Simple Models for Diaphragm-Type Chlorine/Caustic Cells I. Dynamic Behavior

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Simple Models for Diaphragm-Type Chlorine/Caustic Cells

I. Dynamic Behavior

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ABSTRACT

A simple model of the dynamic behavior of a diaphragm-type chlorine/caustic cell is presented. The model is based upon measurable diaphragm properties and the mass transfer of hydroxyl ion through the diaphragm. The anolyte is modeled simply as a region in which the OH⁻ ion concentration is fixed, the diaphragm is modeled as a plug-flow reactor with an electrochemical reaction occurring at the catholyte/diaphragm interface where the cathode is placed, and the catholyte is modeled as a completely stirred flow reactor. Analytical integration of the governing equations for these models yields two mathematical expressions: one for the concentration distribution of hydroxyl ion within the diaphragm and one for the effluent concentration. Both of these expressions are functions of time, independent operating variables, diaphragm properties, and physical constants. They are used to show how the concentration distribution of OH⁻ within the diaphragm and the cell effluent change when subjected to a step change in the current density. Also, presented is a numerical method of solution for the model equations to predict the required change of the cell head subject to an arbitrary time-dependent change in the current density at a fixed cell effluent concentration.

Diaphragm-type cells are used extensively in the United States to produce chlorine and caustic (1). The diaphragm is the key to efficient cell operation, because the diaphragm properties affect the voltage loss, the yield, and the effluent caustic concentration. Recently (2, 3, 4), measurable diaphragm properties have been proposed and used to predict the performance of these cells under steady-state conditions. A simple model of the cell is presented here to predict the effect of these diaphragm properties on the dynamic behavior of the caustic yield.

The time-dependent or dynamic behavior of diaphragm-type cells is of interest during start-up and in situations where a differential cost structure for electricity provides an opportunity to reduce the cost of production by operating the cells accordingly. This may mean a high production rate during the night and a low production rate during the day, for example. The model presented in this paper can be used to predict the changes in the operating conditions e.g., current density and differential head) which would be required to maintain a fixed caustic effluent concentration or a fixed caustic yield.

In a diaphragm-type chlorine/caustic cell (see Fig. 1), hydroxyl ions are produced at the cathode according to the following electrochemical reaction

$$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \frac{1}{2} \text{H}_2$$  \[1\]

The buoyancy of the hydrogen gas causes stirring in the catholyte and this compartment is consequently assumed to be completely mixed. A similar statement could be made concerning the anolyte and the chlorine gas generated at the anode. This is, however, not necessary here since the anolyte is modeled simply as a region in which the OH⁻ ion concentration is fixed at a known value that depends on the fixed anolyte pH. As shown in Fig. 1, a differential head force anolyte to percolate through the diaphragm from the anolyte to the catholyte. This percolation rate decreases the loss of OH⁻ ions from the catholyte to the anolyte due to diffusion and migration. However, this percolation rate should not be too large because the catholyte OH⁻ concentration decreases as the percolation rate increases which leads to a larger steam requirement if the cell effluent is to be concentrated to 50 weight percent NaOH. Increasing the current density increases the OH⁻ ion concentration in the catholyte but also increases the voltage drop through the diaphragm and hence increases the loss of OH⁻ ions due to migration. Also, the diaphragm characteristics affect the loss of OH⁻ ions due to diffusion, migration, and percolation velocity. The time-dependent behavior of the caustic yield depends upon these losses of OH⁻ ions from the catholyte, the volume of the catholyte, and other operating variables and parameters, as discussed below.

Literature

In a recently reported experiment (2), two measurable quantities were used to characterize the diaphragm in a metal-anode CI₂/NaOH electrolyzer when the velocity was specified (3, 4). These two properties are the MacMullin number, Nₘ, and the diaphragm thickness, L. The MacMullin number is defined (2-8) in terms of readily measurable quantities and can be thought of as the ratio of the diaphragm tortuosity and porosity

$$N_m = \frac{\rho_c}{\rho_a} = \frac{\tau}{\epsilon}$$  \[2\]

Fig. 1. A schematic of a diaphragm-type chlorine/caustic cell

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1The phrase "simple model" is used here to mean a model with a linear potential gradient through the diaphragm.
The ratio $\rho_i/\rho_o$ represents the resistivity of an electrolyte-saturated porous medium to that of the pure electrolyte. This ratio denoted here as $N_{M}$ has been referred to by others as the formation factor (7) and the labyrinth factor (8). Other diaphragm properties have also been proposed (9-15), but none of these is measurable directly, even though they have been shown to be equivalent to the product $N_{M}$ (3, 4, 16).

