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Modified Reverse Osmosis System for Treatment of Produced Waters

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ABSTRACT

This report describes work performed during the second year of the project "Modified reverse osmosis system for treatment of produced waters." We performed two series of reverse osmosis experiments using very thin bentonite clay membranes compacted to differing degrees. The first series of 10 experiments used NaCl solutions with membranes that ranged between 0.041 and 0.064mm in thickness. Our results showed compaction of such ultra-thin clay membranes to be problematic. The thickness of the membranes was exceeded by the dimensional variation in the machined experimental cell and this is believed to have resulted in local bypassing of the membrane with a resultant decrease in solute rejection efficiency. In two of the experiments, permeate flow was varied as a percentage of the total flow to investigate results of changing permeate flow on solute rejection. In one experiment, the permeate flow was varied between 2.4 and 10.3% of the total flow with no change in solute rejection. In another experiment, the permeate flow was varied between 24.6 and 52.5% of the total flow. In this experiment, the solute rejection rate decreased as the permeate occupied greater fractions of the total flow. This suggests a maximum solute rejection efficiency for these clay membranes for a permeate flow of between 10.3 and 24.6% of the total; flow. Solute rejection was found to decrease with increasing salt concentration and ranged between 62.9% and 19.7% for chloride and between 61.5 and 16.8% for sodium. Due to problems with the compaction procedure and potential membrane bypassing, these rejection rates are probably not the upper limit for NaCl rejection by bentonite membranes. The second series of four reverse osmosis experiments was conducted with a 0.057mm-thick bentonite membrane and dilutions of a produced water sample with an original TDS of 196,250 mg/l obtained from a facility near Loco Hill, New Mexico, operated by an independent. These experiments tested the separation efficiency of the bentonite membrane for each of the dilutions. We found that membrane efficiency decreased with increasing solute concentration and with increasing TDS. The rejection of SO_4^{2-} was greater than Cl^-. This may be because the SO_4^{2-} concentration was much lower than the Cl^- concentration in the waters tested. The cation rejection sequence varied with solute concentration and TDS. The solute rejection sequence for multi-component solutions is difficult to predict for synthetic membranes; it may not be simple for clay membranes either. The permeate flows in our experiments were 4.1 to 5.4% of the total flow. This suggests that very thin clay membranes may be useful for some separations. Work on development of a spiral-wound clay membrane module found that it is difficult to maintain compaction of the membrane if the membrane is rolled and then inserted in the outer tube. A different design was tried using a cylindrical clay membrane and this also proved difficult to assemble with adequate membrane compaction. The next step is to form the membrane in place using hydraulic pressure on a thin slurry of clay in either water or a nonpolar organic solvent such as ethanol. Technology transfer efforts included four manuscripts submitted to peer-reviewed journals, two abstracts, and chairing a session on clays as membranes at the Clay Minerals Society annual meeting.

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EXECUTIVE SUMMARY

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Technology transfer efforts included four manuscripts submitted to peer-reviewed journals, two abstracts, and chairing a session on clays as membranes at the Clay Minerals Society annual meeting.

INTRODUCTION

In the United States, more than 20 billion barrels of water are produced each year during oilfield operations. Disposal of produced water can be expensive. For example, produced water in the San Juan Basin of New Mexico and Colorado is currently disposed of by deep-well injection at a cost of approximately $1.75 per bbl. In other areas the cost of water disposal is typically between $0.25 and $0.50 per barrel for pipeline transport and $1.50 per barrel for trucked water.

In many parts of the country, deep injection wells, or use of produced water for waterflood operations, may not be available disposal options. The EPA commonly will not allow surface disposal of produced waters because of the high content of dissolved solids. Therefore, in many areas, produced water will need to be treated prior to disposal so that it can meet EPA standards for various uses such as surface disposal, fresh water aquifer recharge, drinking water, irrigation, or release to streams.

PROJECT OBJECTIVES

The work this year focused on testing clays for use as reverse osmosis membranes to remove dissolved solids from oilfield-produced waters. Geologists have known that clays exhibit osmotic or membrane properties for many years. A semi-permeable membrane is defined as a material that will permit the passage of some molecules but not others (Noggle, 1984). As defined, the membrane would be perfect, *i.e.*, it would absolutely preclude the passage of certain molecular species. Such perfect membranes probably do not exist in nature (Fritz, 1986). Therefore, a better working definition for a semi-permeable geological membrane is any lithology that allows one solution component to pass through more easily than another. Clays fit this definition of a membrane.

A number of laboratory experiments have demonstrated that clays exhibit membrane properties (Marshall, 1948; Wyllie, 1948, 1949; Kemper, 1960, 1961; McKelvey and Milne, 1960, Berstein, 1960; McKelvey and Milne, 1963; Milne et al, 1963; Milne et al., 1964; Kemper and Rollins, 1966; Olsen, 1969,1972; Kharaka and Berry, 1973; Coplen and Hanshaw, 1973; Srivastava and Jain, 1975; Kharaka and Smalley, 1976; Fritz and Marine, 1983; Benzel and Graf, 1984; Fritz and Eady, 1985; Campbell, 1985; Haydon and Graf, 1986; Demir, 1988, Fritz *et al.*, 1987; Fritz and Whitworth, 1994, Whitworth and Fritz, 1994, Whitworth and DeRosa, 1997, Whitworth and Gu, 2001). However, investigation of potential practical uses of clays as membranes has been limited. Ishiguro et al. (1995) performed some preliminary tests using a 0.5mm-thick modified montmorillonite (SWy-1 Wyoming bentonite obtained from the Clay Source Repository) membrane to investigate the reverse osmosis potential of clay. They concluded that the montmorillonite membrane exhibited characteristics typical for a charged membrane by rejecting NaCl less efficiently with increasing solute concentration. They also concluded that the rejection capability of the montmorillonite membrane for small organic solutes was very low and that the separation of amino acids greatly depended on the charge of the amino acid molecule.

Clay membranes may reject solutes on the basis of size and/or electrical restrictions (Gregor and Gregor, 1978). If a geological material has a net electrical charge, then electrical restrictions become important. For example, bentonite clays have a net negative charge due to ion substitution in the lattice (Grim, 1968). In bentonite membranes, electrical restrictions

contribute to solute rejection for charged species such as electrolytes. However, the net negative charge should have no direct effect on uncharged ion pairs or non-electrolytes in solution. In this case, separation is accomplished because the non-electrolyte species enter and traverse the membrane more slowly than the aqueous solvent. If a membrane material has no net charge, like kaolinite at neutral pH (Grim, 1968) then electrolyte rejection must be primarily attributed to rejection on the basis of molecular size.

Commercial reverse osmosis processes use a flow configuration that sweeps the upper surface of the membrane with a turbulent, high-velocity flow that destroys any concentration build-up adjacent to the membrane due to solute rejection (Figure 1). A fraction of the water passes through the membrane and another fraction of the feed water passes out of the other port on the upper side of the membrane. The membrane removes a significant portion of the dissolved solutes from the water that passes through the membrane (the permeate) and thus purifies it. The solute that is removed from the permeate remains in solution above the membrane and exits the unit with the fraction of the flow that did not pass through the membrane. This flow is called the concentrate because its concentration is higher than that of the feed or input solution. Ishiguro et al's (1995) experimental apparatus utilized a layer of clay smeared between two Millipore filter papers contained between two porous steel frits in a similar flow configuration. Most of the clay membrane experiments referenced above used different experimental conditions than those shown in Figure 1 and were designed to test potential membrane effects in the subsurface. See Alexander (1990) for a summary of clay membrane experimental conditions in literature published prior to 1986.

We report herein on a series of cross-flow experiments using bentonite clay membranes. The experiments are divided into two series. The first series used NaCl solutions, and the second series used dilutions of a produced water.

TESTING CONSTRUCTION OF ULTRA-THIN CLAY MEMBRANES

INTRODUCTION

Our previous experiments used relatively thick (0.5mm) clay membranes. For a reverse osmosis membrane to be cost effective, the flow through the membrane must be maximized. Thinner membranes offer less resistance to flow. Therefore we conducted several experiments using compacted, 0.04 to 0.06mm-thick bentonite membranes. The goal of these experiments was to test a procedure for constructing ultra-thin clay membranes and to investigate if such ultra-thin clay membranes could be compacted so as to be increasingly efficient membranes.

METHODS AND MATERIAL STUDIED

We used a commercially available Wyoming bentonite (Wyo-Ben Hydrogel) which X-ray analysis showed to be a Na-bentonite. We used this commercially available clay in preference to a reference clay because commercially available clay would be used to construct clay reverse osmosis membranes if these membranes prove to have commercial potential.

The first step in preparation of the bentonite clay for use in the bench-scale cross-flow membrane experiments is to separate the 0.2 μm and smaller size fraction. This was done using standard sedimentation techniques. Following size separation, the clay was dialyzed and then freeze-dried using a Model 4.5 Labconco benchtop freeze dryer. The method used was that reported by Whitworth and Fritz (1994). Bentonite is quite fluffy after freeze drying: every gram of freeze-dried bentonite has a volume of approximately 100 ml. After freeze-drying, the clay is stored in nested, tightly sealed ziplock bags to prevent moisture from contacting the clay. The purpose of freeze drying is to remove the moisture content of the clay. Vacuum freeze-drying removes non-adsorbed water (Zimmie and Almaleh, 1976, Fritz and Marine, 1983).

A flat-leaf experimental cell was designed for reverse osmosis experiments using clays as the membrane (Figure 1). This cell was constructed from 316 stainless steel by the R&ED machine shop at New Mexico Tech. This cell uses a piston to compress the clay. This feature is not present in commercially available reverse osmosis experimental cells, but is necessary to control the compaction of the clay in these experiments. The membrane area in this cell is 136.5 cm^2.

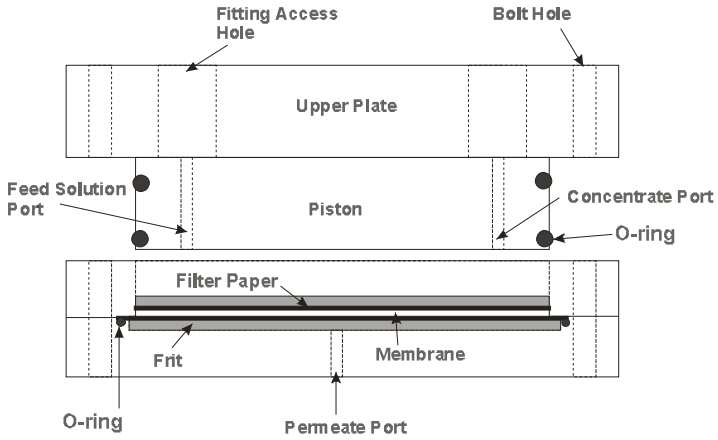

Figure 1. Schematic of cross-flow experimental cell designed for clay membranes.

The clay membranes were prepared by first assembling the lower part of the experimental cell using bolt holes not shown in Figure 1. The 316 stainless steel frit was covered with two layers of Millipore 0.1 μm filter paper. The filter paper extends past the frit and is sealed by an O-ring inset into the bottom plate. Next, a thin clay slurry (2.00 grams of freeze-dried bentonite thoroughly mixed with 150 ml of deionized water) was poured into the cavity above the filter paper. The clay was allowed to settle for approximately 10 hours and then a vacuum pump was attached to the permeate port and the remaining water removed. This procedure forms a very thin and uniform layer of clay on the Millipore filter paper.

Next, the piston is inserted and gently pressed into place using an arbor press and then the upper plate is set into place and the retaining bolts are loosely assembled into position. The entire assembly is then transferred to a 75 ton hydraulic press and the membrane is compacted at the desired pressure for 24 hours. At the end of the compaction period, the nuts are tightened to hold the cell together and the cell is moved to the lab bench.

The first step in the experimental procedure is to measure the permeability of the clay membrane to deionized water. To prevent complications from entrained air, the cell is placed under vacuum for four hours prior to starting deionized water through the system. The deionized water is also vacuum degassed before use.

The flow configuration used in these experiments is shown in Figure 2. Both deionized water and salt solutions are pumped through the system using an ISCO Model LC 5000 syringe pump. This pump has a capacity of 500ml and provides a pulseless and exceptionally stable steady flow rate. Pressure gages are provided both before and after the experimental cell and a 0.2 μm in-line filter is used in the concentrate line to prefilter samples before analysis.

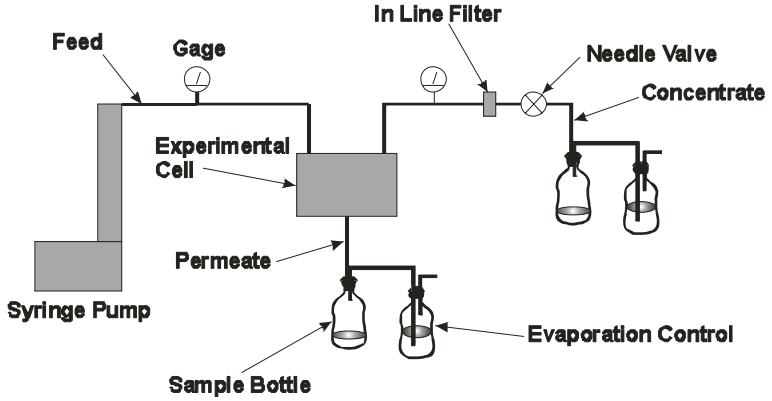

Figure 2. Schematic of experimental setup.

During permeability measurement, the needle valve in the concentrate line is closed so that all of the flow must pass through the clay membrane. Samples are collected at specified time intervals and the volume collected is determined by weighing to ±0.01 g. Since the density of deionized water is very close to 1.00, the weight of the water collected gives a precise measure of the volume collected for that time interval. Samples are collected until three consecutive samples, each taken at least an hour apart, show no change in volume collected per unit time. This is deemed steady state and the permeability is calculated from these last measurements via Equation 1

$$L_P = \frac{J_V}{\Delta P} \quad (1)$$

where L_p is the membrane's coefficient of permeability for water, J_v is the water flux at steady state in cm/s, and ΔP is the applied hydraulic pressure in dynes/cm^2.

Next the syringe pump is emptied and refilled with the feed solution to be used for the specific experiment. The pump is filled and emptied a minimum of three times to minimize any dilution effects due to the small dead space at the piston head in the pump. Then the needle valve is opened and the solution is started through the experimental cell. The needle valve is adjusted to achieve the desired back-pressure on the upper side of the membrane. Both permeate and concentrate samples are periodically collected for analysis. Samples are also collected from the stock solution and from the feed solution in the syringe pump for analysis. Feed solutions were changed between experimental runs to investigate the response of the membrane to differing solute concentrations.

To prevent evaporation during sample collection, an evaporation control system was used. A rubber stopper was placed into the sample flask. Two tubes passed through the stopper. One was the effluent line that was connected to the membrane cell. The other was a capillary tube that also passed through another rubber stopper inserted into a second flask. The end of this capillary tube remained below the liquid level in the second flask ensuring that no evaporation takes place. Another short length of capillary tube was inserted into the stopper in the second flask and was open to the atmosphere. The feed solution tanks remained tightly sealed during the experiments.

At the end of the experiments the cells were disassembled and the clay membrane thickness was measured using digital calipers. Thickness values were obtained by averaging a minimum of six measurements located at various places on the membrane.

Ion Chromatography (IC) was used for low concentrations of chloride (below 0.0056M after dilution). The ion chromatograph was a Dionex 600 with an AS50 autosampler and chromatography compartment, CD25 conductivity detector and a GP50 gradient pump. The column was a Dionex AS14. Calibration was done by injecting a series of standard solutions. Low concentrations of chloride were analyzed using the Dionex 600 with an AS50 autosampler and chromatography compartment, CD25 conductivity detector and a GP50 gradient pump. Internal reference standards were run near the beginning and end of each IC run. Occasionally, calibration checks were run every 20-30 samples if it was a large run. If it was known that some samples had particularly high concentration, a blank was run after these samples. A duplicate sample was run every 10-12 samples. Internal reference standards of Cl = 0.00114M were periodically run. The results of these analyses were Cl = 0.00114M, 0.00115M, and 0.00113M.

High chloride concentrations (above 0.0056M) were analyzed by using a Lachat QuikChem 8000® flow injection analysis automated ion analyzer (FIA) made by Zellweger Analytics, INC. The method used was QuikChem Method 10-117-07-1-J. This method covers the determination of chloride in drinking, ground, and surface waters, and domestic and industrial wastes. The applicable range is 0.0056M to 0.705M Cl. The method detection limit is 0.00021M. Dilutions were made when concentrations were above this range. Calibration was done by injecting a series of standard solutions. Triplicate analysis was conducted for each standard solution and a 0.5% RSD was set as replicate criteria.

Cation analysis (Na^+) was conducted by using Varian Model 110 Flame Atomic Absorption (FAA), SIPS-10 Sample Introduction Pump System, and SPS-5 Sample Preparation

System and Dilutor. Calibration check samples were run at the beginning and end of each run, and every 10-12 samples if there are more than 20 samples in a run. A duplicate sample was run every 10-12 samples. The instrument was checked for zero readings between samples and re-zeroed if necessary, re-sloped every 10-12 samples and re-calibrated every 20-24 samples. Analytical accuracy and precision of chemical measurements are presented in Table 1.

Table 1. Summary of analytical methods, accuracy, and precision for chemical analyses.

Species	Equipment	Method Number	Accuracy	Precision
Chloride (<200ppm)	IC	EPA300.0	< 1%	< 0.5%
Sodium	FAA	EPA7000	2%	1%
Chloride (>200ppm)	FIA	QuikChem 10-117-07-1-J	0.5%	0.5%

Note: Accuracy and precision are stated at one standard deviation. Error bars on graphs are at plus or minus two standard deviations.

RESULTS AND ANALYSES

We report on 10 experiments using four ultra-thin bentonite clay membranes and NaCl solutions. Clay membrane compaction pressures ranged between 21.6 MPa and 43.3 MPa. The NaCl concentrations used were 0.107, 0.218, 0.302, 0.375, 0.518, 0.802, and 0.989 molar.

Rejection rates R in percent were calculated using

$$R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \cdot 100 \qquad (2)$$

Because Na^+ takes part in ion exchange reactions with the clay and Cl^- is conservative, rejection rates calculated for Cl^- should be more representative, although both are reported.

A summary of the results of the ten experiments is presented in Table 2. Each membrane was constructed using 2.00 g of freeze-dried bentonite. Experiments P30C01, P40C01, P50C01 and P60C01 used differing compaction pressures and the same feed solution concentration. The remaining experiments varied the feed concentration for a single membrane at one compaction pressure.

Table 2. Summary of experimental results.

Experiment No.	Compaction Level (MPa)	Membrane Thickness (mm)	Lp ($cm^3/s \cdot dyne$)	Solution Concentration and Type	Cl^- Rejection Rate (%)	Na^+ Rejection Rate (%)	Average Permeate Flow (%)	Total flow rate (ml/min)	Pressure (MPa)
P30C01	21.6	0.044	5.54E-13	0.101M NaCl	21.6	21.0	47.2	0.494	3.34
P40C01	28.9	0.064	5.98E-14	0.092 M NaCl	62.9	61.5	6.9	0.434	5.24
P50C01	36.1	0.057	5.71E-14	0.105 M NaCl	55.9	52.3	5.4	0.413	5.78
P60C01	43.3	0.041	7.62E-14	0.103 M NaCl	53.6	51.4	8.7	0.429	5.77
P60C02	43.3	0.041	7.62E-14	0.210 M NaCl	39.8	38.2	11.9	0.473	7.61
P60C03	43.3	0.041	7.62E-14	0.302 M NaCl	31.7	35.0	8.5	0.524	6.63
P60C04	43.3	0.041	7.62E-14	0.375 M NaCl	27.6	30.2	8.7	0.427	6.72
P60C05	43.3	0.041	7.62E-14	0.518 M NaCl	27.3	27.8	8.2	0.437	6.85
P60C08	43.3	0.041	7.62E-14	0.802 M NaCl	23.7	23.1	6.4	0.451	6.39
P60C10	43.3	0.041	7.62E-14	0.989 M NaCl	19.7	16.8	7.8	0.447	6.85

Figure 3 shows the results of the experiment P30CO1 that used a bentonite membrane compacted to 21.6MPa. The initial rise of the permeate and concentrate concentrations occurs because the deionized water previously used to measure the permeability is being displaced from the system. During this experiment the permeate flow was varied between 24.6% and 52.5% of the total flow with an average hydraulic pressure of 3.34 MPa (485 psi). The average permeate flow rate was 47.2% of the total flow rate. Figure 4 shows the relationship between permeate flow rate and solute rejection rate. The average solute rejection for both chloride (Fig. 3A) and sodium (Fig. 3B) was slightly over 20%.

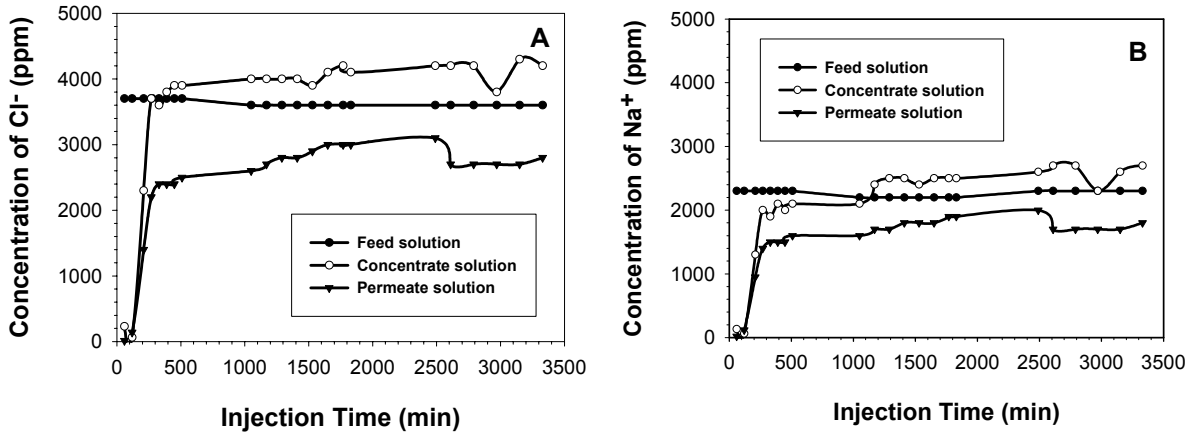

Figure 3. Results of Experiment P30C01 using a bentonite clay membrane compacted to 21.6 MPa.

