

Modeling $\text{Al}^{3+}/\text{H}^{+}$ Ion Transport in Donnan Membrane Process for Coagulant Recovery

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*A single-step Donnan Membrane Process (DMP) has recently been investigated for selective recovery of Al^{3+} from water treatment plant residuals using cation exchange membranes. The DMP works on an electrochemical potential gradient and is not susceptible to fouling even in the presence of high concentration of particulates and natural organic matter (NOM). A step-wise algorithm is presented to predict the kinetics of $\text{Al}^{3+} - \text{H}^{+}$ coupled transport using the Nernst-Planck equation. The model includes the effect of solvent osmosis. Two characteristically different cation exchange membranes, namely the homogeneous Nafion 117 and the heterogeneous Ionac MC 3470, were included in the study. Both the membranes have hydrophilic properties when compared with recognized hydrophobic material, such as the polytetrafluoroethylene (PTFE) surface. The average $\text{Al}^{3+} - \text{H}^{+}$ interdiffusion coefficient ($\bar{D}_{\text{Al-H}}$) value determined under nearly identical experimental conditions was an order of magnitude greater for the Nafion 117 membrane ($10^{-10} \text{ m}^2/\text{s}$) in comparison with Ionac MC 3470 membrane ($10^{-11} \text{ m}^2/\text{s}$). The lower diffusion coefficient values for Ionac MC 3470 membrane was attributed to the presence of nonionogenic pockets in the membrane phase that offer greater diffusional resistance to ion transport. A step-wise protocol for the coupled transport of Al^{3+} and H^{+} during DMP successfully predicted the Al^{3+} recovery profile for both homogeneous and heterogeneous membranes. The Nafion 117 membrane could selectively recover Al^{3+} from water treatment plant residuals and could exclude dissolved organic carbon (DOC) in the recovered solution through Donnan co-ion exclusion. © 2004 American Institute of Chemical Engineers *AIChE J*, 51: 333–344, 2005*

Keywords: Ion exchange membrane, Donnan principle, coupled transport, coagulant recovery, interdiffusion coefficient.

Introduction

Donnan membrane process (DMP), also referred to as Donnan Dialysis, is a widely recognized ion-exchange membrane separation process that can selectively remove ions from a dilute feed solution and can simultaneously enrich them in a sweep solution until conditions of Donnan equilibrium^{1–4} are achieved. It has been utilized to concentrate metal cations in water treatment and hydrometallurgical operations,^{5,6} and for concentrating anions, such as nitrate, fluoride, chromate and cyanide.^{7–9} Previous studies to date, however, did not involve slurry or sludge with a high

concentration of particulates and natural organic matter (NOM), often responsible for membrane fouling.

In water treatment plants, alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, is used as a coagulant for efficient removal of particulate solids and colloids from surface water supply. The process generates water treatment residuals (WTR) in these utilities every day^{10,11} and they contain insoluble aluminum hydroxide, a major component (50–75%) of the solids in the WTR, along with suspended inorganic particles, NOM, and trace amounts of heavy metal precipitates.¹² Recovery of alum from these residuals is in accordance with the objectives of waste management. Donnan membrane process had been applied earlier in coagulant recovery, wherein coagulant feed ion Al^{3+} was selectively recovered from alum based water treatment plant residuals generated at the Allentown Water Treatment Plant in Pennsylvania,^{13,14} with near-complete rejection of NOM or dissolved

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organic carbon (DOC), and without any noticeable evidence of membrane fouling.

The general premise of this study is to investigate the coupled transport of Al^{3+} and H^+ ions during the DMP through (a) a homogeneous cation exchange membrane (Nafion 117), and (b) a heterogeneous cation exchange membrane (Ionac MC 3470). The specific objectives of the article are to present a step-wise model to (1) compute the membrane phase interdiffusion coefficient and the self diffusion coefficient values of Al^{3+} and H^+ ions, and (2) predict Al^{3+} recovery rates for both the homogeneous and heterogeneous membranes. Model predictions are subsequently validated by laboratory experimental data.

Theory

Let us consider aluminum sulfate and sulfuric acid solutions in a Donnan membrane cell divided into two chambers by a cation-exchange membrane that allows only cations to migrate from one side to the other, but rejects any passage of anions according to Donnan's co-ion exclusion principle.¹⁵ Chamber I or the feed side primarily consists of the feed cation Al^{3+} , while Chamber II or the sweep side predominantly consists of the sweep cation H^+ . At equilibrium, the electrochemical potential of aluminum ion Al^{3+} $\bar{\mu}$ in the electrolyte solution on the lefthand side (LHS) of the membrane will be the same as that in the electrolyte solution on the righthand side (RHS), that is

$$\bar{\mu}_{\text{Al}}^{\text{L}} = \bar{\mu}_{\text{Al}}^{\text{R}} \quad (1)$$

$$\text{or } \mu_{\text{Al}}^{\circ} + RT \ln a_{\text{Al}}^{\text{L}} + zF\phi^{\text{L}} = \mu_{\text{Al}}^{\circ} + RT \ln a_{\text{Al}}^{\text{R}} + zF\phi^{\text{R}} \quad (2)$$

where superscripts "o", "L", and "R" refer to the standard state, LHS and RHS and, $\bar{\mu}$, a , F and ϕ denote electrochemical potential (Joules/mole), chemical potential (Joules/mole), activity (moles/ m^3), Faraday Constant (Coul/mole) and electrical potential (Volts), respectively. The "z" refers to the charge of the diffusing ion. Similar expression can be derived for H^+ ions. Assuming that nonideality effects are about the same on both sides of the membrane, activities can be replaced by molar concentrations and the condition for Donnan equilibrium is

$$\left(\frac{C_{\text{Al}}^{\text{R}}}{C_{\text{Al}}^{\text{L}}} \right) = \left(\frac{C_{\text{H}}^{\text{R}}}{C_{\text{H}}^{\text{L}}} \right)^3 \quad (3)$$

If the ratio $C_{\text{H}}^{\text{R}}/C_{\text{H}}^{\text{L}}$ is 10, it means that C_{Al}^{R} (moles/ m^3) is 1,000 times greater than C_{Al}^{L} . Thus, by maintaining high hydrogen ion concentration on the RHS side of the membrane, aluminum ions can be driven from the LHS to the RHS even against a positive concentration gradient, that is, from a lower concentration region to a higher concentration one.

Figure 1 depicts the conceptualized selective alum recovery from WTR, highlighting the following: (1) aluminum hydroxide precipitates can be dissolved and then concentrated on the righthand side; (2) negatively charged NOM, sulfate and chloride cannot permeate through the membrane; and (3) the transmembrane pressure does not influence the Al^{3+} transfer flux. As shown in Figure 2a, the start of the process is characterized by a concentration gradient across the cation-exchange mem-

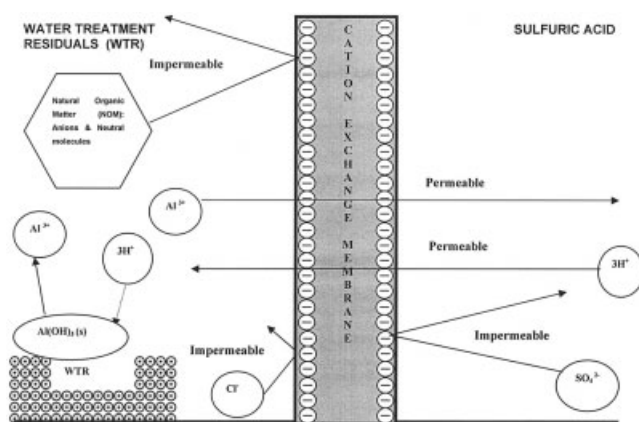


Figure 1. Donnan membrane process illustrating underlying principles.