Simple steady-state models of the diaphragm-type cell for chlor-alkali cells have been presented and reviewed recently (3, 4). More complete models have also been presented (5, 17). One of these models (5) was used to analyze steady-state phenomena, including the assumption of a reaction plane for dissolved chlorine species in the diaphragm; however, only the essence of the model was presented for proprietary reasons. The other model (17) used numerical integration to analyze the distribution of Na+, Cl-, and OH-, and a nonlinear potential gradient in the diaphragm, but again, neglect diaphragm properties. These investigators (22, 17) used numerical integration of the time-dependent, dilute solution convective diffusion equations for their models. Unfortunately, the results were limited for one of the models (22) because the numerical integration did not converge for steep gradients in the concentration. In the other model, the concentrations of Na+, Cl-, and OH- were included together with a nonlinear potential gradient through the diaphragm. However, again the authors (17) did not include diaphragm properties in their work but instead claim that the diaphragms used in their comparison with data were very inhomogeneous.

**Model**

The model will be presented by first reviewing the time-dependent material balance equation and the flux equation for species $i$ in a porous medium by presenting the assumptions of the model and the development of the equations.

A time-dependent material balance equation for a charged species within a porous region has been formulated in terms of average quantities (23-25). For the case of no electrochemical or homogeneous reactions, the material balance equation for species $i$ can be written (24) as follows

$$\frac{\partial(\rho c_i)}{\partial t} = -\nabla \cdot \mathbf{N}_i.$$  \hspace{1cm} \[3\]

where

$$\frac{N_i}{\epsilon} = -(D_{i,o} + \frac{D_{c_i}}{\epsilon}) \nabla c_i + z_i u_i F \frac{c_i}{\epsilon} \rho + \frac{v c_i}{\epsilon}$$  \hspace{1cm} \[4\]

In Eq. [4], $v$ is the superficial velocity (i.e., the volumetric flow rate entering the diaphragm divided by the projected diaphragm area, $A_{D}$) and $\nabla \cdot \mathbf{N}_i$ is the velocity in the pores. Also, according to Newman and Tiedemann (24), the ionic diffusion coefficient, $D_{i,o}$, the axial dispersion coefficient, $D_{i}$, the ionic mobility $u_i$, in Eq. [4] are all corrected for the tortuosity of the pores, $\tau$, but not for the porosity, $\epsilon$.

The assumptions of the model presented here are: (i) only the OH- ion is important, and it exists only in the diaphragm and catholyte; (ii) dilute solution theory (26) applies, and the cell is isothermal; (iii) only the spatial coordinate through the diaphragm in the direction of flow is important; (iv) the diaphragm porosity, MacMullin number, permeability, and thickness are constant with time; (v) the diffusion coefficient, $D_{i}$, is negligible and the effective diffusion coefficients in the porous diaphragm can be written in terms of the measurable property $N_{M}$ as follows

$$D_{i,o} = \epsilon D_{i,o} = D_{i}/(\epsilon) = D_{i}/N_{M}$$  \hspace{1cm} \[5\]

The current density through the diaphragm is simply related to the potential gradient through the diaphragm by an effective average specific conductivity (3) as follows

$$i = \frac{-\kappa}{N_{M}} \frac{d\Phi}{dx}$$  \hspace{1cm} \[6\]

The percolation velocity through the diaphragm is related to the differential head, $h$, according to Darcy’s law, with an average viscosity for the solution within the diaphragm and a pressure drop through the diaphragm given by $\rho gh$ where $\rho$ is the density of the anolyte as follows

$$\frac{v}{\mu} = \frac{\rho gh}{L}$$  \hspace{1cm} \[7\]

(viii) water vapor loss from the anolyte and catholyte is negligible, so that the velocity of the feed to the cell and the velocity of the effluent are equal; (ix) the gas generation provides sufficient mixing so that the catholyte is a completely mixed flow reactor; (x) hydroxyl ions do not participate in any homogeneous reactions.

With these assumptions, the unsteady-state material balance for the hydroxyl ion (i = 1) in the diaphragm (Eq. [3]) for one spatial coordinate can be written

$$\frac{\partial c_1}{\partial t} + \frac{v c_1}{\epsilon} = \frac{\partial}{\partial x} \left[ \frac{\epsilon D_{c_1}}{\partial x} \right] + \frac{v c_1}{\epsilon}$$  \hspace{1cm} \[8\]