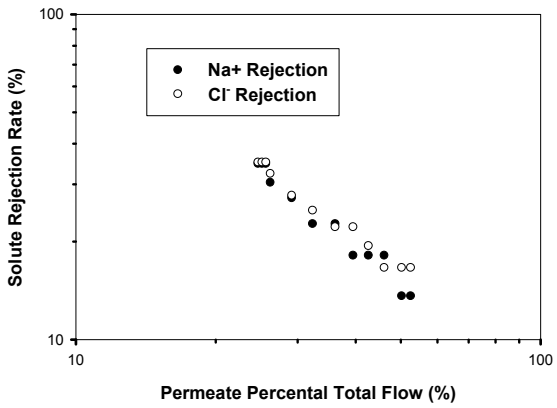

Figure 4. Relationship between permeate flow rate and solute rejection for experiment P30C01.

Figure 5 shows the results of experiment P40CO1 that used a bentonite membrane compacted to 28.9 MPa. The average hydraulic pressure was 5.24 MPa (759 psi). The initial rise of the permeate and concentrate concentrations occurs because the deionized water previously used to measure the permeability is being displaced from the system. During this experiment the permeate flow was varied between 2.7% and 10.3% of the total flow. The average permeate flow rate was 6.9% of the total flow rate. Figure 6 shows the relationship between permeate flow rate and solute rejection rate. The rejection for both Chloride (Fig. 5A) and sodium (Fig. 5B) averaged 62.9 and 61.5 %, respectively.

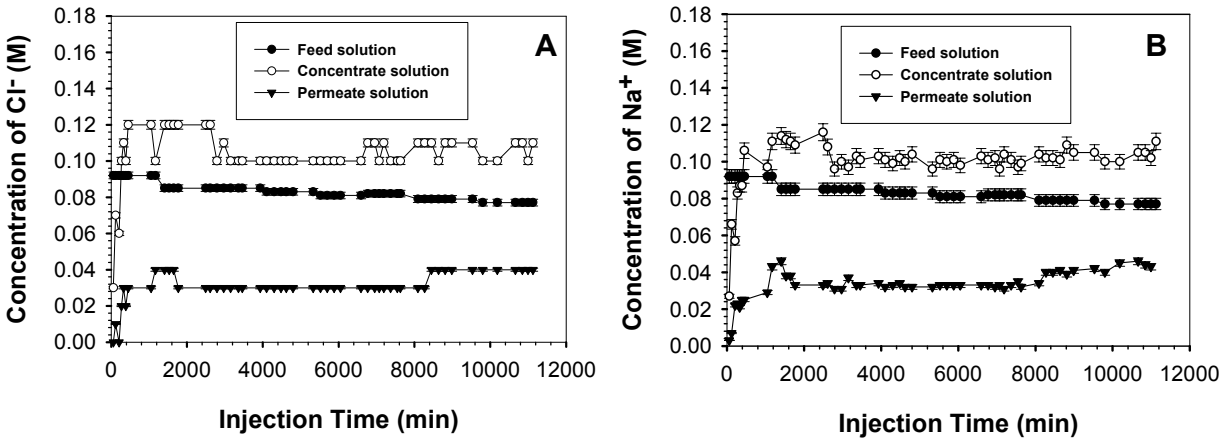

Figure 5. Results of Experiment P40C01 using a bentonite membrane compacted to 28.9 MPa.

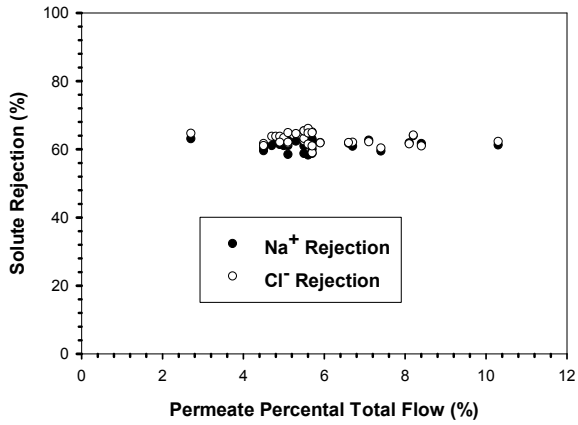

Figure 6. Relationship between permeate flow rate and solute rejection for Experiment P40C01.

Figure 6 shows the results of an experiment (P50CO1) that used a bentonite membrane compacted to 36.1 MPa. The hydraulic pressure was 5.78 MPa (838 psi). The results are similar to those in experiment P40CO1 (Fig. 5). The chloride rejection averaged 55.9% (Fig. 7A) and the sodium rejection averaged 52.3% (Fig. 7B). Notice that this is a slight decrease in solute rejection from the previous experiment. The permeate flow rate was 5.4% of the total flow rate. The initial rise of the permeate and concentrate concentrations occurs because the deionized water previously used to measure the permeability is being displaced from the system.

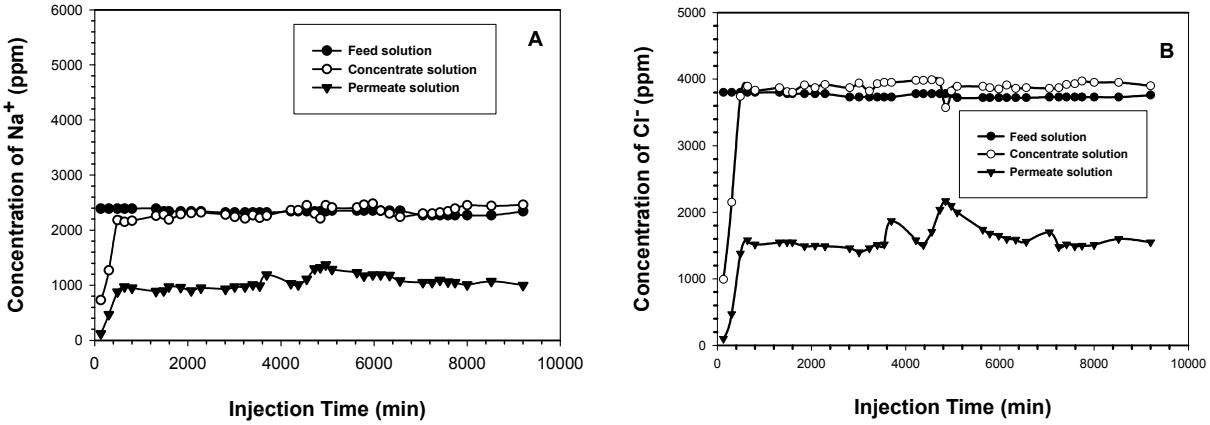

Figure 7. Results of Experiment P50C01 using a bentonite membrane compacted to 36.1 MPa.

Figure 8 shows the results of experiment P60C01 that used a bentonite membrane compacted to 43.3 MPa. The hydraulic pressure was 5.77 MPa (836 psi). This is the first experiment in which this particular membrane was used, so there is an initial rise of the permeate and concentrate concentrations because the deionized water previously used to measure the permeability is being displaced from the system. The solute rejection showed a slight decrease

from the previous two experiments. The chloride rejection was 53.6% (Fig. 8A) and the sodium rejection was 51.4% (Fig. 8A). The permeate flow rate was 8.7% of the total flow.

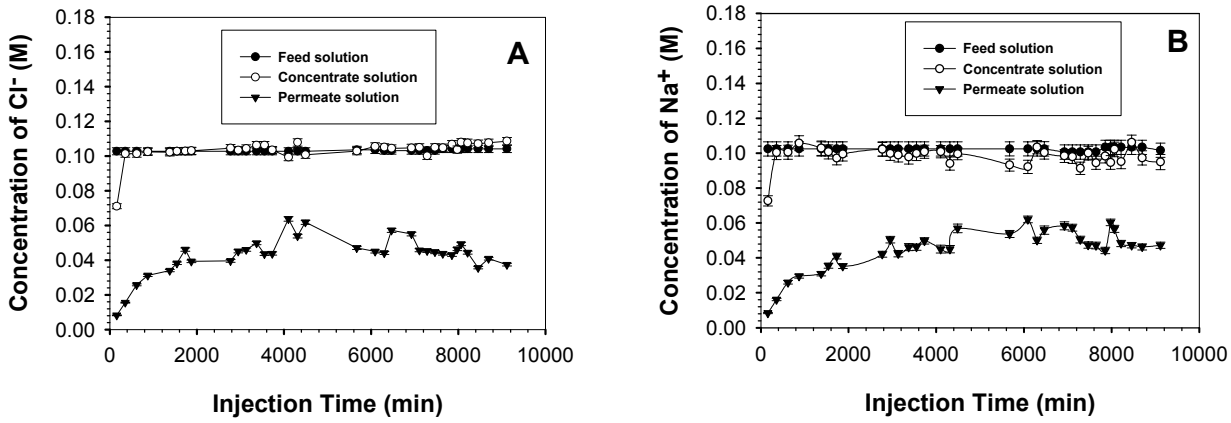

Figure 8. Results of Experiment P60C01 using a bentonite membrane compacted to 43.3 MPa.

Figure 9 presents the results of experiment P60C02 that permeated 0.218M NaCl solution through a bentonite membrane compacted to 43.3 MPa. The hydraulic pressure was 7.61 MPa (1104 psi). Notice that the solute rejection was reasonably stable over time and averaged 39.8% for chloride (Fig. 9A) and 38.2% for sodium (Fig. 9B). The permeate flow was 11.9% of the total flow.

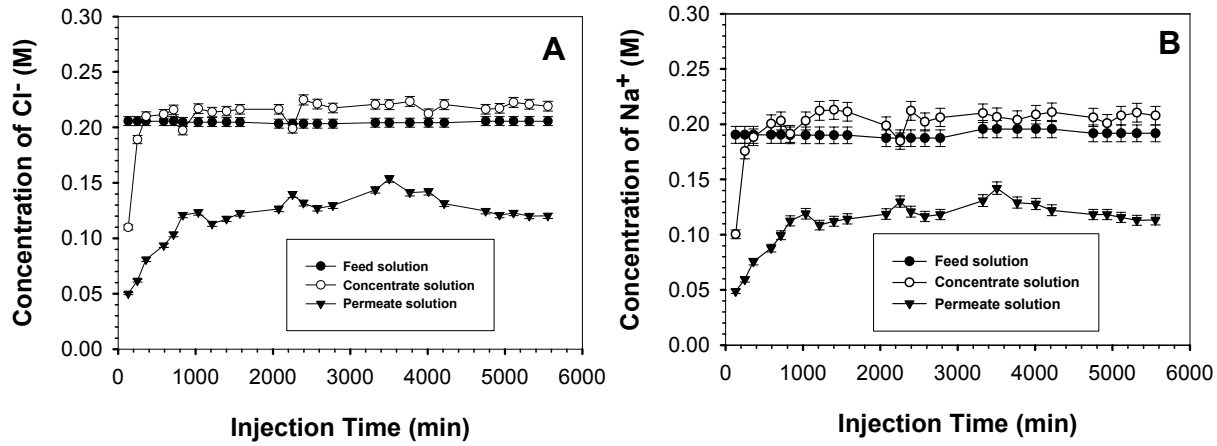

Figure 9. Results of Experiment P60C02 which used a bentonite membrane compacted to 43.3 MPa exposed to 0.2M NaCl solution.

Figure 10 presents the results for experiment P60C03 in which a 0.302M NaCl solution was passed through the same membrane used in experiment P60C01. The hydraulic pressure was 6.63 MPa (961 psi). Notice that for this experiment, the concentration of the permeate and

concentrate rise and the more dilute solution previously used is removed from the system. The chloride rejection was 31.7% (Fig. 10A) and the sodium rejection was 34.9% (Fig. 10B). There is a small decrease in solute rejection at the end of the experimental run. Since the same membrane was used in the following experiment and showed no signs of deterioration, this solute rejection decrease may be an analysis or sample collection error. The permeate flow was 8.5% of the total flow.

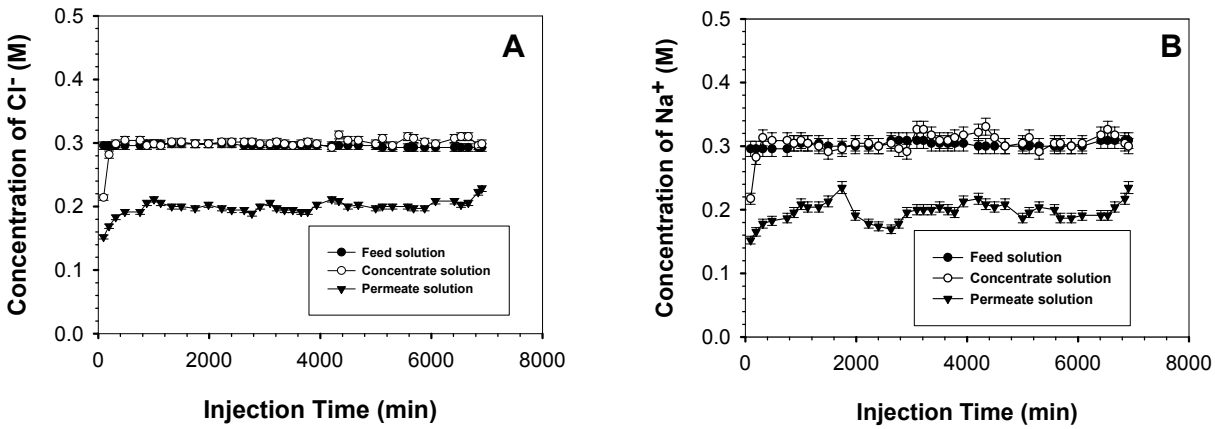

Figure 10. Results of Experiment P60C03 which used a bentonite membrane compacted to 43.3 MPa exposed to 0.3M NaCl solution.

Figure 11 presents results for experiment P60C04 that exposed a bentonite membrane compacted to 43.3 MPa to a 0.375M NaCl solution. The hydraulic pressure was 6.72 MPa (975 psi). The average chloride (Fig. 11A) and sodium (Fig 11B) rejection averaged 27.6% and 30.2%. The permeate flow was 8.7% of the total flow. The solute rejection remained reasonably stable for the duration of the experiment.

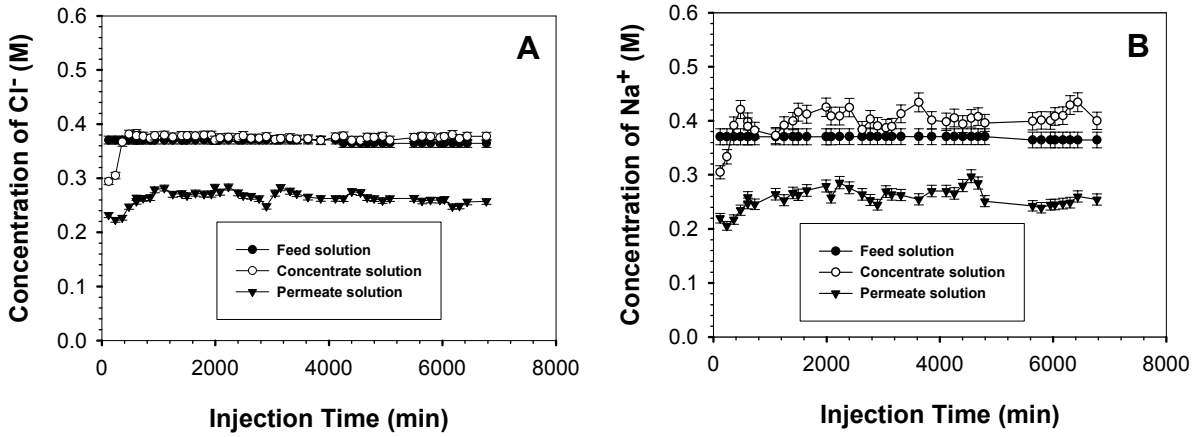

Figure 11. Results of Experiment P60C04 which used a bentonite membrane compacted to 43.3 MPa exposed to 0.4M NaCl solution.

Figure 12 presents data for experiment P60C05 that exposed the same membrane used in the previous experiment to 0.518M NaCl solution. The hydraulic pressure was 6.85 Mpa (994 psi). The chloride rejection was 27.3 % (Fig. 12A) and the sodium rejection was 27.7 % (Fig. 12B). The permeate flow was 8.2% of the total flow. The solute rejection remained essentially stable during the experiment.

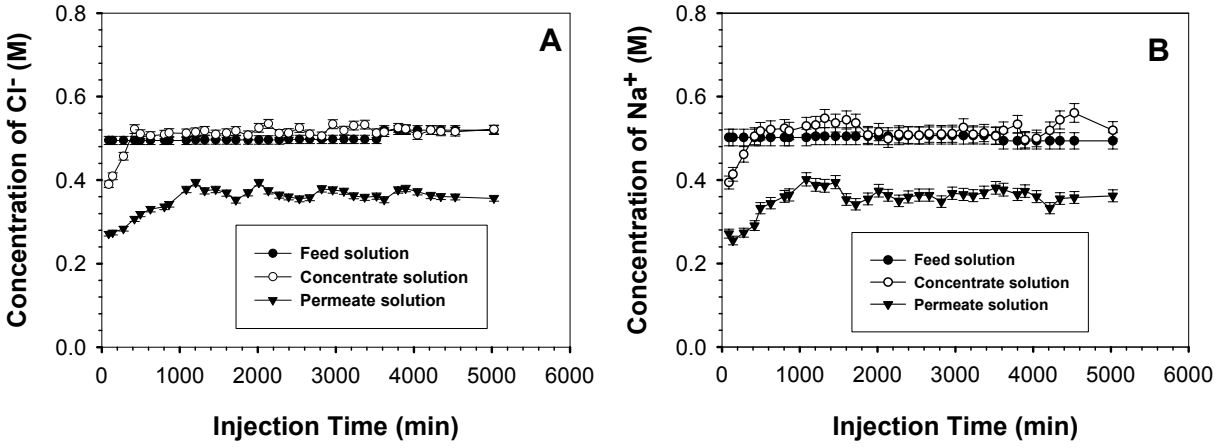

Figure 12. Results of Experiment P60C05 which used a bentonite membrane compacted to 43.3 MPa exposed to 0.5M NaCl solution.

Figure 13 presents data for Experiment P60C08. In this experiment, the membrane was exposed to a 0.802M NaCl solution. The hydraulic pressure was 6.39 MPa (926 psi). The chloride rejection was 23.7% (Fig. 13A) and the sodium rejection was 23.1% (Fig. 13B). The permeate flow was 6.4% of the total flow.

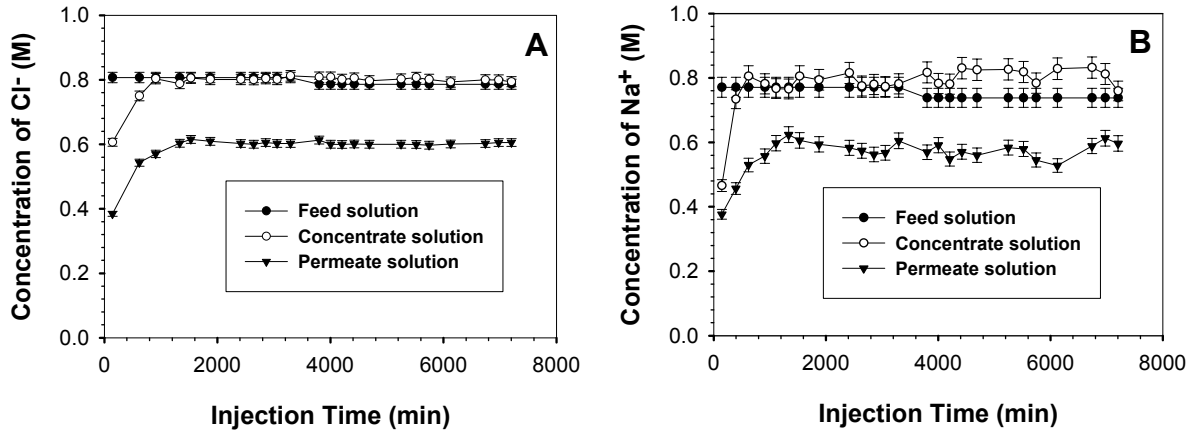

Figure 13. Results of Experiment P60C08 which used a bentonite membrane compacted to 43.3 MPa exposed to 0.8M NaCl solution.

Figure 14 presents data for experiment P60C10. This experiment used a bentonite membrane exposed to 0.989M NaCl solution. The hydraulic pressure was 6.85 MPa (994 psi). The rejection rate for chloride was 19.7% (Fig. 14A) and the rejection rate for sodium was 16.8% (Fig 14B). In this experiment, the permeate was 7.8% of the total flow. Solute rejection was reasonably steady during the experiment.