brane. The high concentration " $q_{\text{Al},\text{I}}$ " (moles/ m^3) of cation Al^{3+} on the membrane surface facing the feed solution (marked "I" in the figures, and addressed as "feed-surface" in the text, henceforth) is attributed to greater preference for trivalent Al^{3+} feed ions over monovalent H^+ ions within the membrane,¹⁶ which is expressed as selectivity coefficient K_{H}^{Al} :

$$K_{\text{H}}^{\text{Al}} = \frac{q_{\text{Al}}^{\text{Z}_\text{H}} C_{\text{H}}^{\text{Z}_\text{Al}}}{C_{\text{Al}}^{\text{Z}_\text{H}} q_{\text{H}}^{\text{Z}_\text{Al}}} \quad (4)$$

assuming similar influence of nonideality in both the feed and the sweep solutions. The membrane selectivity is reversed on sweep side due to large electrolyte concentration, which leads to " $q_{\text{H},\text{II}}$ " or H^+ concentration being much higher on the membrane surface facing the sweep solution (marked "II" in figures and addressed as "sweep-surface" in the text, henceforth). The sum total of the equivalent concentration of the ionic species Al^{3+} and H^+ is equal to the ion-exchange capacity " Q " (moles/ m^3) of the membrane. The resulting coupled transport, where the movement of the feed ion Al^{3+} from the "feed-surface" to the "sweep-surface" is compensated for in the other direction by the movement of the sweep ion H^+ , leads to the Donnan equilibrium condition which is characterized by the absence of any concentration gradient. At conditions of Donnan equilibrium, $q_{\text{Al},\text{I}} = q_{\text{Al},\text{II}}$ and $q_{\text{H},\text{I}} = q_{\text{H},\text{II}}$, as represented in Figure 2b.

The fundamental assumptions and conditions for coupled transport that involve the Nernst-Planck equation have been discussed in several articles,^{17,18} and can be applied to the ionic species Al^{3+} and H^+ . The associated flux J ($\text{m}^3/\text{m}^2 \text{ h}$) can be described by a contribution of driving forces

$$J_{\text{Al}} = -\bar{D}_{\text{Al}} \left(\frac{\partial q_{\text{Al}}}{\partial x} + z_{\text{Al}} * q_{\text{Al}} * \frac{F}{RT} * \frac{\partial \phi}{\partial L} \right) \quad (5)$$

$$J_{\text{H}} = -\bar{D}_{\text{H}} \left(\frac{\partial q_{\text{H}}}{\partial x} + z_{\text{H}} * q_{\text{H}} * \frac{F}{RT} * \frac{\partial \phi}{\partial L} \right) \quad (6)$$

where " J " and " q " (moles/ m^3) are the flux and the concentration of ions in the ion-exchange membrane, and F , R , T and ϕ

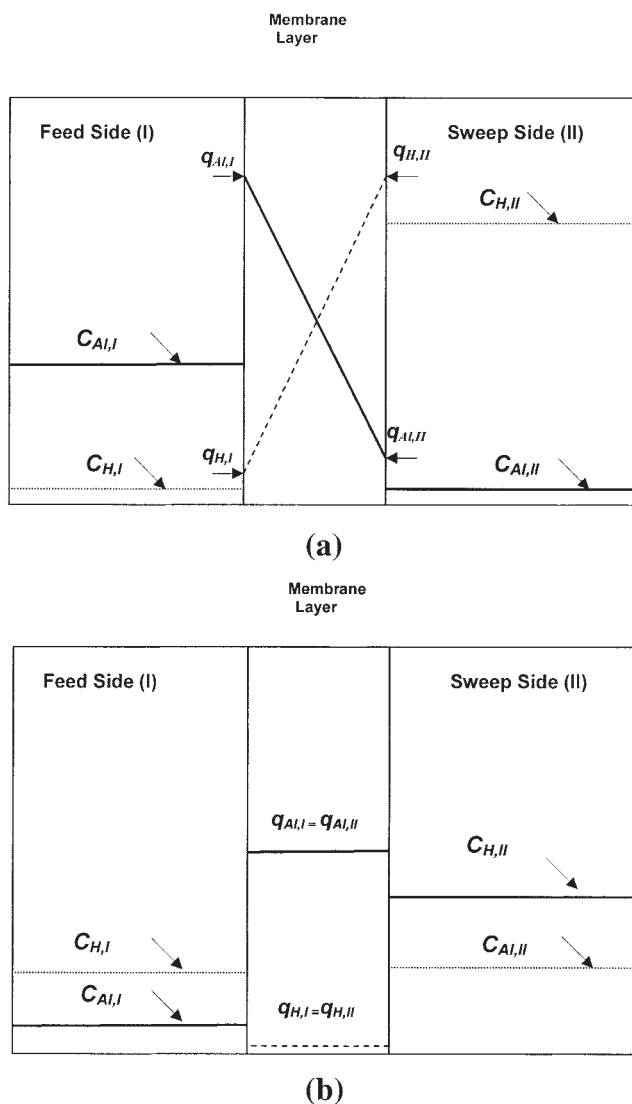


Figure 2. (a) Instantaneous ion concentration in the liquid phase and in the membrane under intramembrane transport limited condition; (b) ion concentration at Donnan equilibrium in the liquid phase and in the membrane under intramembrane transport limited condition.

are Faraday's constant, the gas constant (Joules/°K mole), the temperature (°K) and electrical potential, respectively. "L" (m) is the thickness of the membrane perpendicular to the membrane-water interface and \bar{D} (m²/s) is the self-diffusion coefficient of the diffusing ion within the membrane. Subscripts "Al" and "H" refer to Al³⁺ and H⁺ ions.

By the principle of electroneutrality, the concentration of all the counter ions is equal to those of the fixed ions viz. the exchange capacity (Q)

$$z_H * q_H + z_{Al} * q_{Al} = Q \quad (7)$$

Because of the condition of zero current, the sum of the flux of feed ions J_{Al} and that of the driving ions J_H is zero

$$z_H * J_H + z_{Al} * J_{Al} = 0 \quad (8)$$

Using Eqs. 5–8, the transfer of feed ion Al³⁺ can be described by

$$J_{Al} = -\bar{D}_H * \bar{D}_{Al} * \left(\frac{z_H^2 q_H + z_{Al}^2 * q_{Al}}{z_H^2 q_H * \bar{D}_H + z_{Al}^2 * q_{Al} * \bar{D}_{Al}} \right) * \frac{\partial q_{Al}}{\partial L} \quad (9)$$

Thus, for the coupled transport of Al³⁺ and H⁺ as presented in Eq. 8, Fick's law can be written as

$$J_{Al} = -\bar{D}_{Al,H} * \frac{\partial q_{Al}}{\partial L} \quad (10)$$

where the Al³⁺–H⁺ interdiffusion coefficient (\bar{D}) is

$$\bar{D}_{Al,H} = \bar{D}_{Al} * \bar{D}_H * \left(\frac{z_H^2 q_H + z_{Al}^2 * q_{Al}}{z_H^2 q_H * \bar{D}_H + z_{Al}^2 * q_{Al} * \bar{D}_{Al}} \right) \quad (11)$$

Equally important point in this mathematical treatment is that the total equivalent strength of the feed, and the sweep solution remains conserved in the transfer, as shown

$$z_{Al} * C_{Al,I} + z_{H,I} * C_{H,I} = C_{T,I} \quad (12)$$

$$z_{Al} * C_{Al,II} + z_{H,II} * C_{H,II} = C_{T,II} \quad (13)$$

where C_T refers to the total equivalent strength of solution expressed in equivalents/m³.

Equation 4 for selectivity coefficient can now be rewritten in terms of equivalent ionic fraction as shown below

$$K_H^{Al} = \frac{y_{Al}}{(1 - y_{Al})^3} * \frac{(1 - x_{Al})^3}{x_{Al}} * \frac{C_T^2}{Q^2} \quad (14)$$

where "y" refers to the equivalent ionic fraction in the membrane and "x" refers to the equivalent ionic fraction in the solution.