The flux expression for Eq. [8] can be obtained from Eq. [4] by using the Nernst-Einstein expression for the ionic mobility (26), so that Eq. [4] becomes

$$N_i = -D_{i,o} \frac{\partial c_i}{\partial x} + \frac{z_i F D_{i,o} c_i}{RT} \frac{\partial \Phi}{\partial x} + \frac{\nu c_i}{\epsilon}$$  \hspace{1cm} \[9\]

which, with assumptions (i)-(viii), becomes

$$N_i = -D_i \frac{\partial c_i}{\partial x} + \left( \frac{z_i F D_{i,o} c_i}{RT \epsilon} + \frac{\rho gh}{\mu L} \right) c_i$$  \hspace{1cm} \[10\]

Thus, the governing partial differential equation for the hydroxyl ion concentration within the diaphragm can be written as

$$\frac{\partial c_1}{\partial t} + \frac{v c_1}{\epsilon} = \frac{\partial}{\partial x} \left[ \frac{\epsilon D_{c_1}}{\partial x} \right] + \left( \frac{z_i F D_{i,o} c_i}{RT \epsilon} + \frac{\rho gh}{\mu L} \right) \frac{\partial c_1}{\partial x}$$  \hspace{1cm} \[11\]

An appropriate set of initial and boundary conditions is

$$c_i(x, t) = c_i(x, 0) = c_i^*(x)$$  \hspace{1cm} \[12\]

for $t > 0$ at $x = 0$

$$c_i(x, t) = c_i(0, t) = E$$  \hspace{1cm} \[13\]

for $t > 0$ at $x = L$

$$N_i(L, t) = -\frac{\rho gh}{\mu L} c_i(L, t) - \frac{i}{F}$$  \hspace{1cm} \[14\]

where $E$ is equal to the square root of the inverse of the equilibrium constant for the reaction between H+ and OH-, which is assumed to occur at the anolyte face of the diaphragm and where $N_i(L, t)$ is given by Eq. [10], evaluated at $x = L$. Equations [11]-[14] can be simplified by defining the following dimensionless variables.
\[ \xi = \frac{x}{L} \quad [15] \]

and

\[ \Theta_i(\xi, t) = \frac{c_i(x, t)}{c_F} \quad [16] \]

where \( c_F \) is the concentration of NaCl in the brine feed to the cell. Substitution of Eq. [15] and [16] into Eq. [11] yields

\[ \gamma \frac{\partial \Theta_i}{\partial t} = \frac{\partial^2 \Theta_i}{\partial \xi^2} - A_i \frac{\partial \Theta_i}{\partial \xi} \quad [17] \]

where

\[ \gamma = \frac{\varepsilon N_m L^2}{D_i} \quad [18] \]

and

\[ A_i = -\frac{F_i N_m L}{R T_k} + \frac{\rho g h P N_m}{\mu D_i} \quad [19] \]

Also, substitution of Eq. [15] and [16] into Eq. [12]-[14] yields the following dimensionless initial and boundary conditions

\[ \text{at } t = 0 \quad \Theta_i(\xi, t) = \Theta_i(0, t) = \frac{c_i^*(x)}{c_F} = \Theta_i(0, 0) = \Theta_i(x, 0) = \varphi_i(\xi) \quad [20] \]

for \( t > 0 \) at \( \xi = 0 \)

\[ \Theta_i(\xi, t) = \Theta_i(0, t) = \frac{E}{c_F} = \Theta_i(0, t) \quad \Theta_i(0, t) = \Theta_i(x, 0) = \varphi_i(\xi) \quad [21] \]

for \( t > 0 \) at \( \xi = 1 \)

\[ \frac{\partial \Theta_i}{\partial \xi} |_{\xi = 1} = -H[\Theta_i(1, t) - B] \quad [22] \]

where

\[ H = \frac{F_i N_m L}{R T_k} \quad [23] \]

and

\[ B = \frac{R T_k}{F_i D_i c_F} \quad [24] \]

As shown in Eq. [20], \( c_i^*(x) \) or \( \varphi_i(\xi) \) corresponds to a steady-state solution of the simple steady-state model, which is a result of a previously set current density \( i^* \). Thus, \( c_i^*(x) \) or \( \varphi_i(\xi) \) is a known quantity that depends only on position within the diaphragm and not on time. This concentration distribution results from the solution of the steady-state material balance equation (3, 4)

\[ \frac{d^2 c_i^*}{d \xi^2} - A_i \frac{d c_i^*}{d \xi} = 0 \quad [25] \]

where

\[ A_i = -\frac{F_i N_m L}{R T_k} + \frac{\rho g h P N_m}{\mu D_i} \quad [26] \]

subject to the boundary conditions

\[ \text{at } \xi = 0 \quad c_i^*(0) = E \quad [27] \]

and

\[ \text{at } \xi = 1 \quad \frac{d c_i^*}{d \xi} \bigg|_{\xi = 1} = -\frac{F_i N_m L}{R T_k} - c_i^*(L) + \frac{i^* N_m L}{D_i F} \quad [28] \]