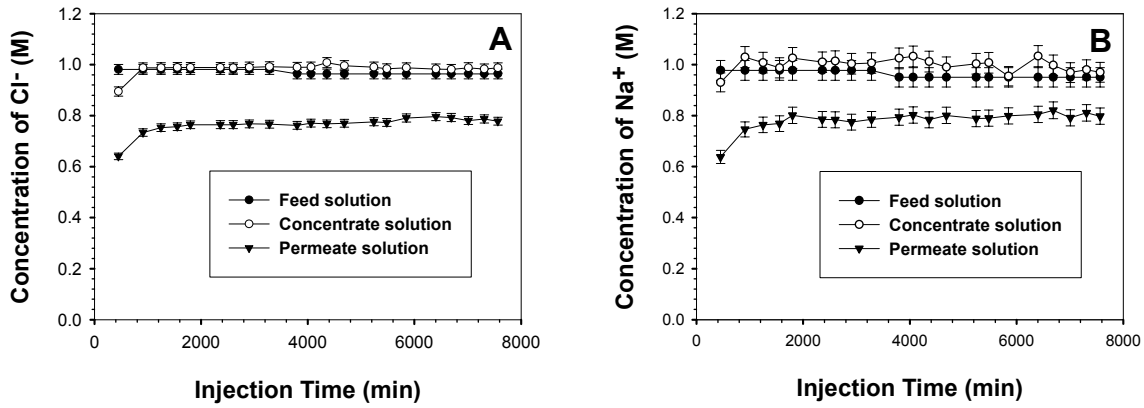

Figure 14. Results of Experiment P60C10 which used a bentonite membrane compacted to 43.3 MPa exposed to 1.0M NaCl solution.

DISCUSSION

The purpose of these experiments was to test the viability of constructing an ultra-thin clay membrane and to test the reverse osmosis solute separation capacity of such an ultra-thin bentonite membrane for NaCl. Of the ten experiments reported here, four tested how well an ultra-thin clay membrane can be compacted in an experimental cell constructed using standard machining techniques and the remaining experiments tested the effects of increasing solute concentration on the membrane efficiency.

During the first two experiments the permeate flow rate was varied to determine possible effects on solute rejection. In experiment P30C01 the permeate flow was varied between 24.6 and 52.5% of the total flow. Chloride rejection decreased from 35.1% to 16.7% as the permeate fraction of flow increased and sodium rejection decreased from 34.8 to 13.6% (Figure 5). In experiment P40C01, the permeate flow was varied between 2.7 and 10.3%. There was no significant change in either chloride or sodium rejection accompanying these flow rate changes Figure 7). These results suggest that clay membranes operated in a cross-flow configuration using porous frits may operate best when the permeate flow is approximately 10% to 24% of the total flow.

Conventional theory suggests that as the pores in a clay become smaller and the electrical double layers overlap or further overlap, the membrane must become increasingly efficient (Fritz, 1986). Compaction pressures of 21.6, 28.9, 36.1, and 43.3 MPa were used on four different bentonite membranes. The membrane thicknesses were 0.044, 0.064, 0.057, and 0.041mm. Each membrane had a higher compaction than the previous experiment. The results of solute rejection versus membrane compaction are shown in Figure 15. Notice that as compaction pressure initially rose, that the solute rejection increased and then as the compaction pressure rose further, the solute rejection decreased slightly and then leveled off.

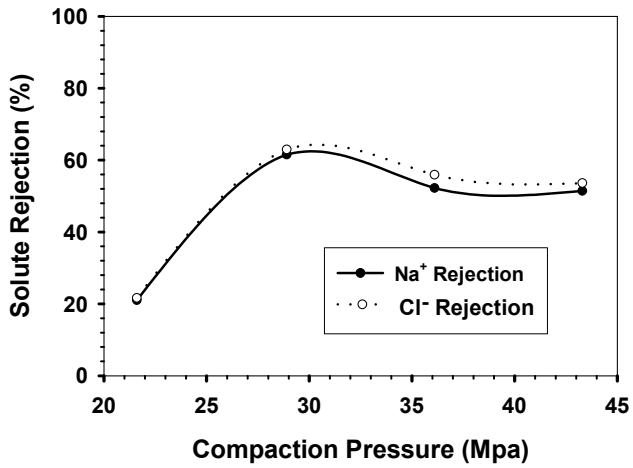

Figure 15. Comparison of solute rejection versus membrane compaction.

It is possible, though unlikely, that clay membrane efficiency, in spite of previous experimental studies (Olsen, 1972, Benzel and Graf, 1984) may decrease with increasing compaction pressure. The most likely explanation for the decrease in solute rejection efficiency accompanying the last two incremental increases in compaction pressure is that the machining precision for pocket depth of the frits or the frit thickness resulted in localized points of contact between the frits where the clay was squeezed out. The 316 stainless steel frit material used in these cells has a surface roughness of approximately ±0.001mm (±40 millionths of an inch). Twice this number is only about 1/20 the thickness of the membranes used in these experiments. Therefore, it is unlikely that contact between minute high spots on the frit material would partially short-circuit the membrane. However, the frit material and depths of the pockets have a dimensional variability that reaches ± 0.025mm (±0.001 inches). Thus a compacted membrane thickness significantly in excess of 0.05mm should be required to prevent the clay being locally squeezed out with resultant membrane bypassing and loss of efficiency at some locations due to dimensional irregularity of the frits and machined pockets for the frits.

Although membrane thickness is not thought to be a factor in clay membrane efficiency (Fritz, 1986), another explanation may be that the clay membranes were too thin. There may be some minimum thickness necessary for clay membranes to obtain optimum efficiency.

If clays are to be useful for practical membrane separations, the clay membranes must be thin enough to allow sufficient fluid throughput. At the same time, these experiments suggest that dimensional irregularities resulting from standard machining practice may place a lower limit on compacted clay membrane thickness and that this limit should be in excess of 0.05 or 0.06mm. If thinner membranes are needed, then higher dimensional tolerances are required.

The remaining experiments exposed the same membrane to differing solute concentrations. As expected, the solute rejection efficiency deceased with increasing solute concentration. For example, chloride rejection decreased from 53.6% for 0.107M NaCl solution to 19.7 % for 0.989M NaCl solution and the sodium rejection decreased from 51.4% to 16.8% (Figure 16). The membrane is the same as used in experiment P60C01 which may have had

some bypassing occurring. Thus, the reported solute rejection levels may not be an upper boundary for the solute rejection capability of bentonite clay compacted to this level.

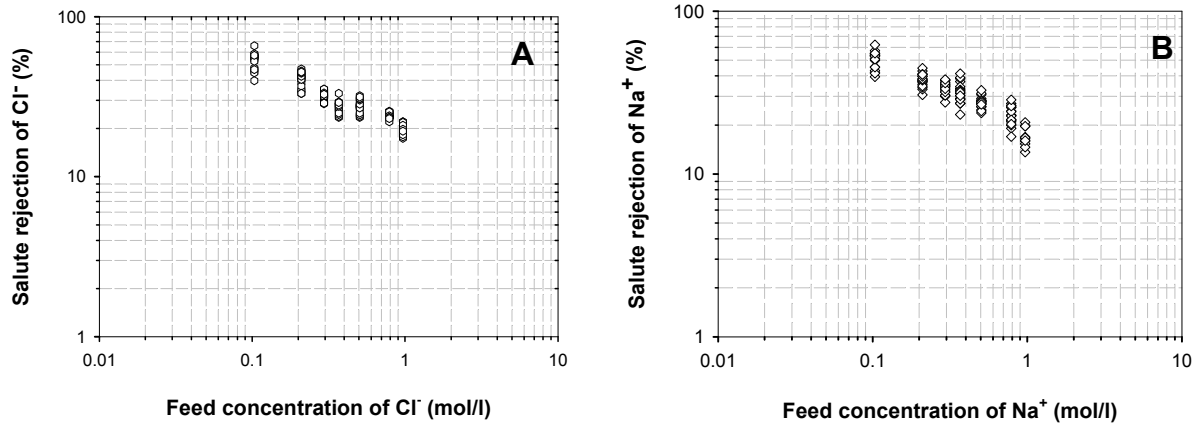

Figure 16. Graph of chloride (A) and sodium (B) rejection versus input concentration for Experiments P60C01, P60C02, P60C03, P60C04, P60C05, P60C08, P60C10.

A common method of characterizing reverse osmosis membranes is calculation of the reflection coefficient σ (Mariñas and Selleck, 1992), a unitless term originated by Staverman (1952) which describes the osmotic efficiency of the membrane. Permissible values of σ range from zero to one (Fritz, 1986). If σ = 0, there is no membrane effect. If σ = 1, the membrane is ideal and no solute can pass. Since in the cross-flow configuration the feed concentration is essentially equal to the concentration at the membrane interface, we can approximate σ via

$$\sigma = \frac{c_0 - c_e}{c_0 + c_e} \tag{3}$$

(Fritz and Marine, 1983) where c_o is the feed concentration and c_e is the permeate concentration. The calculated values of σ (Equation 3) for these experiments ranged from 0.45 to 0.10 (Table 3).

Table 3. Calculated values of the reflection coefficient σ for each experiment. Values are averaged for Cl^- and Na^+.

Experiment	σ
P30C01	0.12
P40C01	0.45
P50C01	0.37
P60C01	0.36
P60C02	0.25
P60C03	0.20
P60C04	0.17
P60C05	0.16
P60C08	0.13
P60C10	0.10

Other published experiments using thicker bentonite clays at lower compaction levels have shown higher sigma values then we report here. For example, Whitworth and DeRosa (1997) performed a series of experiments using various solutions and bentonite membranes and obtained generally higher σ values (Table 4). However, the concentrations they used were significantly lower than the ones we used in our experiments. The value of σ is expected to decrease with increasing solute concentration (Fritz, 1986), therefore our results may be reasonable and membrane bypassing may have been minor. The values of Lp reported by Whitworth and DeRosa (1997) (Table 4) are three to four orders of magnitude greater than our Lp measurements (Table 3). However, if some of the compaction force in our experiments was transferred through point to point contact on the frits instead of through the clay, then our calculated values of Lp may be misleading.

Table 4. Results of Whitworth and DeRosa's (1997) bentonite membrane experiments.

Experiment	Membrane Thickness (mm)	Compaction Pressure (MPa)	Solution Type	Input Concentration (M)	Lp ($cm^3/s \cdot dyne$)	σ
WRRI2	0.64	3.14	$CuCO_2$	0.0071	4.97E-11	0.90
WRRI4	0.64	0.50	$CuCO_2$	0.0036	5.37E-10	0.95
WRRI5	0.97	2.45	$PbCl_2$	0.023	9.00E-11	0.74
WRRI6	0.94	1.66	$PbCl_2$	0.0074	6.34E-11	0.49
WRRI7	0.61	0.63	$CuCO_2$	0.002	2.21E-11	0.59
WRRI8	0.94	6.72	$CuCl_2$	0.029	7.21E-11	0.96
WRRI9	0.94	6.39	$CoCl_2$	0.077	6.69E-11	0.88

Based on the relatively low rejection rates we obtained using bentonite clays for reverse osmosis removal of NaCl, it is doubtful that clay membranes can directly compete with synthetic membranes in desalination applications. However, higher compaction pressures with no

membrane bypassing may yield significantly higher rejection rates than we achieved in these experiments. Also, certain types of modified clays might prove to be more effective membranes as well.

Perhaps the most likely use of clay membranes for desalination might be as an inexpensive first stage of a two-stage reverse osmosis treatment unit. Two-stage RO is defined as running two reverse osmosis systems in series with the permeate from the first feeding the second reverse osmosis system. Staged or series operation is typically used when a single-stage RO system does not produce the required quality of product water.

One possible use of poorly-compacted clay membranes, perhaps in under-developed nations, might be for removal of cryptosporidium oocysts and other microbiological contaminants. Cryptosporidium, for example, is very resistant to commonly used disinfection methods (Knops and Franklin, 2000). Clays are inexpensive and might be useful for treating water supplies in small villages and towns that cannot afford commercial water treatment systems.

CONCLUSIONS

Sedimentation followed by vacuum filtration is a viable method for constructing ultra-thin clay membranes. The membranes constructed for the experiments reported herein ranged between 0.064 and 0.041mm in thickness. However, compaction of such ultra-thin clay membranes proved problematic. The thickness of the membranes was exceeded by the dimensional variation in the machined experimental cell and this is believed to have resulted a decrease in effective compaction pressure and in local bypassing of the membrane with a resultant decrease in solute rejection efficiency. Another possibility that clay membranes have some minimum effective thickness and these clay membranes were too thin to reach maximum efficiency.

The permeate flow was varied as a percentage of the total flow in two of the experiments to investigate results of changing permeate flow on solute rejection. In one experiment, the permeate flow was varied between 2.7 and 10.3% of the total flow with no significant change in solute rejection. In another experiment, the permeate flow was varied between 24.6 and 52.5% of the total flow. In this experiment, the solute rejection rate decreased as the permeate occupied greater fractions of the total flow. This suggests a maximum solute rejection efficiency for these clay membranes for a permeate flow of between 10.3 and 24.6%.

Solute rejection was found to decrease with increasing salt concentration. It ranged between 62.9% for 0.101 M Cl^- and 19.7% for 0.989 M Cl^- and between 61.5 for 0.101 M Na+ and 16.8% for 0.989 M Na+. Due to problems with the compaction procedure and potential membrane bypassing, these rejection rates may not be the upper limit for bentonite membrane solute rejection.

CROSS-FLOW EXPERIMENTS WITH PRODUCED WATER

INTRODUCTION

We ran a series of four reverse osmosis experiments using a 20%, 40%, 60%, and 80% dilution of a produced water sample. The bentonite membrane used in these experiments was 0.057mm thick.

METHODS

We used a commercially available Wyoming bentonite (Wyo-Ben Hydrogel) which X-ray analysis showed to be a Na-bentonite. We chose a commercially available clay because it is the most likely candidate for use if clay membranes prove to have practical potential.

The first step in preparation of the bentonite clay was to separate the 0.2 μm and smaller size fraction using standard sedimentation techniques. Following sedimentation, most of the water in the clay slurry was evaporated. The clay slurry was then dialyzed, freeze-dried in a Model 4.5 Labconco benchtop freeze dryer, and the freeze-dried clay was stored in nested, tightly sealed Ziplock™ bags.

A flat-leaf experimental cell was designed for reverse osmosis experiments using clays as the membrane (Figure 1). This cell was constructed from 316 stainless steel by the R&ED machine shop at New Mexico Tech. The clay membrane was compacted to 36.1 Mpa in a hydraulic press via the integral piston. The membrane area in this cell is 136.5 cm^2.

The clay membranes were prepared by first assembling the lower part of the experimental cell (using bolt holes not shown in Figure 1). The bottom 316 stainless steel frit was covered with two layers of Millipore 0.1 μm filter paper. The filter paper extends past the frit and is sealed by an O-ring when the center ring is bolted in place. Then a thin clay slurry (2.00 grams of freeze-dried bentonite thoroughly mixed with 150 ml of deionized water) was poured into the cavity above the filter paper. The clay was allowed to settle for 10 hours and then a vacuum pump was attached to the permeate port and the remaining water removed under vacuum. This procedure formed a very thin and uniform layer of clay on the Millipore filter.

Next, the piston was inserted and gently pressed into place using an arbor press and then the upper plate was set into place and the retaining bolts were loosely fastened. The entire assembly was then transferred to a 75-ton hydraulic press and the membrane was compacted at pressure 36.1 Mpa for 24 hours. At the end of the compaction period, the bolts were tightened to hold the cell together and the cell was moved to the lab bench.

The next step was to measure the permeability of the clay membrane to deionized water. To prevent complications from entrained air, the cell was placed under vacuum for four hours prior to starting deionized water through the system. The deionized water was also vacuum-degassed before use.

The flow configuration used in these experiments is shown in Figure 2. Both deionized water and diluted produced water solutions were pumped through the system using an ISCO Model LC 5000 syringe pump. This pump has a capacity of 500ml and provides a pulseless and exceptionally stable flow rate. Pressure gages are provided both before and after the experimental cell and a 0.2 μm in-line filter is used in the concentrate line to prefilter samples before analysis.

During permeability measurement, the needle valve in the concentrate line was closed so that all of the flow had to pass through the clay membrane. Samples were collected at specified time intervals and the volume collected was determined by weighing to ±0.01 g. Since the density of deionized water is very close to 1.00, the weight of the water collected gave a precise measure of the volume collected for that time interval. Samples were collected until three consecutive samples, each taken at least an hour apart, showed no change in both volume collected per unit time and the hydraulic pressure. This was deemed steady-state and the permeability was averaged from these last measurements via Equation 4.

$$L_P = \frac{J_V}{\Delta P} \tag{4}$$

where L_p is the membrane's coefficient of permeability for water, J_v is the water flux at steady state in $cm^3/cm^2 \cdot s$, and ΔP is the applied hydraulic pressure in $dynes/cm^2$.

Next the syringe pump was emptied and refilled with the feed solution. The pump was filled and emptied a minimum of three times to minimize dilution effects caused by the small dead space in the pump. Then the needle valve was opened and the solution was started through the experimental cell. The needle valve was adjusted to achieve the desired back-pressure on the upper side of the membrane. Both permeate and concentrate samples were periodically collected for analysis. Samples were also collected from the stock solution and from the feed solution in the syringe pump for analysis.

To prevent evaporation during sample collection, an evaporation control system was used. A rubber stopper was placed into the sample flask and two tubes passed through the stopper. One was the permeate line, which was connected to the membrane cell. The other was a capillary tube that also passed through another rubber stopper inserted into a second flask. The end of this capillary tube remained below the liquid level in the second flask ensuring that no evaporation took place. Another short length of capillary tube was inserted into the stopper in the second flask and was open to the atmosphere. The feed solution tanks remained tightly sealed during the experiments.

At the end of the experiments, the cell was disassembled and the clay membrane thickness was measured using digital caliper. Thickness values were obtained by averaging a minimum of six measurements located at various places on the membrane.

The produced water (Table 1) was obtained from a facility near Loco Hills, New Mexico. The produced water sample was first filtered through 0.7µm Whatman® filter paper to remove suspended solids. Because dissolved organics would damage the ion-exchange column during anion analysis by Ion Chromatography (IC), they were removed by adsorption onto granular active carbon. To do this, 1.0% weight percent of 20~40 mesh Darco® granular active carbon was added to the filtered produced water and allowed to settle for 12 hours. The granular activated carbon was then removed by filtering first with 0.7µm Whatman® filter paper and next with 0.22µm Millipore filter paper. The pretreated produced water was then diluted for use in the experiments.

Table 5. Chemical Analysis of produced water sample.

Analyte	Concentration
pH	6.98
Total Dissolved Solids	196,250 mg/l
Bicarbonate	820 mg/l
Chloride	115,453 mg/l
Sulfate	4,271 mg/l
Phosphate	<0.5 mg/l
Sodium	71,000 mg/l
Potassium	845 mg/l
Magnesium	1,191 mg/l
Calcium	3,080 mg/l
Bromide	93 mg/l
Arsenic	0.01 mg/l

Ion Chromatography (IC) was used for analysis of sulfate (SO_4^{2-}) concentrations and low concentrations of chloride (below 0.0056M after dilution). The ion chromatograph was a Dionex 600 with an AS50 autosampler and chromatography compartment, CD25 conductivity detector and a GP50 gradient pump. The column was a Dionex AS14. Calibration was performed by injecting a series of standard solutions. Internal reference standards were run near the beginning and end of each IC run. For large runs, calibration checks were run every 20-30 samples. A duplicate sample was run every 10-12 samples. Internal reference standards of Cl = 0.00114M were periodically run. The results of these analyses were Cl = 0.00114M, 0.00115M, and 0.00113M.

High chloride concentrations (above 0.0056M) were analyzed using a Lachat QuikChem 8000® flow injection analysis automated ion analyzer (FIA). The method was QuikChem Method 10-117-07-1-J. This method covers the determination of chloride in drinking, ground, and surface waters, and domestic and industrial wastes. The applicable range is 0.0056M to 0.705M Cl. The method detection limit is 0.00021M. Therefore, dilutions were necessary when concentrations were above this range. Calibration was performed by injecting a series of standard solutions. Triplicate analysis was conducted for each standard solution and a 0.5% RSD was set as replicate criteria.

Cation analysis (Na^+, K^+, Mg^{2+} and Ca^{2+}) was conducted using a Varian model 110 flame atomic absorption spectrophotometer (FAA) with a SIPS-10 sample introduction pump system, and SPS-5 sample preparation system and dilutor. Calibration check samples were run at the beginning and end of each run, and every 10-12 samples if there were more than 20 samples in a run. A duplicate sample was run every 10-12 samples. The instrument was checked for zero readings between samples and re-zeroed if necessary, re-sloped every 10-12 samples, and re-calibrated every 20-24 samples. Analytical accuracy and precision of chemical measurements are presented in Table 2.

Table 6. Summary of analytical methods, accuracy, and precision for chemical analyses.

Species	Equipment	Method Number	Accuracy	Precision
Chloride (<200mg/l)	IC	EPA300.0	< 1%	< 0.5%
Chloride (>200mg/l)	FIA	QuikChem 10-117-07-1-J	0.5%	0.5%
Sulfate (SO_4^{2-})	IC	EPA300.0	< 1%	< 0.5%
Cation (Na^+, K^+, Mg^{2+}, Ca^{2+})	FAA	EPA7000	2%	1%

Note: Accuracy and precision are stated at one standard deviation. Error bars on graphs are at plus or minus one standard deviations for IC and FIA analysis and plus or minus two standard deviations for FAA analysis.

RESULTS

Four room-temperature solute rejection experiments were conducted with a compacted, very thin (0.057mm) bentonite membrane and 80%, 60%, 40%, and 20% dilutions of a produced water. The membrane was compacted to 36.1Mpa. A summary of the experimental parameters is presented in Table 3, and the chemical composition of each dilution is given in Table 4.

Table 7. Experimental parameters.

Experiment No.	Compaction Level (MPa)	Membrane Thickness (mm)	Solution Concentration and Type	Average Permeate Flow (% of total)	Total flow rate (ml/min)	Pressure (MPa)
P5002Co	36.1	0.057	80% dilution	4.78%	0.512	5.6
P5004Co	36.1	0.057	60% dilution	4.13%	0.534	5.6
P5006Co	36.1	0.057	40% dilution	5.41%	0.419	5.7
P5008Co	36.1	0.057	20% dilution	4.51%	0.489	6.1

Table 8. Chemical analysis of feed solutions used in the experiments.