Step-wise Modeling Protocol

Experimental results from our previous studies¹⁴ demonstrated that the diffusional resistance in the liquid phase is negligible under representative experimental conditions and intramembrane transport is the rate-limiting step for the alum recovery process. The following provides a step-wise protocol for the determination of self-diffusion coefficient values and the alum recovery rate for the DMP.

Step 1. Ion-exchange capacity and Al³⁺/H⁺ isotherm data

The ion-exchange capacity of the membranes is determined using the standard protocols.¹⁹ Equilibrium data for equivalent ionic fractions of Al³⁺ and H⁺ in the aqueous phase and the corresponding fraction in the membrane phase are then experimentally determined for a given total ionic concentration C_T

expressed in eq/m³. Average selectivity value is subsequently generated using Eq. 4.

Step 2. Determination of aluminum flux

A 24 h experiment (Run 1) is performed for a given feed and sweep solution to generate concentration values of Al³⁺ in the two solutions at different times. From these concentration values, the average flux data between time t_1 and t_2 can be generated using the following equation

$$J_{Al} = \frac{(C_{Al,sweep,t2} - C_{Al,sweep,t1}) \times V_{sweep}}{(t_2 - t_1) \times A} \quad (15)$$

where A is the membrane area of exchange and V_{sweep} is the volume of sweep solution.

Step 3. Determination of interdiffusion coefficient

Once the flux data is available, the average interdiffusion coefficient during that time period is given by Eq. 10 as

$$J_{Al} = -\bar{D}_{Al,H} * \frac{q_{Al,I} - q_{Al,II}}{L} \quad (16)$$

Local equilibrium is assumed at the membrane-water interface. Thus, q_{Al} values at both the feed surface ($q_{Al,I}$) and the sweep surface ($q_{Al,II}$) can be computed using the computed average selectivity coefficient value in Step 1, and the known aqueous phase compositions from Step 2. Since J_{Al} , $q_{Al,I}$, $q_{Al,II}$, and the membrane thickness L are known, the interdiffusion coefficient can be calculated. Note that $\bar{D}_{Al,H}$ is not constant and it changes with time with the change in membrane composition.

Step 4. Determination of membrane phase self-diffusion coefficient values

Equation 11 can be arranged as follows

$$\frac{1}{\bar{D}_{Al,H}} = \frac{1}{\bar{D}_{Al}} + \frac{\bar{D}_{Al} - \bar{D}_H}{\bar{D}_H * \bar{D}_{Al}} * \left(\frac{1}{1 + \frac{z_H^2 q_H}{z_{Al}^2 q_{Al}}} \right) \quad (17)$$

Considering $z_H=1$, $z_{Al} = 3$ and $y_{Al} + y_H = 1$, Eq. 17 becomes

$$\frac{1}{\bar{D}_{Al,H}} = \frac{1}{\bar{D}_{Al}} + \frac{\bar{D}_{Al} - \bar{D}_H}{\bar{D}_H * \bar{D}_{Al}} * \left(\frac{1}{1 + \frac{1}{9} \frac{(1 - y_{Al})}{y_{Al}}} \right) \quad (18)$$

From experimental data, the values of $1/\bar{D}_{Al,H}$ are plotted against $1/(1 + (1/9)((1 - y_{Al})/y_{Al}))$. Since the membrane has a high selectivity for trivalent aluminum ion over monovalent hydrogen ion, H⁺ ions are essentially the minor species within the membrane phase. The intercept of Eq. 18 can be used to calculate \bar{D}_{Al} and it can be substituted in the expression for slope to obtain \bar{D}_H . This approach can only be applied as a first approximation, as overall interdiffusion coefficient has been used to represent the interdiffusion coefficient value on a membrane surface. This assumption is not true, since interdif-

fusion coefficient is a function of ionic distribution and is unique at each point across the membrane. It is hypothesized in this model that while the true value of self-diffusion coefficient \bar{D}_{Al} and \bar{D}_H needs to be calculated separately from the model, the relative deviation from the true value in the linear regression approach described in Eq. 18 is the same for both Al³⁺ and H⁺. Therefore, the ratio \bar{D}_{Al}/\bar{D}_H determined from the plot for Eq. 18 is the same as the ratio for the true values obtained from the model.

Step 5. Aluminum ion concentration profile

A numerical integration technique is applied to calculate the aluminum ion concentration at intermediate times. The input parameters are (a) Initial concentration of the ions in the feed and the sweep solutions: $C_{Al, feed}$, $C_{Al, sweep}$, $C_{H, feed}$ and $C_{H, sweep}$, (b) volume of the two solutions: V_{feed} and V_{sweep} , (c) area of exchange A, (d) self-diffusion coefficient \bar{D}_{Al} and \bar{D}_{Al}/\bar{D}_H determined from Step 4, and (e) wet membrane thickness L. Two sets of equations are generated from the isotherm plot for feed and sweep conditions, relating the ionic fraction of Al³⁺ in the membrane phase to that in the aqueous phase. These equations coupled with the Nernst Planck equations discussed in the theory are applied in a model that uses \bar{D}_{Al} as an operating parameter to predict Al³⁺ concentration profile in the feed and sweep solutions.

Step 6. Incorporation of osmosis effect

To incorporate dilution effect, a separate experiment is carried out with known concentration of NaCl on the sweep side and deionized water on the feed side of the membrane to determine the osmosis of water. Water flux is related to the difference in electrolyte strength of the two solutions and has been validated in previous studies.²⁰ For the current work, it can be assumed that the water flux $\hat{J}_{Osmosis}$ (m³/m² h) is proportional to the difference of ionic concentration in the two solutions

$$\hat{J}_{Osmosis} = k_{osmosis} \Delta C \quad (19)$$

where $\Delta C = C_{sweep} - C_{feed}$, C is the summation of molar concentration of all ionic species in the given solution and “ $k_{osmosis}$ ” is the proportionality constant or the “Osmosis Parameter”. The value of “ $k_{osmosis}$ ” was determined from this experiment as 1.13×10^{-7} m⁴/moles h, and was used in the modeling program.

Materials and Methods

Feed and sweep solution

The feed solution consisted of a known concentration of Al₂(SO₄)₃·14H₂O (Fisher Scientific) at a C_T value of 222 eq/m³. The pH was approximately 3.0 ensuring that most of Al₂(SO₄)₃·14H₂O was dissolved in the water. The sweep side solution consisted of 10% or 2N sulfuric acid (E M Science). In experiments involving the study of osmosis, 2N NaCl (Fisher Scientific) was used. Acidified feed solution generated from the water treatment residuals was used during alum recovery experiments; the WTR obtained from the Allentown Water Treatment Plant (AWTP) in Pennsylvania. Poly(tetrafluoroethylene)

Table 1. Properties of Cation-Exchange Membranes

| | Nafion 117 | Ionac MC 3470 |
|--------------------------------|------------------------|--|
| Type | Homogeneous | Heterogeneous |
| Ionic form as shipped | H ⁺ | Na ⁺ |
| Exchange capacity (dry basis)* | 1694 eq/m ³ | 2099 eq/m ³ |
| Exchange capacity (wet basis)* | 1372 eq/m ³ | 1896 eq/m ³ |
| Membrane thickness (dry basis) | 0.187 mm | 0.381 mm |
| Membrane thickness (wet basis) | 0.200 mm | 0.466 mm |
| Reinforcement | No | Yes, strong fabric base and a chemically stable binder |

(PTFE) tapes purchased from the Home Depot were used for hydrophilicity experiments.

Donnan membrane cell

The Donnan membrane cell was made of Plexiglas, with dimensions of L=30 cm, W=14 cm and H=40 cm divided into two chambers. Fixed volumes of feed and sweep solutions were used for every run; the ratio of feed volume to sweep volume could be adjusted independently in the test cell. The solutions in both chambers were agitated using instrument quality compressed air at 1 psig. The area available for exchange was adjusted to a maximum of 415 cm².