Integration of Eq. [25] with Eq. [27] and [28] yields an expression for \( c_i^* \) and the dimensionless OH\(^{-}\) concentration \( \varphi_i(\xi) \) at \( t = 0 \)

\[ \varphi_i(\xi) = \frac{E}{c_F} + G_i \left[ \exp (A_i \xi) - 1 \right] \quad [29] \]

where

\[ G_i = \frac{\frac{i^* N_m L}{D_i F} - \frac{F_i N_m L}{R T_k}}{\rho g h P N_m} \exp \left( \frac{A_i \xi}{4 \gamma} \right) \quad [30] \]

The governing partial differential equation for \( \Theta_i(\xi, t) \), Eq. [17], can be integrated analytically subject to Eq. [20]-[22] by using the transformation suggested by Bastian and Lapidus (27, 28) as shown in the Appendix. The resulting expression for the dimensionless concentration of OH\(^{-}\) ion in the diaphragm can be written as follows

\[ \Theta_i(\xi, t) = \text{EP} \]

\[ \text{EP} \left[ \frac{A_i \xi}{2} - A_i \frac{\xi^2}{4 \gamma} \right] \quad [31] \]

where

\[ G = \frac{H B - H E P}{\rho g h P N_m} \exp \left( A_i \xi - H \right) \quad [32] \]

and

\[ \text{and} \]

\[ F_i = \frac{4 \lambda_n}{(2 \lambda_n + \sin 2 \lambda_n)} \left[ \begin{array}{c} G_i \left( \lambda_n + \left( A_i^* - A_i \frac{\sin \lambda_n - \lambda_n \cos \lambda_n}{2} \exp \left( \frac{A_i^* - A_i}{2} \right) \right) \right) \\
\left( A_i^* - A_i \frac{\sin \lambda_n + \lambda_n \cos \lambda_n}{2} \exp \left( \frac{-A_i}{2} \right) \right) \\
\left( G_2 - G_1 \right) \left( \lambda_n - \frac{A_i^*}{2} \sin \lambda_n + \lambda_n \cos \lambda_n \right) \exp \left( \frac{-A_i}{2} \right) \\
\frac{A_i^2}{4} + \lambda_n^2 \\
\end{array} \right] \quad [33] \]

and where the eigenvalues, \( \lambda_n \), are the roots of

\[ \lambda_n \cot \lambda_n + (H + A_i) = 0 \quad [34] \]

Next, consider the unsteady-state material balance for the OH\(^{-}\) ions in the catholyte, which, with assumptions (iii)-(x), can be written as follows
\[
\frac{dc_{\text{eff}}}{dt} = \frac{vA_d}{V_e} c_i(L, t) - \frac{vA_d}{V_e} c_{\text{eff}}
\]  

where \( v \) is given by Eq. [7] and \( V_e \) is the volume of the catholyte. Recall that, according to assumption (ix), the catholyte is a completely mixed flow reactor, which means that the effluent concentration \( c_{\text{eff}} \) is the same as the catholyte concentration, and the inlet concentration to the catholyte compartment, \( c_i(L, t) \), is typically different from \( c_{\text{eff}} \) during transients. An appropriate initial condition for the catholyte concentration is its value at steady state before a transient

\[
c_{\text{eff}}(t = 0) = c_i^*(L) \tag{36}
\]

Equation [35] can be integrated analytically by using Eq. [31] to obtain an expression for \( c_i(L, t) \) (i.e., \( c_F(0, t) \)). That is

\[
c_{\text{eff}}(t) = c_F \left[ \exp \left( \frac{vA_d t}{V_e} \right) \right] = \frac{vA_d}{V_e} \int c_p(1, t) \exp \left( \frac{vA_d t}{V_e} \right) dt + G_{so} \tag{37}
\]

where \( G_{so} \) is an integration constant. Evaluation of \( G_{so} \) by using Eq. [36] yields

\[
c_{\text{eff}}(t) = c_f \left[ EP + G_0 \right] \left[ 1 - \exp \left( -\frac{vA_d t}{V_e} \right) \right] + c_i^*(L) \exp \left( \frac{-vA_d t}{V_e} \right)
\]

\[
- \frac{vA_d}{V_e} \left[ A_1 \right] - \frac{A_1^2}{4y} \sum_{n=0}^{\infty} G_1 n \sin \left( \frac{\lambda_n^2 t}{y} \right) + c_i^*(L) \exp \left( \frac{-vA_d t}{V_e} \right)
\]

where

\[
G_1 = \frac{vA_d}{V_e} \frac{A_1^2}{4y} - \frac{\lambda_n^2}{y} \tag{38}
\]