Experiment No.	TDS (mg/l)	Cl^- Concentration (mmol/l)	SO_4^{2-} Concentration (mmol/l)	Na^+ Concentration (mmol/l)	K^+ Concentration (mmol/l)	Mg^{2+} Concentration (mmol/l)	Ca^{2+} Concentration (mmol/l)
P5002Co	37,212	614.3	7.8	592.6	3.1	5.0	19.3
P5004Co	74,147	1218.6	17.6	1196.0	6.6	10.6	29.2
P5006Co	115,092	1905.9	25.2	1830.4	9.7	15.4	53.9
P5008Co	154,097	2617.7	32.8	2377.1	11.6	19.0	60.6

Note: TDS, total dissolved solid in feed solution

Figures 17-22 present the solute rejection results for Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} for experiment P5002Co, which used an 80% dilution of the produced water with a TDS of 37,212 mg/l. The concentration of permeate and concentrate increased initially (Figs. 17-22) because the deionized water previously used to measure the permeability was being displaced from the frit and membrane in the experimental cell. The average permeate flow was 4.78% of the total flow and the total flow rate was 0.512 ml/min.

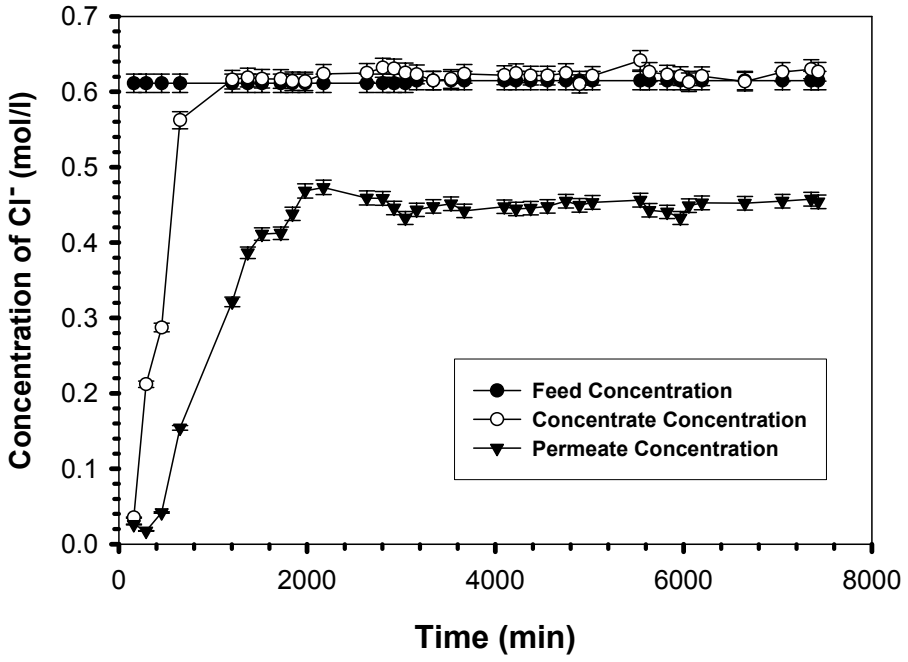

Figure 17. Results of experiment P5002Co for Cl^- in which the feed solution was an 80% dilution of produced water.

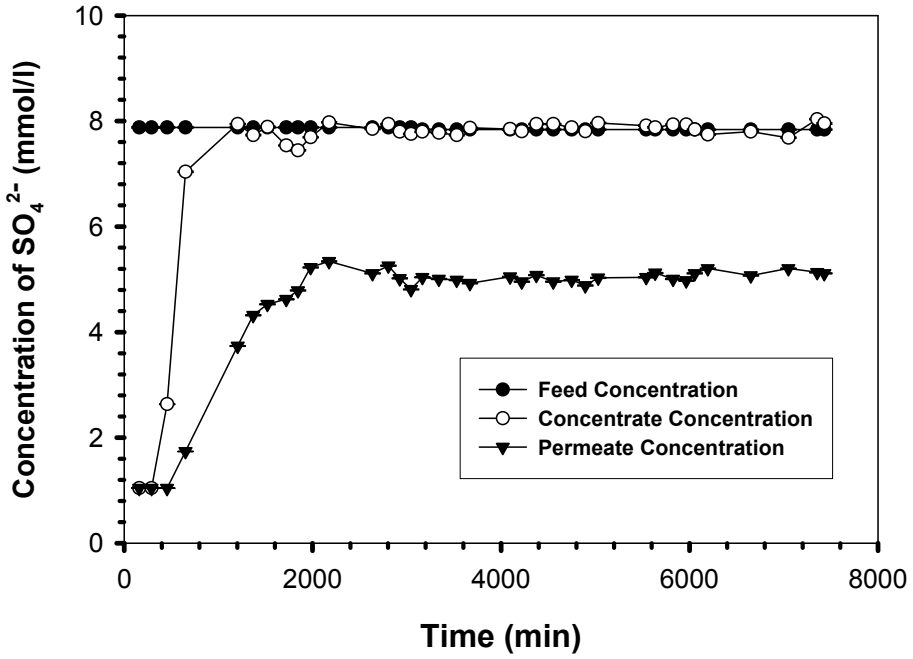

Figure 18. Results of experiment P5002Co for SO_4^{2-} in which the feed solution was an 80% dilution of produced water.

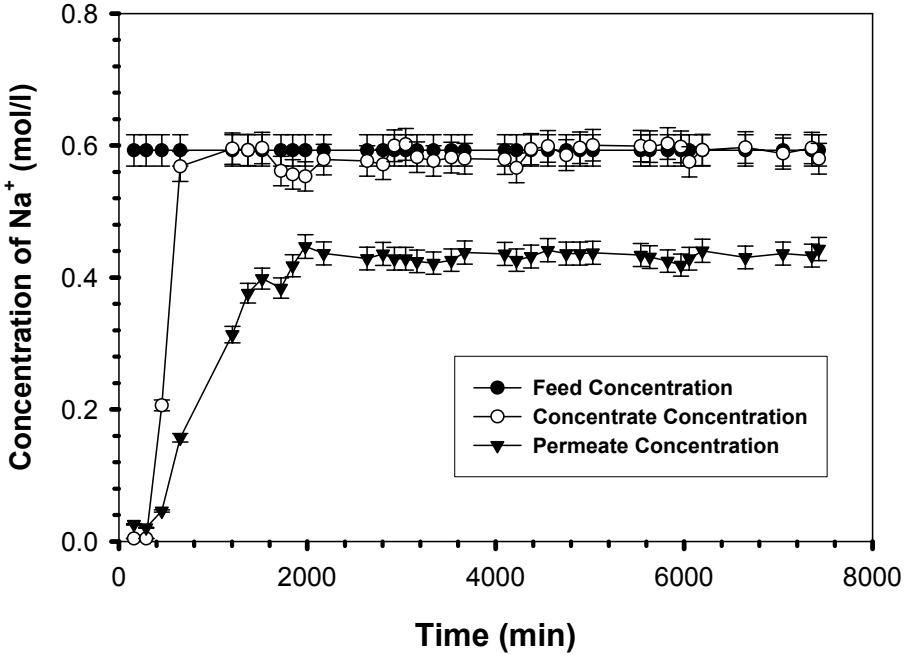

Figure 19. Results of experiment P5002Co for Na^+ in which the feed solution was an 80% dilution of produced water.

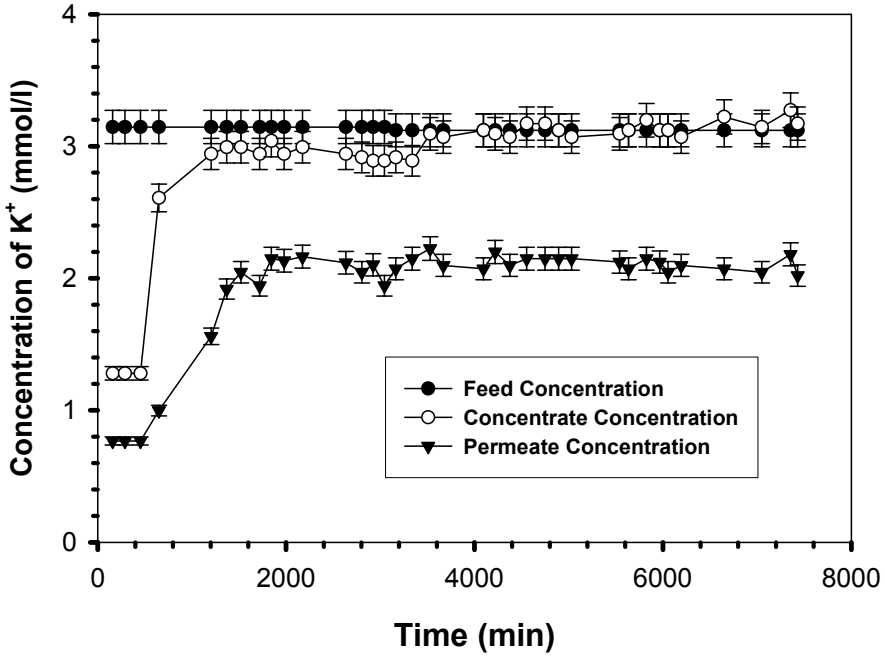

Figure 20. Results of experiment P5002Co for K^+ in which the feed solution was an 80% dilution of produced water.

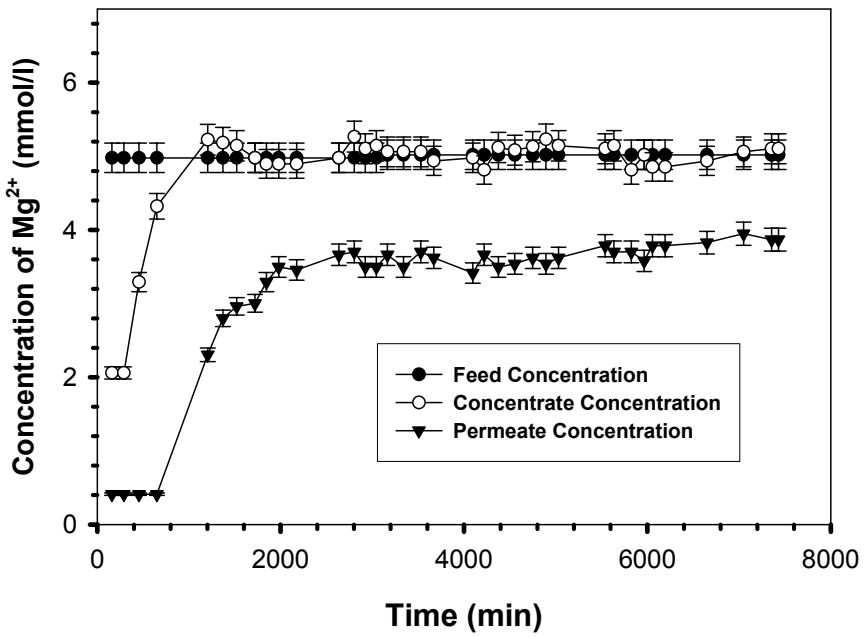

Figure 21. Results of experiment P5002Co for Mg^{2+} in which the feed solution was an 80% dilution of produced water.

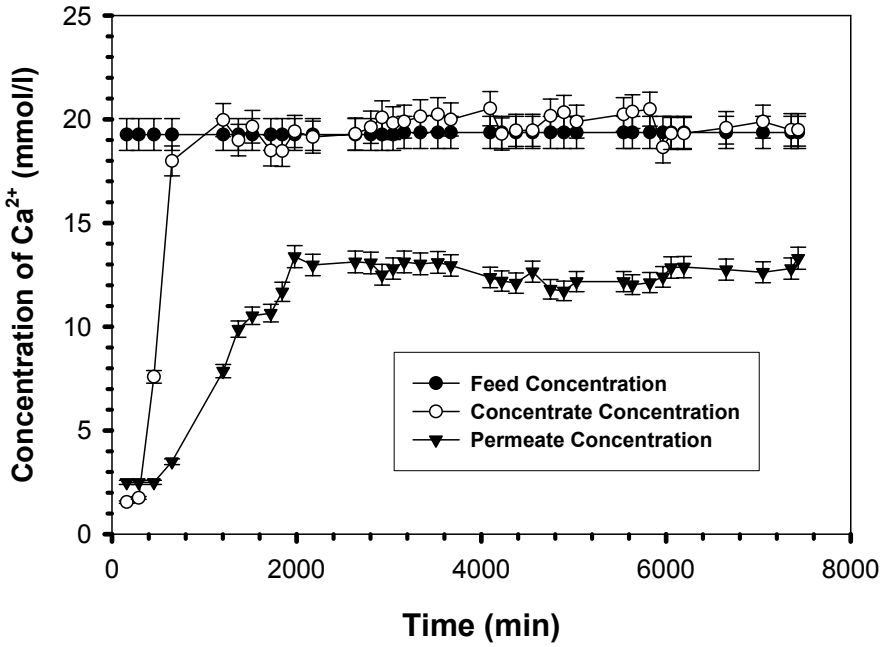

Figure 22. Results of experiment P5002Co for Ca^{2+} in which the feed solution was an 80% dilution of produced water.

Figures 23-28 present the solute rejection of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} for experiment P5004Co, which used a 60% dilution of the produced water. The total dissolved solids in this feed solution was 74,147 mg/l. The permeate flow ranged from 3.7% to 4.8% and averaged 4.1% of the total flow. The hydraulic pressure was 5.6 Mpa. The concentration of both the permeate and concentrate (Figs. 23-28) increase from an initial value that is close to the feed concentration in experiment P5002Co, due to flushing of the previous, less concentrated solution out of the experimental cell. Since each experiment was conducted with feed solutions of increasing concentration, this initial increase in concentration of the permeate was exhibited in each of the experimental runs.

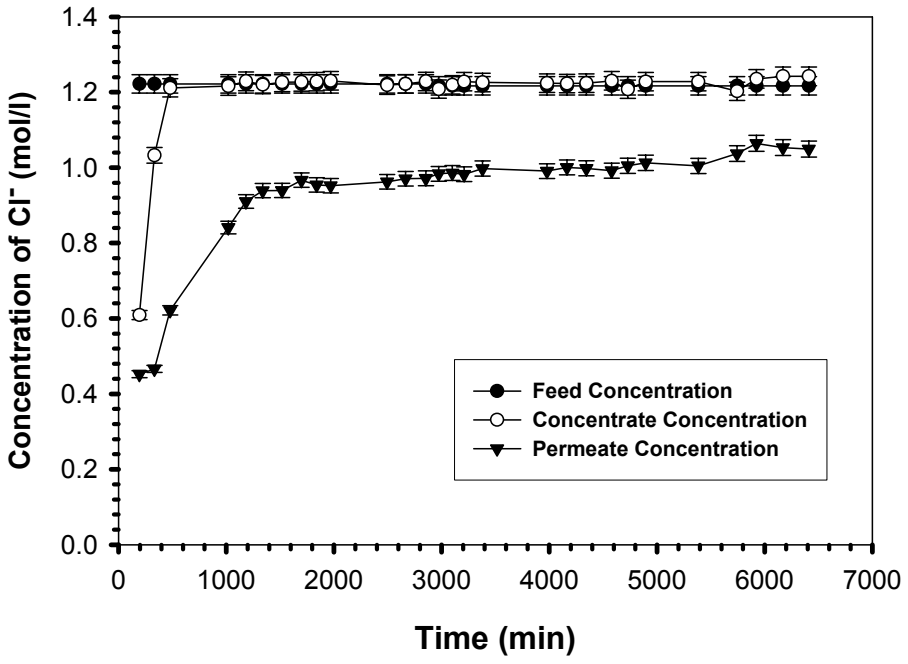

Figure 23. Results of experiment P5004Co for Cl^- in which the feed solution was a 60% dilution of produced water.

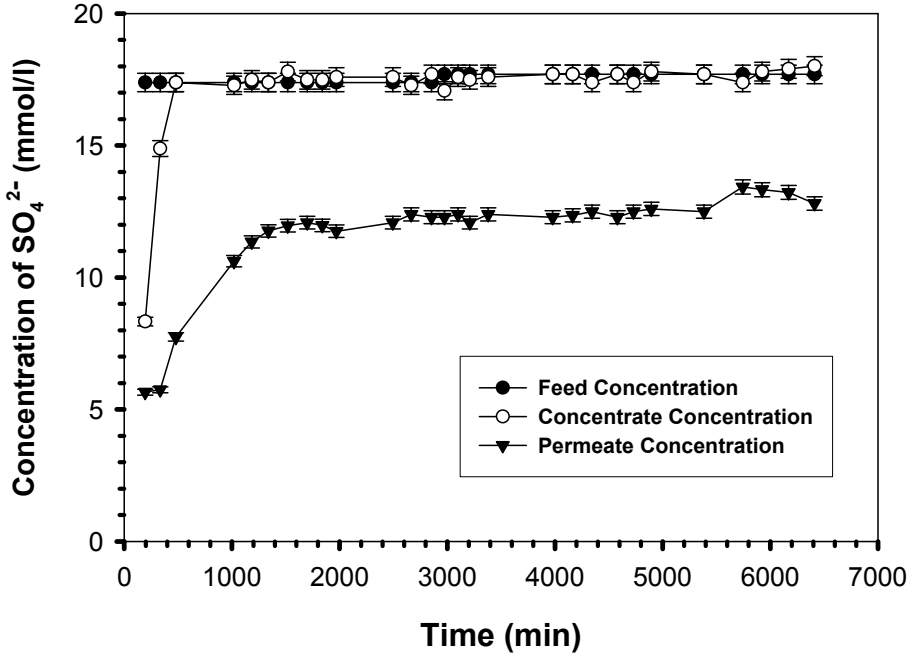

Figure 24. Results of experiment P5004Co for SO_4^2 in which the feed solution was a 60% dilution of produced water.

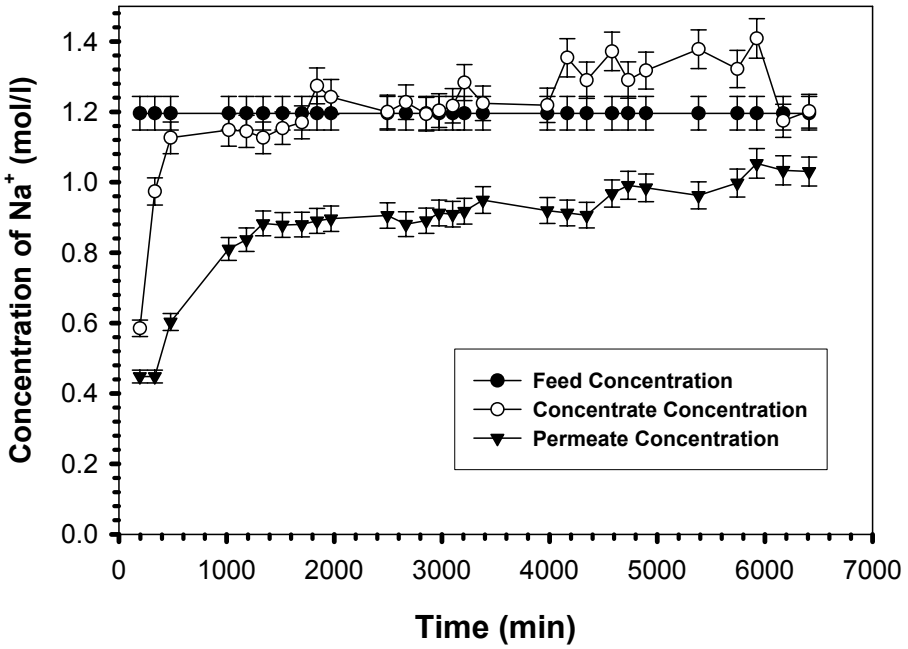

Figure 25. Results of experiment P5004Co for Na^+ in which the feed solution was a 60% dilution of produced water.

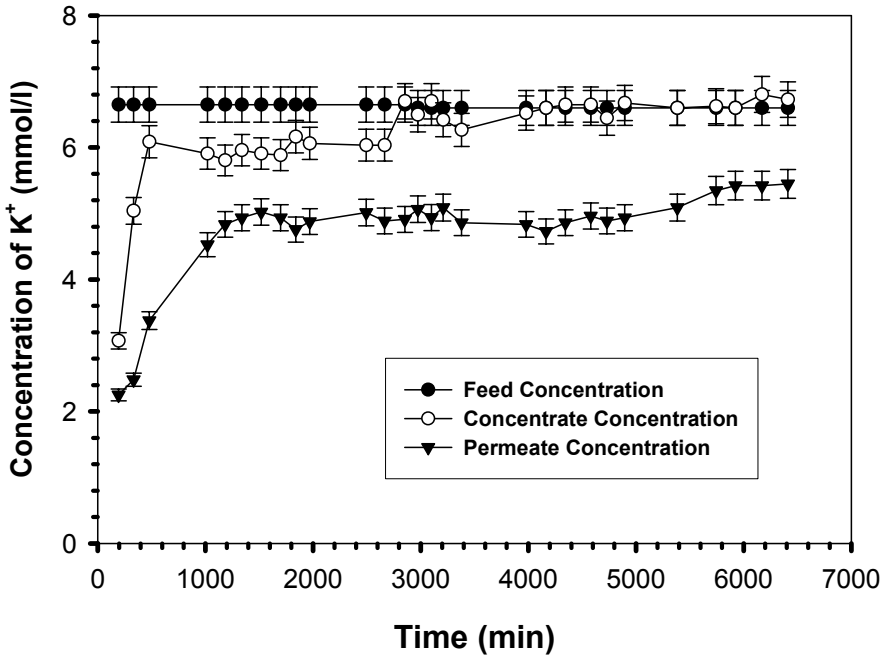

Figure 26. Results of experiment P5004Co for K^+ in which the feed solution was a 60% dilution of produced water.