Two different classes of membranes were used in the Donnan membrane cell. These were the homogeneous membrane Nafion 117 from Dupont and heterogeneous membrane Ionac MC 3470 from Sybron Chemicals. Table 1 shows a summary of the properties of these two membranes. Most of the data was available from the manufacturers, and the exchange capacity data shown in (*) were determined in the laboratory.

Hydrophilicity of membranes

Experiments were performed to measure the hydrophilicity of the membranes. For this purpose, the two membranes Nafion 117 and Ionac MC 3470 were dipped in the WTR solution for over 48 h. Samples were viewed under a Goniometer, to measure the contact angle of water with the membrane surface. For this purpose, a small sheet of the membrane surface was kept under observation, a drop of water added by a syringe on the surface and the drop allowed to settle for a few minutes. The contact angle made by the drop with the surface was measured manually. The angle was compared against that for a standard hydrophobic material. For this purpose, PTFE sheet was used. Figure 3 shows the different contact angles for the three surfaces. It can be observed that the contact angle for Nafion 117 surface is the lowest at 60°, for Ionac MC 3470 surface it is approximately 70° and the PTFE surface has a contact angle of approximately 120°. This result is an indication of the hydrophilic nature of the two membranes and it suggests that the cation-exchange membranes may be resistant to membrane fouling by hydrophobic NOM during the Donnan membrane process.

Procedure for DMP experiments

The aluminum sulfate (or acidified WTR) feed solution was allowed to exchange Al³⁺ ions with H⁺ ions from the sweep solution of sulfuric acid for a period of 24 h. Samples were collected at regular intervals from both feed and the sweep side. Mild agitation with instrument quality air was provided at 1 psig. This was done to ensure that there was no film forma-

tion on the membrane surface. A smaller Donnan Cell was selected for osmosis experiment in which the feed solution side consisted of 0.5*10⁻³ m³ of DI water and the receiver solution side had 0.2*10⁻³ m³ of 2N electrolyte solution of NaCl. The area of contact was 50 cm². Total water transport from feed to receiver solution was measured at different time intervals and water flux \hat{J}_{Osmosis} calculated from the obtained data.

Exchange capacity (Q) of membranes

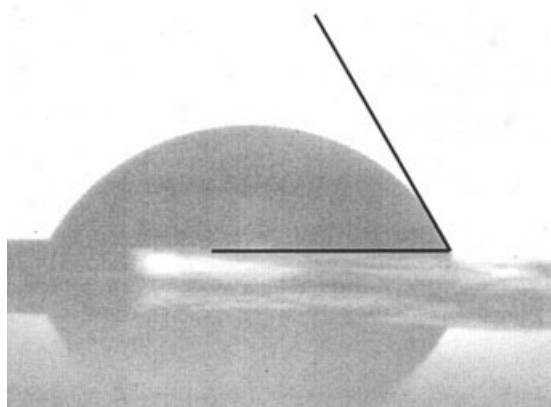
For exchange capacity determination for Nafion membranes, a 10 cm*10 cm membrane was completely converted to Na⁺ form by allowing it to exchange with 2N NaCl solution for 48 h in two consecutive experimental runs of 24 h each. The membrane was cleaned thoroughly in deionized water, dried with filter paper and then stripped of Na⁺ ions in two batches by exchanging with H⁺ ions in a 2N H₂SO₄ solution for 48 h, as before. The Na⁺ concentration was measured using an atomic absorption spectrometer (PerkinElmer Model 2380). The expansion of membrane was taken into consideration in calculating the exchange capacity of the wet membrane. For Ionac MC 3470, the exchange capacity was determined the same way, keeping in mind that the membrane was originally in Na⁺ form and that it needed just one stripping step to get the Na⁺ ions in solution. The expansion in aqueous phase was taken into account in this case too.

Isotherm plot generation

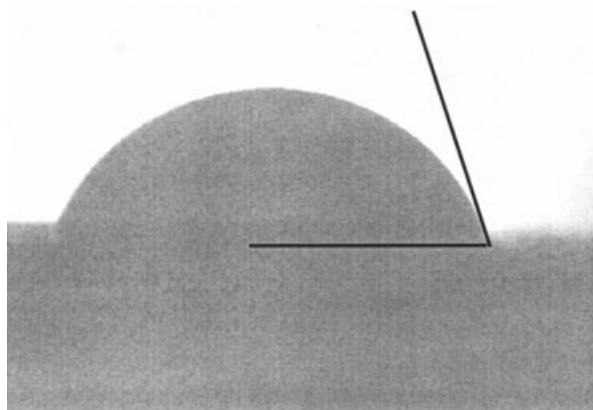
The membrane was converted to H⁺ form and dipped in an Al³⁺ - H⁺ electrolyte solution of known strength C_T, and the solution was stirred for 24 h to attain equilibrium. Aluminum ion uptake by the membrane was determined by mass balance. Several sets of such equilibrium experiments were carried out using different masses/areas of both Nafion 117 and Ionac MC 3470. From these experiments, it was possible to determine y_{AI}. Four values of X_{AI} were selected, and the experiment was run for different C_T values, such as 50, 1,000 and 2,000 meq/L (or eq/m³) in case of Nafion 117. For Ionac MC 3470, the same was carried out with the C_T value of 50 meq/L.

SEM-XRF Analysis and analytical technique

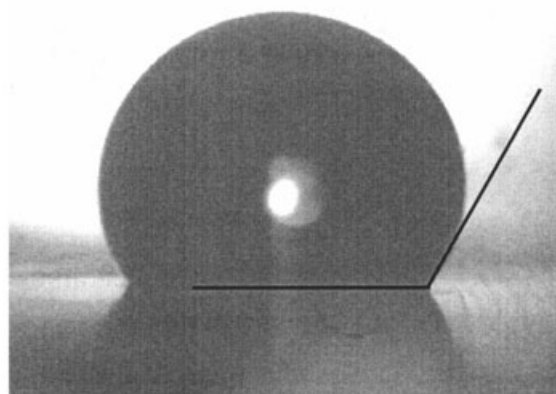
A ½ in. by ½ in. square piece of the two membranes was taken and converted to Na⁺ form. Since the Sybron membranes are available in Na⁺ form, they were treated "as received". For Nafion 117, the membrane was converted to Na⁺ form. For this purpose, the membrane was dipped in a 2% NaOH solution (for 30 min, stir) followed by a DI water wash (or soak) and then rinsed. The process was repeated three times with "fresh" NaOH. 200 mL of 2% NaOH was used for each treatment step. Once the membrane was converted to Na⁺ form, it was dried,



Nafion 117: Contact Angle = 60 degrees



Ionac MC 3470: Contact Angle = 71 degrees



Teflon: Contact Angle = 118 degrees

Figure 3. Contact angle as a measure of hydrophilicity of (a) Nafion 117; (b) Ionac MC 3470, and (c) PTFE.

a cross-section of the sample taken and mounted for scanning electron microscopy (SEM). A “dot-map” of the Na^+ was performed using X-ray fluorescence (XRF). The sample was taken from the sample’s center to eliminate edge effect. The

Sybron membrane was also soaked in DI water and after hydration, the membrane was air-dried before preparing a cross-section sample for analysis. Aluminum ion was analyzed using UV-vis spectrometer. This analysis involved the Eriochrome Cyanine R Method described in Standard Methods.²¹ For pH measurement, Fisher Scientific Accumet pH meter 900 was used. All experiments were conducted at ambient temperature and no significant difference in temperature was noticed between the feed and sweep samples. SEM-XRF analysis was carried out with ThermoNORAN Quest, which is a combination SEM and XRF. The contact angles for hydrophilicity studies were measured with a Goniometer (Rame-Hart), and pictures taken with a digital camera (Redlake MotionPro Model 2000).