Equation [38] can be used to obtain an expression for the time-dependent caustic yield, \( \eta(t) \), (often referred to as the caustic current efficiency) by using the following definition

\[
\eta(t) = \frac{P_{\text{ph}} g F c_{\text{eff}}}{\mu L_i} \tag{40}
\]

Discussion

The model presented above can be used to investigate the dynamic behavior of a diaphragm cell in terms of step changes in either the current density or the differential head (not discussed here). The model also allows consideration of two distinct initial conditions; that is, the behavior of the cell can be analyzed during start-up, where the initial concentration is a constant for all \( \xi \), or during a change from one steady state to another, where the initial concentration is a function of \( \xi \). Figures 2-4 show the predictions of the model for the two different initial conditions when the parameters of Table I are used. Figure 2 shows the concentration profiles in the diaphragm during start-up for an initial concentration of \( \text{OH}^- \) of \( 10^{-12} \text{M} \) (corresponding to no current) and a step change in current density from \( 0 \) to \( 0.1543 \text{A/cm}^2 \) at \( t = 0 \). Figure 3 presents the concentration profiles in the diaphragm for a step change in current density from \( 0.054 \) to \( 0.1543 \text{A/cm}^2 \) at \( t = 0 \). In both Fig. 2 and 3, the final steady state is achieved approximately after 56 min. This rather quick response illustrates that the response time of the diaphragm is not on the order of \( \gamma \) (i.e., \( 8h \) for Table I values), as would be expected in a system governed solely by diffusion, but instead is faster because of the convection-like term

\[
\left( A_1 \frac{\partial c_e}{\partial \xi} \right)
\]

in Eq. [17]. On the other hand, Fig. 4 shows that the time-dependent responses of the cell effluent concentration for the cases shown in Fig. 2 and 3 are on the order of 10h (i.e., \( \approx 63\% \) of the final steady-state value), as would be expected from Eq. [35], since \( V_e/(vA_d) \) is on the order of 9h.

Table I. Parameters for calculations shown in Fig. 2-5

<table>
<thead>
<tr>
<th>Physical Constants</th>
<th>( D_i )</th>
<th>( D_f )</th>
<th>( E )</th>
<th>( \mu )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_i )</td>
<td>( 5.00 \times 10^{-4} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 3.50 \times 10^{-4} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 1.00 \times 10^{-4} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
</tr>
<tr>
<td>( E )</td>
<td>( 1.00 \times 10^{-10} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 1.00 \times 10^{-10} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 1.00 \times 10^{-10} \text{mol/cm}^3 \text{s}^{-1} )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.10 \times 10^{-4} \text{g/cm}^{-1} \text{s}^{-1} )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
<td>( 1.17 \text{g/cm}^3 )</td>
</tr>
</tbody>
</table>

Diaphragm Properties

| \( A_d V_e \) | \( 0.20 \text{cm}^{-1} \) |
|-------------------|---------|---------|---------|---------|
| \( A_d V_e \) | \( 2.00 \) | \( 5.00 \times 10^{-11} \text{cm}^3 \text{s}^{-1} \) | \( 1.00 \text{cm}^{-1} \) | \( 0.50 \text{cm}^{-1} \) |

Operating Variables

| \( h^* \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) |
| \( h \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) | \( 25.0 \text{cm} \) |
| \( i^* \) | \( \text{see figure captions and text} \) | \( \text{see figure captions and text} \) | \( \text{see figure captions and text} \) | \( \text{see figure captions and text} \) |
| \( T \) | \( 358.15 \text{K} \) | \( 358.15 \text{K} \) | \( 358.15 \text{K} \) | \( 358.15 \text{K} \) |
Instead of determining the response of the cell to a step change in \( (i) \), it may be more desirable to maintain the effluent concentration at a previous steady-state value \( c_{\text{cell}} \) and simply increase or decrease the production rate by adjusting the head and current densities simultaneously. This change in the production rate might be desirable if, for example, a differential cost structure for electricity provided an incentive for a high production rate at night and a low production rate during the day. In such a case, a constant effluent concentration may simplify the operation of evaporators that are connected in series to the electrolyzers.

Unfortunately, the analytical solution presented above cannot be used to predict the time-dependent head required to maintain a constant effluent concentration because \( A_i \) is a function of time in this case. However, Eq. [17] can be integrated numerically. To do this, implicit stepping accurate to \( O(\Delta t) \) was used with a finite difference technique accurate to \( O((\Delta \xi)^2) \) (29-31) in a manner similar to that in Ref. (32, 33) and then with a finite difference technique accurate to \( O((\Delta \xi)^4) \) (34) to first verify the profiles of Fig. 2 and 3 and then to produce (16) Fig. 5.