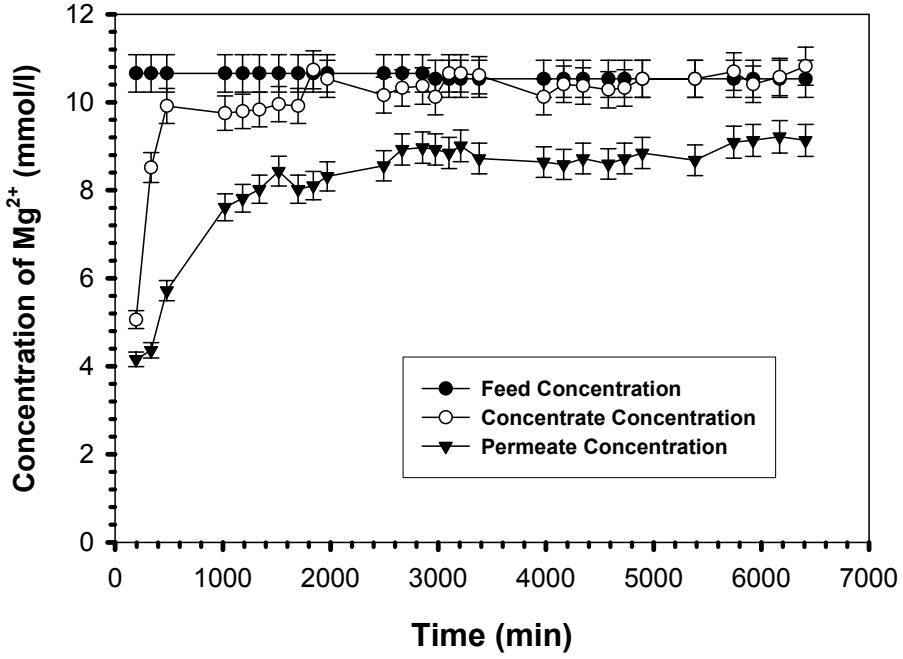

Figure 27. Results of experiment P5004Co for Mg^{2+} in which the feed solution was a 60% dilution of produced water.

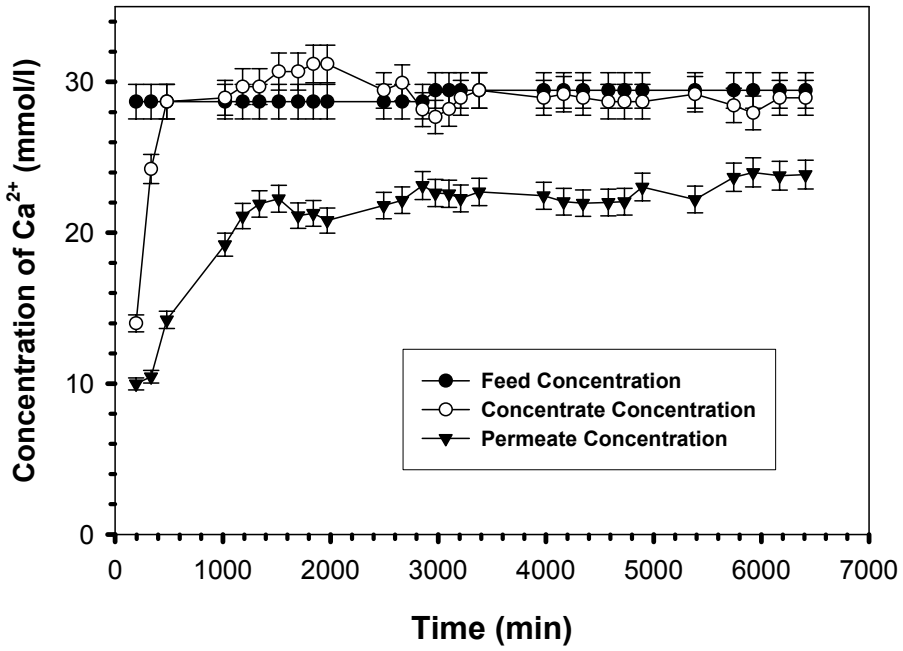

Figure 28. Results of experiment P5004Co for Ca^{2+} in which the feed solution was a 60% dilution of produced water.

Figures 29-34 present the solute rejection of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} in experiment P5006Co, in which the feed solution was a 40% dilution of the produced water sample and had a TDS of 115,092 mg/l. The average permeate flow was 5.4% of total flow and the hydraulic pressure in this experiment was 5.7 Mpa.

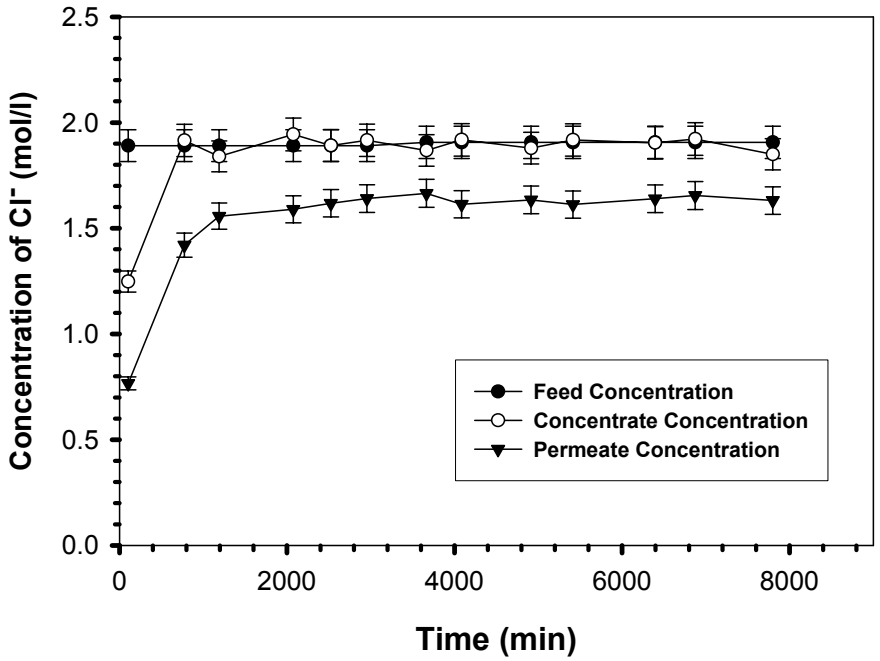

Figure 29. Results of experiment P5006Co for Cl^- in which the feed solution was a 40% dilution of produced water.

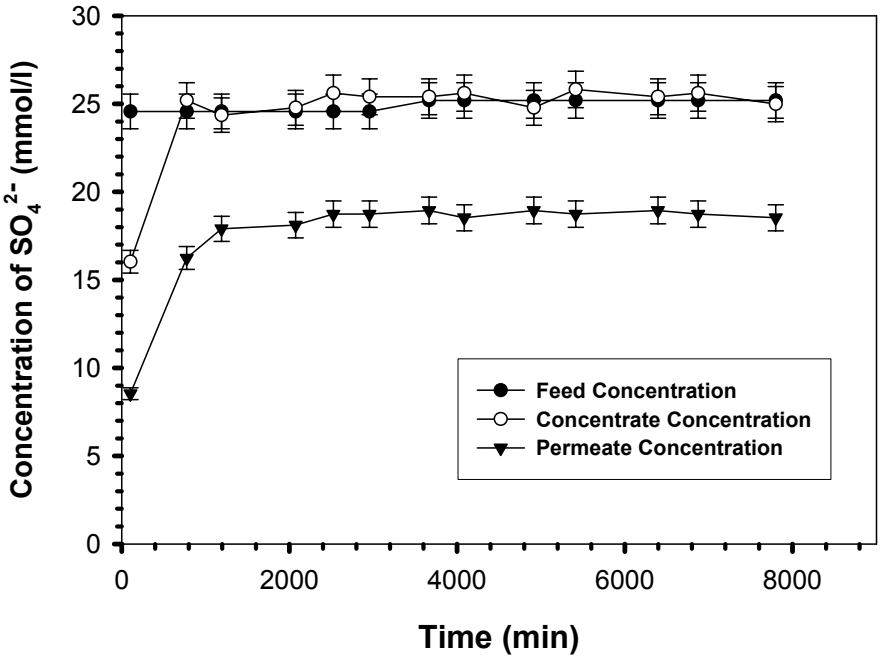

Figure 30. Results of experiment P5006Co for SO_4^{2-} in which the feed solution was a 40% dilution of produced water.

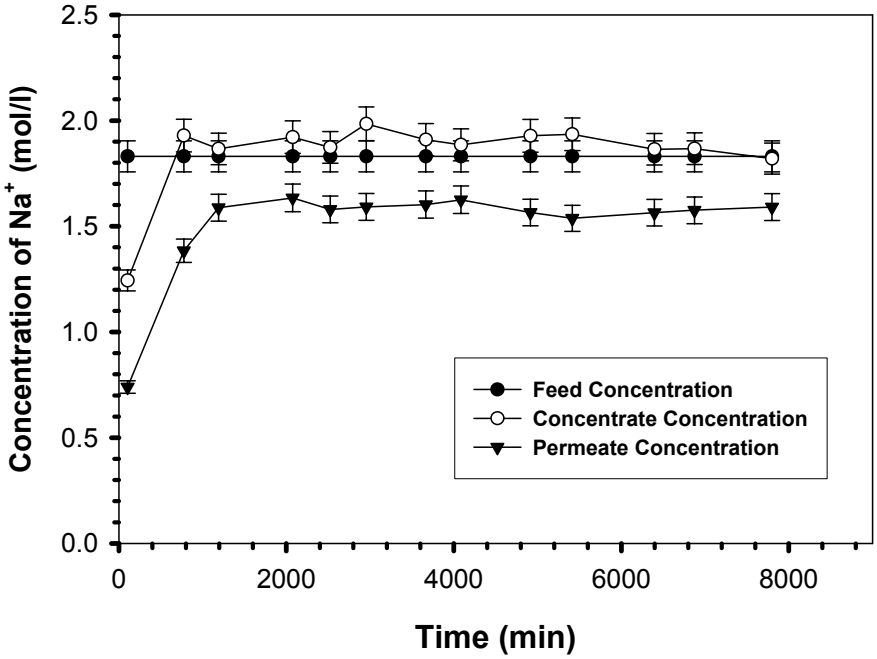

Figure 31. Results of experiment P5006Co for Na^+ in which the feed solution was a 40% dilution of produced water.

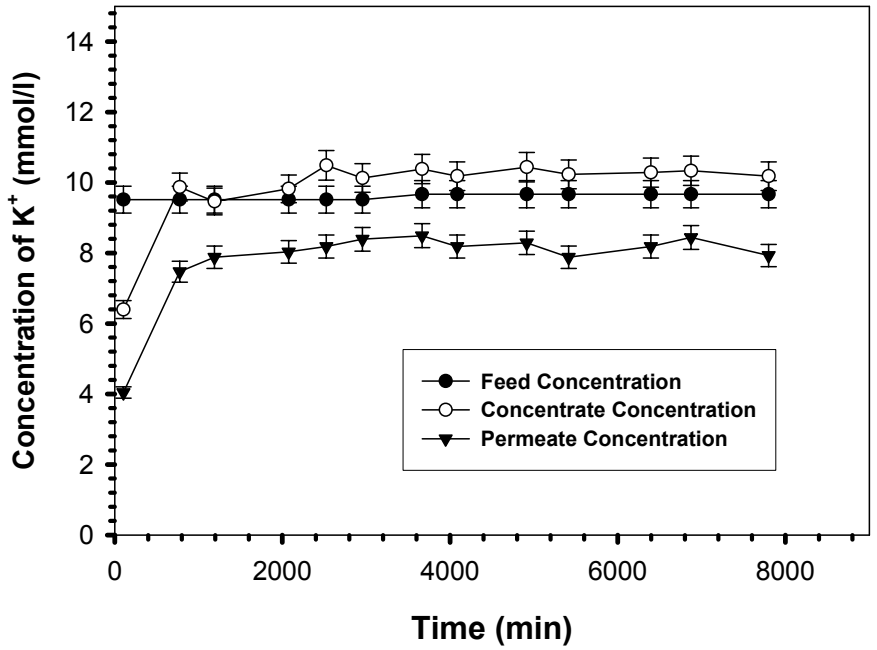

Figure 32. Results of experiment P5006Co for K^+ in which the feed solution was a 40% dilution of produced water.

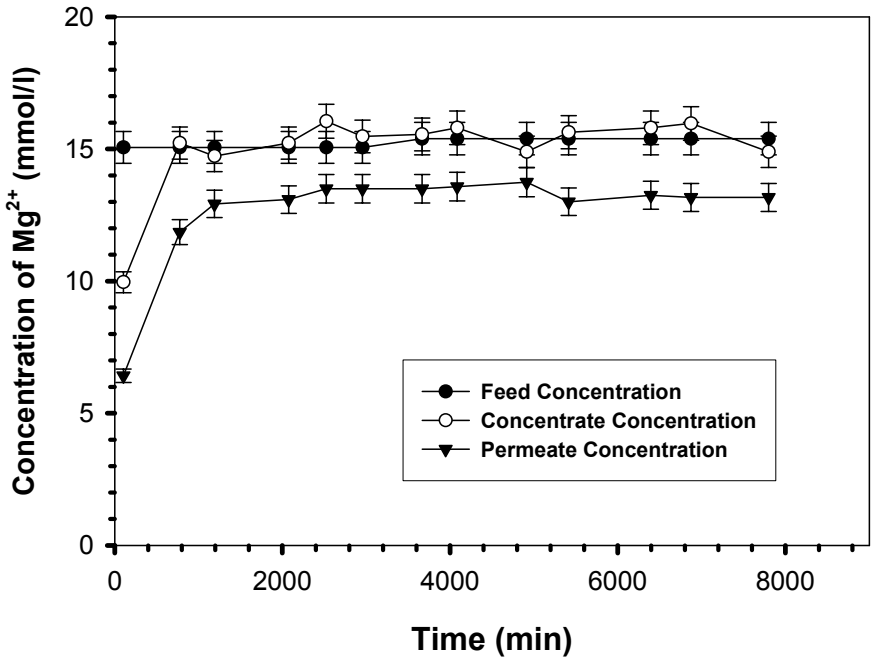

Figure 33. Results of experiment P5006Co for Mg^{2+} in which the feed solution was a 40% dilution of produced water.

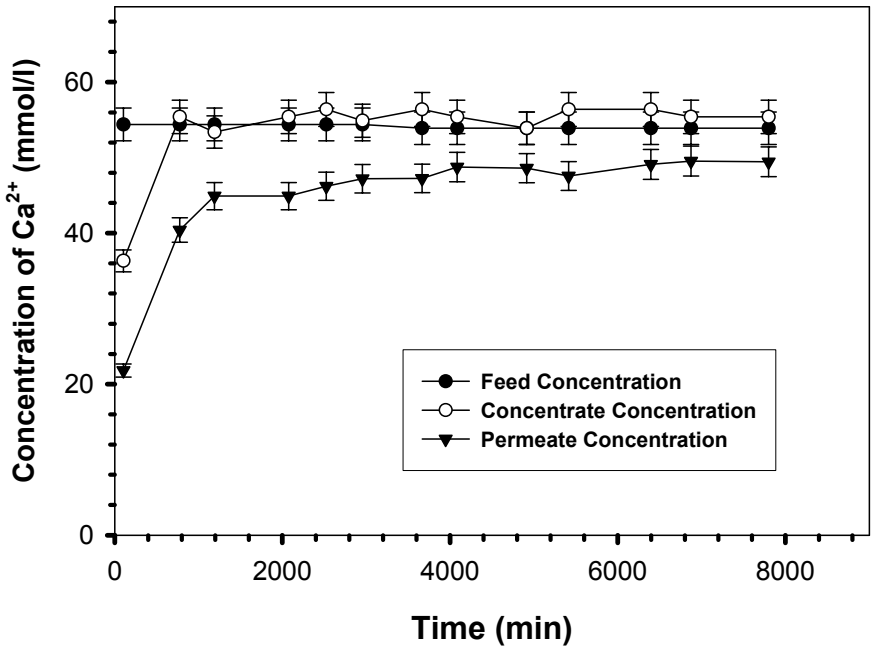

Figure 34. Results of experiment P5006Co for Ca^{2+} in which the feed solution was a 40% dilution of produced water.

Figures 35-40 present the solute rejection of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} in experiment P5008Co, which used a 20% dilution of the produced water with a TDS of 154,097 mg/l as the feed solution. The average permeate flow was 4.5% of the total flow. The hydraulic pressure was 6.1 Mpa.

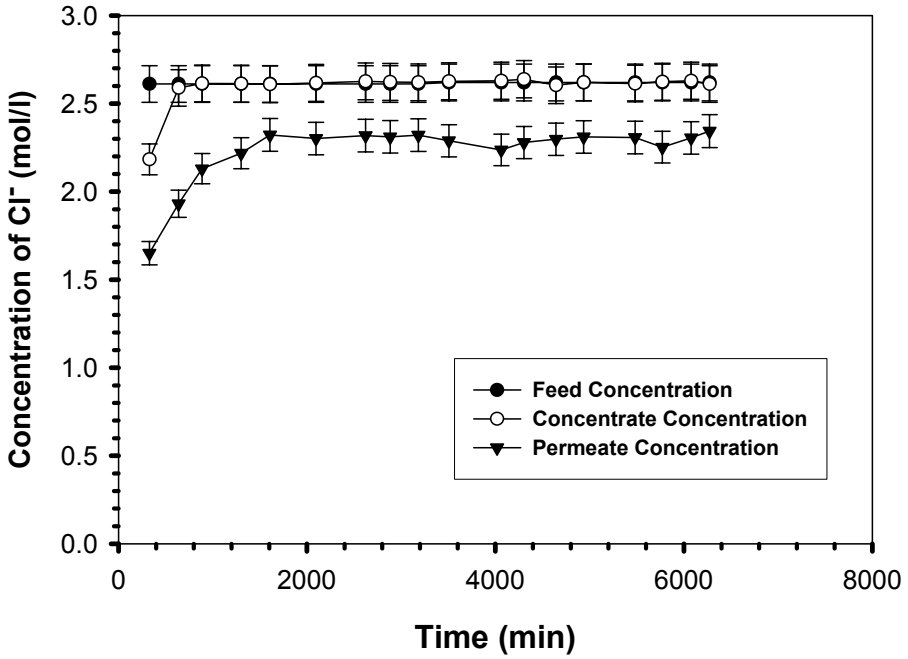

Figure 35. Results of experiment P5008Co for Cl^- in which the feed was a 20% dilution of produced water.

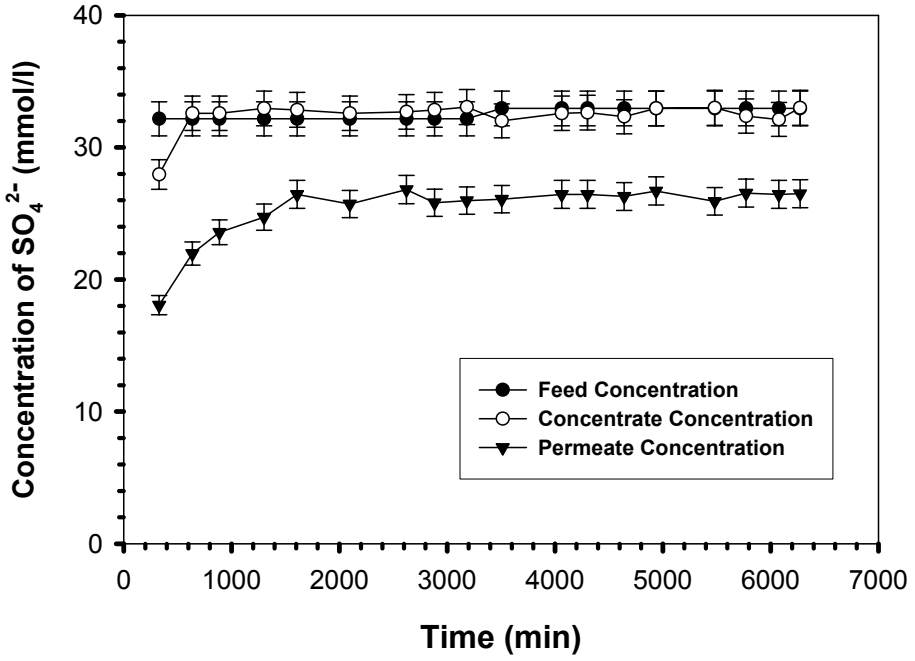

Figure 36. Results of experiment P5008Co for SO_4^{2-} in which the feed solution was a 20% dilution of produced water.

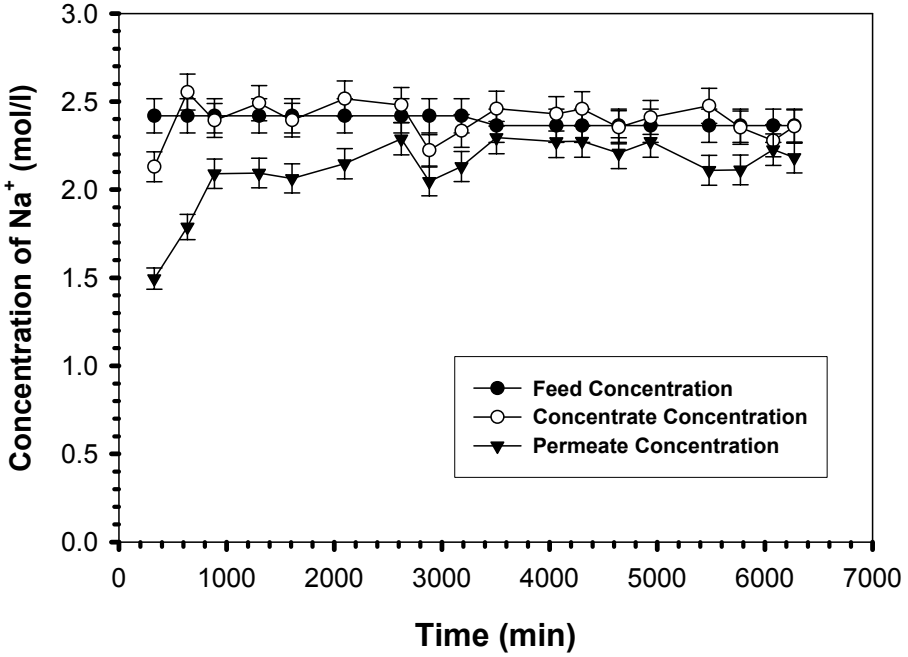

Figure 37. Results of experiment P5008Co for Na^+ in which the feed solution was a 20% dilution of produced water.

