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REMOVAL OF CADMIUM AND CHROMIUM FROM A PRETREATED WASTEWATER WITH REVERSE OSMOSIS

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This document is dedicated to Lieutenant Commander Wiz Withers and to Mr. and Mrs. James Zapp who were very supportive and encouraging throughout the author's graduate program.

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ABSTRACT

Zapp, Karen Marie, Lieutenant, Civil Engineer Corps, United States Navy. MSE, Purdue University, May 1992. Removal of Cadmium and Chromium from a Pretreated Wastewater with Reverse Osmosis. Major Professor: Benito J. Mariñas.

The purpose of this research project was to investigate the removals of cadmium(II) and chromium(VI) from a simulated wastewater by reverse osmosis (RO). The project was one very focused aspect of a major U.S. Navy multi-year research project aimed at achieving zero-discharge from its Industrial Wastewater Treatment Plants. The effects of varied operating conditions on the performance of a thin-film composite brackish water RO membrane were investigated: feed solutions of 1000, 2000, and 3000 mg/l NaCl; 2000 mg/l NaCl at pH 5, 6 and 7; and background feed composition solutions of NaCl and Na_2SO_4 at four different mix ratios. The effects of temperature in the range of 20 to 36°C, and operating pressures of 400, 300 and 200 psi were also investigated. In nearly all cases metal concentrations were 10 mg/l; a 100 mg/l test was also performed.

Typical RO behaviors were observed with water and solute permeation. Both water permeation and solute passage decreased with time due to membrane compaction. On the other hand, water permeation increased with applied pressure.

The best rejections for the metals were obtained in feed solutions of sodium chloride and sodium sulfate. A maximum rejection of 99.9 percent was observed for cadmium(II) at a feed solution mole fraction of approximately 0.95 sodium sulfate and a pH of 6. The highest chromium(VI) rejection observed was 99.1 percent at a 0.5 mole fraction of sodium sulfate and pH of 6.

CHAPTER 1

INTRODUCTION

This research project was sponsored by the Naval Civil Engineering Laboratory (NCEL), Port Hueneme, CA. It is a small piece of a more comprehensive U.S. Navy research project entitled "The IWTP of the Third Millennium," where IWTP stands for Industrial Wastewater Treatment Plants. The U.S. Navy has the goal of zero-discharge from its IWTP's in order to meet stringent environmental requirements anticipated for the next century.

The objective of the overall research project is to investigate a combination of chemical, sorption/desorption, and membrane processes which will result in zero-discharge. If the necessary technologies are not currently available, then they will be developed. This objective includes reducing the use of flocculation/precipitation in favor of advanced membrane technology. The large volumes of sludge generated from flocculation/precipitation practices are no longer acceptable. In addition to eliminating sludge, contaminants to be eliminated from the discharge stream include toxic organics, heavy metals, and microbials.

The focus of research efforts carried out at Purdue University was narrow in comparison to the grand project just described. The contaminants investigated were heavy metals, and the technology selected was reverse osmosis (RO). The decision to study only heavy metals and RO was made primarily because of a combination of time constraint and analytical apparatus availability.

The U.S. Navy has prepared a list of priority pollutants including the heavy metals: cadmium(II), copper(II), chromium(III), chromium(VI), nickel(II), silver(I), lead(II), and zinc(II). Cadmium(II) and chromium(VI) were selected for this study because they represent metals with cationic and anionic characteristics, respectively. In the absence of complexing chemical agents, the predominant metal species in aqueous solutions at the pH range of 5 to 7 are the cation Cd^{++} for cadmium(II), and anions bichromate ($HCrO_4^-$) and chromate ($CrO_4^=$) for chromium (VI).

Research Objectives

The major objectives of this research project were:

(1) Investigate the removals of cadmium(II) and chromium(VI) by a commercially available RO membrane.

(2) Determine the effect of operating pressure, and feed solution temperature, pH, concentration and composition on membrane performance.

CHAPTER 2

LITERATURE REVIEW

Chemical Principles

The chemistry of cadmium(II) and chromium(VI) in aqueous solution is presented in this section. Only those chemical principles that might affect the performance of the RO process are discussed.

Cadmium(II) Chemistry

The cation Cd^{++} is the predominat dissolved cadmium(II) species in water at acidic, neutral and slightly basic pH levels. However, as a result of hydrolysis reactions other dissolved cadmium species tend to form as pH increases. In addition, cadmiun hydroxide will also tend to precipitate under certain conditions primarily at relatively high dissolved cadmium(II) concentrations.

Cd^{++} ions tend to hydrolyze in aqueous solutions undergoing the following reactions:

$$Cd^{++} + OH^- \Leftrightarrow Cd(OH)^+ \qquad \text{(R1)}$$

$$Cd^{++} + 2\,OH^- \Leftrightarrow Cd(OH)_2^{\circ} \qquad \text{(R2)}$$

$$Cd^{++} + 3\,OH^- \Leftrightarrow Cd(OH)_3^- \qquad \text{(R3)}$$

$$Cd^{++} + 4\,OH^{-} \Leftrightarrow Cd(OH)_4^{=} \qquad \text{(R4)}$$

The equilibria for Reactions R1 to R4 at 25°C are defined by the following expressions (Benefield *et al.*, 1982):

$$K_1 = 10^{4.17} = \frac{[Cd(OH)^{+}]}{[Cd^{++}]\,[OH^{-}]} \qquad (2-1)$$

$$K_2 = 10^{8.33} = \frac{[Cd(OH)_2^{0}]}{[Cd^{++}]\,[OH^{-}]^2} \qquad (2-2)$$

$$K_3 = 10^{9.02} = \frac{[Cd(OH)_3^{-}]}{[Cd^{++}]\,[OH^{-}]^3} \qquad (2-3)$$

$$K_4 = 10^{8.62} = \frac{[Cd(OH)_4^{=}]}{[Cd^{++}]\,[OH^{-}]^4} \qquad (2-4)$$

If cadmium hydroxide precipitation occurs then the following solubility equilibrium reaction applies:

$$Cd(OH)_2(s) \Leftrightarrow Cd^{++} + 2\,OH^{-} \qquad \text{(R5)}$$

The equilibrium expression for Reaction R5 at 25°C is (Benefield *et al.*, 1982):

$$K_{sp} = 10^{-14} = [Cd^{++}]\,[OH^{-}]^2 \qquad (2-5)$$

The hydroxide ions are also at equilibrium with water following the reaction (Stumm and Morgan, 1981):

$$H_2O \Leftrightarrow H^{+} + OH^{-} \qquad \text{(R6)}$$

where the equilibrium at 25°C is represented by the expression:

$$K_w = 10^{-14} = [H^+][OH^-] \qquad (2-6)$$

The total concentration of dissolved cadmium $C_{T,Cd}$ is:

$$C_{T,Cd} = [Cd^{++}] + [Cd(OH)^+] + [Cd(OH)_2^\circ] + [Cd(OH)_3^-] + [Cd(OH)_4^=] \qquad (2\text{-}7)$$

The system of Equations 2-1 to 2-6 can be solved to obtain expressions for the concentration of each cadmium species (in terms of $pC = -\log_{10}C$) as a function of solution pH. The results from this effort are:

$$p[Cd^{++}] = 2pH - 14.3 \qquad (2\text{-}8)$$

$$p[Cd(OH)^+] = pH - 4.47 \qquad (2\text{-}9)$$

$$p[Cd(OH)_2^\circ] = 5.37 \qquad (2\text{-}10)$$

$$p[Cd(OH)_3^-] = 18.68 - pH \qquad (2\text{-}11)$$

$$p[Cd(OH)_4^=] = 33.08 - 2pH \qquad (2\text{-}12)$$

Equations 2-8 to 2-12 are plotted in the pC-pH diagram shown in Figure 2-1. The total dissolved cadmium concentration $C_{T,Cd}$ (see Equation 2-7) at equilibrium with solid $Cd(OH)_2(s)$ is also depicted in the figure.

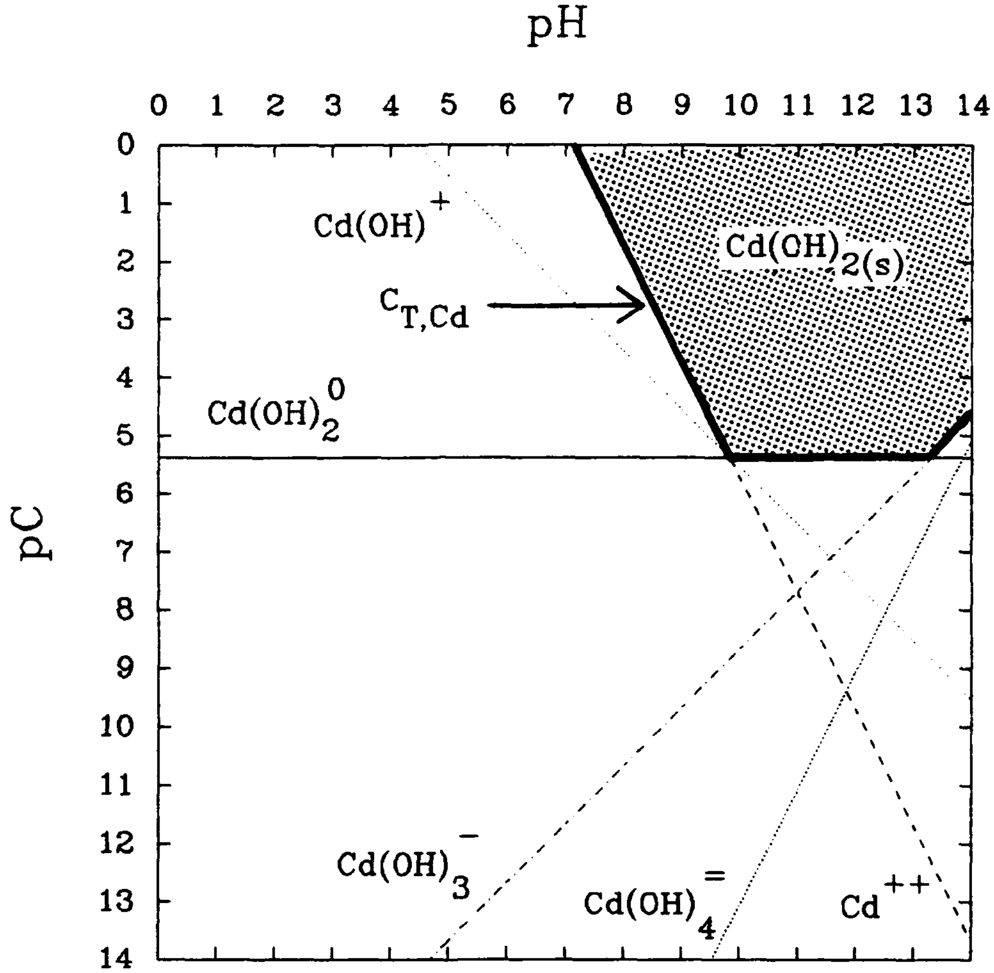

Figure 2-1. Solubility of total cadmium(II) $C_{T,Cd}$ in water versus pH at 25°C.

Chromium(VI) Chemistry

There are three dissolved chromium(VI) species that occur in water: chromic acid (H_2CrO_4), bichromate ion ($HCrO_4^-$), and chromate ion ($CrO_4^=$). The equilibria between these species is defined by the following acid-base equilibrium reactions:

$$H_2CrO_4 \Leftrightarrow HCrO_4^- + H^+ \qquad (R7)$$

$$HCrO_4^- \Leftrightarrow CrO_4^= + H^+ \qquad (R8)$$

The equilibrium expressions for Reactions R7 and R8 at 25°C are (Benefield *et al.*, 1982):

$$K_{a,1} = 10^{-0.74} = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]} \qquad (2-13)$$

$$K_{a,2} = 10^{-6.5} = \frac{[CrO_4^=][H^+]}{[HCrO_4^-]} \qquad (2-14)$$

Under most conditions, chromium(VI) is very soluble in water. Assuming that compounds with which chromium(VI) tend to form complexes are not present in solution, then the total concentration of dissolved chromium(VI) is given by the expression:

$$C_{T,Cr} = [H_2CrO_4] + [HCrO_4^-] + [CrO_4^=] \qquad (2\text{-}15)$$

Equations 2-13 to 2-15 can be solved simultaneously to obtain the following expressions for the concentration of each individual chromium(VI) species:

$$H_2CrO_4 = \frac{[H^+]^2 C_{T,Cr}}{[H^+]^2 + [H^+]K_{a,1} + K_{a,1}K_{a,2}} \qquad (2-16)$$

$$\mathrm{HCrO_4^-} = \frac{[\mathrm{H^+}]K_{a,1}\,\mathrm{C_{T,Cr}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_{a,1} + K_{a,1}K_{a,2}} \qquad (2-17)$$

$$\mathrm{CrO_4^=} = \frac{K_{a,1}K_{a,2}\,\mathrm{C_{T,Cr}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_{a,1} + K_{a,1}K_{a,2}} \qquad (2-18)$$

Equations 2-16 to 2-18 are plotted against solution pH in Figure 2-2.

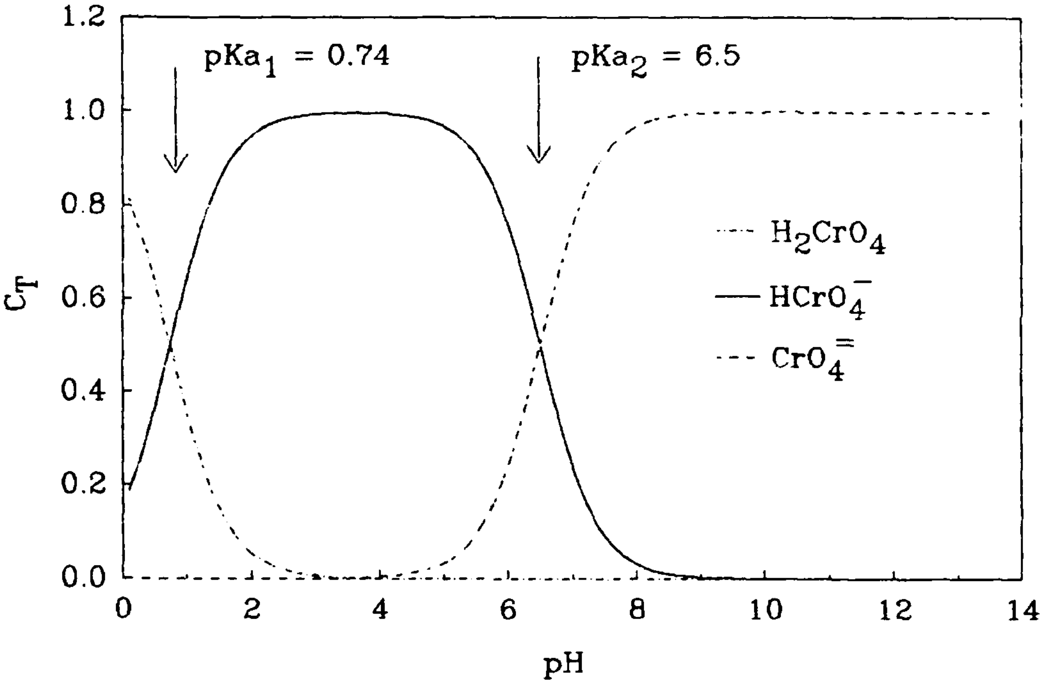

Figure 2-2. Chromium(VI) speciation as a function of water pH at 25°C.

Reverse Osmosis Process

Reverse osmosis (RO) is a pressure-driven membrane separation process. RO is a modification of the natural process called osmosis. In osmosis, when an ideally semipermeable membrane separates solutions of different concentrations, water permeates from the low concentration solution through the membrane into the higher concentration solution. Water permeates until the osmotic pressure (i.e., concentration in the case of identical low and high concentration solution compositions) is the same on both sides of the membrane.

A hydraulic pressure in excess of the osmotic pressure difference between high and low concentration solutions is applied in the high concentration side for the RO process. As a result the water flow is reversed and permeates from the high concentration to the low concentration side. RO membranes also allow a fraction of the solute to permeate through. In contrast to water permeation, the permeation of solutes is always in the same direction for both osmosis and RO, i.e., from the high to the low concentration side.

A schematic of an RO unit is shown in Figure 2-3. The unit is divided into two compartments, feed and permeate channels, by an RO membrane. The feed water is pressurized and pumped into the feed channel of the unit at a flow rate Q_f. As a result of the applied pressure, a portion of the feed water permeates through the membrane into the permeate channel at an overall flow rate Q_p. Water permeates through RO membranes more rapidly than most solutes and therefore a solute-depleted permeate is produced.