Results and Discussion

Recovered alum quality in DMP treatment

The composition of recovered alum, based on AWTP WTR was compared with the composition of recovered alum obtained from the acid digestion process (ADP), a process that simply involves dissolution of solids in WTR through acid addition.¹⁴ The DMP concentrates aluminum ions to a higher value (~ 2 times) than the ADP, and in addition the DOC concentration in the recovered solution is very low due to its Donnan co-ion exclusion by the negatively charged cation-exchange membranes. The sweep solution is, therefore, virtually free of DOC. This is clearly visible in the yellow coloration of recovered alum solution obtained through ADP in Figure 4.

Equilibrium isotherm plot

The exchange capacity of Nafion 117 on a wet basis was calculated as 1372 eq/m^3 . The Nafion 117 isotherm plot for $\text{Al}^{3+} - \text{H}^+$ equilibrium is shown in Figure 5a. The experimental data was generated for C_T values of 50, 1,000 and 2,000 meq/L. Using these plots and based on the selectivity coefficients calculated from Eq. 4, a theoretical plot for $C_T = 222 \text{ meq/L}$ and $C_T = 2,000 \text{ meq/L}$ is obtained. These two C_T values

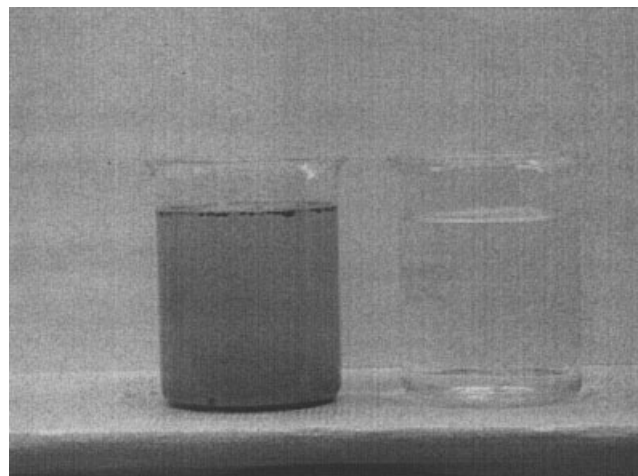


Figure 4. Recovered alum from Water Treatment Plant Residuals using Acid Digestion Process (left) and Donnan Membrane Process (right).

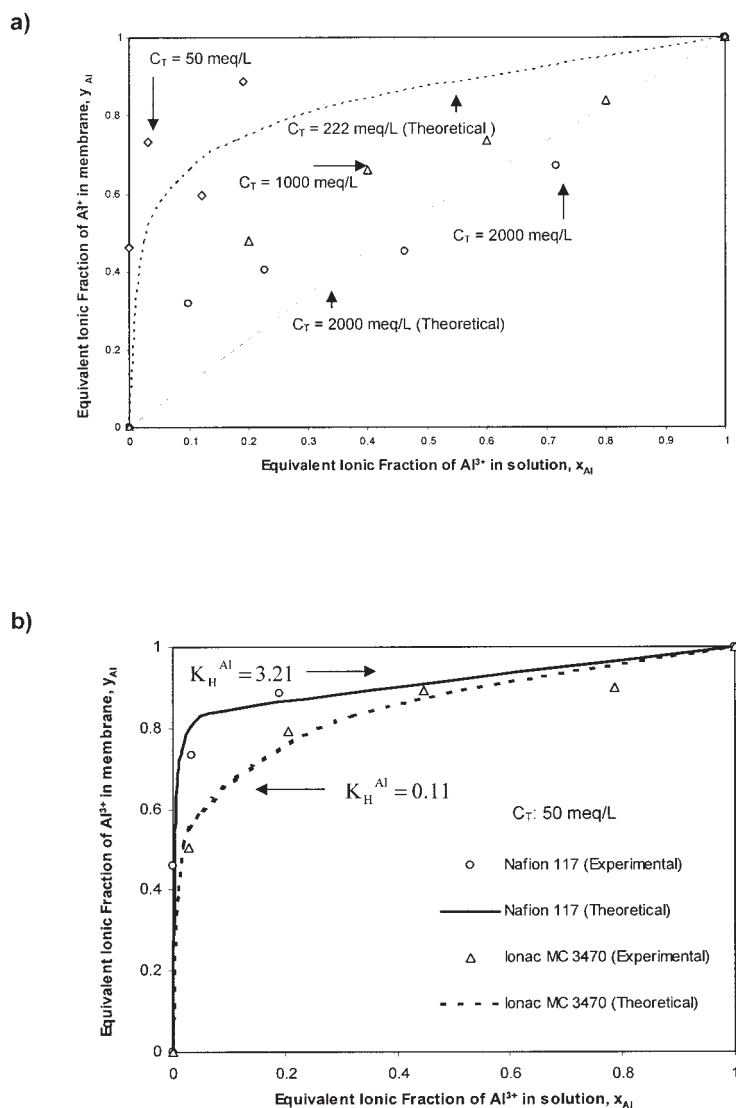


Figure 5. $\text{Al}^{3+}\text{-H}^+$ Isotherm plot (a) for Nafion 117 b) comparison between Nafion 117 and Ionac MC 3470.

represent the electrolyte concentration in the experiments performed. These plots were used in the model to predict theoretical concentrations in the feed and sweep solution. It can be seen from Figure 5a that for a low C_T value of 50 meq/L, the isotherm is close to a rectangular plot. For higher C_T values of 1,000 and 2,000 meq/L, the plot approaches linearity. The drop in selectivity with increasing values of C_T is on predictable lines, as for a given ionic fraction in solution, the membrane fraction is inversely proportional to the square of C_T , as observed in Eq. 14. This implies that with increasing C_T , the isotherm plot approaches linearity and at a later stage, changes from “convex-up” configuration to “convex-down”.

A study was done to compare the isotherm plots of Nafion 117 and Ionac MC 3470. The comparison in Figure 5b shows that Nafion 117 has a more rectangular isotherm than Ionac MC 3470, indicating that the homogeneous membrane has a higher selectivity for Al^{3+} ions. In fact, the average selectivity coefficient K_H^{Al} was determined to be 3.21 for Nafion 117 and 0.11 (over 30 times lower) for Ionac MC 3470.

Kinetic treatment of alum recovery in Nafion 117

As discussed in Step 1 in the model, the exchange capacity for the membrane and the $\text{Al}^{3+}\text{-H}^+$ equilibrium isotherm data were generated, as shown in Figure 5. Step 2 involved determining the aluminum ion recovery profile using a synthetic solution. The recovery profile for an experiment labeled Run 1 is plotted in Figure 6. For this experiment, a feed solution of 6 liters ($C_T = 222$ meq/L) and a sweep solution of 1.5 liters ($C_T = 2000$ meq/L) were used. In the same figure, aluminum flux, calculated from Eq. 15 is also shown. For a given feed and sweep aluminum ion fraction “ x_{Al} ” determined from this experimental run, the corresponding fraction “ y_{Al} ” in the membrane surface exposed to the solution and its concentration was determined using Figure 5a. With the aluminum ion transfer flux data available and the membrane thickness provided, it was possible to determine the experimental interdiffusion coefficient value $\bar{D}_{\text{Al,H}}$ with the aid of Fick’s law in Eq. 10. This plot is shown in Figure 7a. It must be noted that this value is

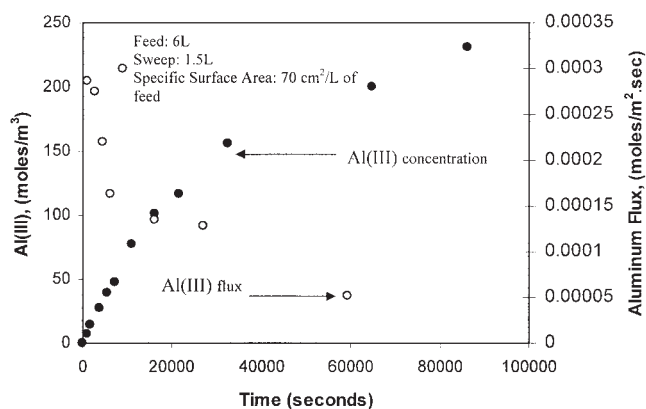


Figure 6. Sweep side Al^{3+} concentration for Run 1 and corresponding aluminum ion flux for Nafion 117 membrane.