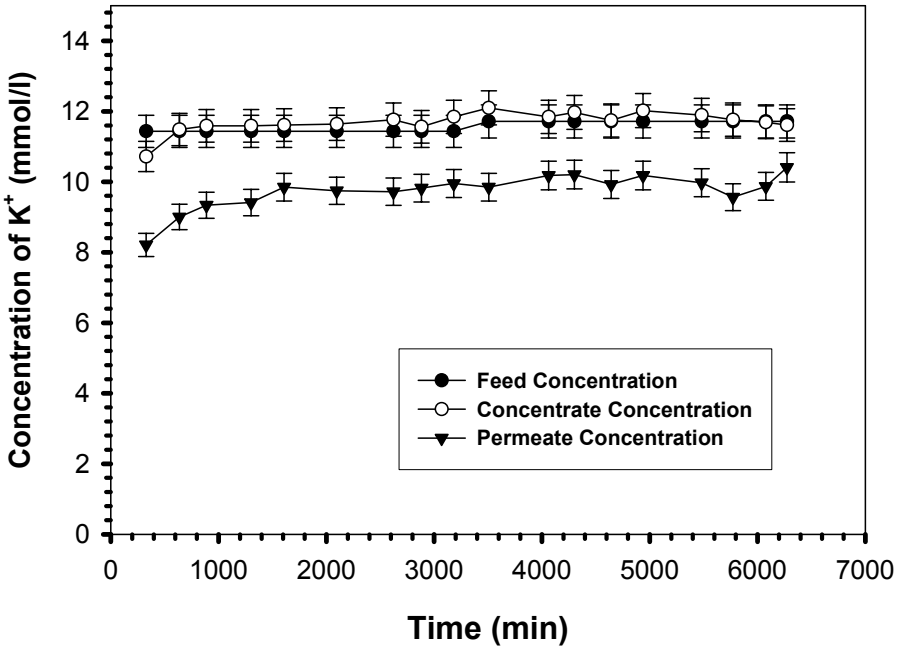

Figure 38. Results of experiment P5008Co for K^+ in which the feed solution was a 20% dilution of produced water.

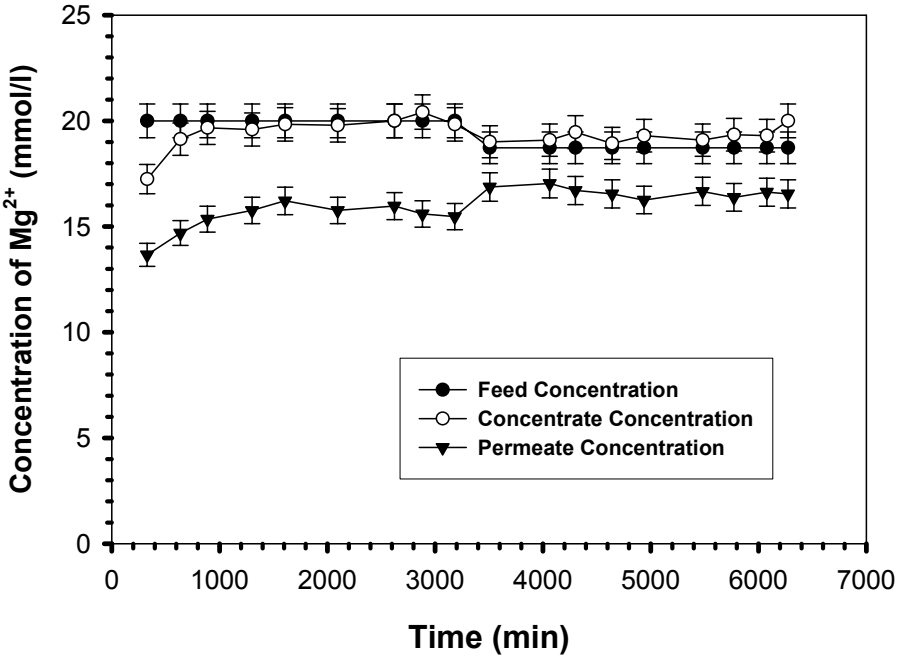

Figure 39. Results of experiment P5008Co for Mg^{2+} in which the feed solution was a 20% dilution of produced water.

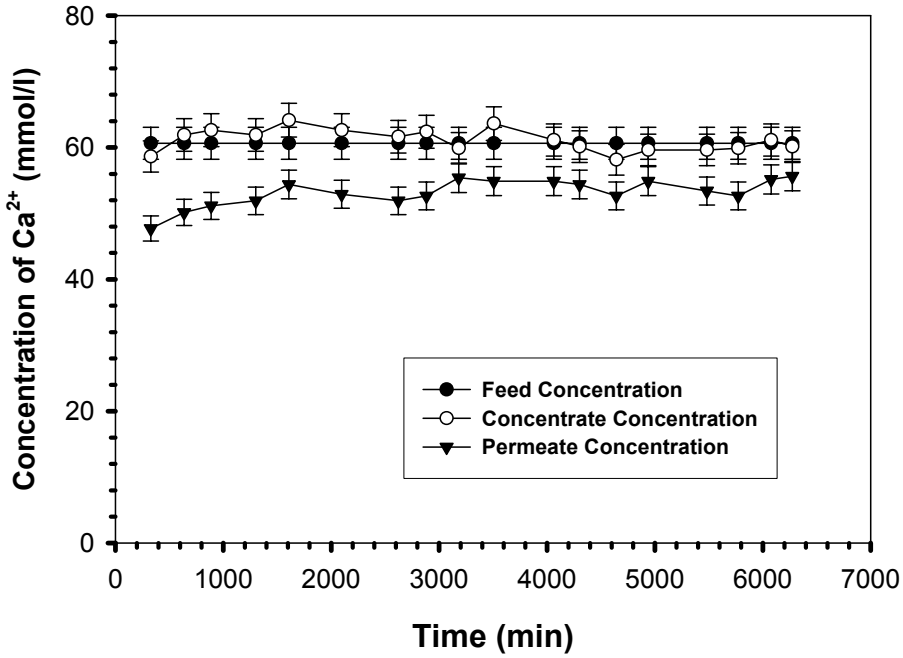

Figure 40. Results of experiment P5008Co for Ca^{2+} in which the feed solution was a 20% dilution of produced water.

DISCUSSION

The main objective of this research was to determine the solute rejection capabilities of a very thin bentonite membrane used in a cross-flow configuration when exposed to waters representative of oilfield produced waters. We tested a single bentonite clay membrane with four different solutions, each prepared as a differing dilution of an actual produced water. The solute rejection rate R was then calculated for each solute by Equation 1 (Table 9).

Table 9. Summary of solute rejection rates.

Experiment No.	Solution Concentration and Type	Cl^- Rejection Rate (%)	SO_4^{2-} Rejection Rate (%)	Na^+ Rejection Rate (%)	K^+ Rejection Rate (%)	Mg^{2+} Rejection Rate (%)	Ca^{2+} Rejection Rate (%)
P5002Co	80% produced water dilution	26.9	35.5	26.9	32.3	26.1	35.9
P5004Co	60% produced water dilution	17.6	29.0	18.3	23.7	16.1	22.6
P5006Co	40% produced water dilution	14.4	25.6	9.6	15.7	13.5	9.4
P5008Co	20% produced water dilution	12.5	20.0	6.2	14.5	11.2	9.8

The rejection rate of each of the solutes decreased with increasing solute concentration in a non-linear manner (Fig. 41). The only exception occurred when Ca^{2+} rejection increased slightly between the 40% and 20% dilutions. Since the rejection was calculated on the basis of a number of chemical analyses, it is unlikely that this is the result of one inaccurate analysis. However, the 0.4% rise in Ca^{2+} rejection rate is within experimental error and may not be real.

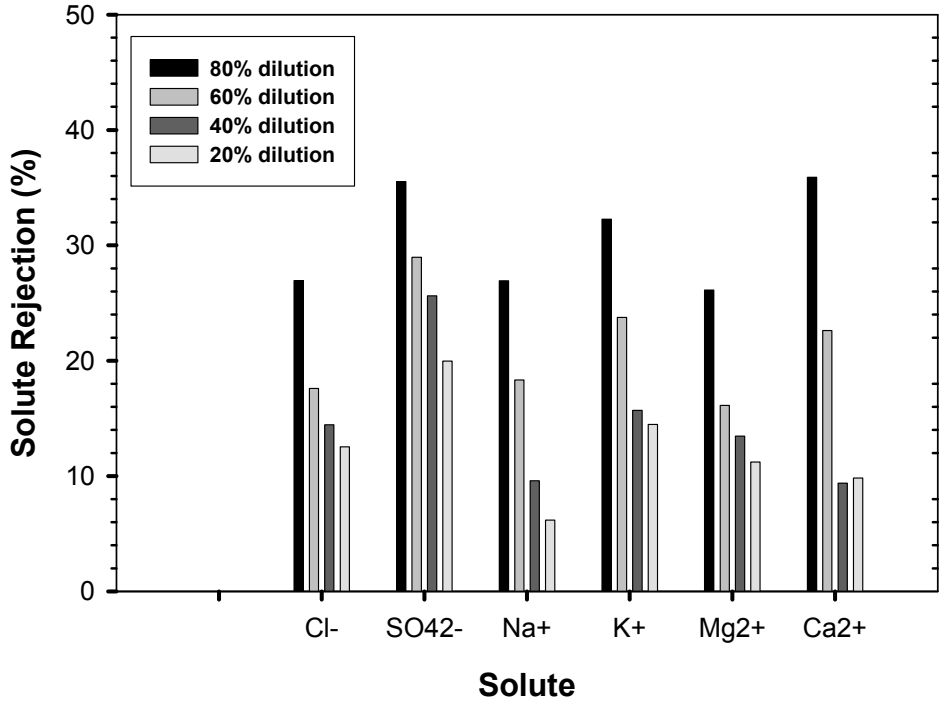

Figure 41. Comparison of solute rejection for differing solutes.

Solute rejection efficiency also decreased as a function of increasing TDS. Sulfate consistently exhibited greater rejection than chloride (Fig. 42). The rejection sequence for cations (Fig. 43) was not as simple. As TDS increased, the Ca^{2+} rejection rate decreased most rapidly and then stabilized below 10%. The cation rejection sequences in order of increasing TDS were 1) $Ca^{2+} > K^{+} > Na^{+} > Mg^{2+}$, 2) $K^{+} > Ca^{2+} > Na^{+} > Mg^{2+}$, 3) $K^{+} > Mg^{2+} > Na^{+} > Ca^{2+}$, and 4) $K^{+} > Mg^{2+} > Ca^{2+} > Na^{+}$. Notice that these cation rejection sequences are not uniform.

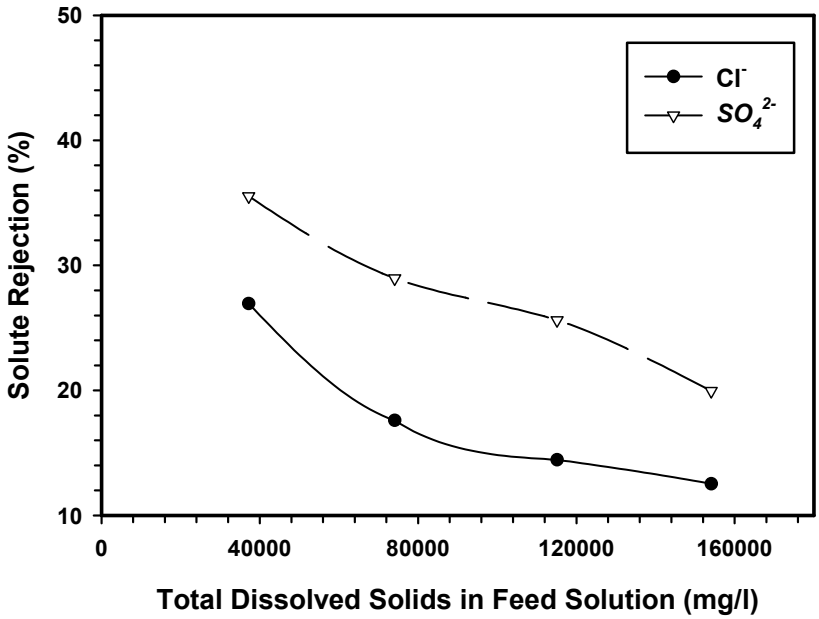

Figure 42. Solute rejection of anions as a function of TDS.

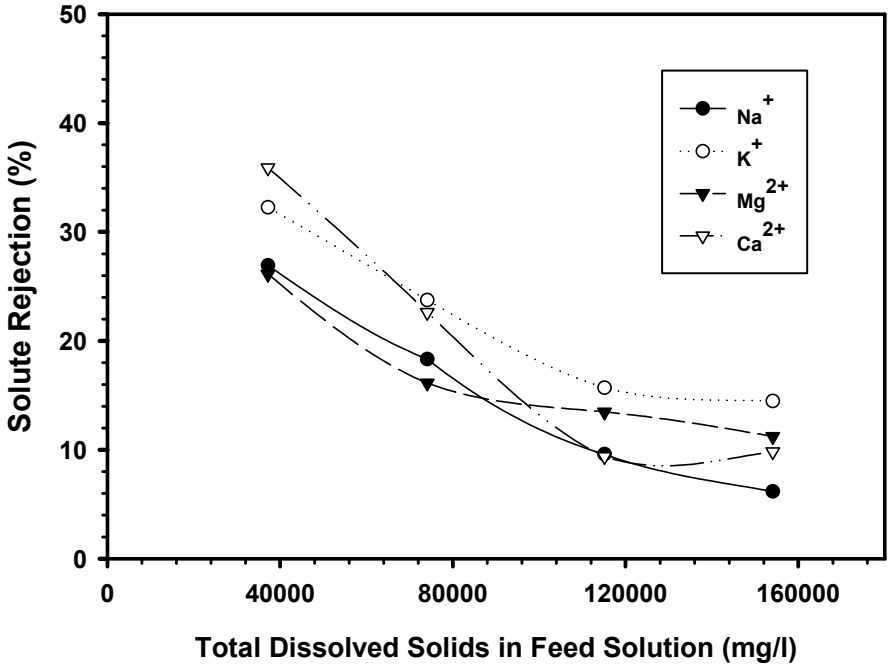

Figure 43. Solute rejection of cations as a function of TDS.

In each of the feed solutions the concentration of K^+ was the lowest, followed in order of increasing concentration by Mg^{2+}, Ca^{2+}, and Na^+. If the concentration of the individual solute was the only factor, then the cation rejection sequence should be $K^+ > Mg^{2+} > Ca^{2+} > Na^+$. This is the cation rejection sequence for the 20% dilution, but not for any of the other dilutions. Prediction of solute rejection sequences for multi-component solutions and synthetic membranes is not clear-cut (Mariñas and Selleck, 1992) and, based on our experiments, it appears that such prediction may be not simple for clay membranes either. Kharakra and Smalley (1976) performed tests on bentonite and kaolinite membranes between 0.18 and 1.47 cm-thick with chloride solutions of alkali and alkaline earth metals and found that solute rejection sequences varied with the clay type and the experimental conditions, so our results are not surprising. The magnitude of solute rejection that was achieved in our experiments ranged between a high of 35.9% for Ca^{2+} for an 80% dilution to a low of 6.2% for Na^+ in a 20% dilution of our produced water sample.

Are the solute rejection results we achieved a maximum for clay membranes? Evidence from published geological literature suggests not. For example, Kharakra and Smalley (1976) performed a series of experiments on a Wyoming bentonite using compaction pressures of 48.3 MPa (7000 psi) and 68.9 MPa (10,000 psi) using a solution with a TDS of 6371 mg/l. Their experiment made no provisions for diminishing CPL buildup in their quasi-cross-flow experimental cell nor were criteria for steady state discussed, but they found that increasing the compaction pressure on their membranes generally increased the solute rejection capability. Kharakra and Berry (1973) used a synthetic sea water with a bentonite clay membrane and found that Na^+ rejection increased from 14.7% to 63.3% as compaction pressure increased from 13.8 MPa (2000 psi) to 65.5 MPa (9500 psi).

Our experiments at a compaction pressure of 36.1 MPa (5236 psi) yielded a 26.9% rejection of Na^+, which is close to the 30.3% Na^+ rejection achieved by Kharakra and Berry (1973) for a compaction pressure of 27.6 MPa for a similar TDS solution. Higher compaction pressures should yield higher solute rejection. Two possible explanations for the fact that our experiments had somewhat lower solute rejection that Kharakra and Berry's (1973) data are 1) our solution had a different chemical composition, and 2) our membrane was very thin, only 0.057mm (0.002 inches) thick. It may be that very thin clay membranes are not as efficient as the 1.9 to 3.2 mm-thick membranes used by Kharakra and Berry (1973), or it may be that some membrane bypassing occurred. The most likely explanation for the lower solute rejection efficiency is that the machining precision for pocket depth of the frits or the frit thickness resulted in localized points of contact between the frits and local bypassing where the clay was squeezed out. The 316 stainless steel frit material used in these cells has a surface roughness of approximately ±0.001mm (±40 millionths of an inch). Twice this number is only about 1/20 the thickness of the membranes used in these experiments. Therefore, it is unlikely that contact between minute high spots on the frit material would partially short-circuit the membrane. However, the frit material and depths of the pockets have a dimensional variability that reaches ± 0.025mm (±0.001 inches). Thus a compacted membrane thickness significantly in excess of 0.05mm should be required to prevent the clay being locally squeezed out with resultant membrane bypassing and loss of efficiency at some locations due to dimensional irregularity of the frits and machined pockets for the frits.

The permeate flows in these experiments averaged between 4.1 and 5.4% of the total flow. Seawater spiral wound reverse osmosis membranes typically have a 7 to 10% recovery (American Water Works Association, 1998). This suggests that very thin clay membranes have

sufficient throughput for practical separations. More compacted clay membranes may also have higher separation efficiencies and may prove useful for first-stage treatment of oilfield produced waters to reduce the TDS to a level manageable by conventional reverse osmosis methods.

SUMMARY AND CONCLUSIONS

A very thin bentonite clay membrane was prepared by vacuum-assisted sedimentation and then compacted using an integral piston to 36.1 MPa in a specially designed experimental cell. Four dilutions of oilfield produced water (80%, 60%, 40%, and 20%) were processed through this bench-scale cross-flow cell and concentrations of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} were analyzed in the feed, permeate, and concentrate solutions. Each experiment was run in turn using the same 0.057mm-thick Wyoming bentonite membrane and each experiment ran 4.5 to 5.5 days. Steady state was achieved before termination of each run.

The results of these experiments indicate that:

- Solute rejection decreased with increasing solute concentration.
- Solute rejection decreased with increasing TDS.
- The anion rejection sequence was $SO_4^{2-} > Cl^-$. This may be because the SO_4^{2-} concentration was always much lower than the Cl^- concentration.
- The cation rejection sequence varied with solute concentration and TDS. Prediction of solute rejection sequences for multi-component solutions and synthetic membranes is not clear-cut and it appears that it may be not simple for clay membranes either.
- The permeate flows in our experiments were 4.1 to 5.4% of the total flow. This suggests that very thin clay membranes may be useful for some separations.

DESIGN OF CLAY MEMBRANE MODULES

Commercial reverse osmosis membranes are most often used in spiral-wound modules. In these modules, the membrane, feed water carrier, and permeate carrier are wound in a spiral around a perforated tube to maximize the surface area of the membrane in the least amount of system volume. Conventional reverse osmosis membranes use synthetic polymer sheets as membranes.

Clay membrane efficiency can be controlled by compaction. Clay membrane efficiency increases with increasing compaction or decreasing porosity (Fritz, 1986). Thus, membranes can be constructed that will allow staged separation of solutes from extremely high TDS produced waters so that unreasonable fluid pressures are not required. This can be shown from one of the fundamental membrane equations developed by Kedem and Katchalsky (1962):

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{5}$$

where J_v = solution flux (cm/s) through the membrane, L_p = water permeation coefficient (cm^3/dyne·s), ΔP = pressure difference across the membrane (dyne/cm^2), σ = reflection coefficient (dimensionless), and $\Delta\pi$ = theoretical osmotic pressure difference across the membrane (dyne/cm^2).

The important parameter in Equation 1 is the reflection coefficient. Permissible values of σ range from zero to one. If $\sigma = 0$, there is no membrane effect. In this case, Equation 1 reduces to a one-dimensional form of Darcy's Law. If $\sigma = 1$, the membrane is ideal and no solute can pass. The value of σ for non-ideal clay membranes must be greater than zero, but less than one. Fritz and Marine (1983) calculated values of σ for a series of six experiments using montmorillonite clay membranes compacted to different porosities and NaCl solutions. The values of σ they determined ranged from 0.04 to 0.89. Fritz and Marine (1983) state that σ is important because it is a measure of osmotic efficiency. Thus, a membrane with a $\sigma = 0.90$ would exhibit 90% of the theoretically predicted osmotic pressure. Therefore, the efficiency of clay membranes can be controlled by adjusting clay membrane compaction, thus changing the value of the reflection coefficient. Hence, a series of increasingly efficient clay membrane modules could be used to treat even highly saturated brines at reasonable hydraulic pressures.