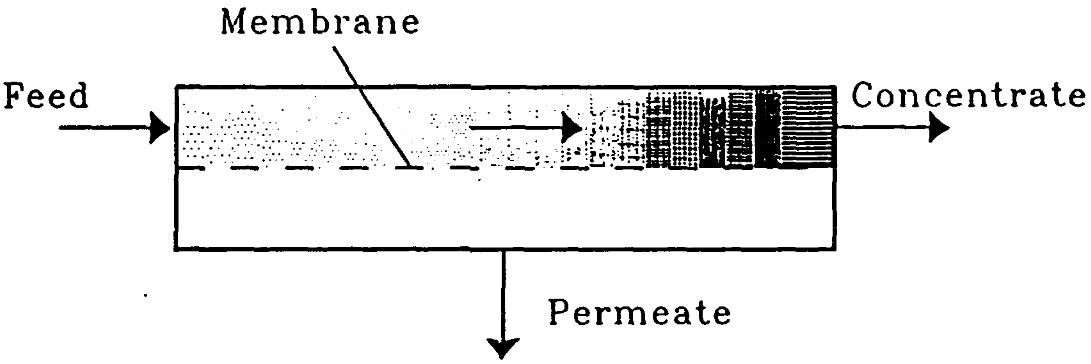

Figure 2-3. Schematic of RO unit.

Because most solutes are rejected by the membrane, the concentration of the solution remaining in the feed channel increases gradually as it advances. Finally, concentrate exits the unit feed channel at a flow rate Q_c. The concentrate is depressurized after exiting the unit and is treated for use or proper disposal.

RO Transport Equations

There are two flux equations which are often used to express the permeation of water and solute across a semi-permeable membrane (Harris, et al., 1976):

$$J_v = A(\Delta p - \sigma\Delta\pi) \qquad (2-19)$$

and

$$J_s = B\Delta c + (1-\sigma)J_v\bar{c} \qquad (2-20)$$

where

J_v = water flux rate (i.e., $J_v = Q_p/S$)
J_s = solute flux rate (i.e., $J_s = J_v \cdot c_p$ at steady state)
A = water permeation coefficient
B = solute permeation coefficient
σ = reflection coefficient
Δp = $p_f - p_p$ = hydraulic pressure gradient
$\Delta\pi$ = $\pi_f - \pi_p$ = osmotic pressure gradient
Δc = $c_f - c_p$ = solute concentration gradient
$\bar{c}$ = $(c_f + c_p)/2$
S = membrane active surface area

The subscripts f, c, and p refer to feed solution, concentrate, and permeate, respectively. The permeation coefficients A, B, and σ are membrane specific and depend on feed water quality parameters such as temperature, pH and ionic strength.

The first term in the right side of Equation 2-20 ($B\Delta c$), represents diffusive permeation, and the second term $(1-\sigma)J_v\bar{c}$ represents convective permeation. For high-rejection RO membranes, $\sigma = 1$ and the solute permeates through the membrane only by diffusion. On the other hand, for low-rejection RO membranes such as those used in nanofiltration, $\sigma < 1$ and convective permeation becomes predominant.

Equation 2-20 together with the expression $J_s = J_v \cdot c_p$ gives the following expression (Mariñas and Selleck, 1991):

$$\frac{c_p}{c_f - c_p} = \frac{1-\sigma}{2\sigma} + \frac{B}{\sigma}\left(\frac{1}{J_v}\right) \qquad (2-21)$$

A plot of experimental results in terms of $c_p/(c_f - c_p)$ against $1/J_v$ should result in a straight line with a slope of B/σ, and a positive intercept with the ordinate of $(1-\sigma)/2\sigma$ if $\sigma < 1$.

The apparent performance of RO membranes with respect to solute permeation is usually represented by a parameter called solute passage

$$SP = \frac{c_p}{c_f} \qquad (2-22)$$

A second common parameter used to describe RO membrane performance is solute rejection defined as

$$SR = 1 - SP, \qquad (2-23)$$

where both SP and SR are commonly expressed in terms of percentage.

Concentration-Polarization

Solutes rejected by an RO membrane accumulate in a thin laminar film next to the membrane. The main result of this is that the membrane is exposed to concentrations c_w which are greater than those in the bulk feed water c_f. This phenomenon is known as concentration-polarization. Steady state values of c_w can be estimated with the expression (Mariñas and Selleck, 1991):

$$\frac{c_w - c_p}{c_f - c_p} = \exp(\alpha_c Sc^{2/3} J_v) \qquad (2-24)$$

where α_c is a constant for a given RO cell geometry and constant feed water flow rate. The Schmidt numbers can be calculated from D and ν values found in the literature for single electrolyte solutions (Sourirajan, 1970).

If concentration-polarization is significant then c_f used in Equations 2-19 through 2-23 should be substituted by c_w.

RO units are designed to minimize concentration-polarization and its detrimental effects. For constant operating conditions, greater concentration-polarization would correspond to higher solute concentration in the permeate, lower permeate flow rate, and greater fouling tendency of membrane surfaces.

Osmotic Pressure

The osmotic pressure π for an aqueous solution is given by the expression (Robinson and Stokes, 1955):

$$\pi = m_T \mathrm{RT} \rho_w \phi \qquad (2-25)$$

in which R is the ideal gas constant (0.08205 atm • L/[mole • K]), T is absolute temperature (K), ρ_w is approximately the density of pure water at temperature T (Kg/L), ϕ is the molal osmotic coefficient (dimensionless), and m_T represents the sum of the molalities (mole/Kg of water) of all ions and molecules in solution. For very dilute solutions $\phi = 1$, but in general, it deviates from unity. The osmotic coefficients for aqueous solutions of many single salts, acids and bases can be found in the literature (Robinson and Stokes, 1955; Harned and Owen, 1958). The method developed by Pitzer (1979) and simplified by Mariñas and Selleck (1991), can be used to estimate average osmotic coefficients for those solutions containing two or more electrolytes.

Effect of Feed Solution Composition on RO Process Performance

Permeation coefficients A and B have been reported to vary significantly with varying feed water composition. An example of this dependency was reported by Mariñas and Selleck (1991). These authors investigated the performance of a high rejection FT-30 membrane (Model SW30). The composition of the feed solutions investigated were combinations of the major electrolytes sodium chloride and sodium sulfate. Tracer amounts of sodium nitrate, sodium selenate, and sodium biselenite were also present. Mariñas and Selleck (1991) found that the passage of all anions (chloride, sulfate, nitrate, biselenite and selenate) present in the feed solutions tested increased with an increase in the fraction of sulfate ion present in solution as shown in Figure 2-4. The experimental results presented in this figure correspond to four tests performed at equal pH, temperature, and net driving force (i.e., $\Delta p - \Delta\pi$).

The pH of the feed solution is another critical parameter. Changes in pH can affect the dissociation of membrane chemical groups and solution weak electrolytes. RO membranes are either positively or negatively charged depending upon the monomer and its reaction with the feed solution. The BW30 has a negative charge as subsequently discussed in Chapter 3.

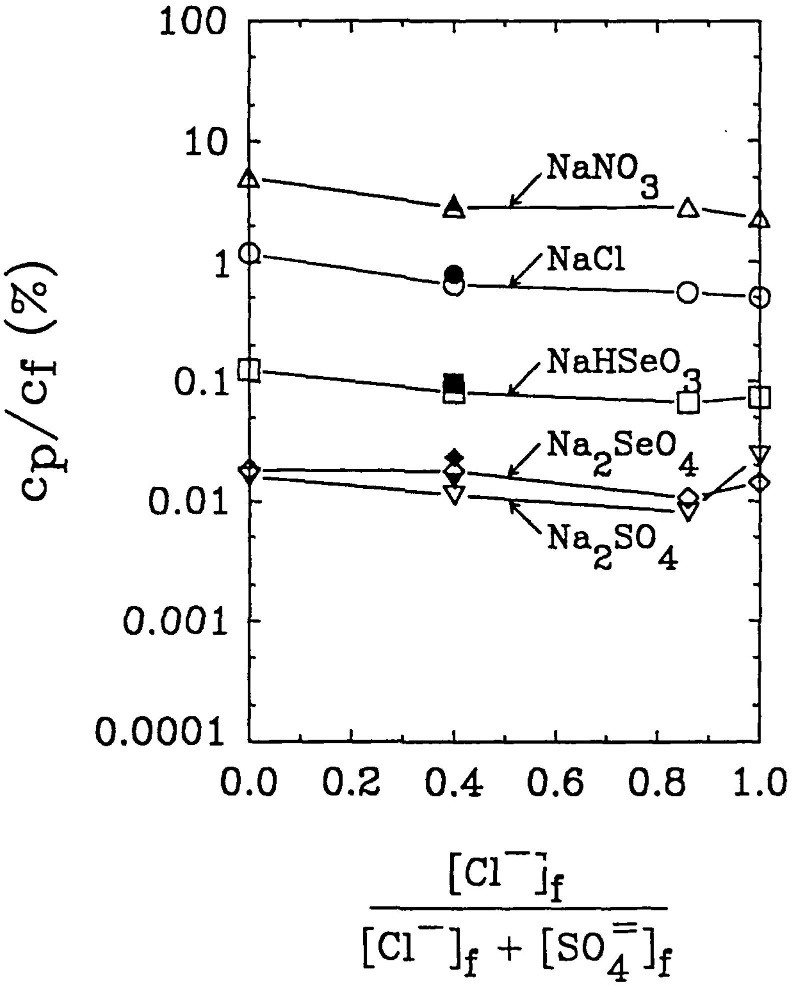

Figure 2-4. Observed anion passages as a function of feed-water chloride-ion mole fraction for FT-30 membrane model SW30 ($\Delta p - \Delta\pi = 400$ psi, feed pH = 5.5, temperature = 25°C).

Predominant weak electrolyte species present in solution can change with changes in pH. For example, in the case of a diprotic acid-base system such as chromic acid, the predominant species in solution could be the neutral chromic acid molecule, the monovalent bichromate ion, or the divalent chromate ion, depending on whether the pH is less than $pK_{a,1}$, between $pK_{a,1}$ and $pK_{a,2}$, or greater than $pK_{a,2}$, respectively. In general, solute passage tends to decrease with an increase in solute electrical charge, and therefore, chromium (VI) will be best rejected by the membrane when the feed solution pH is greater than $pK_{a,2}$.

Temperature Dependence

Both water and solute permeations through RO membranes are sensitive to feed solution temperature. These dependencies are primarily contained in the permeation coefficients A, B, and possibly σ. Arrhenius-type expressions are commonly used to represent the effect of temperature on A and B, or

$$\frac{A_{T_2}}{A_{T_1}} = \exp(\alpha_T) \qquad (2-26)$$

and

$$\frac{B_{T_2}}{B_{T_1}} = \exp(2 \cdot \alpha_T) \qquad (2-27)$$

where

$$\alpha_T = K_T\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (2-28)$$

in which K_T is a constant, T is the absolute temperature, and the subscripts 1 and 2 refer to two different temperatures. Expressions for the dependence of σ on temperature were not available.

Membrane Compaction

The active layer of RO membranes tend to compact with time as a result of relatively high hydraulic pressures commonly used in the RO process. The result is changes in membrane resistance to water and solute molecules permeation. The changes in A and B parameters with operating time can be expressed as (Mariñas and Selleck, 1991):

$$\frac{A_{t_2}}{A_{t_1}} = \exp\{\alpha_A(t_2 - t_1)\} \qquad (2-29)$$

and

$$\frac{B_{t_2}}{B_{t_1}} = \exp\{\alpha_B(t_2 - t_1)\}, \qquad (2-30)$$

respectively. The parameters α_A and α_B, respectively called the water and solute compaction factors, typically increase with the feed water pressure and temperature.

CHAPTER 3

METHODS AND MATERIALS

This section presents a description of the RO membrane, feed solutions, test apparatus, experimental design and analytical methods used in this study.

RO Membrane

The RO membrane investigated was the thin-film composite FilmTec FT-30 Type BW30 provided by FilmTec Corporation, Minneapolis, Minnesota. This membrane is used in the manufacture of commercial spiral-wound elements utilized for brackish water desalination.

A schematic representing the thin-film composite structure of the FT-30 membrane is shown in Figure 3-1. An active RO film approximately 0.25 μm thick is supported by a 50 μm thick microporous polysulfone layer with pore diameters of about 0.02 to 0.03 μm at the confluence with the active layer. These two layers are further supported by a 120 μm thick non-woven polyester web (Larson et al, 1983).

The active layer of the FT-30 membrane is a homogeneous film of fully aromatic polyamide resulting from the reaction of *m*-phenylenediamine and trimesoylchloride (Petersen et al, 1982). The monomer structure for this polymeric material is shown in Figure 3-2. Performance specifications for a commercial spiral-wound element manufactured with the FT-30 membrane used in this study are presented in Table 3-1.

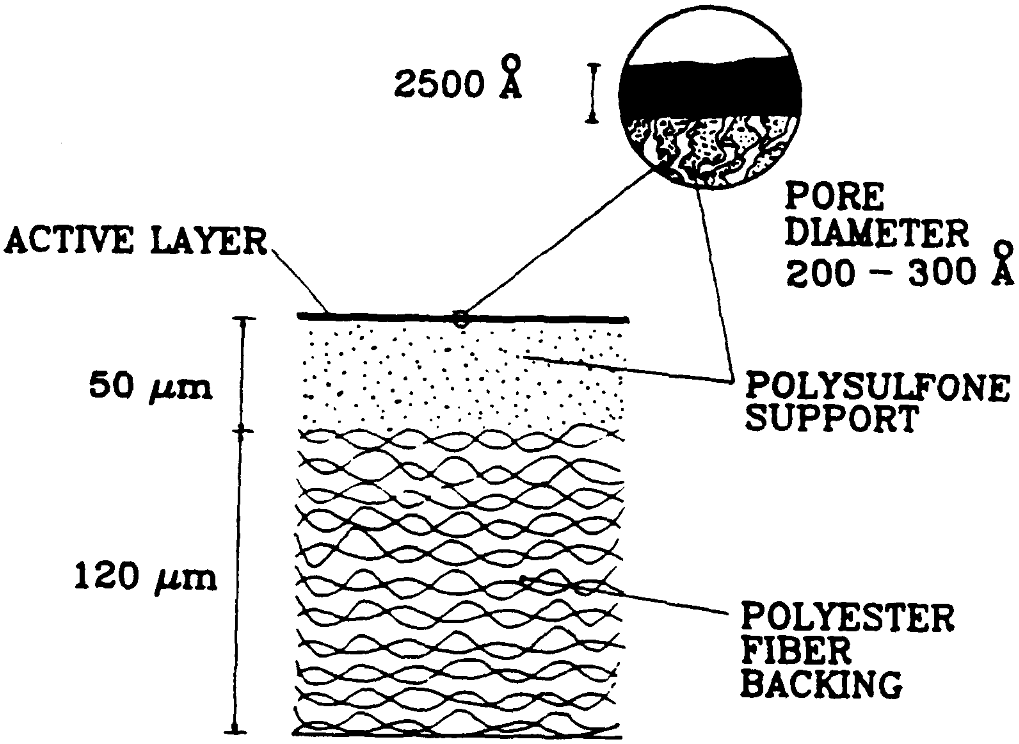

Figure 3-1. Schematic of thin-film composite FT-30 membrane.

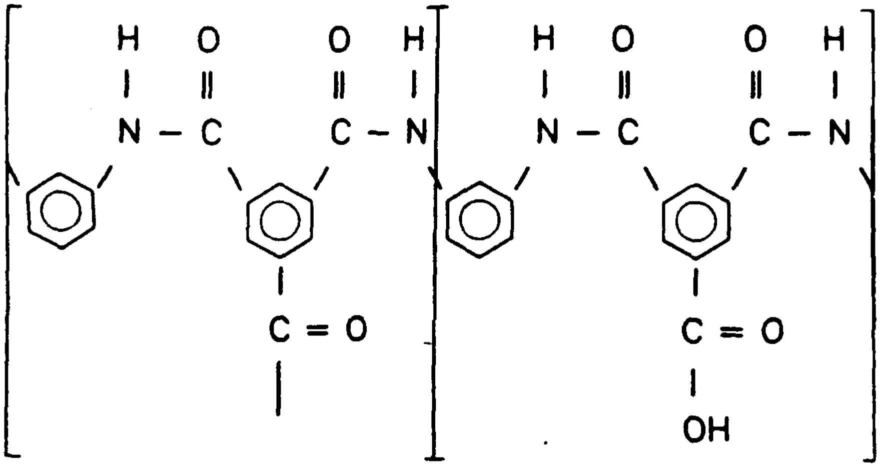

Figure 3-2. Structure of FT-30 membrane monomer.

Table 3-1. Specifications for the FT-30 spiral-wound element model BW30-8040.

Dimensions	
Nominal Diameter (in)	8
Length (in)	40
Estimated Membrane Active Area (ft^2)	300
Feed Water Conditions	
Composition	2,000 mg/L NaCl
Pressure (psi)	225
Temperature (°C)	25
pH	8
Element Performance[a]	
Water Productivity[b] (gpd)	7,500
Product Water Recovery (%)	15
Solute Rejection (%)	
Average	98
Minimum	96

[a] Subsequent to 30 minutes of operation under the specified feed water composition

[b] Individual element productivity may vary ±15 percent from the stated value

Feed Solutions

The feed solutions were prepared and mixed in an 80-L tank by adding reagent grade chemicals to water produced from a centralized water purification system which includes cation, anion and mixed-bed ion exchange plus granular activated carbon adsorption processes. The compositions of ten (10) feed solutions tested are presented in Table 3-2.