only an approximate value of interdiffusion coefficient, as actual values vary across the cross-section of the membrane with varying charge distribution. Using this approximate value of interdiffusion coefficient, the linearization technique described in Step 4 in the modeling section was implemented. The values of $1/\bar{D}_{\text{Al,H}}$ from Run 1 were plotted against $1/(1 + (1/9)((1 - y_{\text{Al}})/y_{\text{Al}}))$ in Figure 7b for surface conditions on “feed-surface”. This plot was used to determine the initial self-diffusion coefficient values and. This approach can only be applied as a first approximation, as overall interdiffusion coefficient has been used to represent the interdiffusion coefficient value on “feed-surface”. The ratio $\bar{D}_{\text{Al}}/\bar{D}_{\text{H}}$ was determined to be 35.0 and was fed into a modeling program. The process was iterated for Run 1 to determine the theoretical recovery. How-

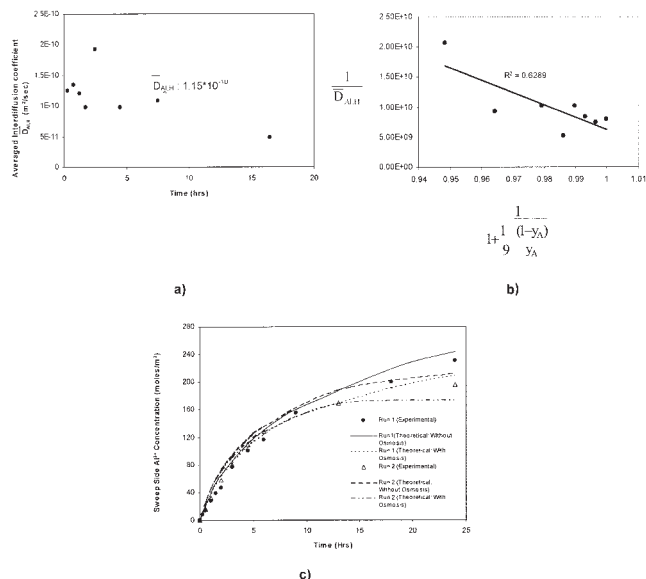


Figure 7. (a) Average interdiffusion coefficient values based on Run 1 (b) self-diffusion coefficient determination for Al^{3+} – H^{+} pair using separation of variables, and (c) recovery profile for Al^{3+} (Theoretical/Experimental values) for Run 1 and Run 2: Nafion 117.

ever, the recovery was modified to take into account the osmosis effect in solutions. The dilution effect was then imposed on the theoretical recovery plot to determine the sweep side concentration with osmosis. The initial self-diffusion coefficient values \bar{D}_{Al} and \bar{D}_{H} determined from Figure 7b underpredicted the experimental findings. So the process was iterated using \bar{D}_{Al} as the operating parameter. When the results matched well with the experimental plot for Run 1, the self-diffusion coefficient values obtained were

$$\bar{D}_{\text{Al}}: 6.5 \times 10^{-12} \text{ m}^2/\text{sec} \text{ and } \bar{D}_{\text{H}}: 2.28 \times 10^{-10} \text{ m}^2/\text{sec}$$

Furthermore to this, another experiment was carried out (Run 2). In this experiment, the feed volume was changed to 3L (from 6L in Run 1), sweep volume to 1L (from 1.5L) and the membrane area to 370 cm^2 (from 415 cm^2). It was observed that the sweep side concentration profile for these self-diffusion coefficient values matched reasonably well with the experimental findings. The results are shown in Figure 7c. The self-diffusion coefficient of H^{+} ions has been investigated earlier,^{18,20} and the current value is close to the values reported for the case of Neosepta C66-5T membrane by Miyoshi ($1.33 \times 10^{-10} \text{ m}^2/\text{s}$) and Sudoh et al. ($1.86 \times 10^{-10} \text{ m}^2/\text{s}$). When self-diffusion coefficient values for H^{+} and Al^{3+} ions in Nafion 117 were compared with the values in the aqueous phase at infinite dilution,²² the ratio of $\bar{D}_{\text{Nafion 117}}/\bar{D}_{\text{Infinite Dilution}}$ was found to be 1/41 and 1/93, respectively for H^{+} and Al^{3+} ions. Miyoshi²³ had earlier found in their work with Na^{+} , K^{+} , Ca^{2+} , Cu^{2+} and Mg^{2+} ions during Donnan membrane process that the drop in self-diffusion coefficient value in the membrane phase was higher for the bivalent ions than for the monovalent ions. This point can be understood from the fact that in their movement across the membrane, trivalent ions have to link themselves with three negative sites, to maintain electroneutrality, while monovalent ions need to link with only one negative site. Therefore, the efficiency with which a multivalent ion hops within an exchange membrane is significantly reduced in comparison with monovalent ions.

Interdiffusion Coefficient Variation on Membrane Surfaces

As mentioned earlier, the interdiffusion coefficient is a variable across the membrane and is dependent on Al^{3+} and H^{+} distribution across the membrane. Using the model q_{H} and q_{Al} , distribution on the two surfaces was determined for Run 1, shown in Figure 8a. The data obtained from this finding was further used to calculate the flux variation with time. The results were compared against the flux obtained from the experimental findings. It could be seen, as shown in Figure 8b, that the flux values based on the interdiffusion coefficient $\bar{D}_{\text{Al,H,I}}$ for “feed-surface” were very well correlated with the experimental flux in comparison with the results obtained for “sweep-surface”. This finding can be used to conclude that the ion transport for this case could be well represented by the Al^{3+} – H^{+} distribution on “feed-surface”, and that the charge distribution on this surface along with the interdiffusion coefficient values on this surface determined the ion transport.

Another important point that can be noted is that the interdiffusion coefficient values are closer to the self-diffusion coefficient value of H^{+} ions and much higher than the values

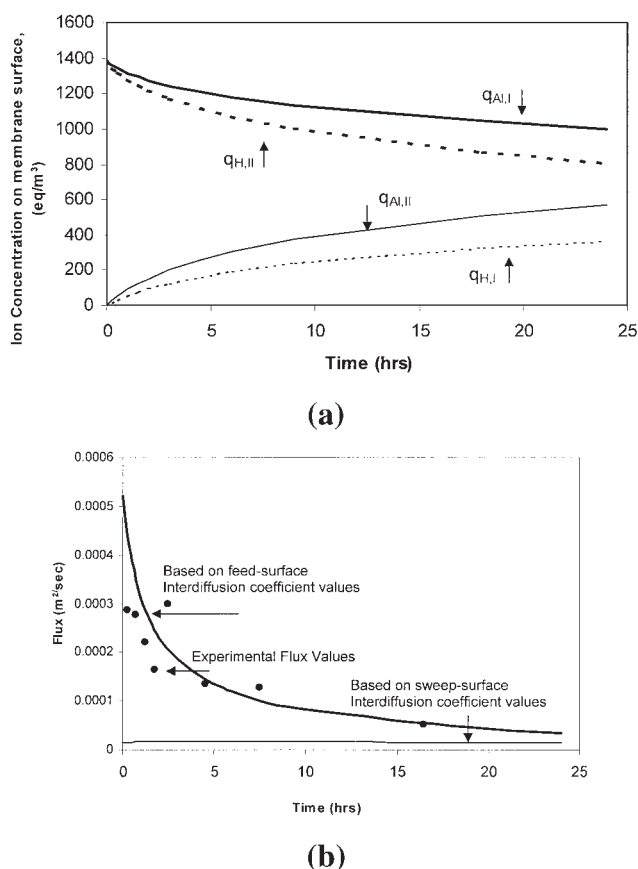


Figure 8. (a) Surface concentration of Al^{3+} - H^+ ions: Run 1; (b) Al^{3+} flux based on experiments with flux, based on interdiffusion coefficient values on feed- surface “I” and sweep- surface “II”.

obtained for Al^{3+} ions, calculations showing that $\bar{D}_{\text{Al,H,I}}/\bar{D}_{\text{Al}}$ ranged from 35 (time “t” = 0 h) to 7 (time “r” = 24 h). In fact, the $\bar{D}_{\text{Al,H}}$ values are significantly greater than self-diffusion coefficients of divalent and trivalent cations within a cation exchanger. For instance, the diffusion coefficient values for multivalent ions in cation exchange resins with 15% crosslinking range between 10^{-12} and 10^{-14} m^2/s .²⁴ This observation of high interdiffusion coefficient ($\bar{D}_{\text{Al,H}}$) value in Nafion 117 is counterintuitive and the following provides a scientific explanation for high $\bar{D}_{\text{Al,H}}$ values observed.