CONSTRUCTION OF SPIRAL WOUND MODULE USING CLAY AS THE MEMBRANE

Method 1. Vacuum filtration to form membrane

The key design elements are to make the membrane as thin as possible, and to precompact the membrane before roll-up. For montmorillonite, overcompaction is good because the membrane will swell in the housing a little bit. Kaolinite clay membranes will not swell.

One way to get a thin, uniform clay layer is by vacuum filtration. To do this a vacuum filtration box was built. The box was vacuum tight on all joints and the upper surface was a porous frit material (Fig. 44). A sheet of filter paper (or more than one) was first cut to fit the porous frit installed on the upper surface of the box. Note there is a lip all around the edge of the box that extends above the porous frit. This is to keep the clay-water slurry from running off the edges during filtration. The box can be made of acrylic sheet or wood—as long as it seals tight at the joints. The porous frit material can be a layer of porous plastic frit material, supported by a wire or metal grid. The important factor is the flatness of the porous frit plate.

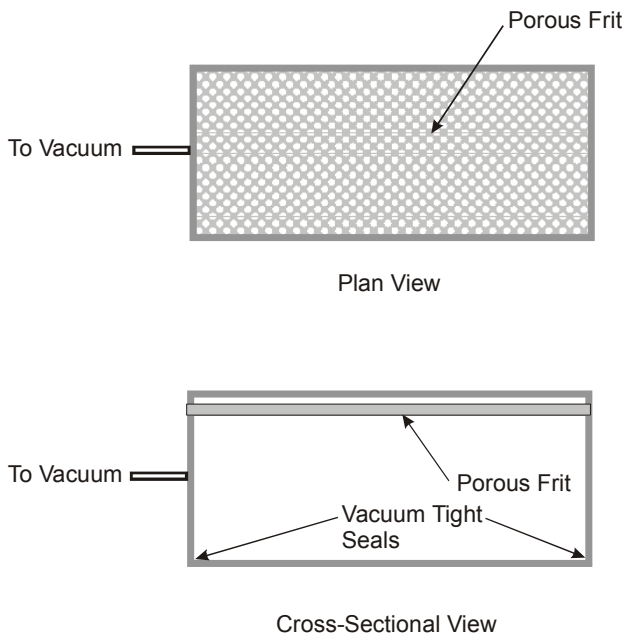

Figure 44. Vacuum filtration box design.

Next, a clay-water slurry was prepared and carefully poured onto the filter paper, making sure to get an even distribution. The vacuum pump was turned on and filtration begins. Once the clay was evenly distributed on the filter paper, an additional sheet of filter paper was added to the upper surface and the filter paper-clay sandwich removed from the vacuum filtration box and placed in a press box.

The press box is built to the same dimensions as the filtration box, only out of stainless steel. The design for the press box is shown below (Fig. 45). Connecting a vacuum pump to the vacuum port during pressing should aid dewatering of the clay and result in somewhat greater compaction with less applied pressure.

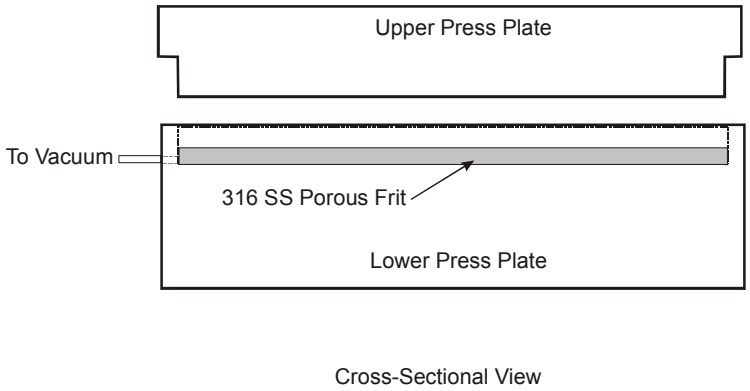

Figure 45. Design of Press Box for making filter paper clay sandwiches.

The next step was to assemble the filter paper-clay sandwich with the appropriate flexible plastic frits as shown in the cross-sectional view in Figure 46.

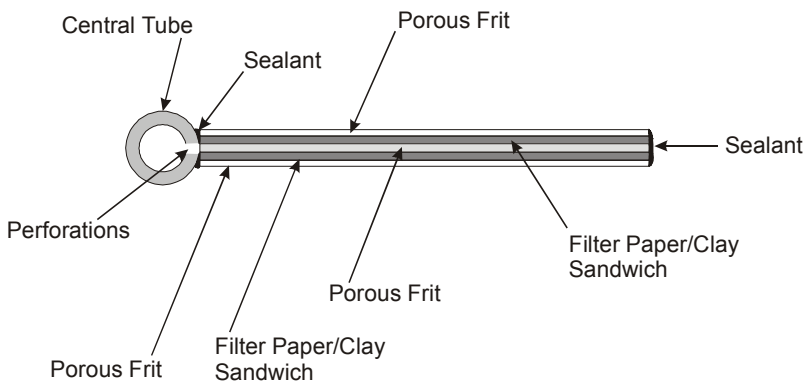

Figure 46. Construction of membrane-frit sandwich.

This complete sandwich is then fixed with a sealant to the central tube (Fig 47) such that the holes in the outer surface of the tube are in contact with the lowermost frit layer. The gluing process should not plug the holes in the center tube. The diameter of the central tube is determined by the flexibility of the membrane-frit stack. The tube diameter much be such that the stack can be rolled around it in a spiral. It is also possible to fasten more than one membrane-frit sandwich to the central tube.

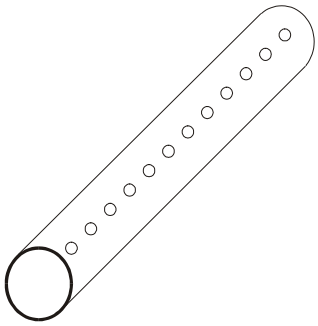

Figure 47. Center tube.

The exposed edge of the membrane stack was selectively sealed where it is exposed along its length before rolling. A flexible sealer is needed such as RTV or silicone.

A thin wedge of plastic or other material may be needed to round off the square edge of the membrane-frit after winding and before placing the assemble in the outer, containment tube. This tube slides over the rolled up membrane assembly. This tube will need O-ring grooves on its outer surface so when the membrane modules slide into the outermost pressure vessel, no flow will bypass the membrane modules. Perforated or slotted end caps are used to keep the membrane in place in the outer tube. The perforations are so that the feed water can flow through the module.

The center tube is constructed so it can be fastened with tube fittings to other modules. The spiral-wound clay membrane modules can then be connected in series in an outer pressure vessel. The ends of the outer pressure vessel can be sealed with o-rings and threaded caps, or by some other means. It may be necessary to use a flexible tubing to make the connections between the modules in the outer pressure vessel. For lab tests or small volume applications, an outer pressure vessel can be built that only holds a single spiral wound module. For the pilot test, more than one module per pressure vessel can be used as can more than one module-pressure vessel assembly.

We encountered the following difficulties in our experiments:

1. It is very difficult to roll the completed membrane sandwich around the center tube and insert it into the outer retaining cylinder and maintain membrane compaction.
2. Keeping the membrane wet during assembly is difficult. If the membrane dries out and cracks, it is ruined. However, wet clay membranes roll up without damage.

Method 2: Development of a cylindrical clay membrane module.

Due to difficulties in inserting a spiral-wound clay membrane sandwich into the tube, we built a module that required only a single wrap (Fig 48 and 49). We designed a compression sleeve (Fig. 49) to precompress the membrane before assembly. We found that it was difficult to develop adequate compaction using this design. Therefore, we began working on developing better ways of creating a compacted clay membrane in place in the module.

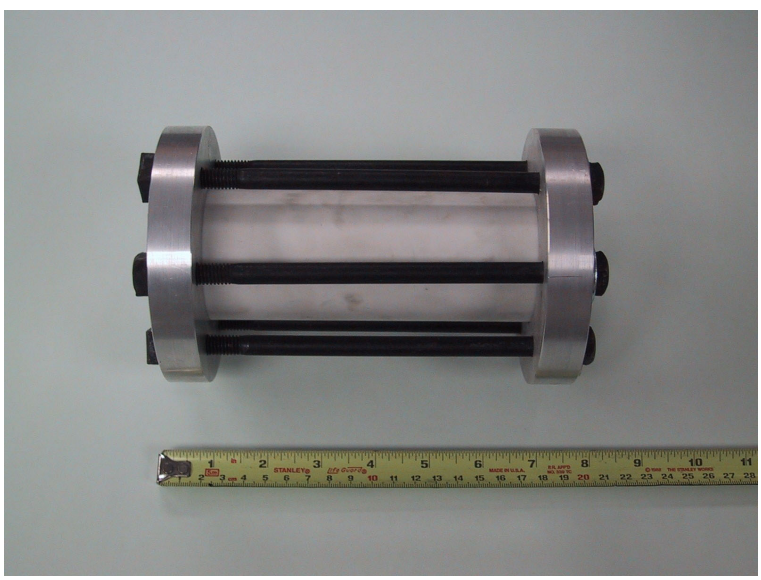

Figure 48. Cylindrical clay membrane module.

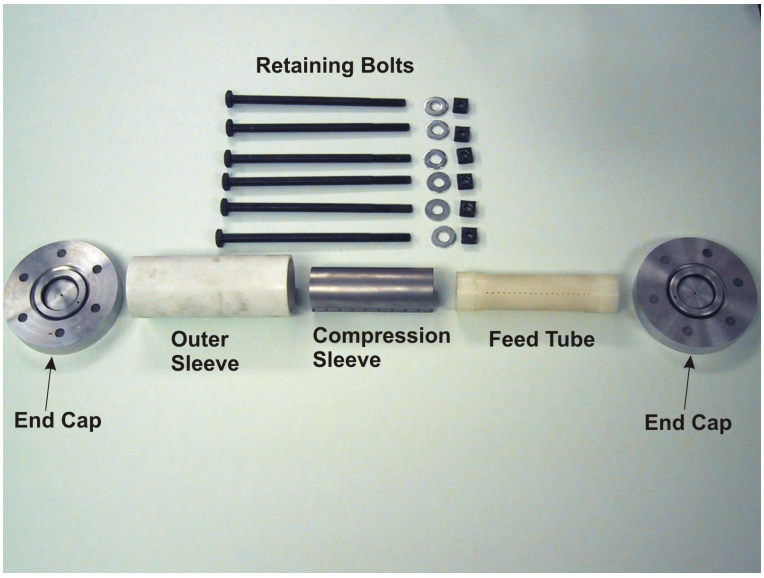

Figure 49. Disassembled cylindrical membrane module. The feed enters the pressure vessel and is constrained to flow through the end caps into the non-sealed frits. It then sweeps across the membrane. The flow that does not pass through the membrane exits as the concentrate. The flow that passes through the membrane flows along the frit between two layers of membrane and passes into the center tube where it exits the system as the permeate.

Method 3: Formation of the membrane in place using hydraulic filtration.

We are still developing this method and it has not yet been tried in the laboratory. The basic principle is to inject a thin clay slurry into the space to be occupied by the membrane. The clay is then filtered out of the slurry and forms the membrane. Compaction is achieved by using sufficient hydraulic pressure. Figure 50 is a diagram of the concept.

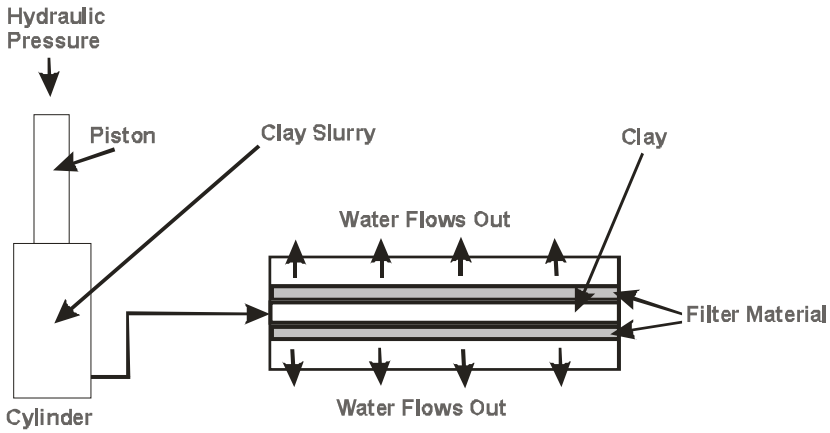

Figure 50. Schematic of system for formation of clay membrane using hydraulic compaction.

The objective is to obtain as dense a clay membrane as possible during hydraulic emplacement and compaction. To do this, the properties of the clay must be considered. In an aqueous solution, clay particles tend to orient themselves in an edge to edge configuration. This edge to edge configuration makes a less effective membrane (Benzel and Graf, 1984). Therefore, we investigated nonpolar organic solvents that should not interact with the clay as does water, which might be used to form the initial slurry.

Small, measured amounts of freeze-dried bentonite were added to stirred beakers containing 1)water, 2) toluene, 3)ethanol, and 4)acetone. The clay mixed in the water formed a non-settling dispersion due to the interaction between the charged clay particles and the water molecules. In each of the beakers containing nonpolar organic solvents, the clay sedimented most rapidly in the toluene, and slightly less rapidly in the acetone and ethanol beakers.

These results suggest that using a slurry composed of clay and ethanol (or some other nonpolar organic solvent) will produce a more tightly compacted membrane at a lower hydraulic pressure. Possible complications include 1) it may be difficult to keep the clay suspended in the slurry during hydraulic injection, and 2) one exposed to water, the swelling pressure exerted by the bentonite clay may exceed the strength of the module. Thus, injection should be fairly rapid to prevent settling and the modules should be designed to accommodate the swelling pressure of the clay.

A support is needed for the filter material that will handle the hydraulic pressures needed to compact the membrane. We are investigating porous materials that can be used. Most porous plastics will compress under pressure. Sintered 316 stainless steel is available made with various grain sizes and in various porosities. In tubular form, it should handle the necessary compaction pressure. Perhaps the best choice is a porous ceramic support. Ceramics offer excellent compressive strength and can be manufactured with a range of pore sizes. However, we have yet to find commercially available porous tubes sized as we need for tubular membrane construction. Porous ceramic supports for use with a spiral-wound system would have to be manufactured to exact specifications.

We have on hand some 316 porous stainless steels tubes that we will use to build a test cell. These tubes can withstand up to 1800 psi without deformation.

Once completed, the clay membrane modules can be assembled in a chain configuration (Fig. 51) or can be inserted into outer cylinders and sealed with O-rings (Fig 52).

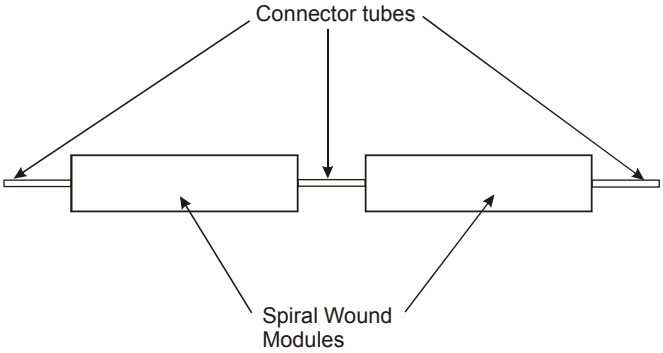

Figure 51. Spiral-Wound Modules with Connection Tubes. Note the first connection tube can either be eliminated or closed with a valve.

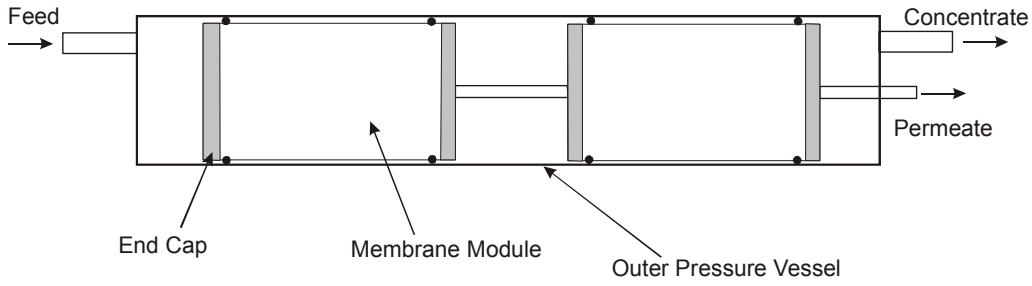

Figure 52. Complete assembly showing fluid flow streams.

TECHNOLOGY TRANSFER

PEER-REVIEWED PUBLICATIONS

Whitworth, T. M. and Lee, Robert, (submitted) Desalting of saline waters: applications to New Mexico, New Mexico Geology.

Whitworth, T. M., Siagian, Ucok. W., and Lee, Robert, (submitted) Reverse osmosis separation of NaCl using a bentonite membrane, Separation and Purification Methods.

Li, Liangxiong, Whitworth, T. M., and Lee, Robert (submitted) Reverse osmosis of oil field produced water using a bentonite membrane, J. Membrane Science.

Li, Liangxiong, Whitworth, T. M., and Lee, Robert (submitted) Construction of an ultra-thin, compacted clay membrane, Clay Science.

ABSTRACTS

Li, Liangxiong, Lee, Robert, and Whitworth, T. M., 2002, Solute rejection capabilities of compacted bentonite membranes, The Clay Minerals Society 39th Annual Meeting, Program and Abstracts, p. 116.

Torres, David, Lee, Robert, and Whitworth, T. M., 2002, Concentration polarization-induced precipitation of NaCl, The Clay Minerals Society 39th Annual Meeting, Program and Abstracts, p. 166.

CHAIRED SESSIONS AT MEETINGS

Clay Membrane Processes, Mike Whitworth, Baolin Deng, Charles Shackleford, and Ning Lu, co-chairs, The Clay Minerals Society, 39th Annual meeting, June 8-13, 2002, Boulder, CO.

SUMMARY AND CONCLUSIONS

We performed two series of reverse osmosis experiments. The first series of 10 experiments used NaCl solutions with bentonite membranes that ranged between 0.041 an 0.064mm in thickness. Our results showed compaction of such ultra-thin clay membranes to be problematic. The thickness of the membranes was exceeded by the dimensional variation in the machined experimental cell and this is believed to have resulted in local bypassing of the membrane with a resultant decrease in solute rejection efficiency. In two of the experiments, permeate flow was varied as a percentage of the total flow to investigate results of changing permeate flow on solute rejection. In one experiment, the permeate flow was varied between 2.4 and 10.3% of the total flow with no change in solute rejection. In another experiment, the permeate flow was varied between 24.6 and 52.5% of the total flow. In this experiment, the solute rejection rate decreased as the permeate occupied greater fractions of the total flow. This suggests a maximum solute rejection efficiency for these clay membranes for a permeate flow of between 10.3 and 24.6% of the total flow. Solute rejection was found to decrease with increasing salt concentration and ranged between 62.9% and 19.7% for chloride and between 61.5 and 16.8% for sodium. Due to problems with the compaction procedure and potential membrane bypassing, these rejection rates are probably not the upper limit for NaCl rejection by bentonite membranes.

The second series of four reverse osmosis experiments were conducted with a 0.057mm-thick bentonite membrane and dilutions of a produced water sample with an original TDS of 196,250 mg/l obtained from a facility near Loco Hill, New Mexico, operated by an independent. These experiments tested the separation efficiency of the bentonite membrane for each of the dilutions. We found that membrane efficiency decreased with increasing solute concentration and with increasing TDS. The rejection of SO_4^{2-} was greater than Cl^-. This may be because the SO_4^{2-} concentration was much lower than the Cl^- concentration in the waters tested. The cation rejection sequence varied with solute concentration and TDS. The solute rejection sequence for multi-component solutions is difficult to predict for synthetic membranes; it may not be simple for clay membranes either. The permeate flows in our experiments were 4.1 to 5.4% of the total flow. This suggests that very thin clay membranes may be useful for some separations.

Work on development of a spiral-wound clay membrane module found that it is difficult to maintain compaction of the membrane if the membrane is rolled and then inserted in the outer tube. A different design was tried using a cylindrical clay membrane and this also proved difficult to assemble with adequate membrane compaction. The next step is to form the membrane in place using hydraulic pressure on a thin slurry of clay in either water or a nonpolar organic solvent such as ethanol.

Technology transfer efforts included four manuscripts submitted to peer-reviewed journals, two abstracts, and chairing a session on clays as membranes at the Clay Minerals Society annual meeting.

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APPENDIX A: TABULATED DATA

Table 10. Cross-flow results of experiment P30C01.