Table 3-2. Target feed solution compositions.

		Concentration (mg/L)			
Target $[Cl^-]/[SO_4^=]$	Code	Cl^-	$SO_4^=$	Cd(II)	Cr(VI)
100/0	I-1-0	603	0	0	0
	I-2-0	1,200	0	0	0
	I-1-10	589	0	10	10
	I-2-10	1,173	0	10	10
	I-3-10	1,656	0	10	10
	I-2-100	1,212	0	100	100
90/10	II-2-10	938	231	10	10
50/50	III-2-10	530	1,249	10	10
25/75	IV-2-10	349	1,696	10	10
0/100	V-2-10	35	1,860	10	10

Solutions I-1-0 and I-2-0 contain only sodium chloride (NaCl). The target concentrations for these solutions were 1,000 and 2,000 mg/L of NaCl, respectively. The latter of these solutions was selected so that the performance of the membrane could be compared to manufacturer's specifications given in Table 3-1.

Solutions I-1-10, I-2-10, and I-3-10 were prepared at target concentrations of 1,000, 2,000 and 3,000 mg/L NaCl, respectively. Cadmium chloride (as Cd) and sodium chromate (as Cr) were also added at 10 mg/L each to all three feed solutions. The target composition of solution I-2-100 was 2,000 mg/L NaCl, 100 mg/L $CdCl_2$ (as Cd), and 100 mg/L Na_2CrO_4 (as Cr).

Solutions II-2-10, III-2-10 and IV-2-10 were combinations of sodium chloride and sodium sulfate with chloride to sulfate target molar ratios of 90/10, 50/50 and 25/75. The only major electrolyte in solution V-2-10 was sodium sulfate. The concentrations of sodium chloride and sodium sulfate added corresponded to a target osmotic pressure of 23.4 psi, equal to that for the 2,000 mg/L NaCl solution. All four solutions also contained 10 mg/L of each $CdCl_2$ (as Cd), and Na_2CrO_4 (as Cr).

With the exception of solution I-2-10, the pH of all other solutions was adjusted to pH 6.0±0.1 with reagent grade concentrate hydrochloric acid and sodium hydroxide. Solution I-2-10 was tested at pH values of 5, 6 and 7.

Test Apparatus

Figures 3-3 and 3-4 show a schematic and a photograph of the experimental apparatus used for this study. The apparatus was a closed loop unit Model SEPA CF-HP (Osmonics, Inc., Minnetonka, Minnesota).

Feed solutions were prepared in a 80-liter feed-tank. The solutions were pressurized and circulated through the RO cell with a positive displacement pump CAT Model 230. This pump was rated at 2.3 gpm and a maximum pressure of 800 psi. A high pressure relief valve was installed on a second discharge port of the pump provided for that purpose and both the concentrate and the permeate were cycled back into the feed tank.

The RO cell was designed to encase a flat-leaf coupon of any thin-film composite RO membrane. A photograph of the cell is shown in Figure 3-5. The cell body, rated at 1,000 psi, consists of two stainless-steel 316 halves. A 34-mil thick spacer web of the type used in commercial spiral-wound elements was inserted in the feed water channel (lower half-cell) to promote turbulence with the goal of minimizing the detrimental effects of concentration-polarization. The membrane sheet was supported by a permeate carrier inserted in upper half-cell. The membrane active surface area exposed to the feed flow was 4 x 6 inches, or approximately 0.165 ft^2.

The two halves of the RO cell were held in place with a hydraulic piston which applied a uniform pressure of 900 psi against the cell during operation (see Figure 3-5). The piston pressure was applied by a hydraulic hand pump. A Viton O-ring was placed in contact with the feed side of the membrane to seal the feed channel from the permeate side.

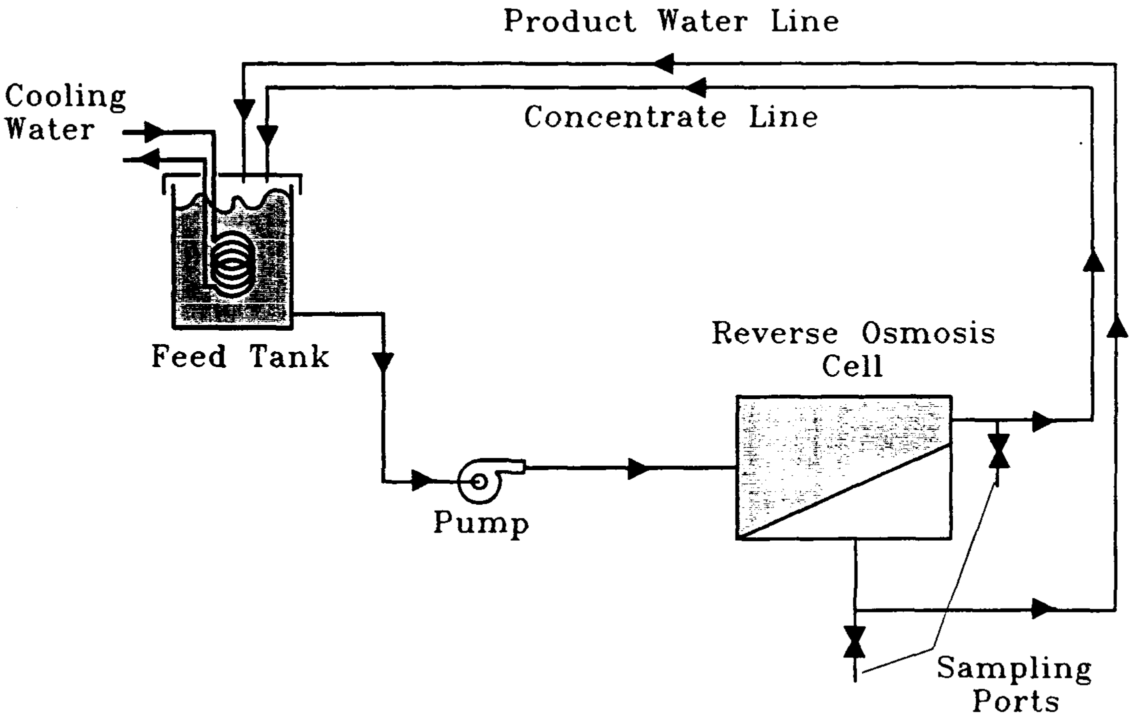

Figure 3-3. Schematic of experimental apparatus.

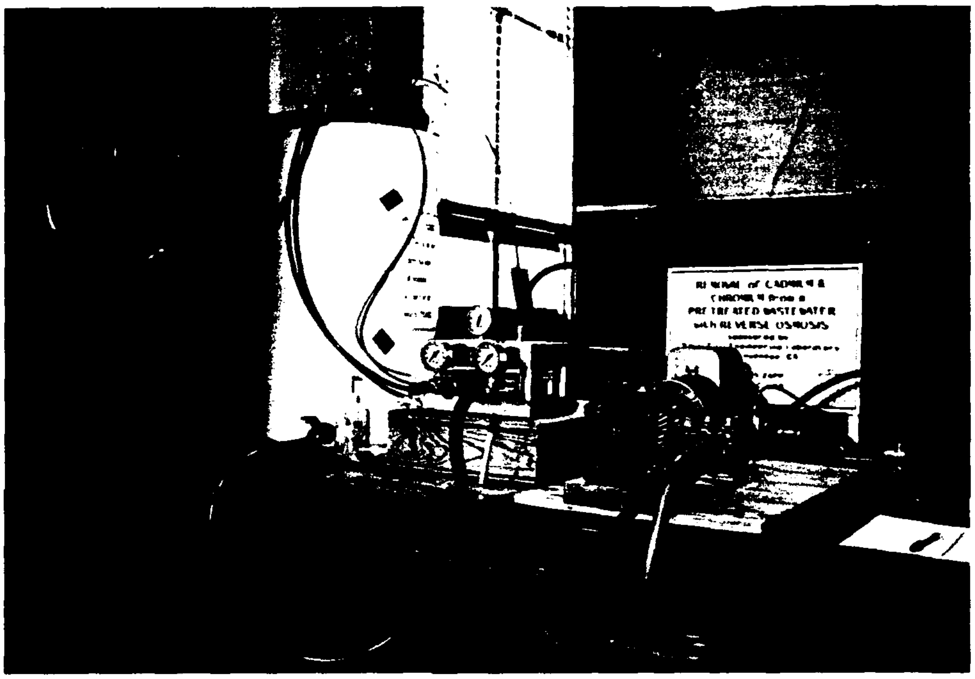

Figure 3-4. Photograph of experimental apparatus.

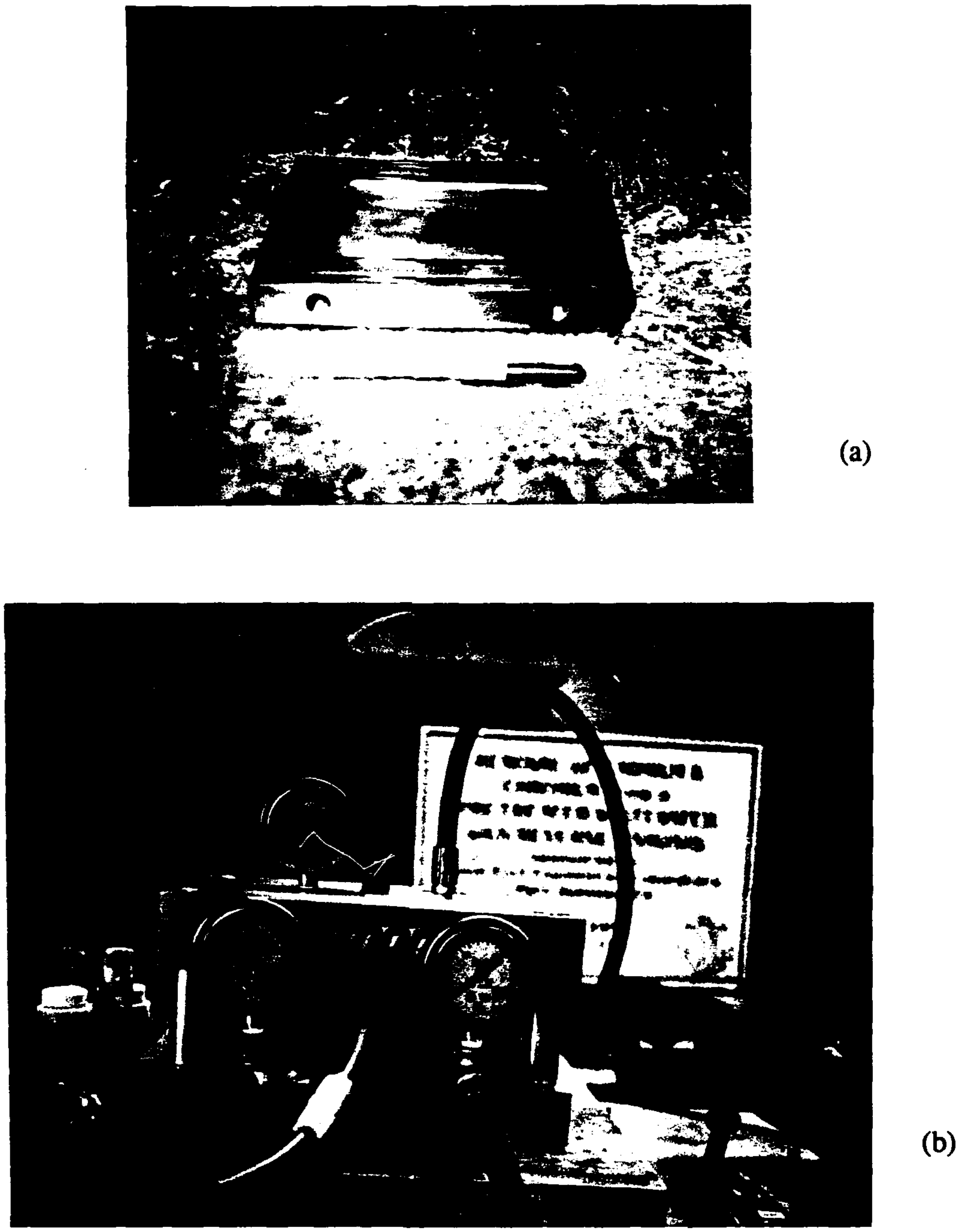

Figure 3-5. Photograph of RO cell(a) and cell holder(b).

The feed water inlet is on the right of the cell body and flow moves through a manifold into the membrane cavity. Here the solution flow is turbulent and moves tangentially across the membrane. The concentrate leaves the cavity, enters a manifold and leaves the cell body on the left side. Again, it was at this port that the needle valve used to control system pressure across the membrane was located.

Feed and concentrate stream pressures were measured with pressure gauges installed immediately next to the cell inlet and outlet ports. A needle valve in the concentrate line was used to set the target operating pressure inside the cell. After depressurization, the concentrate stream was sampled and finally returned to the feed tank.

The permeate flows through the top half-cell permeate carrier and into holes 1.4 mm in diameter located in the center of the half-cell. The permeate leaving the cell was sampled and returned to the feed tank so that the feed solution concentration was maintained approximately constant.

The pH of the feed solution inside the feed tank was monitored continuously with a pH meter Orion Model 501. A glass thermometer attached to a stainless steel rod was used to monitor the feed tank temperature.

Feed solution temperature was controlled at 25°C with cold tap water circulated through a 1/4-inch stainless steel tubing coil immersed in the feed tank. The target temperature was not always obtainable because of fluctuations in tap water temperature. A needle valve was installed on the water line to minimize these effects.

Concentrate and permeate flow rates were measured volumetrically with a graduated cylinder. The turbulence created by the returning concentrate flow rate of 2.3 gpm was sufficient to provide good mixing inside the feed tank.

Experimental Design

A number of experiments were performed with the experimental apparatus previously described. Preliminary testing was followed by an initial assessment of membrane stabilization as well as the effects of temperature and operating pressure on membrane performance. Subsequently, the effects of feed solution concentration, pH, and composition on membrane performance were also investigated.

Preliminary Testing

The first experimental task was to run some preliminary tests with the goal of removing debris from the surfaces of the unit components that might eventually have produced membrane fouling to some extent. The RO unit was operated with solution I-2-0 and a sacrificial membrane coupon during a twenty (20) hour period for this purpose.

Initial Tests without Metals

A second membrane coupon was installed after the preliminary runs were completed. All experiments described subsequently were performed with this coupon. A summary of all tests performed and their corresponding operating conditions is presented in chronological order in Table 3-3.

The objective for the first set of tests performed was to investigate membrane compaction. Solution I-2-0 (see Table 3-2) was tested for 54.4 hours at constant feed pressure of 400 psi. The target temperature for most tests was 25°C. Temperature dependence was investigated in the range of 20 to 36°C between operating times 47.8 and 54.4 hours.

An additional test with solution I-2-0 was performed between operating times 139.7 and 150.0 hours.

The effect of varying operating pressure on membrane performance was investigated between operating times 54.4 and 63.3. The two additional pressures studied were 200 and 300 psi.

A test was also performed with solution I-1-0 (see Table 3-2) between operating times 63.3 and 67.8 hours. The objective of this experiment was to assess the effect of feed solution concentration on membrane performance in the absence of metals.

Concentration Dependence Tests

The effect of feed solution composition on membrane performance in the presence of metals was studied between operating times 67.8 and 109.8 hours. The solution tested were I-1-10, I-2-10, and I-3-10 corresponding to target feed concentrations of 1,000, 2,000, and 3,000 mg/L of NaCl and 10 mg/L each of cadmium (II) and chromium (VI) in all cases (see Table 3-2). Each solution was tested at operating pressures of 200, 300 and 400 psi, a temperature of 25°C, and a pH of 6.

Table 3-3. Summary of experiments performed and target operating conditions.

		Target Experimental Conditions		
Testing Period (hrs)	Solution Code	Temperature (°C)	pH	Pressure (psi)
0 - 47.8	I-2-0	25	6	400
47.8 - 54.4	I-2-0	20 - 36	6	400
54.4 - 59.5	I-2-0	25	6	300
59.5 - 63.3	I-2-0	25	6	200
63.3 - 67.8	I-1-0	25	6	400
67.8 - 71.0	I-1-10	25	6	400
71.0 - 75.3	I-1-10	25	6	300
75.3 - 78.6	I-1-10	25	6	200
78.6 - 83.6	I-1-10	25	6	400
83.6 - 86.9	I-1-10	25	6	300
86.9 - 90.2	I-1-10	25	6	200
90.2 - 94.4	I-2-10	25	6	400
94.4 - 96.4	I-2-10	25	6	300
96.4 - 99.7	I-2-10	25	6	200
99.7 - 104.0	I-3-10	25	6	400
104.0 - 106.3	I-3-10	25	6	300
106.3 - 109.8	I-3-10	25	6	200
109.8 - 114.0	III-2-10	25	6	400
114.0 - 116.3	III-2-10	25	6	300
116.3 - 119.7	III-2-10	25	6	200
119.7 - 124.0	IV-2-10	25	6	400
124.0 - 126.3	IV-2-10	25	6	300
126.3 - 129.3	IV-2-10	25	6	200

Table 3-3, continued.