Curve A in Fig. 5 shows how to change the head with time so that \( c_{\text{eff}} \) remains constant at \( 3.54 \times 10^{-3} \) mol/cm\(^3\) when the current density is increased linearly from 0.054 to 0.1543 A/cm\(^2\) in 15 min. Similarly, curve B shows how to decrease the head as the current density is decreased linearly from 0.1543 to 0.054 A/cm\(^2\) so that \( c_{\text{eff}} \) remains constant at \( 3.54 \times 10^{-3} \) mol/cm\(^3\). For the results shown in

\[\text{Fig. 3. Concentration profiles for a step change in current density from } i^* = 0.0540 \text{ A/cm}^2 \text{ to } i = 0.1543 \text{ A/cm}^2.\]

\[\text{Fig. 4. Effluent concentration and caustic yield profiles corresponding to Fig. 2 and 3.}\]

\[\text{Fig. 5. Relationship between current density and head required to maintain a constant caustic effluent concentration of } 3.541 \times 10^{-3} \text{ mol/cm}^3.\]

\[\text{Fig. 5, the caustic yield, } \eta(t), \text{ changes from about } 0.96 \text{ to } 0.99 \text{ for curve A and then from } 0.99 \text{ to } 0.96 \text{ for curve B while the molar production rate of NaOH (} \beta c_{\text{cell}} \text{ with } \beta \text{ given by Eq. [7]} \text{ is increased and then decreased by a factor of three in curves A and B, respectively; that is, } h \text{ changes from } 25 \text{ cm at } t = 0 \text{ to } 75 \text{ cm at } t = \infty \text{ for curve A and from } 75 \text{ cm at } t = 0 \text{ to } 25 \text{ cm at } t = \infty \text{ for curve B.}\]

\[\text{Conclusions}\]

The development of a simple time-dependent model for OH\(^-\) ion in the diaphragm and the catholyte in terms of measurable diaphragm properties and cell geometry provides a design equation that could be used for future comparison of experimental data and theoretical predictions. A numerical solution of the model equations provides a method that could be used in a control scheme to maintain a constant hydroxyl ion concentration in the effluent, subject to an arbitrary change of the current density.

\[\text{Acknowledgment}\]

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\[\text{APPENDIX}\]

The governing partial differential equation for OH\(^-\) in the diaphragm is

\[\gamma \frac{\partial \Theta_i}{\partial t} = \frac{\partial^2 \Theta_i}{\partial \xi^2} - A_i \frac{\partial \Theta_i}{\partial \xi} \quad [A-1]\]

and the initial and boundary conditions are

\[\begin{align*}
\text{at } t &= 0 & \Theta_i(\xi, 0) &= \phi_i(\xi) & [A-2] \\
\text{for } t > 0 \text{ at } \xi &= 0 & \Theta_i(0, t) &= EP & [A-3]
\end{align*}\]
for $t > 0$ at $\xi = 1$ \[ \frac{\partial \Theta_1}{\partial \xi} \bigg|_{\xi=1} = -H[\Theta_1(1, t) - B] \] \[ [A-4] \]

where $H$ and $B$ are given respectively by Eq. [23] and [24] in the text.

The solution to these equations can be obtained by assuming a solution of the form

\[
\Theta_1(\xi, t) = Y_1(\xi, t) + \Gamma_1(t) 
\]

Substitution of Eq. [A-5] into Eq. [A-1] gives an expression that can be divided arbitrarily into two equations

\[
\frac{d^2 Y_1}{d \xi^2} - A_1 \frac{d Y_1}{d \xi} = 0 \quad \text{[A-6]}
\]

\[
\gamma \frac{d Y_1}{d \xi} = \frac{d Y_1}{d \xi} - A_1 \frac{d Y_1}{d \xi} \quad \text{[A-7]}
\]

Similarly, the initial conditions and boundary conditions are separable and can be written

\[
Y_1(\xi, 0) = \psi_1(\xi) - \Gamma_1(\xi) \quad \text{[A-8]}
\]

\[
Y_1(0, t) = 0 \quad \text{[A-9]}
\]

\[
\Gamma_1(0) = EP \quad \text{[A-10]}
\]

\[
Y_1(1, t) = \psi_1(1) - \Gamma_1(1) \quad \text{[A-11]}
\]

\[
\frac{d \Gamma_1}{d \xi} \bigg|_{\xi=1} = -H[\Gamma_1(1, t) - B] \quad \text{[A-12]}
\]

Integration of Eq. [A-6] twice yields

\[
\Gamma_1(\xi) = V_1 + V_2 \exp (A_1 \xi) \quad \text{[A-13]}
\]

where $V_1$ and $V_2$ are constants of integration that can be obtained from application of Eq. [A-10] and [A-12] to Eq. [A-13], which yields

\[
\Gamma_1(\xi) = EP + G_1 \exp (A_1 \xi) - 1 \quad \text{[A-14]}
\]

where $G_1$ is defined by Eq. [32] in the text.