The composition of the membrane with respect to Al^{3+} and H^+ content (that is, q_{Al} and q_{H}) varies across the membrane, influencing the Al^{3+} - H^+ interdiffusion coefficient as discussed earlier in Eq. 11, and revised as below

$$\bar{D}_{\text{Al,H}} = \bar{D}_{\text{H}} * \bar{D}_{\text{Al}} * \left(\frac{q_{\text{H}} + 9 * q_{\text{Al}}}{q_{\text{H}} * \bar{D}_{\text{H}} + 9 * q_{\text{Al}} * \bar{D}_{\text{Al}}} \right) \quad (20)$$

The relative distribution of Al^{3+} and H^+ in the membrane governs the value of $\bar{D}_{\text{Al,H}}$. Nafion is a strong-acid cation exchange membrane and exhibits significantly greater affinity for ions with higher valence. Equilibrium experiments revealed earlier that binary separation factor, which is a measure of relative affinity for two competing ions for an ion exchanger,

was equal to 70 for Al^{3+} over H^+ for Nafion 117 at 50 meq/L solution concentration. Thus, at anytime during the process, q_{Al} is significantly greater than q_{H} within the ion-exchange membrane. In fact, the $q_{\text{Al,I}}/Q$ value on “feed-surface” was never below 0.75 during the entire period of experiment. Considering the extreme case where hydrogen ion is essentially a trace species compared to aluminum ion, that is, $q_{\text{Al}} \gg q_{\text{H}}$, Eq. 20 reduces to

$$\bar{D}_{\text{Al,H}} = \bar{D}_{\text{H}} \quad (21)$$

For the alum recovery process, the H^+ ion is a minor species within the membrane. Consequently, the value of interdiffusion coefficient $\bar{D}_{\text{Al,H}}$ approaches that of the faster diffusing hydrogen ion \bar{D}_{H} . The composition of the membrane changes with the progress of the process, thus, altering the values $\bar{D}_{\text{Al,H}}$, but they always remain significantly greater than the self-diffusion coefficient of aluminum ions. From an application viewpoint, this phenomenon leads to a high mass transfer or alum recovery rate.

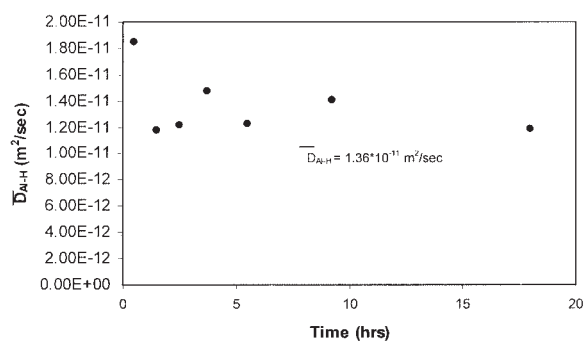
Self-Diffusion Coefficient Comparison in Nafion 117 and Ionac MC 3470

Experiments were carried out with Ionac MC 3470 to determine the self-diffusion coefficient values for H^+ and Al^{3+} in the coupled transport. Data points were used from the experiment involving 2N acid sweep solution in Figure 9b, presented later. These values formed the basis for aluminum transport rate or flux (J_{Al}) calculation at different time intervals. The equilibrium data generated in Figure 5b were used in conjunction with Eq.16 to determine the interdiffusion coefficient values. Local equilibrium was assumed at the membrane-water interface. Figure 9a shows computed $\bar{D}_{\text{Al,H}}$ values for this membrane. When compared with $\bar{D}_{\text{Al,H}}$ values for Nafion 117, it was noticed that the drop in interdiffusion coefficient values was not so steep, indicative of slow kinetics. The model discussed earlier was applied to determine the self-diffusion coefficient values of aluminum and hydrogen ions in Ionac MC 3470 membrane. A notable point was that the osmosis effect was not taken into account in this case, as no significant osmosis was observed in a separate experiment. Two experiments were carried out. Run 1 is the standard run and is the basis for generation of Figure 9a. In Run 2, a 2L sweep solution was used instead of 1L to verify the findings from Run 1. The findings from the model are presented in Figure 9b. The self-diffusion coefficient values were determined to be

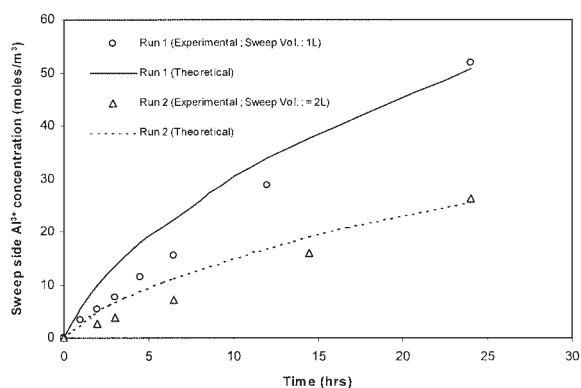
$$\bar{D}_{\text{Al}}: 5.00 * 10^{-13} \text{ m}^2/\text{sec}$$

$$\bar{D}_{\text{H}}: 3.75 * 10^{-11} \text{ m}^2/\text{sec}$$

Even for Ionac MC 3470, it was the H^+ ion which was the trace species. A comparison of the diffusion coefficient values for the two membranes is presented in Table 2. From this table, it can be observed that the self-diffusion coefficient values for aluminum and hydrogen ions are similarly lowered as the experimental interdiffusion coefficient value. This lowering is about 1 order for both the cases. Explanation for low $\bar{D}_{\text{Al,H}}$



(a)



(b)

Figure 9. (a) Interdiffusion coefficient values for aluminum ion transfer in Ionac MC 3470; (b) Recovery profile for Al^{3+} (theoretical/experimental values) for Run 1 and Run 2: Ionac MC 3470.

values in the heterogeneous membrane is desired, as it explains the slow transport kinetics in heterogeneous membrane.

Influence of Heterogeneity on Transport Properties of Nafion 117 and Ionac MC 3470

Several researchers have studied the influence of nonuniformity of ion-exchange membranes on various transport properties of membranes, such as electrical conductivity, transport numbers and diffusion permeability.^{25–27} A typical membrane may be considered to be a system of two or more phases. Timashev²⁸ proposed a two-phase model with a hydrophobic backbone, and a hydrophilic ion-exchange group, including sorbed water. Zabolotsky and Nikonenko²⁹ suggested that a membrane can be represented as a combination of two phases: (1) a conducting phase (that included a gel phase with a relatively uniform distribution of ionogenic groups and hydrophilic parts of the matrix polymer chains, and an electroneutral solution filling the interstices between the elements of the gel

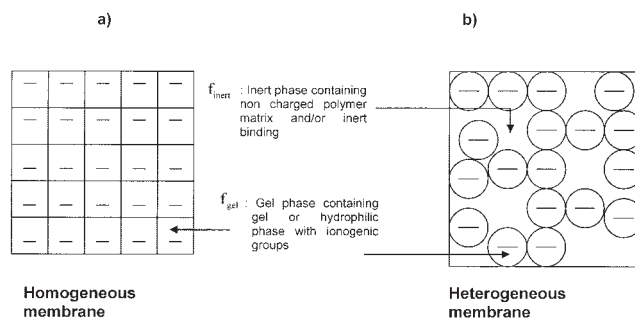


Figure 10. Conceptualized distribution of ionogenic groups within cation exchange membranes for (a) homogeneous membrane, and (b) heterogeneous membrane.

phase), and (2) an inert phase formed from hydrophobic parts of the polymer matrix and/or from the inert binder introduced during the synthesis stage. It can, therefore, be said that the membrane morphology is represented by two constituents or phases:

(a) The conducting fraction f_{gel} that includes the conducting gel or hydrophilic phase with ionogenic groups.