		Target Experimental Conditions		
Testing Period (hrs)	Solution Code	Temperature (°C)	pH	Pressure (psi)
129.3 - 134.0	V-2-10	25	6	400
134.0 - 136.2	V-2-10	25	6	300
136.2 - 139.7	V-2-10	25	6	200
139.7 - 150.0	I-2-0	25	6	400
150.0 - 155.2	I-2-10	25	5	400
155.2 - 157.5	I-2-10	25	5	300
157.5 - 161.5	I-2-10	25	5	200
161.5 - 166.5	I-2-10	25	7	400
166.5 - 168.8	I-2-10	25	7	300
168.8 - 172.0	I-2-10	25	7	200
172.0 - 176.3	I-2-10	25	6	400
176.3 - 178.4	I-2-10	25	6	300
178.4 - 181.6	I-2-10	25	6	200
181.6 - 187.2	I-2-100	25	6	400
187.2 - 189.8	I-2-100	25	6	300
189.8 - 193.0	I-2-100	25	6	200
193.0 - 198.3	II-2-10	25	6	400
198.3 - 201.5	II-2-10	25	6	300
201.5 - 205.5	II-2-10	25	6	200

The 2,000 mg/L sodium chloride feed solution was also tested (between operating times 181.6 and 193.0 hours) with 100 mg/L each of cadmium (II) and chromium (VI) to study the effect of varying metal concentration on membrane performance.

Composition Dependence Tests

The effect of solution composition was investigated between operating times 109.8 and 139.7 hours, and between 193.0 and 205.5 hours. Tests were performed with feed solutions of sodium sulfate and combination of sodium chloride and sodium sulfate in addition to the sodium chloride solutions. As in previous tests, the target concentration for cadmium (II) and chromium (VI) were 10 mg/L each (see Table 3-2). Each solution was tested at operating pressures of 200, 300 and 400 psi, a temperature of 25°C, and pH 6.

pH Dependence Tests

The dependence of membrane performance on feed solution pH was studied between operating times 150.0 and 181.6 hours. The pH investigated were 5, 6 and 7. The feed solution selected for these tests was I-2-10, or 2,000 mg/L sodium chloride, and 10 mg/L each of cadmium (II) and chromium (VI) (see Table 3-2). Each solution was tested at operating pressures of 200, 300 and 400 psi, and a temperature of 25°C.

Experimental Procedures

The following precautions were taken to ensure that the RO membrane coupon would not leak or rupture during installation. The back surface of the membrane coupon (i.e., support side) was first rinsed with deionized water and then with a 2000 mg/L solution of sodium chloride. This was done to avoid membrane rupture as a result of an osmotic shock.

Next, the permeate carrier was also soaked with the 2,000 mg/L sodium chloride solution so that it would remain in place during assembly of the cell body. Subsequently, the two half-cells were coupled after inserting the membrane coupon and the feed spacer. Finally, the hydraulic hand pump was used to activate the hydraulic press until a pressure of 900 psi was achieved. A small needle valve was used to control a small leak in the hydraulic pump which resulted in a slow loss of pressure with time.

The first task for each operating day was to start the RO pump after checking that the pressure control valve was fully open. Next, the control valve was slowly closed until the desired operating pressure was reached. After setting the pressure, the membrane was allowed to stabilize for approximately four hours before taking samples and measuring the flow rate. When pressure was changed in the middle of an experimental day, it was observed that only two (2) hours of stabilization were required when changing the pressure from 400 to 300 psi, and three (3) hours were necessary when changing from 330 to 200 psi. The unit was shut off at the end of each experimental day throughout the course of the experiments. Before turning off the RO pump, the pressure control valve was slowly, gently open to avoid osmotic shocks. This process took approximately 10 minutes.

Analytical Methods

Feed and permeate samples were analyzed for chloride and sulfate ion concentrations with an ion chromatograph Dionex Model 2000i/SP in accordance with Method 4110, (eluant composition: 0.0028M $NaHCO_3$, 0.0022M Na_2CO_3; and regenerant composition: 0.025N H_2SO_4) described in Standard Methods for the Examination of Water and Wastewater.

Cadmium and total chromium concentrations were determined by emission spectroscopy using inductively coupled plasma (ICP). The analyses were performed at Naval Air Warfare Center-Aircraft Division-Indianapolis analytical facilities with a Thermo Jerrell Ash ICP Model Atomscab 25. With the exception of sample preparation (i.e., samples were neither filtered nor digested), Method 3120B described in Standard Methods for the Examination of Water and Wastewater was followed. Concentrations reported are the average of four replicate measurements. The method detection limits were 0.01 ppm for cadmium, and 0.02 ppm for total chromium.

CHAPTER 4

RESULTS AND DISCUSSION

Experimental observations for all tests described in Chapter 3 are contained in Tables A-1 and A-2 of the Appendix. These data include operating conditions (elapsed time, applied hydraulic pressure, and temperature), permeate flow rate, and feed water and permeate quality data (pH, and chloride, sulfate, cadmium (II) and chromium (VI) concentrations). This information was analyzed to determine the effect of operating conditions and feed water quality on FT-30 membrane performance efficiency. The results from these efforts are presented in this chapter.

Solute concentrations from Table A-2 in the Appendix were used with Equation 2-25 to calculate the osmotic pressure of feed solutions for all tests. The concentration of sodium, not determined analytically, was assumed to be that required to achieve electrical neutrality in all solutions.

Permeate flux values were calculated by dividing the observed permeate flow rates presented in Table A-1 of the Appendix by the active membrane area in the RO cell. The resulting permeate fluxes were then divided by the corresponding net driving force, i.e., $(\Delta p - \Delta\pi)$, to estimate water permeation coefficients A according to Equation 2-19. For this calculation, the hydraulic pressure gradient Δp was assumed equal to the applied hydraulic pressure p_f given in Table A-1 of the Appendix, or $p_p = 0$, and the permeate osmotic pressure π_p was neglected, or $\Delta\pi \approx \pi_f$.

Calculated values for feed osmotic pressure, permeate flux and water permeation coefficients are presented in Table 4-1. Feed and permeate concentrations contained in Table A-2 of the Appendix for chloride, sulfate, cadmium (II), and chromium (VI) were also used to compute the apparent solute passage parameters using Equation 2-22. The results from this effort are presented in Table 4-2.

The performance of the flat leaf BW30 membrane coupon is comparable to the FT-30 spiral-wound model BW30-8040. The system was operated at 200 psi with a 2000 mg/L sodium chloride solution (pH 6; 25°C) for this purpose and the solute rejection was 97.4 percent (Table 4-2; 63.25 hours) which is within the manufacturer's specifications cited in Table 3-1.

Effect of Temperature on Water Permeation

The continued pressurization/depressurization cycle in the closed loop unit resulted in tendency for the temperature of the feed solution to increase. For this reason, cold tap water was circulated through a cooling coil immersed in the feed tank. Although for most tests the temperature was maintained at approximately the target of 25°C, oscillations in the range of 22 to 28°C were observed during days in which the tap water temperature tended to oscillate.

Experiments were performed to determine the effect of temperature in the range of 20 to 36°C on both water and solute passage (see Tables A-1 and A-2 in the Appendix).

These were performed in a narrow operating time range, i.e., between 47.75 and 54.42 hours, to minimize the simultaneous effect of membrane compaction which is analyzed in the next section.

Table 4-1. Feed solution osmotic pressure, permeate flux, and water permeation coefficient.

Feed Solution Code[a]	Time t (hour)	Feed Osmotic Pressure π_f (psi)	Permeate Flux J_v (gpd/ft^2)	Water Permeation Coefficient A (gpd/ft^2)
I-2-0	4.00	20.5	50.611	1.960
	8.00	20.5	43.940	1.702
	14.00	21.1	41.984	1.629
	23.75	22.7	41.409	1.613
	31.50	22.6	40.029	1.559
	36.50	22.1	38.189	1.486
	43.75	22.9	42.329	1.650
	47.75	22.9	37.958	1.480
	50.25	22.9	31.057	1.211
	52.42	22.9	46.240	1.803
	54.42	22.9	53.832	2.098
	59.50	23.2	26.456	1.405
	63.25	23.2	16.104	1.339
I-1-0	67.75	11.8	37.038	1.403
I-1-10	71.00	11.3	37.958	1.436
	75.33	11.3	27.376	1.394
	78.58	11.3	17.944	1.398
	83.60	11.5	36.658	1.349
	86.85	11.5	26.456	1.348
	90.18	11.5	17.599	1.372
I-2-10	94.43	22.7	34.048	1.327
	96.43	22.7	25.076	1.329
	99.68	22.7	16.104	1.335
I-3-10	104.00	31.8	32.207	1.286
	106.33	31.8	21.855	1.198
	109.75	31.8	14.723	1.287

[a] See Table 3-2 for target feed solution composition

Table 4-1, continued.

Feed Solution Code[a]	Time t (hour)	Feed Osmotic Pressure π_f (psi)	Permeate Flux J_v (gpd/ft^2)	Water Permeation Coefficient A (gpd/ft^2)
III-2-10	114.00	22.4	30.482	1.187
	116.33	22.4	19.554	1.036
	119.67	22.4	13.288	1.095
IV-2-10	124.00	23.2	27.031	1.055
	126.25	23.2	19.324	1.026
	129.33	23.2	12.883	1.071
V-2-10	134.00	18.9	27.606	1.065
	136.17	18.9	19.784	1.035
	139.67	18.9	12.860	1.044
I-2-0	145.00	21.7	25.306	0.983
	150.00	21.7	27.606	1.073
I-2-10	155.17	20.3	26.456	1.024
	157.50	20.3	19.324	1.016
	161.50	20.3	12.883	1.054
	166.50	21.6	25.306	0.983
	168.83	21.6	19.554	1.033
	172.00	21.6	12.423	1.024
	176.25	21.6	25.076	0.974
	178.42	21.6	19.278	1.018
	181.58	21.6	12.423	1.024
I-2-100	187.17	23.4	25.306	0.988
	189.83	23.4	18.404	0.978
	193.00	23.4	11.733	0.977
II-2-10	198.33	20.4	27.606	1.069
	201.50	20.4	18.404	0.968
	205.50	20.4	11.963	0.979

[a] See Table 3-2 for target feed solution composition

Table 4-2. Calculated solute passages (*SP*) for chloride, sulfate, cadmium(II) and chromium (VI).

		SP (%)			
Feed Solution Code[a]	Time t (hour)	Chloride	Sulfate	Cadmium (II)	Chromium (VI)
I-2-0	4.00	1.71	--	--	--
	8.00	1.52	--	--	--
	14.00	1.33	--	--	--
	23.75	1.43	--	--	--
	31.50	1.43	--	--	--
	36.50	1.44	--	--	--
	43.75	1.37	--	--	--
	47.75	1.28	--	--	--
	50.25	1.29	--	--	--
	52.42	1.37	--	--	--
	54.42	1.43	--	--	--
	59.50	1.97	--	--	--
	63.25	2.63	--	--	--
I-1-0	67.75	1.98	--	--	--
I-1-10	71.00	4.37	--	2.35	4.19
	75.33	5.36	--	3.02	4.98
	78.58	6.45	--	3.14	5.77
	83.60	5.83	--	3.49	5.92
	86.85	6.22	--	3.15	5.92
	90.18	7.7	--	4.17	6.77
I-2-10	94.43	6.5	--	4.38	6.34
	96.43	6.75	--	3.92	6.47
	99.68	8.19	--	4.61	7.12
I-3-10	104.00	8.51	--	3.89	6.38
	106.33	7.82	--	5.72	7.03
	109.75	9.07	--	6.41	7.43

[a] See Table 3-2 for target feed solution composition

Table 4-2, continued.

Feed Solution Code[a]	Time t (hour)	SP (%)			
		Chloride	Sulfate	Cadmium (II)	Chromium (VI)
III-2-10	114.00	2.61	1.48	0.55	1.10
	116.33	2.69	1.41	0.44	0.88
	119.67	3.36	1.42	0.44	0.88
IV-2-10	124.00	2.26	1.18	0.59	1.87
	126.25	2.55	1.17	0.59	1.77
	129.33	2.97	1.16	0.20	2.18
V-2-10	134.00	5.43	1.17	0.39	1.99
	136.17	5.91	1.15	0.10	2.19
	139.67	6.93	1.22	0.39	2.58
I-2-0	145.00	2.31	--	--	--
	150.00	2.55	--	--	--
I-2-10	155.17	2.86	--	1.60	2.69
	157.50	3.14	--	1.63	2.79
	161.50	3.88	--	1.81	3.12
	166.50	3.36	--	1.32	2.28
	168.83	3.55	--	1.13	2.20
	172.00	4.21	--	1.39	2.35
	176.25	3.72	--	1.65	2.82
	178.42	4.01	--	1.54	2.79
	181.58	4.79	--	1.65	3.08
I-2-100	187.17	3.46	--	2.32	3.10
	189.83	3.69	--	2.52	2.99
	193.00	4.08	--	2.27	3.16
II-2-10	198.33	3.05	2.41	1.65	2.92
	201.50	3.49	2.59	1.71	3.03
	205.50	4.48	3.71	1.78	3.42

[a] See Table 3-2 for target feed solution composition

Equation 2-26 was used to analyze the effect of temperature on the water permeation coefficients given in Table 4-1. A semilog plot of A against 1/T values is presented in Figure 4-1. The linearity of the data in this plot supports the validity of Equation 2-26. The resulting expression is:

$$\log A = 4.69 - \frac{1,350}{\mathrm{T}} \qquad (4-1)$$

In principle, Equation 4-1 only applies to the operating time range of 47.75 to 54.42 hours. However, even though the absolute value of A at a given temperature changes with time as a result of membrane compaction, the slope of the Arrhenius type plot might not change with operating time. If this assumption is valid, then the following expression could be used to correct all A values to the target temperature of 25°C:

$$A_{25} = A_{\mathrm{T}} 10^{1,350\left(\frac{1}{\mathrm{T}} - \frac{1}{298}\right)} \qquad (4-2)$$

where T is in Kelvin.

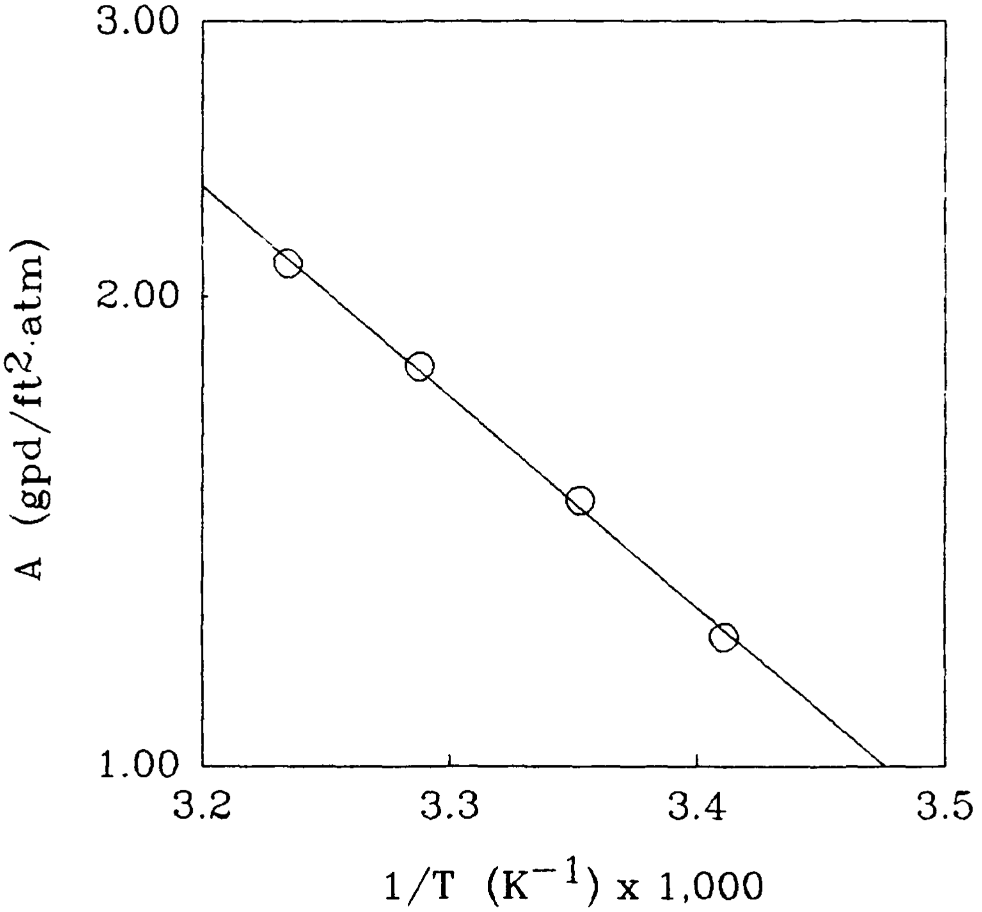

Figure 4-1. Temperature dependence of *A* coefficient.