Equation [A-7] can be integrated by using the transformation suggested by Bastain and Lapidus (27, 28); that is, let

\[
Y_1(\xi, t) = w_1(\xi, t) \exp \left[ \frac{A_1 \xi}{2} - \frac{A_1 t}{4\gamma} \right] \quad \text{[A-15]}
\]

so that Eq. [A-7] becomes

\[
\gamma \frac{\partial w_1}{\partial t} = \frac{\partial^2 w_1}{\partial \xi^2} \quad \text{[A-16]}
\]

and the initial and boundary conditions become

\[
w_1(\xi, 0) = \psi_1(\xi) - \Gamma_1(\xi) \exp \left( -\frac{A_1 \xi}{2} \right) \quad \text{[A-17]}
\]

\[
for \ t > 0 \ at \ \xi = 0 \quad w_1(0, t) = 0 \quad \text{[A-18]}
\]

\[
for \ t > 0 \ at \ \xi = 1 \quad \frac{\partial w_1}{\partial \xi} \bigg|_{\xi=1} = -\left( H + \frac{A_1}{2} \right) \quad \text{[A-19]}
\]

Equation [A-16] can be integrated with the method of separation of variables by assuming that

\[
w_1(\xi, t) = U(\xi) Z(t) \quad \text{[A-20]}
\]


\[
\gamma \frac{d Z}{d t} = \frac{1}{U} \frac{d U}{d \xi} = -\lambda \gamma \quad \text{[A-21]}
\]

and the boundary conditions become

\[
f or \ t > 0 \ at \ \xi = 0 \quad U(0) = 0 \quad \text{for all} \ Z(t) \quad \text{[A-22]}
\]

\[
f or \ t > 0 \ at \ \xi = 1 \quad \frac{d U}{d \xi} \bigg|_{\xi=1} = -\left( H + \frac{A_1}{2} \right) \quad \text{for all} \ Z(t) \quad \text{[A-23]}
\]

Thus $Z(t)$ and $U(\xi)$ have the general forms

\[
Z(t) = G_s \exp \left( -\frac{\lambda \gamma t}{2} \right) \quad \text{[A-24]}
\]

and

\[
U(\xi) = G_s \sin \left( \lambda \xi \right) + G_s \cos \left( \lambda \xi \right) \quad \text{[A-25]}
\]

where $G_s$, $G_a$, and $G_b$ are integration constants.


\[
G_s = 0 \quad \text{[A-26]}
\]

and application of Eq. [A-23] to Eq. [A-25] yields the eigenvalues, which are roots of the following equation

\[
\lambda \cot \lambda + \left( H + \frac{A_1}{2} \right) = 0 \quad \text{[A-27]}
\]

Thus the complete general solution for $w_1(\xi, t)$ is

\[
w_1(\xi, t) = \sum_{n=0}^{\infty} F_n \sin \left( \lambda_n \xi \right) \exp \left( -\frac{\lambda_n^2 t}{2} \right) \quad \text{[A-28]}
\]

The constants $F_n$ in Eq. [A-28] can be evaluated using the initial condition and the principle of orthogonality. That is, at $t = 0$

\[
\sum_{n=0}^{\infty} F_n \sin \left( \lambda_n \xi \right) \sin \left( \lambda_n \xi \right) \exp \left( -\frac{\lambda_n^2 t}{2} \right) \quad \text{[A-29]}
\]

Multiplying both sides of Eq. [A-29] by $\sin (\lambda_n \xi)$ and integrating yields

\[
\sum_{n=0}^{\infty} F_n \int_0^1 \sin \left( \lambda_n \xi \right) \sin \left( \lambda_n \xi \right) d\xi = \int_0^1 \left[ \psi_1(\xi) - \Gamma_1(\xi) \right] \sin \left( \lambda_n \xi \right) \sin \left( \lambda_n \xi \right) d\xi \quad \text{[A-30]}
\]

The left-hand side of Eq. [A-30] is zero for $N \neq M$; thus

\[
F_n = \frac{4 \lambda_n}{(2 \lambda_n - \sin 2 \lambda_n)} \int_0^1 \left[ \psi_1(\xi) - \Gamma_1(\xi) \right] \sin \left( \lambda_n \xi \right) \sin \left( \lambda_n \xi \right) d\xi \quad \text{[A-31]}
\]

which after integration yields the expression given by Eq. [33] in the text.