(b) The nonconducting fraction f_{inert} that includes the nonconducting polymer matrix and/or inert binding without ionogenic groups.

In a homogeneous membrane, the nonconducting fraction f_{inert} is much lower than in a heterogeneous membrane. Homogeneous membranes are, therefore, coherent ion-exchanger gels and heterogeneous membranes consist of colloidal ion-exchanger particles embedded in an inert binder. Conceptually, this information can be represented in Figure 10a and 10b. Figure 10a depicts the distribution of the ionogenic groups within a homogeneous membrane, while Figure 10b represents the same inside a heterogeneous membrane. It may be noted that the nonconducting inert fraction f_{inert} is significantly greater within the heterogeneous membrane. Under nonequilibrium conditions, a diffusing cation hops from one charged site to the next within the membrane and that constitutes the primary ion transport mechanism for homogeneous membranes as illustrated in Figure 11a. For heterogeneous membranes, the nonconducting or inert fraction offers resistance to ion transport in the following two ways: first, the tortuosity or the path length of ion transfer through the membrane is increased; and second, the stagnant inert phase with minimal or no ionogenic groups is always less conducive to transport of ions. For counter-transport of aluminum and hydrogen ions in a heterogeneous membrane, Figure 11b illustrates the foregoing effects of the inert phase.

A SEM-XRF analysis was done to verify this hypothesis by identifying the distribution of charged sites within Nafion 117 and Ionac MC 3470. A dot-map of Na^+ in Figures 12a and 12b showed that sodium ions were uniformly distributed in the

Table 2. Diffusion Coefficient Value Comparison in Nafion 117 and Ionac MC 3470

| | \bar{D}_H (m ² /sec) | \bar{D}_{Al} (m ² /sec) | $\bar{D}_{Al,H}$ (m ² /sec) |
|---------------|-----------------------------------|--------------------------------------|--|
| Nafion 117 | 2.28×10^{-10} (6.1) | 6.5×10^{-12} (13.0) | 1.15×10^{-10} (8.45) |
| Ionac MC 3470 | 3.75×10^{-11} | 5×10^{-13} | 1.36×10^{-11} |

Figures in () indicate ratio of diffusion coefficient in Nafion 117 over Ionac MC 3470.

homogeneous Nafion 117 membrane, while they were unevenly distributed in clusters in the Ionac MC 3470. It suggests that there are regions of nonfunctional reinforcement in Ionac MC 3470, which are absent in the unsupported Nafion 117 membrane. This reinforced region is characterized by absence of ionogenic groups.

Conclusions

Donnan membrane process or DMP was investigated for recovering alum from water treatment plant residuals using two different types of cation exchange membranes, namely, homogeneous Nafion 117 membrane and heterogeneous Ionac MC 3470 membrane. The process was selective and allowed high recovery of aluminum with near-complete rejection of natural organic matter. A stepwise design protocol was developed to determine the Al^{3+} – H^+ interdiffusion coefficient values within these membranes for coupled transport of these two ions. Subsequently, the self-diffusion coefficient values of Al^{3+} and H^+ were also computed using the experimental data. It was found that the diffusion coefficient value for Al^{3+} ions was of the order 10^{-12} m^2/s while that of H^+ ion was of the order 10^{-10} m^2/s in the case of the homogeneous Nafion 117 membrane. For the heterogeneous membrane Ionac MC 3470, these diffusion coefficient values were 5–10 times lower. This difference was attributed to the presence of nonionogenic regions in heterogeneous membranes. However, both the membranes were sufficiently hydrophilic, when compared to the hydrophobic PTFE surface. The equilibrium isotherm plot for Al^{3+} – H^+ indicated that the Nafion 117 membrane had a selectivity coefficient (K_{H}^{Al}) that was over 30 times greater than that of Ionac MC 3470. The interdiffusion coefficient value was closer to the self-diffusion coefficient value for H^+ ion, which was the trace species in both the membranes. The stepwise design protocol developed in this study was able to

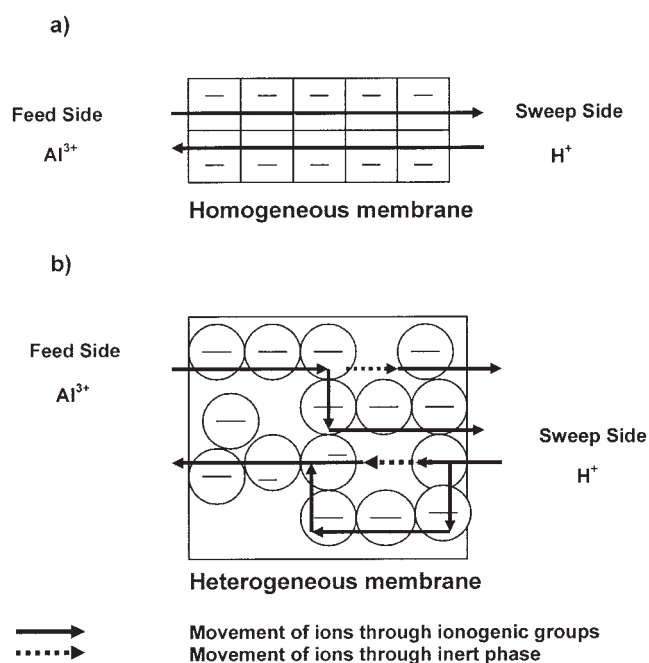
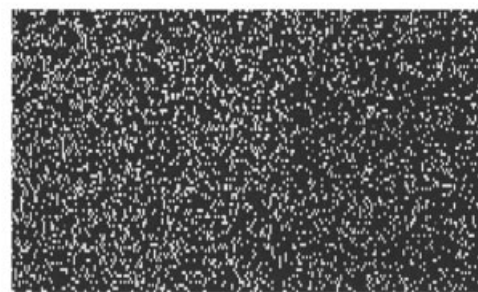


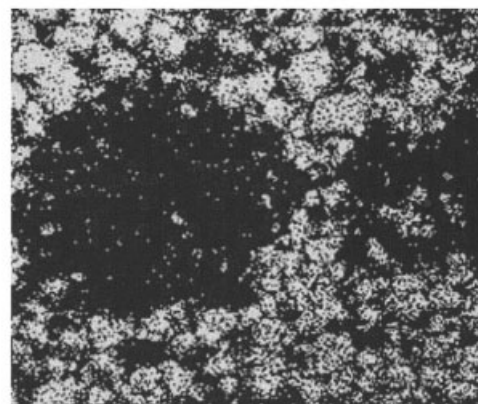
Figure 11. Counter-transport of Al^{3+} and H^+ through homogeneous and heterogeneous membranes.

(a)



Nafion 117

(b)



Ionac MC 3470

Figure 12a,b. SEM-XRF "Dot map" of Na^+ in a cross-section of (a) Nafion 117, and (b) Ionac MC 3470.

It may be noted that the charged sites are more uniformly distributed in homogeneous membrane Nafion 117, while heterogeneous membrane Ionac MC 3470 has non-conducting pockets shown by dark space.

predict the alum recovery rate for both the membranes under varying operating conditions.

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