Effect of Membrane Compaction on Water Permeability

Equation 4-2 was used to normalize all A coefficients to 25°C. The resulting coefficients A_{25} for all solutions tested are presented versus elapsed operating time in the semilog plot shown in Figure 4-2. With the exception of the first few operating hours, the time dependence for A_{25} follows Equation 2-26. The expression representing the plot in Figure 4-2 is:

$$A_{25} = 1.73\exp(-0.001363t) \qquad (4-3)$$

The results shown in Figure 4-2 indicate that water permeation was not affected by feed solution composition or concentration within the ranges investigated.

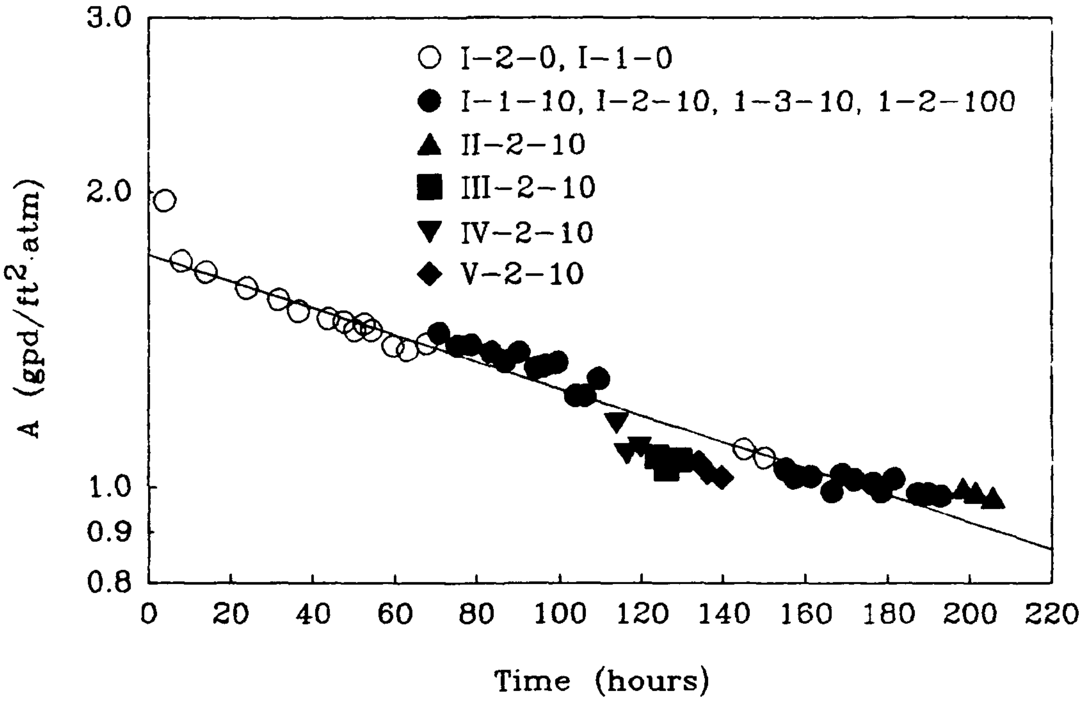

Figure 4-2. Effect of membrane compaction on A_{25} .

Linear Plot Analysis of Solute Permeation Results

Solution I-2-0 (see Table 3-2), the first feed solution tested at varying applied hydraulic pressures, was tested at 400, 300 and 200 psi after 47.75, 59.50, and 63.25 hours of operation, respectively. The permeate fluxes and solute passages (chloride ions) for these tests (see Tables 4-1 and 4-2) were used to calculate SP/SR and $1/J_v$ values plotted in Figure 4-3 according to Equation 2-21. Assuming negligible concentration-polarization, the linearity of the data in this plot supports the validity of Equation 2-21, even after neglecting the effects of membrane compaction and fluctuations in feed temperature (see table A-1 in Appendix). The intercept with the vertical axis $((1-\sigma)/2\sigma)$ and the slope of the line (B/σ) were used to compute the solute permeation and reflection coefficients $B = 0.0375$ ft/day and $\sigma = 0.9818$ which are also presented in Table 4-3.

Compaction is known to affect solute permeation coefficients (Mariñas and Selleck, 1991). Unfortunately the only feed solution composition that was tested more than once (but only twice), at the three levels of hydraulic pressure (i.e., 400, 300 and 200 psi) required to determine B and σ was solution I-2-10. The first of these two sets of tests was performed between operating times 94.43 and 99.68 hours, and the second between 176.25 and 181.58 hours. Linear plots of SP/SR ratios versus $1/J_v$ for these two tests are shown in Figures 4-4, 4-5 and 4-6, for chloride, cadmium (II), and chromium (VI), respectively. The B and σ coefficients calculated for the vertical axis interception and slope are presented in Table 4-3. Both solute permeation coefficients decreased significantly for all three solutes. For example, in the case of chloride, B decreased 52 percent from 0.0762 to 0.0366 ft/day, and $(1 - \sigma)$ decreased 43 percent from 0.0902 to 0.0513.

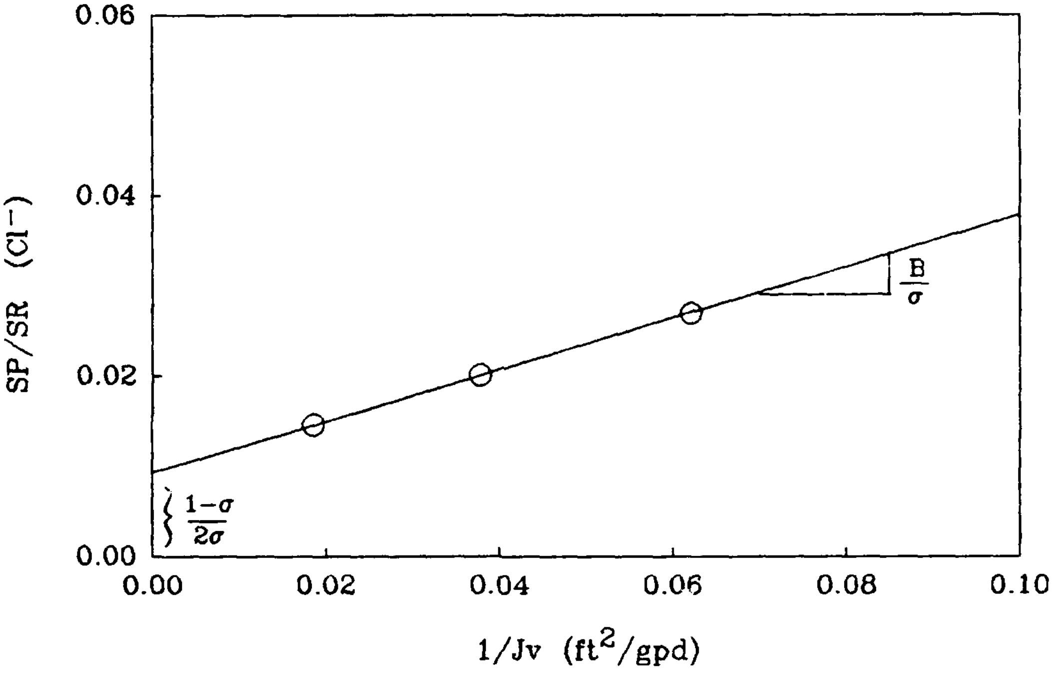

Figure 4-3. Linear plot of solute permeation data for tests performed between elapsed times 47.75 and 63.25 hours with feed solution I-2-0.

Table 4-3. Solute Permeation and Reflection Coefficients (*B* in ft/day, and σ dimensionless)

		Chloride		Sulfate		Cadmium (II)		Chromium (VI)	
Code	t (hr)	*B*	σ	*B*	σ	*B*	σ	*B*	σ
I-2-0	47.75 59.50 63.25	0.0375	0.9818	--	--	--	--	--	--
I-1-10	71.00 75.33 78.58	0.0981	0.9495	--	--	0.0327	0.9631	0.0732	0.9442
I-1-10	83.60 86.85 90.18	0.0954	0.9274	--	--	0.0379	0.9520	0.0435	0.9066
I-2-10	94.43 96.43 99.68	0.0762	0.9098	--	--	0.0146	0.9263	0.0338	0.8947
I-3-10	104.00 106.33 109.75	0.0255	0.8593	--	--	0.0932	0.9588	0.0378	0.8938
III-2-10	114.00 116.33 119.67	0.0246	0.9623	NS[a]	0.9702	NS[a]	0.9880	NS[a]	0.9761
IV-2-10	124.00 126.25 129.33	0.0240	0.9683	NS[a]	0.9762	NS[a]	0.9797	0.0117	0.9713
V-2-10	134.00 136.17 139.67	0.0505	0.9218	0.00157	0.9779	0.00191	0.9957	0.01958	0.9713
I-2-10 pH = 5	155.17 157.50 161.50	0.0357	0.9641	--	--	0.00750	0.9730	0.0148	0.9559
I-2-10 pH = 7	166.50 168.83 172.00	0.0291	0.9515	--	--	0.00407	0.9781	0.00314	0.9581
I-2-10	176.25 178.42 181.58	0.0366	0.9487	--	--	0.00073	0.9689	0.00972	0.9516
I-2-100	187.17 189.83 193.00	0.0181	0.9428	--	--	NS[a]	0.9513	0.00267	0.9424
II-2-10	198.33 201.50 205.50	0.0425	0.9633	NS[a]	0.9759	0.00364	0.9693	0.0148	0.9515

[a] Negative slope

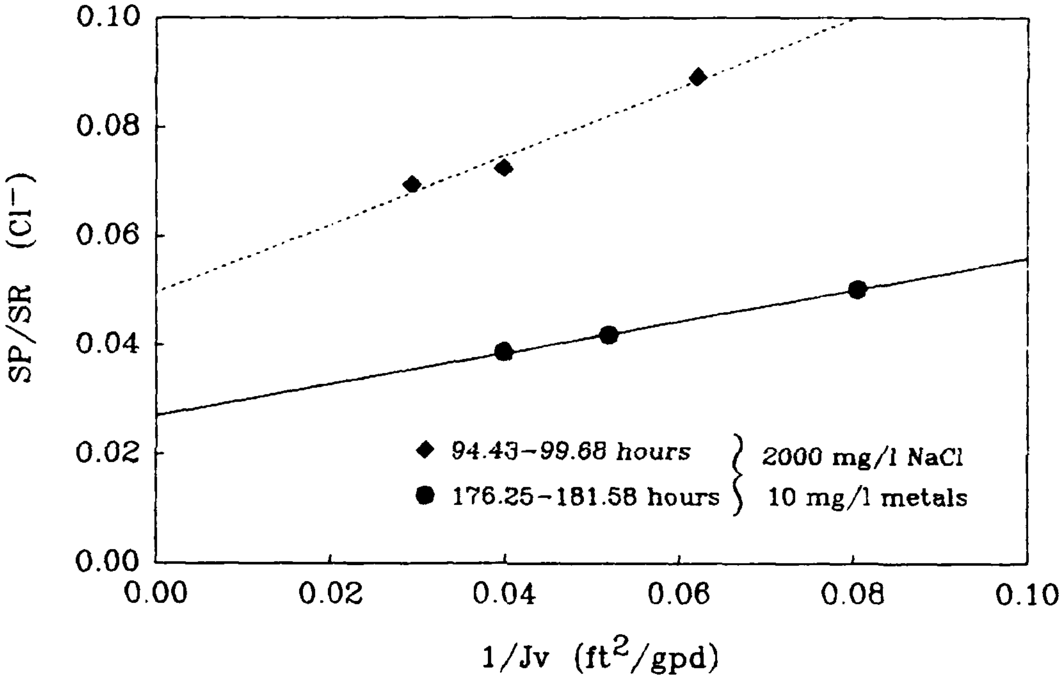

Figure 4-4. Effect of compaction on chloride permeation (tests performed between elapsed times 94.43 and 104.00 hours, and between 176.25 and 181.58 hours with feed solution I-2-10 defined in Table 3-2).

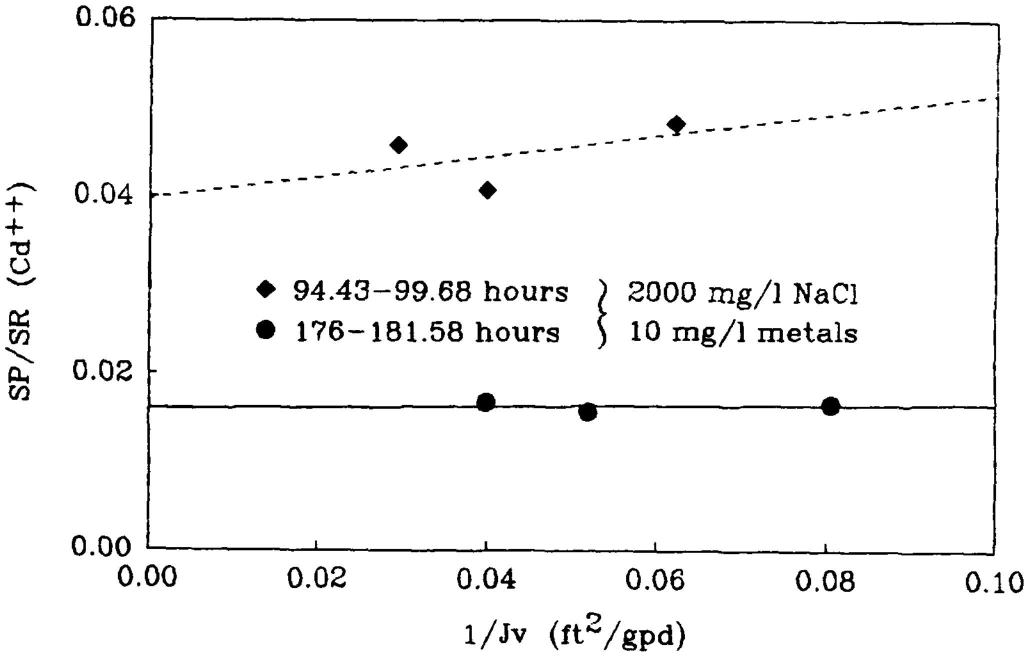

Figure 4-5. Effect of compaction on cadmium (II) permeation (tests performed between elapsed times 94.43 and 104.00 hours, and between 176.25 and 181.58 hours with feed solution I-2-10 defined in Table 3-2).

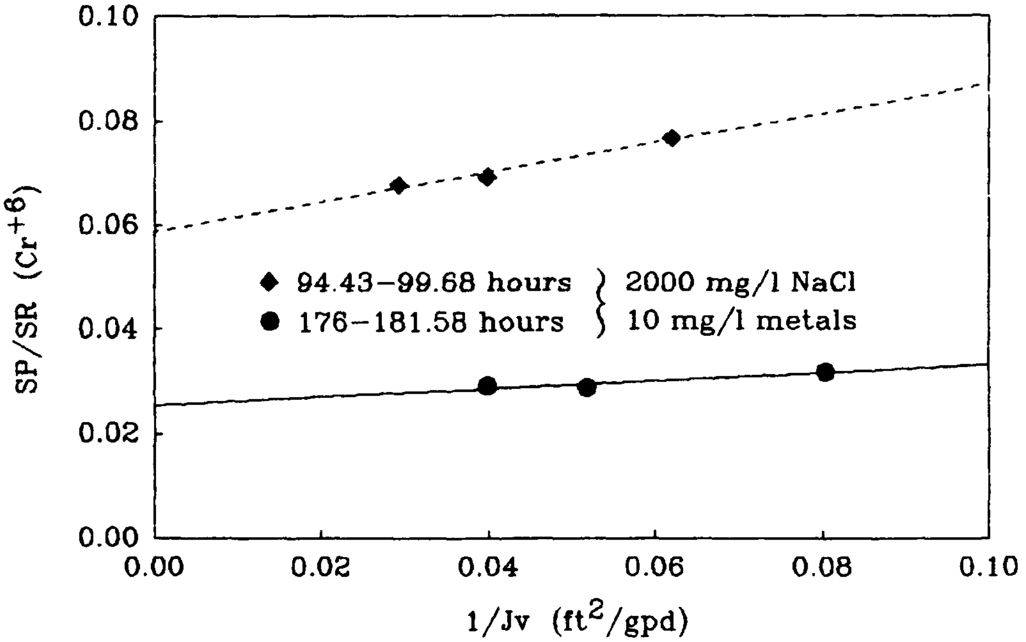

Figure 4-6. Effect of compaction on chromium (VI) permeation (tests performed between elapsed times 94.43 and 104.00 hours, and between 176.25 and 181.58 hours with feed solution I-2-10 defined in Table 3-2).