Finally, the complete solution for $\Theta_1(\xi, t)$ can be written by using Eq. [A-5], [A-14], [A-15], and [A-28]

\[
\Theta_1(\xi, t) = EP + G_1 \exp (A_1 \xi) - 1 \quad \text{[A-32]}
\]

\[ \text{LIST OF SYMBOLS} \]

- $A_4$, area of the diaphragm, cm²
- $A_{1r}$, $A_{r*}$ dimensionless driving force at $t > 0$ and $t = 0$, respectively, see Eq. [19] and [26]
- $B$ see Eq. [24], dimensionless
- $c_i$, $c_i(x, t)$ concentration of species $i$, mol/cm³
- $c_i^*, c_i^*(x)$ concentration of OH⁻ ion at $t > 0$, mol/cm³
- $c_i^{eff}$, $c_i^{eff}(x)$ effluent NaOH concentration, mol/cm³
- $C_{NaCl}$ NaCl feed concentration, a constant reference quantity, mol/cm³
- $D_1$, free-stream diffusion coefficient of species $i$, cm²/s
- $D_1^s$, free-stream diffusion coefficient of OH⁻ ion, cm²/s
- $D_a$, axial dispersion coefficient in porous region, cm²/s
$D_{e}$
- effective diffusion coefficient of species $i$, cm$^2$/s

$D_{o}$
- free-stream diffusion coefficient divided by tortuosity, cm$^2$/s

$E$
- equilibrium concentration of OH$^-$ ion at anolyte/diaphragm interface (e.g., $10^{-4}$ mol/cm$^3$ at 298 K)

$EP$
- dimensionless equilibrium concentration, see Eq. [21]

$F$
- Faraday's constant, 96,487 C/mol of electrons

$G_{i}$
- see Eq. [30], dimensionless

$G_{i0}$
- see Eq. [32], dimensionless

$G_{i1}$
- integration constant, mol/cm$^3$

$G_{i2}$
- see Eq. [39], dimensionless

$g$
- acceleration due to gravity, cm/s$^2$

$h$
- dimensionless potential gradient, see Eq. [23]

$h^{*}$
- differential head at $t > 0$ and $t = 0$, respectively, cm

$i$
- current density at $t > 0$ and $t = 0$, respectively, A/cm$^2$

$L$
- diaphragm thickness, cm

$M$
- summation indexes

$N_{u}$
- MacMullin number, see Eq. [2], dimensionless

$N_{i}$
- flux of species $i$, mol/cm$^2$-s

$P$
- Darcy's law permeability, cm$^2$

$R$
- gas constant, 8.3143 J/mol-K

$T$
- temperature of the cell, K

$t$
- time, s

$u$
- ionic mobility of species $i$, cm$^2$-mol/J-s

$V$
- volume of catholyte, cm$^3$

$v$
- superficial velocity vector, cm/s

$V$
- superficial velocity through the diaphragm, cm/s

$x$
- diaphragm dimensional coordinate, cm

$z$
- ionic charge of species $i$, $z_i = -1$, dimensionless

Greek

$\nabla$
- divergence vector, cm$^{-1}$

$\epsilon$
- porosity, dimensionless

$\eta_{i}(t)$
- caustic yield or caustic current efficiency, see Eq. [40], dimensionless

$\gamma$
- diaphragm time constant, see Eq. [18], s$^{-1}$

$\kappa$
- average solution conductivity, $\Omega$-cm$^{-1}$

$\lambda_{s}$
- eigenvalues see Eq. [34], dimensionless

$\mu$
- average solution viscosity, g/cm-s

$\Phi$, $\Delta \Phi$
- dimensional voltage, voltage drop through the diaphragm, V

$\psi_{i}(\xi)$
- dimensionless concentration at $t = 0$ see Eq. [29]

$\rho$
- anolyte solution density, g/cm$^3$

$\rho_{e}$
- resistivity of diaphragm filled with electrolyte, $\Omega$-cm

$\rho_{e}$
- resistivity of the electrolyte, $\Omega$-cm

$\tau$
- tortuosity of diaphragm, dimensionless

$\Theta_{i}(\xi, t)$
- dimensionless concentration of OH$^-$ ion at position $\xi$ and time $t$

$\xi$
- dimensionless coordinate, see Eq. [15]

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