Fluxes are plotted for the three possible operating cases as a function of dimensionless length. In this figure, when the membrane length becomes larger than about 0.1, fluxes decrease abruptly. These results suggest that the modular lengths greater than 0.1 are uneconomical under these conditions and that other methods are needed to treat this stream further. For example, the tubular membrane length required is about 100 m to achieve this condition, when treating feed solution with flow rate of 70 m³/min.

One of the objectives of this study is to estimate the performance of shell–and–tube-type membrane modules and eventually to determine the operation conditions for two sizes and two operation modes. In order to compare performances of these four different situations, the feed and strip concentration changes are estimated as a function of the dimensionless length. However, it is difficult to directly compare each of the four configurations to the other using the same axis, since each independent variable includes only the average flow velocity in the flow channel, and does not consider the treatment capacity. In order to compare the performances of four different cases, it is useful to use the ratio of dimensionless length per unit feed volume to be treated:

$$W_F = \left(\frac{z}{\overline{Q}_F}\right) \Big/ \left(\frac{s^2 R^2}{D_{\overline{MR}}}\right) \tag{37}$$

This equation uses the average volumetric flow rate of the feed solution ($\overline{Q}_F$) instead of the average flow velocity ($\bar{v}^F$). The variable W_F allows one to compare directly the performances of four different cases, even though this variable is not dimensionless. W_F gives a measure of the performance of tubular module per membrane area. Figure 9 plots feed concentration changes with W_F for the four different cases stud-

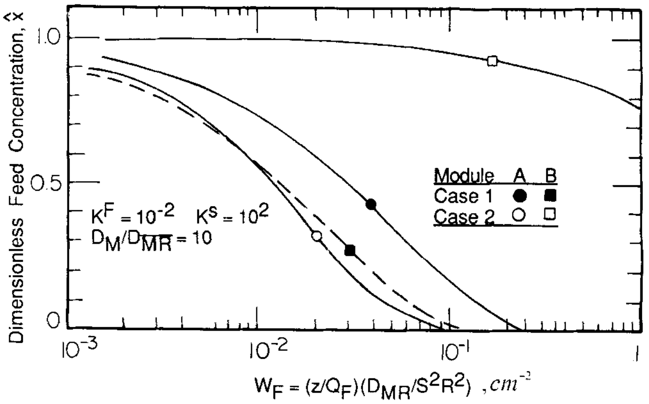

Figure 9. Comparison of shell–and–tube-type membrane module performance for four cases.

Table 2. Volumetric Flow Rates (cm^3/min) of Strip Solutions Required for $\bar{Q}_F = 10$ cm^3/min

Operation	Module A	Module B
Mode 1	1.4	71
Mode 2	50	2.0

ied. In this figure, the more steeply the feed concentration decreases, the better the membrane module performance. This figure shows that better performance for the module A can be obtained when operated by operation mode 2, in which the strip solution stream flows inside the tube and the feed solution flows in the annular region, while for module B the better performance is obtained under operation mode 1 condition, in which the feed solution stream flows inside the tube and the strip solution flows in the annular region.

These results are consistent with the volumetric flow rate of strip solution required to operate under the no-pressure difference condition across the membrane at a given feed solution amount. The volumetric flow rates of strip solution required to maintain no-pressure difference across the membrane calculated are tabulated in Table 2. From the comparison of the performance results in Figure 9 with the calculated results in Table 2, it is seen that the performance of tubular membrane modules is improved, as the volumetric flow rate of strip solution increases for each of the four cases studied.

These results also show that the strip solution affects the performance of tubular membrane modules, since the interfacial reactions take place at both interfaces, and these two interfacial reactions play a role in controlling the membrane performance. As the strip solution flow rate increases, the strip solution concentration decreases (C_M^{S*} in Eq. 15 becomes very small). Thus, the interfacial strip reaction rate at the strip side interface (R^S in Eq. 15) increases by the decrease of the reverse reaction rate ($k_{+S}C_M^{S*}$ term in Eq. 15). Consequently, the overall mass-transfer rate through the membrane increases. This result, shown in Figure 9 and Table 2, suggests that better performance is obtained for the higher flow rates of the strip solution under the studied conditions.

Conclusions

Numerical calculations were executed to estimate the performance of shell–and–tube-type membrane modules prepared for metal ion removal from aqueous streams, and to predict the operating conditions for four possible operation modes. The first operation mode (mode 1) is that feed solution flows inside the membrane tube and strip solution flows in the annular region in the shell–and–tube-type module. The second operation mode (mode 2) is that strip solution flows inside the membrane tube and feed solution flows in the annular region in the module. Also, extraction performances of two different size tubular modules (modules A and B) were estimated for each different operating mode. In this study, tubular modules of α-alumina/silica ceramic membranes were selected as a model, since the performance of such membranes in disk geometry was evaluated experimentally (Yi and Tavlarides, 1992). The dimension of the tubular membrane prepared is 0.6 cm I.D., 0.75 cm outside diameter, and 25 cm long. The case system studied was copper ion extraction from acidic solutions employing 2-hydroxy-5-nonylacetophenone oxime (Henkel) impregnated in α-alumina/silica ceramic membranes (Coors Ceramic Co.). The conditions employed were copper sulfate feed solution of 0.03 gmol/L, feed solution pH of 3, strip solution of 1.5 gmol/L sulfuric acid, and impregnation solution concentration of 3.2 gmol/L.

Model equations incorporate the effects of both the boundary layer mass-transfer resistances and the kinetic rate resistances at the interfaces. Modeling results show that the performance of shell–and–tube-type membrane module depends on the sizes and operation methods. In these calculations, the operation condition of no-pressure difference across the membrane were imposed on the design. This condition is accomplished by the ratio adjustment of the average flow velocity of the feed and strip solutions flowing within the inside and annular region in the tubular modules. Results also show that for increasing flow rate of the strip solution for a given module design, the metal concentration in the feed stream decreases more steeply. The strip solution concentration increase however becomes smaller due to the high dilution. Thus, for practical operation, the strip solution can be operated in a recycle mode while maintaining high flow rates of the strip solution stream (module A operated by mode 2 with strip solution recycle). In this operation situation, the required no-pressure difference across the membrane is achieved, yet small processing volumes of the strip solution can be used to effect a desired separation of a given feed stream.

Model equations of the shell–and–tube-type membrane modules reported herein could provide a basis for the design and scale-up of these units. Also, these models can serve as the basis to select more promising chelation agent systems and desirable operating conditions for high separation efficiencies.

Notation

C_M^i = metal ion concentration at the i side, $i = F$ or S
f = dimensionless feed concentration
g = dimensionless metal complex concentration
k_{+i}, k_{-i} = interfacial rate coefficient at i side
P_0^i = fluid pressure at the inlet of i stream
P_L^i = fluid pressure at the outlet of i stream
r = radial position of the tube
R^i = interfacial reaction expression at the i side
t = time
u = dimensionless strip concentration
v^i = flow velocity expression of stream i, $i = F$ or S
v^s = flow velocity of the strip solution
$\bar{v}^F$ = average flow velocity of the feed
$\bar{v}^S$ = average flow velocity of the strip solution
x = dimensionless radial distance
$\hat{X}$ = average feed concentration at the outlet
y = dimensionless axial distance down the tubular module
$\hat{Y}$ = average strip concentration at the outlet
z = axial position of the tube
ϵ = ratio of diffusivities
τ = dimensionless time

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