Concentration Dependence

The dependence of solute permeation on solution concentration was also investigated. Three sets of tests were performed with solutions I-1-10, I-2-10, and I-3-10 to study the effect of sodium chloride concentration on chloride, cadmium (II), and chromium (VI) removal. The target concentrations for these solutions were 1,000, 2,000 and 3,000 mg/L of sodium chloride, and 10 mg/L each of cadmium (II) and chromium (VI) (see Table 3-2). Each feed solution was tested at hydraulic pressures of 400, 300 and 200 psi.

The water fluxes observed are plotted versus applied hydraulic pressure in Figure 4-7. This figure presents an alternative for obtaining the water permeation parameter A with A being the slope of each of the three linens shown in Figure 4-7. Previously in Figures 4-1 and 4-2, A was calculated for each individual data point.

The slope for the three lines presented in Figure 4-7 are approximately identical. This demonstrates that the effect of concentration-polarization was negligible inside the RO cell because otherwise the slope of the lines should have decreased with increasing feed concentration (Mariñas and Selleck, 1991).

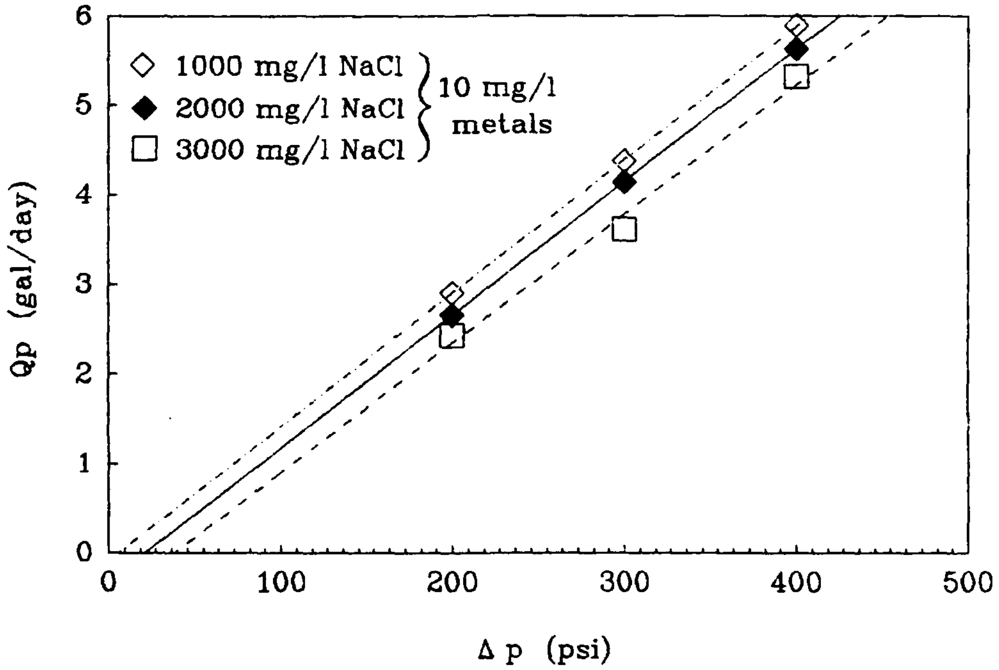

Figure 4-7. Water flux data corresponding to tests performed with feed solutions I-1-10, I-2-10, and I-3-10 after 83.60-90.18 hours, 94.43-99.68 hours, and 104.00-109.75 hours, respectively.

Linear plots for the chloride, cadmium (II), and chromium (VI) permeation data are shown in Figures 4-8, 4-9, and 4-10, respectively. The corresponding B and σ coefficients are presented in Table 4-3. No satisfactory explanation could be found for the apparently erratic behavior of the I-3-10 solution for chloride and cadmium (II). In the case of chromium (VI), feed solution concentration did not affect the permeation coefficients significantly. This behavior is consistent with observations from previous work with the FT-30 membrane model SW30 (Mariñas and Selleck, 1991).

A set of tests was performed with solution I-2-100 containing 2,000 mg/L sodium chloride plus cadmium (II) and chromium (VI) concentrations of 100 mg/L each between operating times 187.17 and 193.00 hours. The results are shown in Figures 4-11, 4-12 and 4-13 in terms of SP/SR ratios versus $1/J_v$ for chloride, cadmium (II) and chromium (VI), respectively. The results corresponding to tests performed with solution I-2-10, the same sodium chloride concentration and only 10 mg/L of the metals, between operating times 176.25 and 181.58 hours are also shown for comparison. The permeations of chloride and chromium (VI) were not affected significantly by the increase in metal concentration. The solute passage of cadmium (II), on the other hand, was approximately 47 percent greater for solution I-2-100 as compared to solution I-2-10.

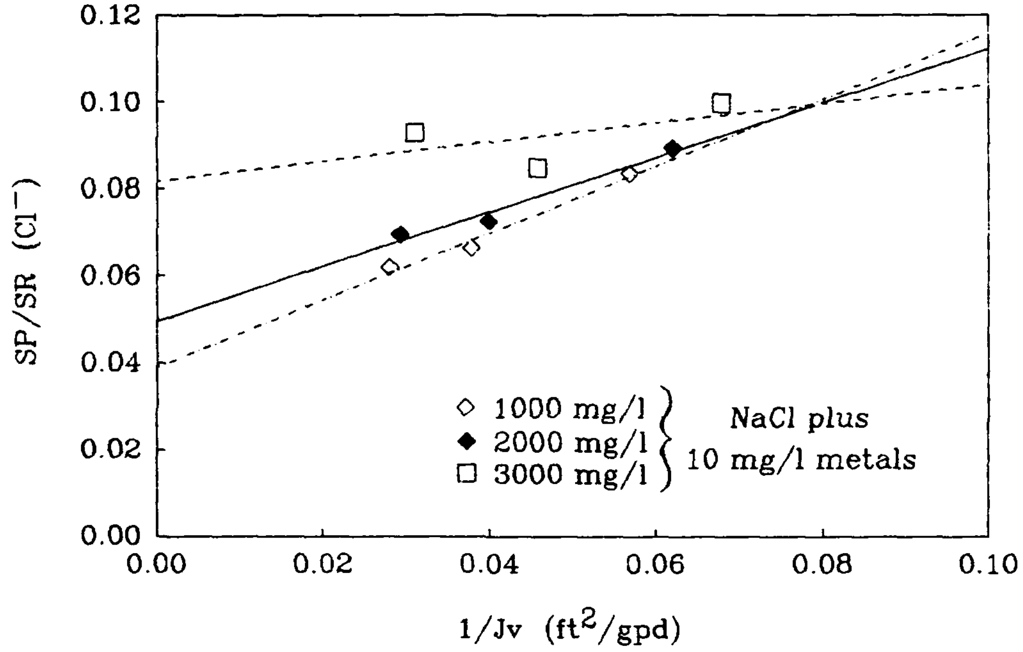

Figure 4-8. Linear plot of chloride permeation data corresponding to tests performed with feed solutions I-1-10, I-2-10, and I-3-10 after 83.60-90.18 hours, 94.43-99.68 hours, and 104.00-109.75 hours, respectively.

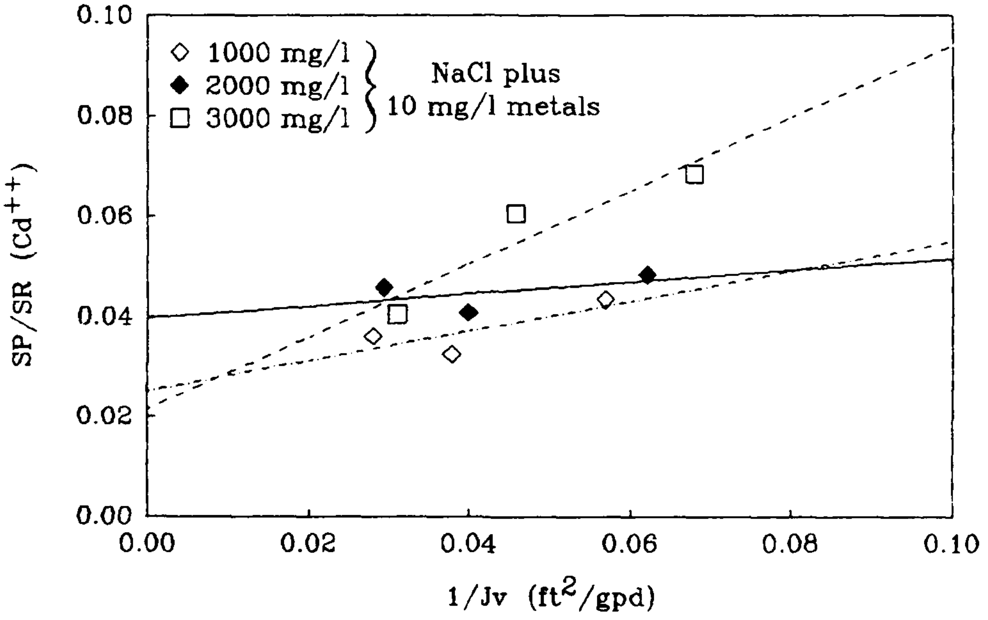

Figure 4-9. Linear plot of cadmium (II) permeation data corresponding to tests performed with feed solutions I-1-10, I-2-10, and I-3-10 after 83.60-90.18 hours, 94.43-99.68 hours, and 104.00-109.75 hours, respectively.

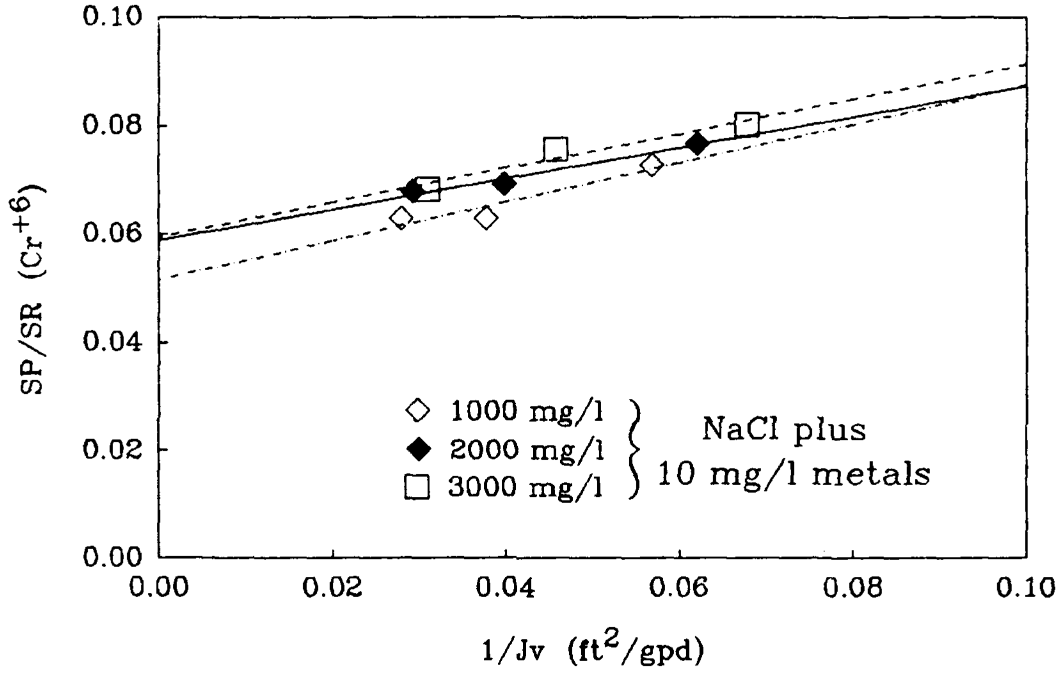

Figure 4-10. Linear plot of chromium (VI) permeation data corresponding to tests performed with feed solutions I-1-10, I-2-10, and I-3-10 after 83.60-90.18 hours, 94.43-99.68 hours, and 104.00-109.75 hours, respectively.

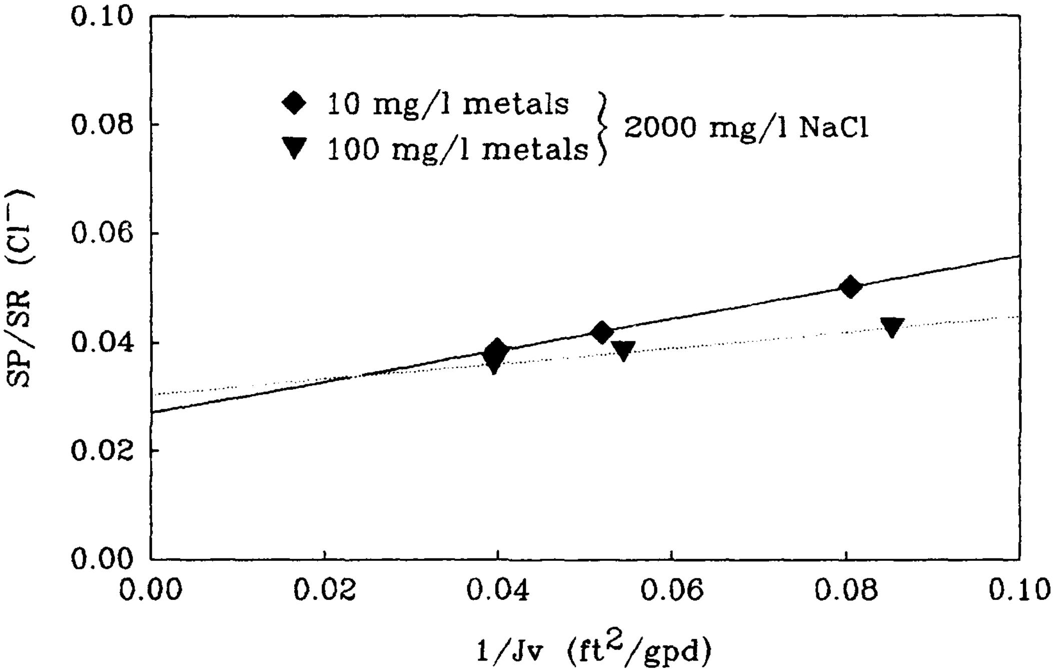

Figure 4-11. Linear plot of chloride permeation data corresponding to tests performed with feed solutions I-2-10, and I-2-100 after 176.25-181.58 hours, and 187.17-193.00 hours of operation, respectively.

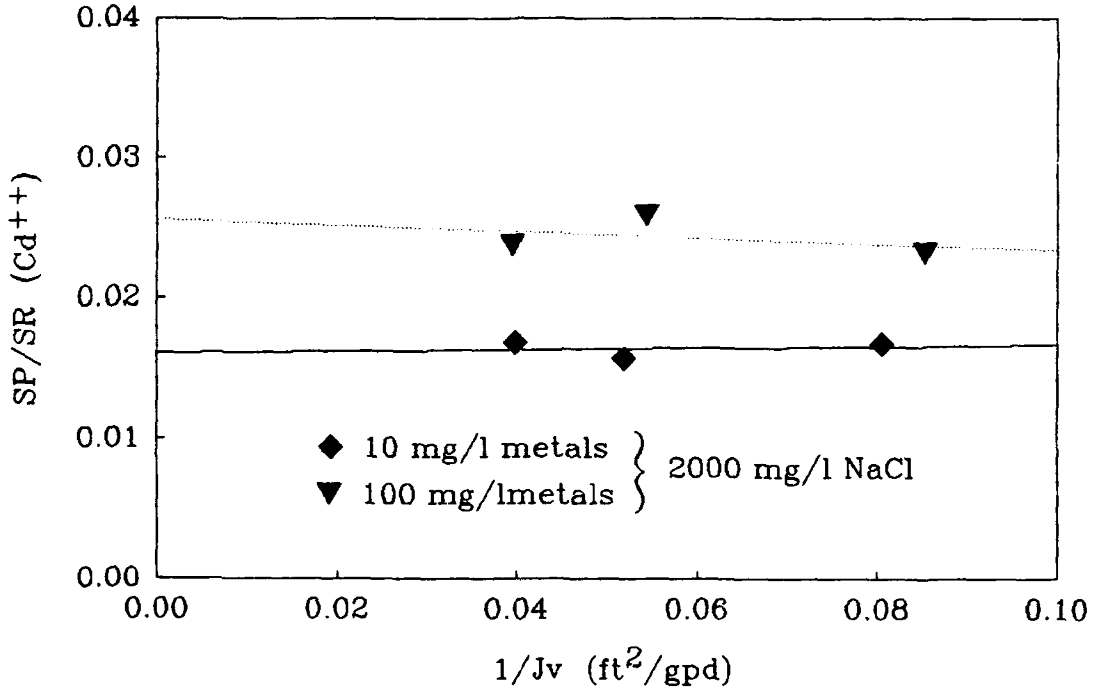

Figure 4-12. Linear plot of cadmium (II) permeation data corresponding to tests performed with feed solutions I-2-10, and I-2-100 after 176.25-181.58 hours, and 187.17-193.00 hours of operation, respectively.

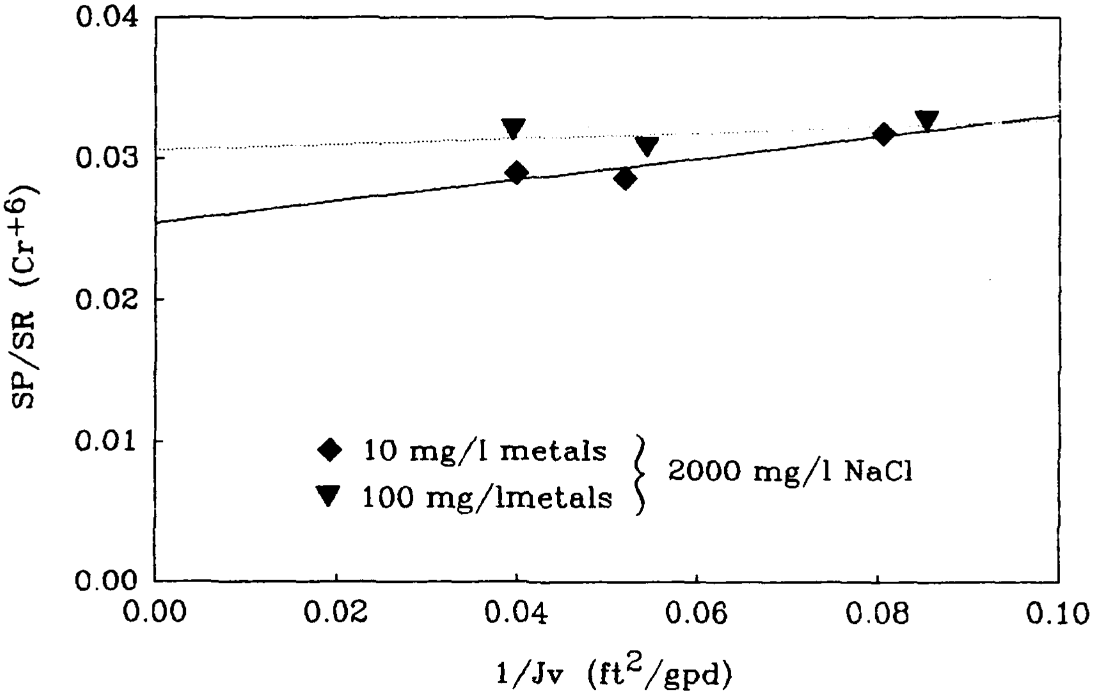

Figure 4-13. Linear plot of chromium (VI) permeation data corresponding to tests performed with feed solutions I-2-10, and I-2-100 after 176.25-181.58 hours, and 187.17-193.00 hours of operation, respectively.

Composition Dependence

The effect of major electrolyte composition on the rejection of all ions in solution was analyzed by comparing the results obtained with a sodium chloride solution (I-2-10 in Table 3-2), a sodium sulfate solution (V-2-10), and three solution mixtures of sodium chloride and sodium sulfate (II-2-10, III-2-10 and IV-2-10), all of which contained 10 mg/L of each cadmium chloride (as Cd) and sodium chromate (as Cr).

The solute passages observed for chloride and sulfate ions, and cadmium (II) and chromium (VI) are shown in Figures 4-14 and 4-15, respectively. The data shown correspond to the applied hydraulic pressure of 400 psi. The results obtained at 300 and 200 psi were comparable.

The passage of chloride and chromium (VI) (see Figures 4-14 and 4-15), both monovalent ions at the operating pH of 6, was apparently lowest for mixtures of sodium chloride and sodium sulfate at approximately balanced molar concentrations for chloride and sulfate ions (i.e., chloride molar fraction of approximately 0.5 percent).

On the other hand, the passages of sulfate and cadmium (II), both divalent ions at the operating pH of 6, were approximately constant for chloride fractions between approximately 0 and 0.5 percent and significantly higher for the two solutions with high chloride mole fractions. The slightly lower passages observed at the lower chloride ion mole fractions in the range of 0 to 0.5 might be the effect of changing membrane permeation characteristics produced by compaction.

Composition Dependence

The effect of major electrolyte composition on the rejection of all ions in solution was analyzed by comparing the results obtained with a sodium chloride solution (I-2-10 in Table 3-2), a sodium sulfate solution (V-2-10), and three solution mixtures of sodium chloride and sodium sulfate (II-2-10, III-2-10 and IV-2-10), all of which contained 10 mg/L of each cadmium chloride (as Cd) and sodium chromate (as Cr).

The solute passages observed for chloride and sulfate ions, and cadmium (II) and chromium (VI) are shown in Figures 4-14 and 4-15, respectively. The data shown correspond to the applied hydraulic pressure of 400 psi. The results obtained at 300 and 200 psi were comparable.

The passage of chloride ions and chromium (VI) (see Figures 4-14 and 4-15), both monovalent ions at the operating pH of 6, was apparently lowest for mixtures of sodium chloride and sodium sulfate at approximately balanced molar concentrations for chloride and sulfate ions (i.e., chloride molar fraction of approximately 0.5 percent).

On the other hand, the passages of sulfate ions and cadmium (II), both divalent ions at the operating pH of 6, were approximately constant for chloride fractions between approximately 0 and 0.5 percent and significantly higher for the two solutions with high chloride mole fractions. The slightly lower passages observed at the lower chloride ion mole fractions in the range of 0 to 0.5 might be an effect of membrane compaction.

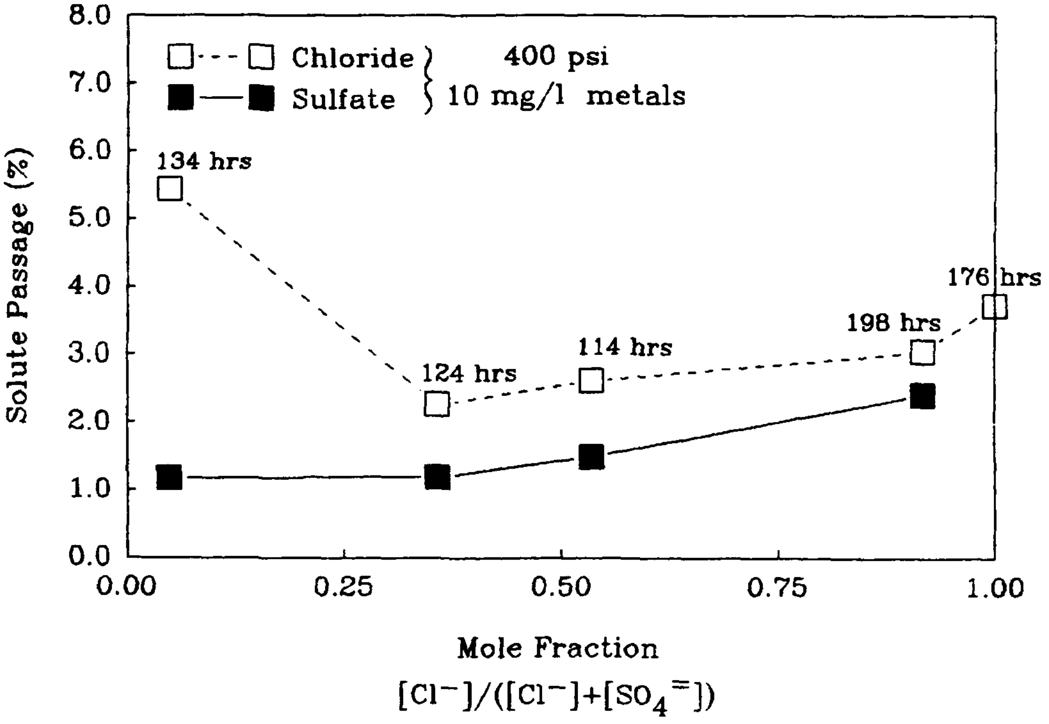

Figure 4-14. Observed solute passages for chloride and sulfate ions corresponding to tests performed with feed solutions I-2-10, II-2-10, III-2-10, IV-2-10, and V-2-10 performed at the operating times indicated.

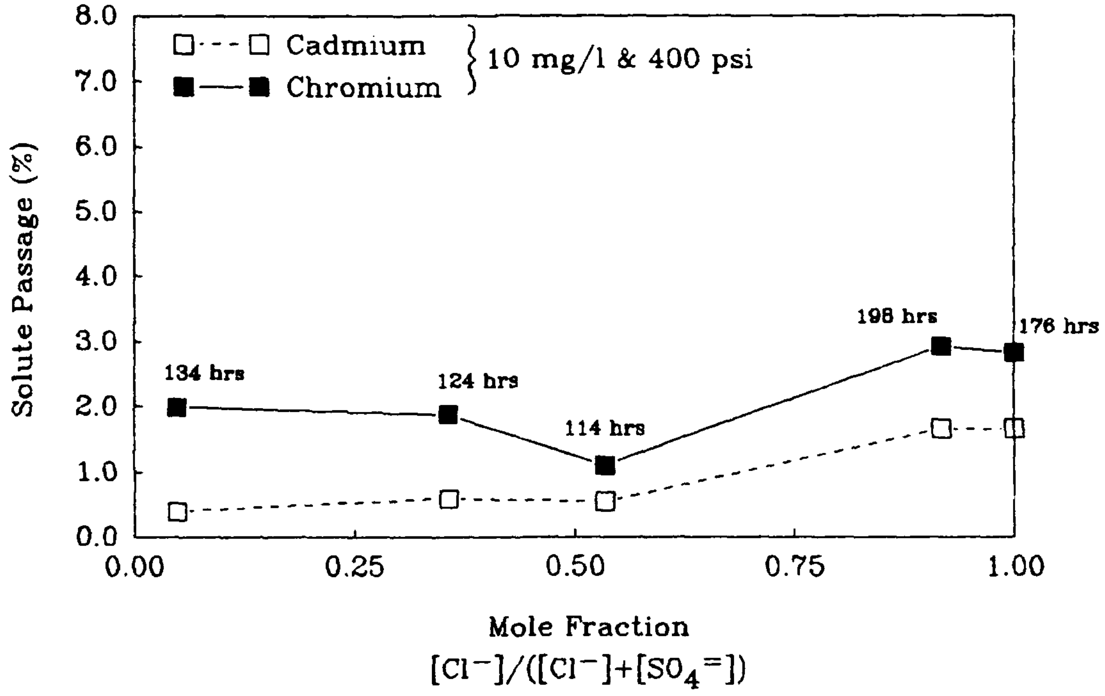

Figure 4-15. Observed solute passages for cadmium (II) and chromium (VI) corresponding to tests performed with feed solutions I-2-10, II-2-10, III-2-10, IV-2-10, and V-2-10 performed at the operating times indicated.

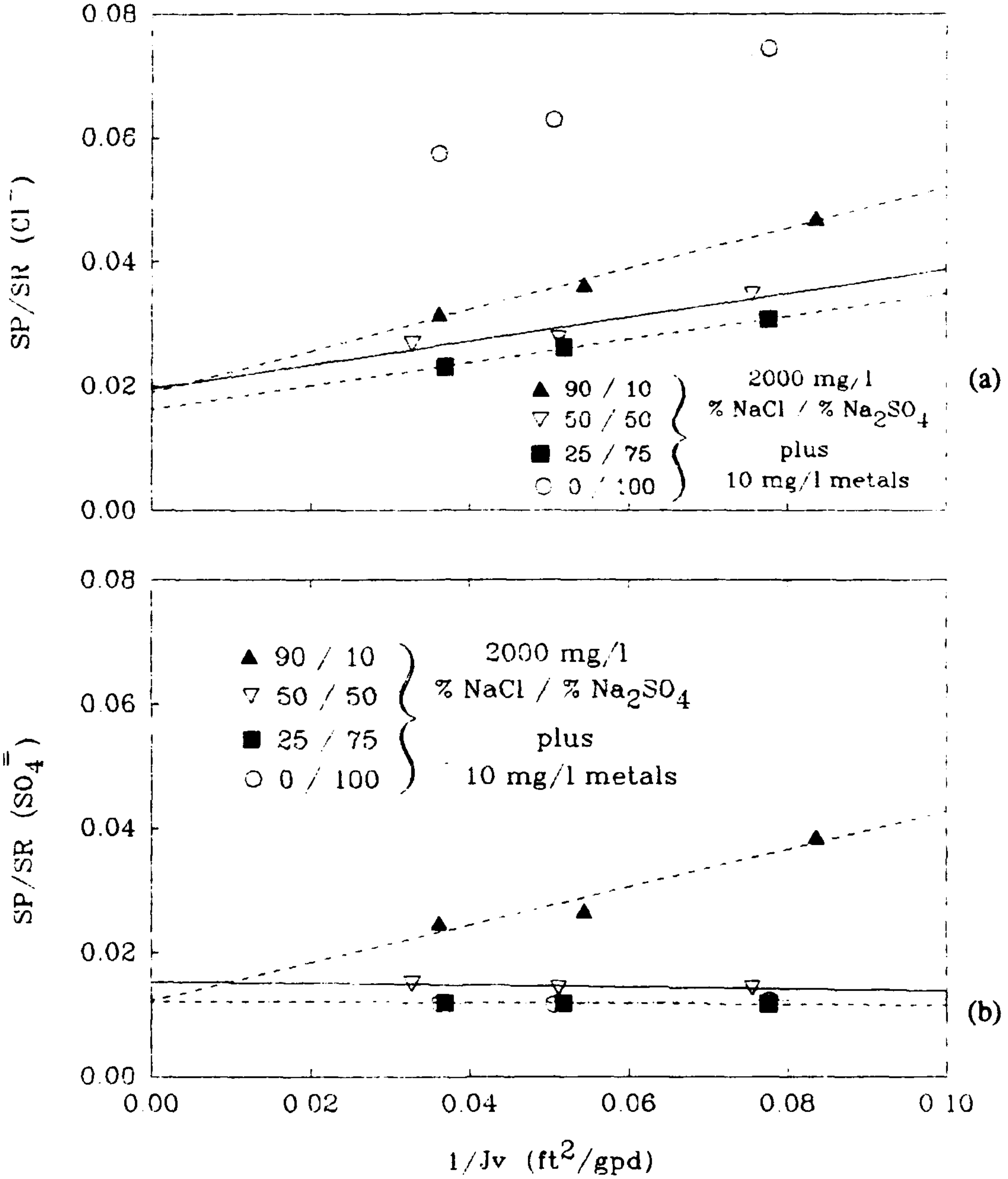

Figure 4-16. Linear plot of chloride (a) and sulfate (b) permeation data corresponding to tests performed with feed solutions II-2-10, III-2-10, IV-2-10 and V-2-10, respectively.

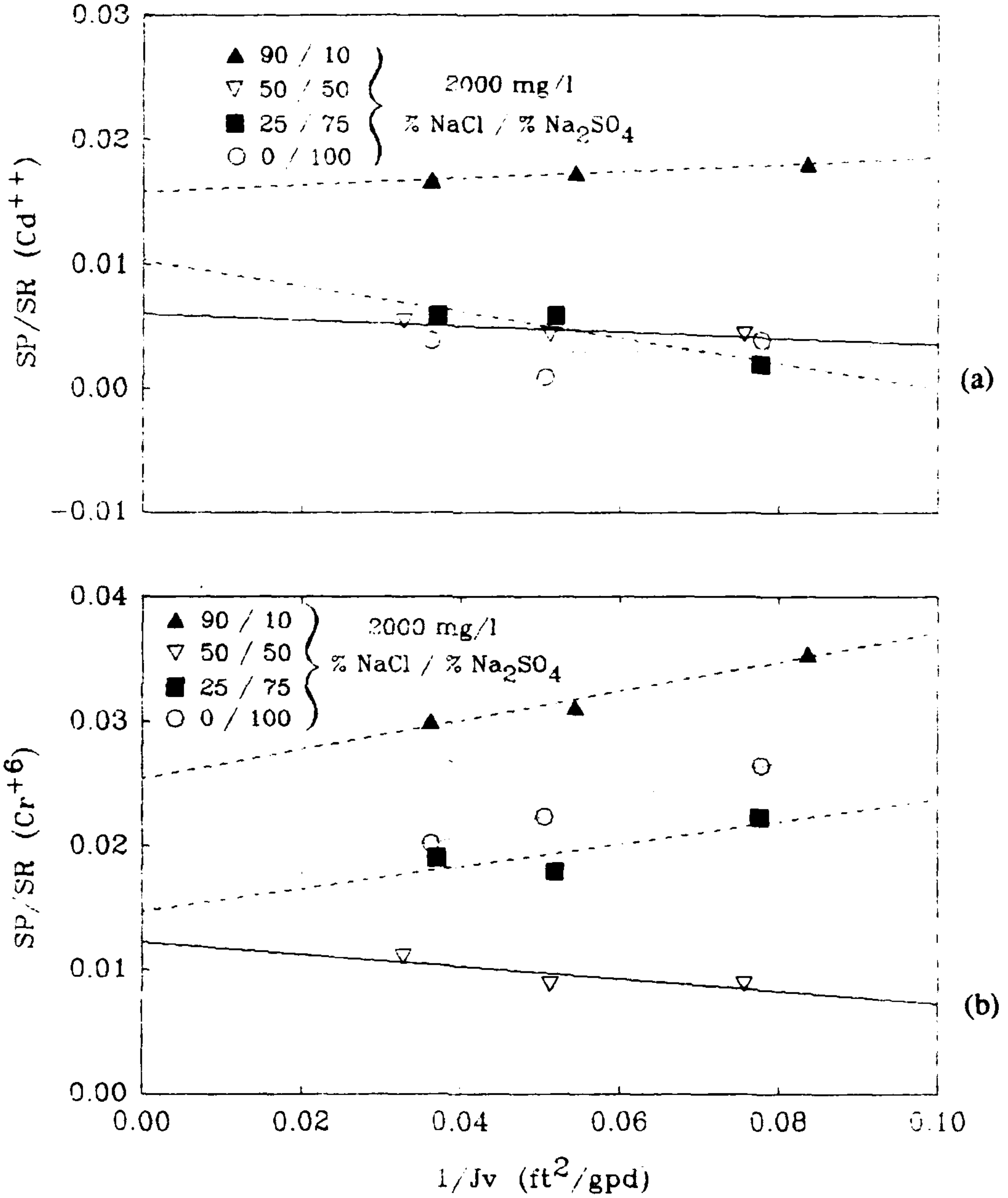

Figure 4-17. Linear plot of cadmium (II) (a) and chromium (VI) (b) permeation data corresponding to tests performed with feed solutions II-2-10, III-2-10, IV-2-10 and V-2-10, respectively.

pH Dependence

A series of experimental runs at pH 5, 6 and 7 revealed that solute passage is dependent upon pH. The observed passage of chloride was lowest at pH5 and 400 psi in Figure 4-18(a). Figures 4-18(b) and (c) refer to cadmium(II) and chromium(VI) respectively where the passage of ions was lowest at pH 7. It is expected that the rejection of the chromium ion improve at the higher pH since the divalent species ($CrO_4^=$) predominates at pH greater than 6.5.

Figure 4-18 also demonstrates the trend for passage of ions to decrease at higher pressures. The variance from this trend for the metal ions is not significant.

It is important to recognize that changes in pH effect the behavior of both the electrolytes and the membrane itself. At higher pH the carboxyl group of the membrane may become negatively charged. The dynamic and complex interactions between the ions, molecules and the membrane may account for the lower solute passage of cadmium(II) at pH 7 even though cadmium always existed as a divalent species under the conditions tested. A similar statement could be made for chloride at pH 5.

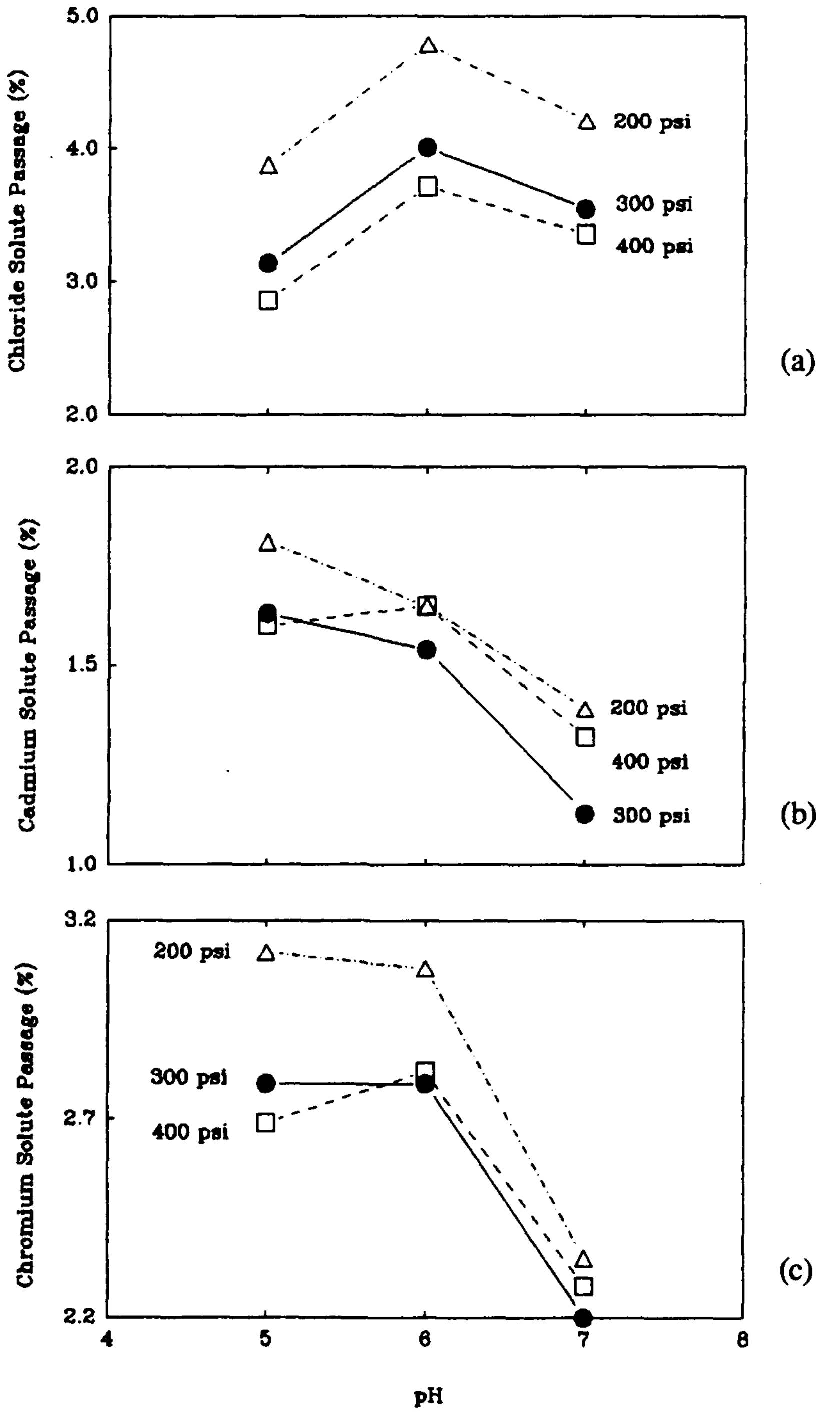

Figure 4-18. Effect of pH on solute passage of chloride(a), cadmium(II)(b), and chromium(VI)(c) at feed solutions I-2-10.

CHAPTER 5

CONCLUSIONS

The FT-30 Type BW30 membrane demonstrated efficient removals of cadmium(II) and chromium (VI) ranging from 92.6 to 99.9 percent. Rejection of the metals was examined over a diverse set of operating conditions such as pressure and feed solution temperature, pH, concentration and composition.

The effects of temperature were examined from 20 to 36°C with a solution of 2000 mg/L sodium chloride (I-2-0). Water permeation increased with temperature as did the solute passage of chloride from approximately 1.29 percent to 1.43 percent for 20 and 36°C respectively. Water permeation was not affected by feed concentration or composition within the ranges investigated (Table 3-2).

The membrane tested experienced compaction over time which caused decreases in water and solute permeabilities. The water permeability coefficient decreased exponentially with time. Unfortunately more extensive testing would be necessary to describe the effect of compaction on solute permeation coefficients. Nonetheless, results confirm findings by others (Mariñas and Selleck, 1991), that for the FT-30 membrane both A and B decrease with time due to compaction.

The effects of background concentration on metal removal were tested with feed solutions of 1000, 2000 and 3000 mg/L NaCl, and 10 mg/L each of cadmium chloride (as Cd) and sodium chromate (as Cr). Changes in concentration had very little effect on the permeation coefficients (β and σ) for chromium(VI), and the erratic behavior of the 3000 mg/L solution (I-3-10) for chloride and cadmium(II) made conclusions for these ions difficult to confirm.

Another concentration dependence investigated was the effect of metal concentrations at 10 and 100 mg/L both with 2000 mg/L NaCl solution. Increasing the metal concentration had an insignificant impact on the permeations of chloride, cadmium(II) or chromium(VI), (see feed solution I-2-10 and I-2-100 in Table 4-2).

The effect of major electrolyte composition on solute rejection was appreciable. Results were compared for a sodium chloride solution (I-2-10), a sodium sulfate solution (V-2-10), and three solution mixtures of sodium chloride and sodium sulfate (II-2-10, III-2-10 and IV-2-10), all of which contained 10 mg/L each of cadmium(II) and chromium(VI). Approximately balanced molar concentrations for chloride and sulfate ions resulted in the lowest passages of chloride and chromium(VI). The sulfate and cadmium ions were approximately constant for low chloride fractions (i.e., less than 0.5 percent), but significantly higher for the higher chloride ion mole fractions.

Finally pH dependence was examined for sodium chloride solutions (I-2-10; pH 5, 6 & 7). Cadmium(II) and chromium(VI) passages were lowest at pH 7. The chloride ion passage on the other hand, was lowest at pH 5.

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APPENDIX

APPENDIX

Table A-1. Operating Conditions and Permeate Flow Rates.

Feed Solution Code[a]	Time t (hour)	Temperature T (°C)	Feed Pressure p_f (psi)	Permeate Flow Rate Q_p (gal/day)
I-2-0	4.00	25.1	400	8.36
	8.00	24.0	400	7.26
	14.00	24.5	400	6.94
	23.75	25.3	400	6.84
	31.50	25.1	400	6.61
	36.50	24.5	400	6.31
	43.75	28.0	400	6.99
	47.75	25.1	400	6.27
	50.25	20.0	400	5.13
	52.42	31.0	400	7.64
	54.42	36.0	400	8.90
	59.50	25.2	300	4.37
	63.25	24.1	200	2.66
I-1-0	67.75	25.0	400	6.12
I-1-10	71.00	25.0	400	6.27
	75.33	25.0	300	4.52
	78.58	25.0	200	2.97
	83.60	24.5	400	5.89
	86.85	25.1	300	4.37
	90.18	25.0	200	2.91
I-2-10	94.43	25.1	400	5.63
	96.43	25.1	300	4.14
	99.68	24.9	200	2.66
I-3-10	104.00	26.0	400	5.32
	106.33	24.0	300	3.61
	109.75	24.9	200	2.43

[a] See Table 3-2 for target feed solution composition

Table A-1, continued.

Feed Solution Code[a]	Time t (hour)	Temperature T (°C)	Feed Pressure p_f (psi)	Permeate Flow Rate Q_p (gal/day)
III-2-10	114.00	25.6	400	5.04
	116.33	23.8	300	3.23
	119.67	24.9	200	2.19
IV-2-10	124.00	24.5	400	4.47
	126.25	24.5	300	3.19
	129.33	25.1	200	2.13
V-2-10	134.00	25.2	400	4.56
	136.17	25.0	300	3.27
	139.67	25.6	200	2.13
I-2-0	145.00	22.0	400	4.18
	150.00	25.0	400	4.56
I-2-10	155.17	24.5	400	4.37
	157.50	24.8	300	3.19
	161.50	25.8	200	2.13
	166.50	24.8	400	4.18
	168.83	25.1	300	3.23
	172.00	25.2	200	2.05
	176.25	24.0	400	4.14
	178.42	25.8	300	3.19
	181.58	25.1	200	2.05
I-2-100	187.17	25.1	400	4.18
	189.83	24.8	300	3.04
	193.00	24.9	200	1.94
II-2-10	198.33	27.0	400	4.56
	201.50	24.4	300	3.04
	205.50	25.1	200	1.98

[a] See Table 3-2 for target feed solution composition

Table A-2. Feed Water and Permeate pH and Solute Concentrations (mg/l).

		pH		Chloride		Sulfate		Cadmium (II)		Chromium (VI)	
Code[a]	t (hr)	feed	perm	feed	perm.	feed	perm.	feed	perm.	feed	per m
I-2-0	4.00	6.11	5.28	1,059	18.13	--	--	--	--	--	--
	8.00	6.05	5.10	1,059	16.14	--	--	--	--	--	--
	14.00	6.05	5.38	1,092	14.58	--	--	--	--	--	--
	23.75	6.09	5.46	1,176	16.8	--	--	--	--	--	--
	31.50	6.07	5.69	1,170	16.78	--	--	--	--	--	--
	36.50	6.01	--	1,143	16.47	--	--	--	--	--	--
	43.75	6.01	--	1,188	16.27	--	--	--	--	--	--
	47.75	6.03	--	1,188	15.25	--	--	--	--	--	--
	50.25	5.99	5.89	1,188	15.36	--	--	--	--	--	--
	52.42	5.99	5.85	1,188	16.33	--	--	--	--	--	--
	54.42	6.04	--	1,188	17.00	--	--	--	--	--	--
	59.50	6.07	5.98	1,200	23.66	--	--	--	--	--	--
	63.25	6.06	--	1,200	31.49	--	--	--	--	--	--
I-1-0	67.75	5.99	--	603.4	11.94	--	--	--	--	--	--
I-1-10	71.00	6.00	6.20	576.6	25.20	--	--	8.93	0.21	8.83	0.37
	75.33	6.00	6.14	576.6	30.92	--	--	8.93	0.27	8.83	0.44
	78.58	6.04	5.96	576.6	37.20	--	--	8.93	0.28	8.83	0.51
	83.60	6.00	6.01	589.5	34.37	--	--	8.88	0.31	8.27	0.49
	86.85	6.00	6.00	589.5	36.69	--	--	8.88	0.28	8.27	0.49
	90.18	6.01	6.02	589.5	45.42	--	--	8.88	0.37	8.27	0.56
I-2-10	94.43	5.99	6.10	1,173	76.19	--	--	8.68	0.38	7.72	0.49
	96.43	6.00	6.09	1,173	79.20	--	--	8.68	0.34	7.72	0.50
	99.68	5.99	5.98	1,173	96.07	--	--	8.68	0.40	7.72	0.55
I-3-10	104.00	6.00	6.14	1,656	140.99	--	--	8.74	0.34	7.68	0.49
	106.33	6.00	6.12	1,656	129.43	--	--	8.74	0.50	7.68	0.54
	109.75	6.00	6.17	1,656	150.23	--	--	8.74	0.56	7.68	0.57

[a] See Table 3-2 for target feed solution composition

Table A-2, continued.

		pH		Chloride		Sulfate		Cadmium (II)		Chromium (VI)	
Code[a]	t (hr)	feed	perm	feed	perm.	feed	perm.	feed	perm.	feed	perm.
III-2-10	114.00	5.97	5.46	529.7	13.85	1,249	18.51	9.11	0.05	4.56	0.05
	116.33	5.98	5.51	529.7	14.23	1,249	17.67	9.11	0.04	4.56	0.04
	119.67	5.98	5.69	529.7	17.80	1,249	17.71	9.11	0.04	4.56	0.04
IV-2-10	124.00	6.03	5.50	348.8	7.87	1,696	20.09	10.17	0.06	9.62	0.18
	126.25	6.04	5.58	348.8	8.91	1,696	19.87	10.17	0.06	9.62	0.17
	129.33	6.00	5.77	348.8	10.38	1,696	19.65	10.17	0.02	9.62	0.21
V-2-10	134.00	6.03	5.55	35.2	1.91	1,860	21.84	10.17	0.04	10.06	0.20
	136.17	6.03	5.58	35.2	2.08	1,860	21.39	10.17	0.01	10.06	0.22
	139.67	6.03	5.88	35.2	2.44	1,860	22.61	10.17	0.04	10.06	0.26
I-2-0	145.00	6.01	5.71	1,121	25.92	--	--	--	--	--	--
	150.00	6.02	5.80	1,121	28.56	--	--	--	--	--	--
I-2-10	155.17	5.01	4.38	1,048	30.00	--	--	9.83	0.16	9.81	0.26
	157.50	5.02	4.36	1,048	32.88	--	--	9.83	0.16	9.81	0.27
	161.50	4.99	4.22	1,048	40.63	--	--	9.83	0.18	9.81	0.31
	166.50	6.99	7.24	1,116	37.52	--	--	8.14	0.11	9.80	0.22
	168.83	6.98	7.32	1,116	39.57	--	--	8.14	0.09	9.80	0.22
	172.00	7.01	7.29	1,116	47.03	--	--	8.14	0.11	9.80	0.23
	176.25	6.00	6.10	1,115	41.49	--	--	8.92	0.15	9.67	0.27
	178.42	6.02	6.10	1,115	44.77	--	--	8.92	0.14	9.67	0.27
	181.58	5.99	6.23	1,115	53.40	--	--	8.92	0.15	9.67	0.30
I-2-100	187.17	5.99	6.27	1,212	41.97	--	--	92.23	2.14	104.55	3.24
	189.83	6.00	6.28	1,212	44.77	--	--	92.23	2.32	104.55	3.13
	193.00	6.01	--	1,212	49.43	--	--	92.23	2.09	104.55	3.31
II-2-10	198.33	5.99	5.96	937.5	28.63	231.0	5.57	9.08	0.15	10.31	0.30
	201.50	6.04	6.00	937.5	32.73	231.0	5.99	9.08	0.16	10.31	0.31
	205.50	6.01	--	937.5	42.04	231.0	8.58	9.08	0.16	10.31	0.35

[a] See Table 3-2 for target feed solution composition