No.	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	60	2.45	0.46	20.7	0.104	0.006	0.000	99.7
2	120	2.55	0.53	20.7	0.104	0.002	0.004	96.2
3	210	2.72	0.54	22.4	0.104	0.065	0.039	62.2
4	270	2.83	0.53	23.8	0.104	0.104	0.062	40.5
5	330	2.86	0.53	24.6	0.104	0.101	0.068	35.1
6	390	2.90	0.53	25.1	0.104	0.107	0.068	35.1
7	450	2.93	0.54	25.6	0.104	0.110	0.068	35.1
8	510	3.00	0.53	26.2	0.104	0.110	0.070	32.4
9	1050	3.55	0.53	29.1	0.101	0.113	0.073	27.8
10	1170	3.70	0.50	32.3	0.101	0.113	0.076	25.0
11	1290	3.96	0.53	36.1	0.101	0.113	0.079	22.2
12	1410	4.14	0.53	39.5	0.101	0.113	0.079	22.2
13	1530	4.27	0.53	42.6	0.101	0.110	0.082	19.4
14	1650	4.48	0.53	46.0	0.101	0.115	0.085	16.7
15	1770	4.69	0.52	50.2	0.101	0.118	0.085	16.7
16	1830	4.79	0.56	52.5	0.101	0.115	0.085	16.7
17	2490	3.00	0.41	57.4	0.101	0.118	0.087	13.9
18	2610	2.96	0.19	62.2	0.101	0.118	0.076	25.0
19	2790	2.96	0.20	64.5	0.101	0.118	0.076	25.0
20	2970	2.93	0.20	65.8	0.101	0.107	0.076	25.0
21	3150	2.93	0.20	68.2	0.101	0.121	0.076	25.0
22	3330	2.93	0.20	68.7	0.101	0.118	0.079	22.2

Table 11. Cross-flow results of experiment P40C01.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	60	2.41	0.037	0.0	0.092	0.030	0.000	100.0
2	120	4.55	0.400	6.2	0.092	0.070	0.010	89.1
3	210	4.55	0.308	5.9	0.092	0.060	0.015	83.7
4	270	4.48	0.543	2.5	0.092	0.100	0.020	78.3
5	330	4.31	0.283	5.9	0.092	0.110	0.030	67.4
6	390	4.48	0.374	7.6	0.092	0.100	0.020	78.3
7	450	4.83	0.348	7.7	0.092	0.120	0.030	67.4
8	1050	3.17	0.348	7.7	0.092	0.120	0.030	67.4
9	1170	4.48	0.426	6.0	0.092	0.100	0.040	56.5
10	1410	4.48	0.397	3.1	0.088	0.120	0.040	54.5
11	1530	4.48	0.412	6.6	0.088	0.120	0.040	54.5
12	1650	4.69	0.463	5.7	0.088	0.120	0.040	54.5
13	1770	4.90	0.455	5.6	0.088	0.120	0.030	65.9
14	2490	4.90	0.417	5.7	0.088	0.120	0.030	65.9
15	2610	4.96	0.401	5.7	0.088	0.120	0.030	65.9
16	2790	4.93	0.446	5.5	0.088	0.100	0.030	65.9
17	2970	4.83	0.457	5.5	0.088	0.110	0.030	65.9
18	3150	4.90	0.445	5.6	0.088	0.100	0.030	65.9
19	3360	4.27	0.267	5.6	0.088	0.100	0.030	65.9
20	3460	4.48	0.453	5.1	0.088	0.100	0.030	65.9
21	3930	5.17	0.460	5.7	0.088	0.100	0.030	65.9
22	4100	4.41	0.484	4.7	0.088	0.100	0.030	65.9
23	4300	4.21	0.444	4.8	0.088	0.100	0.030	65.9
24	4480	4.34	0.451	4.9	0.085	0.100	0.030	64.7
25	4620	4.48	0.464	5.0	0.085	0.100	0.030	64.7
26	4800	4.48	0.450	5.1	0.085	0.100	0.030	64.7
27	5330	5.24	0.472	5.3	0.085	0.100	0.030	64.7
28	5520	5.17	0.474	4.9	0.085	0.100	0.030	64.7
29	5700	4.48	0.482	4.5	0.085	0.100	0.030	64.7
30	5880	4.62	0.450	5.1	0.085	0.100	0.030	64.7
31	6050	5.38	0.455	6.7	0.085	0.100	0.030	64.7
32	6590	5.10	0.452	4.5	0.085	0.100	0.030	64.7
33	6770	5.38	0.446	5.9	0.085	0.110	0.030	64.7
34	6950	5.93	0.301	6.6	0.085	0.110	0.030	64.7
35	7070	6.21	0.461	7.1	0.085	0.100	0.030	64.7
36	7190	6.89	0.465	8.1	0.085	0.110	0.030	64.7
37	7370	7.24	0.450	8.2	0.085	0.100	0.030	64.7
38	7550	7.24	0.463	8.4	0.085	0.100	0.030	64.7
39	7630	6.76	0.481	7.4	0.085	0.100	0.030	64.7
40	8090	9.31	0.467	10.3	0.085	0.110	0.030	64.7

Table 12. Cross-flow results of experiment P50C01.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	130	5.52	0.037	0.0	0.107	0.028	0.003	97.4
2	305	6.21	0.400	6.2	0.107	0.061	0.013	87.6
3	490	6.72	0.308	5.9	0.107	0.105	0.039	63.7
4	640	5.38	0.543	2.5	0.107	0.110	0.045	58.4
5	800	5.52	0.283	5.9	0.107	0.108	0.043	60.0
6	1320	6.62	0.374	7.6	0.107	0.109	0.044	59.2
7	1485	5.93	0.348	7.7	0.106	0.107	0.044	59.0
8	1595	5.38	0.348	7.7	0.106	0.107	0.044	59.0
9	1850	5.86	0.426	6.0	0.106	0.110	0.042	60.6
10	2075	6.55	0.397	3.1	0.106	0.109	0.042	60.3
11	2285	6.52	0.412	6.6	0.106	0.110	0.042	60.6
12	2810	3.45	0.430	5.5	0.105	0.109	0.041	60.9
13	3010	3.86	0.419	5.5	0.105	0.111	0.039	62.5
14	3230	4.00	0.463	5.7	0.105	0.108	0.041	60.9
15	3395	5.52	0.455	5.6	0.105	0.111	0.043	59.5
16	3545	6.55	0.417	5.7	0.105	0.111	0.043	59.2
17	3695	3.79	0.401	5.7	0.105	0.111	0.053	49.9
18	4215	6.07	0.446	5.5	0.106	0.112	0.045	58.2
19	4375	5.72	0.457	5.5	0.106	0.112	0.043	60.1
20	4555	6.14	0.445	5.6	0.106	0.112	0.048	54.8
21	4725	6.14	0.267	5.6	0.106	0.112	0.057	46.0
22	4845	6.21	0.453	5.1	0.106	0.101	0.061	42.6
23	4965	6.34	0.460	5.7	0.106	0.108	0.059	44.4
24	5095	5.86	0.453	2.7	0.105	0.110	0.056	46.2
25	5635	5.72	0.484	4.7	0.105	0.110	0.049	53.2
26	5785	6.21	0.444	4.8	0.105	0.109	0.047	54.8
27	5975	5.93	0.451	4.9	0.105	0.108	0.046	55.6
28	6145	5.10	0.464	5.0	0.105	0.110	0.045	57.0
29	6335	4.69	0.450	5.1	0.105	0.109	0.045	57.3
30	6560	4.34	0.472	5.3	0.105	0.109	0.044	58.1
31	7050	4.34	0.474	4.9	0.105	0.109	0.048	54.4
32	7250	5.24	0.482	4.5	0.105	0.109	0.042	60.3
33	7415	5.86	0.450	5.1	0.105	0.110	0.043	59.2
34	7590	5.86	0.455	6.7	0.105	0.111	0.042	60.1
35	7740	3.45	0.452	4.5	0.105	0.112	0.042	59.8
36	8000	5.17	0.446	5.9	0.105	0.111	0.043	59.5
37	8520	6.62	0.301	6.6	0.105	0.111	0.045	57.1
38	9200	6.76	0.461	7.1	0.106	0.110	0.044	58.8

Table 13. Cross-flow results of experiment P60C01.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	160	2.21	0.342	3.0	0.103	0.071	0.008	92.0
2	355	2.48	0.416	3.1	0.103	0.101	0.016	84.9
3	615	2.14	0.431	2.8	0.103	0.101	0.026	74.9
4	870	2.14	0.424	2.8	0.103	0.102	0.031	69.6
5	1375	3.31	0.427	3.5	0.103	0.102	0.034	66.9
6	1540	2.55	0.430	3.1	0.103	0.103	0.038	62.8
7	1730	2.93	0.403	3.9	0.103	0.103	0.046	55.1
8	1870	3.10	0.474	4.2	0.103	0.103	0.039	61.7
9	2770	7.24	0.428	7.6	0.103	0.105	0.040	61.4
10	2950	6.55	0.417	8.7	0.103	0.103	0.045	56.1
11	3130	5.58	0.459	9.7	0.103	0.104	0.046	55.2
12	3370	7.24	0.416	9.4	0.103	0.106	0.050	51.5
13	3550	5.17	0.428	6.6	0.103	0.106	0.044	57.6
14	3730	6.89	0.461	9.6	0.103	0.104	0.044	57.4
15	4100	5.86	0.416	13.9	0.103	0.099	0.064	37.9
16	4310	4.90	0.391	6.2	0.103	0.108	0.054	47.5
17	4490	5.38	0.454	7.1	0.103	0.101	0.062	39.8
18	5670	5.65	0.517	7.0	0.104	0.103	0.047	54.5
19	6090	6.21	0.514	9.6	0.104	0.106	0.045	56.5
20	6300	6.21	0.430	9.7	0.103	0.105	0.044	57.3
21	6465	5.52	0.440	9.3	0.103	0.104	0.057	44.6
22	6925	5.86	0.422	9.4	0.103	0.105	0.055	46.7
23	7105	6.21	0.419	8.9	0.103	0.105	0.046	55.7
24	7285	6.27	0.434	9.2	0.103	0.100	0.045	56.0
25	7465	6.55	0.436	9.3	0.103	0.105	0.045	56.7
26	7645	6.27	0.423	8.6	0.104	0.105	0.044	58.0
27	7855	6.55	0.435	9.2	0.104	0.107	0.043	58.6
28	7975	5.86	0.408	8.9	0.104	0.104	0.046	55.4
29	8065	5.45	0.431	7.5	0.104	0.108	0.049	52.6
30	8215	6.21	0.426	8.7	0.104	0.108	0.044	57.4
31	8455	6.21	0.436	9.3	0.104	0.107	0.036	65.8
32	8695	6.55	0.427	9.5	0.104	0.108	0.041	60.7
33	9115	6.55	0.415	9.8	0.104	0.109	0.037	64.0

Table 14. Cross-flow results of experiment P60C02.

No.	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	130	5.45	0.422	7.4	0.206	0.110	0.050	75.6
2	250	5.79	0.423	7.8	0.206	0.189	0.062	70.0
3	360	5.86	0.423	8.2	0.206	0.210	0.081	60.7
4	590	8.91	0.234	16.6	0.206	0.212	0.094	54.5
5	715	6.55	0.456	9.2	0.206	0.216	0.103	49.7
6	835	5.58	0.495	6.4	0.205	0.197	0.121	41.0
7	1035	5.90	0.513	7.9	0.205	0.217	0.123	39.8
8	1215	6.21	0.500	8.1	0.205	0.214	0.113	44.8
9	1400	6.74	0.518	8.7	0.205	0.215	0.117	42.6
10	1575	7.79	0.486	10.6	0.205	0.216	0.123	40.2
11	2075	8.27	0.439	13.3	0.203	0.216	0.126	37.8
12	2255	6.29	0.307	7.8	0.203	0.199	0.139	31.4
13	2395	7.25	0.454	9.1	0.203	0.225	0.132	35.2
14	2575	7.62	0.337	9.7	0.203	0.221	0.127	37.5
15	2775	7.58	0.408	14.6	0.203	0.217	0.130	36.3
16	3325	12.76	0.386	21.2	0.204	0.221	0.144	29.7
17	3505	6.55	0.356	10.5	0.204	0.221	0.154	24.8
18	3770	8.14	0.535	12.9	0.204	0.223	0.141	30.9
19	4010	8.14	0.357	13.9	0.204	0.212	0.142	30.5
20	4215	7.38	0.378	13.3	0.204	0.221	0.131	35.7
21	4750	6.76	0.344	8.1	0.206	0.216	0.125	39.5
22	4930	6.22	0.365	9.2	0.206	0.217	0.121	41.2
23	5110	7.12	0.460	8.4	0.206	0.223	0.123	40.3
24	5315	7.25	0.272	12.8	0.206	0.221	0.120	41.6
25	5555	5.52	0.363	9.0	0.206	0.219	0.120	41.5

Table 15. Cross-flow results of experiment P60C03.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	95	5.72	0.381	5.9	0.296	0.214	0.152	48.6
2	195	5.68	0.582	6.4	0.296	0.282	0.169	42.9
3	315	6.09	0.432	6.9	0.296	0.299	0.183	38.1
4	480	5.86	0.436	7.7	0.296	0.304	0.192	35.2
5	755	6.21	0.449	8.4	0.296	0.304	0.192	35.2
6	875	5.64	0.597	4.9	0.299	0.296	0.206	31.1
7	1005	6.21	0.404	8.1	0.299	0.299	0.211	29.2
8	1125	5.38	0.372	4.6	0.299	0.296	0.206	31.1
9	1325	6.76	0.456	5.7	0.299	0.301	0.200	33.0
10	1495	6.89	0.466	5.0	0.299	0.301	0.200	33.0
11	1745	6.58	0.462	4.9	0.299	0.299	0.197	34.0
12	1985	6.24	0.448	4.0	0.299	0.299	0.203	32.1
13	2225	6.21	0.446	5.2	0.299	0.301	0.197	34.0
14	2405	5.90	0.452	5.1	0.299	0.301	0.194	34.9
15	2630	6.58	0.459	5.0	0.296	0.301	0.194	34.3
16	2770	6.43	0.452	4.9	0.296	0.301	0.189	36.2
17	2915	5.86	0.434	3.1	0.296	0.299	0.200	32.4
18	3095	6.55	0.448	3.9	0.296	0.299	0.206	30.5
19	3215	6.58	0.480	4.8	0.296	0.301	0.197	33.3
20	3355	6.34	0.443	4.8	0.296	0.299	0.194	34.3
21	3505	6.21	0.452	4.5	0.296	0.296	0.194	34.3
22	3655	6.21	0.460	4.4	0.296	0.299	0.192	35.2
23	3775	6.58	0.444	5.1	0.296	0.301	0.192	35.2
24	3935	6.51	0.418	4.5	0.296	0.299	0.203	31.4
25	4335	7.24	0.428	10.3	0.296	0.313	0.208	29.5
26	4495	7.17	0.294	14.3	0.296	0.304	0.200	32.4
27	4685	6.89	0.328	11.3	0.296	0.304	0.203	31.4
28	5000	7.24	0.418	9.1	0.296	0.299	0.197	33.3
29	5120	7.37	0.257	13.0	0.293	0.307	0.200	31.7
30	5300	6.76	0.402	9.1	0.293	0.296	0.200	31.7
31	5575	6.55	0.250	13.6	0.293	0.310	0.200	31.7
32	5680	7.26	0.264	13.7	0.293	0.307	0.197	32.7
33	5880	6.89	0.338	12.4	0.293	0.301	0.197	32.7
34	6075	6.89	0.264	11.9	0.293	0.299	0.208	28.8
35	6415	6.69	0.256	13.6	0.293	0.307	0.208	28.8
36	6535	7.48	0.484	15.6	0.293	0.310	0.203	30.8
37	6665	6.51	0.421	12.8	0.293	0.310	0.206	29.8
38	6845	6.39	0.197	12.0	0.293	0.296	0.223	24.0
39	6910	6.85	0.383	13.9	0.293	0.299	0.228	22.1

Table 16 Cross-flow results of experiment P60C04.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	120	6.89	0.299	10.3	0.370	0.294	0.232	37.4
2	240	6.89	0.447	8.8	0.370	0.305	0.223	39.8
3	360	6.89	0.428	8.5	0.370	0.367	0.227	38.7
4	480	6.89	0.429	9.0	0.370	0.381	0.247	33.2
5	610	6.89	0.418	9.8	0.370	0.382	0.257	30.6
6	730	6.89	0.386	9.6	0.370	0.377	0.263	29.0
7	1100	6.89	0.446	8.3	0.370	0.379	0.282	24.0
8	1250	6.55	0.427	7.7	0.370	0.376	0.270	27.0
9	1405	6.89	0.425	8.9	0.370	0.379	0.272	26.7
10	1500	6.89	0.436	9.4	0.370	0.379	0.268	27.8
11	1650	6.89	0.427	9.7	0.370	0.378	0.272	26.5
12	1990	6.55	0.435	8.7	0.371	0.370	0.283	23.7
13	2080	6.76	0.410	8.2	0.371	0.375	0.274	26.0
14	2230	7.93	0.430	8.5	0.371	0.375	0.284	23.5
15	2400	6.89	0.414	9.6	0.371	0.375	0.273	26.4
16	2630	6.55	0.434	8.0	0.371	0.374	0.267	28.0
17	2770	6.89	0.409	8.0	0.371	0.374	0.262	29.3
18	2900	7.24	0.411	9.1	0.371	0.377	0.248	33.1
19	3050	7.03	0.384	9.0	0.371	0.371	0.272	26.5
20	3150	6.89	0.392	8.8	0.371	0.373	0.283	23.8
21	3315	6.55	0.371	9.3	0.371	0.375	0.276	25.5
22	3630	6.83	0.379	9.1	0.371	0.373	0.265	28.4
23	3855	6.62	0.336	11.2	0.371	0.370	0.263	29.2
24	4115	7.10	0.357	11.4	0.371	0.376	0.263	29.2
25	4255	6.76	0.486	8.1	0.365	0.378	0.262	28.1
26	4405	6.48	0.447	7.2	0.365	0.370	0.275	24.5
27	4555	6.21	0.464	8.4	0.365	0.370	0.274	25.0
28	4675	6.21	0.459	7.0	0.365	0.375	0.264	27.5
29	4795	6.89	0.473	8.2	0.365	0.375	0.262	28.1
30	5640	7.58	0.444	8.8	0.365	0.377	0.258	29.2
31	5790	7.10	0.468	8.2	0.365	0.377	0.260	28.7
32	5955	6.69	0.463	8.1	0.365	0.374	0.259	28.8
33	6035	7.03	0.477	8.8	0.365	0.377	0.261	28.5
34	6175	6.34	0.442	7.6	0.365	0.380	0.248	32.1
35	6300	7.03	0.452	8.5	0.365	0.373	0.248	31.8
36	6435	6.96	0.441	8.2	0.365	0.377	0.256	29.7
37	6775	6.93	0.421	9.1	0.365	0.377	0.257	29.5

Table 17. Cross-flow results of experiment P60C05.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	90	6.55	0.440	7.3	0.495	0.390	0.272	45.1
2	140	7.24	0.482	7.8	0.495	0.409	0.274	44.6
3	280	5.72	0.456	5.5	0.495	0.457	0.283	42.7
4	420	6.27	0.459	6.8	0.495	0.522	0.307	38.0
5	495	6.96	0.487	8.9	0.495	0.510	0.319	35.6
6	625	6.89	0.468	7.2	0.495	0.506	0.330	33.2
7	805	7.03	0.427	7.2	0.495	0.509	0.336	32.2
8	865	7.34	0.447	8.2	0.495	0.513	0.342	30.8
9	1085	6.83	0.484	6.9	0.495	0.512	0.377	23.7
10	1205	6.76	0.383	8.2	0.496	0.515	0.394	20.6
11	1320	7.10	0.392	7.8	0.496	0.518	0.374	24.5
12	1460	6.89	0.464	8.3	0.496	0.509	0.378	23.9
13	1600	6.62	0.476	7.5	0.496	0.512	0.369	25.6
14	1720	6.69	0.414	7.5	0.496	0.518	0.352	29.0
15	1875	6.89	0.422	8.2	0.496	0.508	0.370	25.5
16	2015	6.62	0.468	7.7	0.496	0.525	0.394	20.6
17	2135	6.69	0.472	7.9	0.496	0.535	0.374	24.5
18	2275	7.03	0.475	8.6	0.496	0.511	0.364	26.6
19	2395	6.34	0.485	7.7	0.497	0.513	0.360	27.7
20	2535	6.96	0.475	8.7	0.497	0.525	0.355	28.6
21	2665	6.72	0.466	8.3	0.497	0.510	0.358	28.0
22	2820	6.52	0.478	7.6	0.497	0.505	0.379	23.8
23	2960	6.62	0.466	8.0	0.497	0.534	0.376	24.3
24	3105	7.10	0.465	8.7	0.497	0.519	0.373	25.0
25	3230	6.76	0.408	8.5	0.497	0.530	0.362	27.2
26	3370	6.79	0.438	8.4	0.497	0.533	0.359	27.9
27	3520	6.96	0.445	8.8	0.497	0.512	0.362	27.3
28	3620	6.62	0.415	8.2	0.520	0.515	0.353	32.1
29	3800	7.03	0.446	7.8	0.520	0.525	0.376	27.6
30	3895	6.76	0.453	8.2	0.520	0.522	0.380	26.9
31	4045	6.96	0.389	8.7	0.520	0.508	0.372	28.4
32	4215	5.93	0.462	7.4	0.520	0.519	0.363	30.1
33	4345	7.24	0.450	9.6	0.520	0.517	0.361	30.6
34	4530	7.21	0.434	8.3	0.520	0.516	0.360	30.8
35	5025	7.72	0.453	9.1	0.520	0.521	0.356	31.4

Table 18 Cross-flow results of experiment P60C08.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	145	6.21	0.466	4.0	0.807	0.606	0.384	52.4
2	620	6.27	0.485	7.2	0.807	0.75	0.543	32.7
3	910	6.24	0.484	7.3	0.807	0.803	0.57	29.4
4	1335	7.52	0.484	6.8	0.807	0.788	0.603	25.3
5	1530	7.45	0.464	6.8	0.807	0.805	0.615	23.8
6	1875	7.07	0.458	7.2	0.807	0.801	0.609	24.5
7	2415	6.48	0.473	5.9	0.807	0.801	0.602	25.4
8	2640	6.27	0.479	6.7	0.807	0.8	0.6	25.7
9	2855	6.41	0.478	7.0	0.807	0.803	0.605	25.0
10	3055	6.62	0.473	7.5	0.807	0.801	0.602	25.4
11	3295	6.00	0.469	6.1	0.807	0.812	0.602	25.4
12	3800	6.34	0.476	6.4	0.786	0.808	0.613	22.0
13	4005	6.14	0.472	6.4	0.786	0.808	0.6	23.7
14	4205	5.38	0.473	6.0	0.786	0.801	0.599	23.8
15	4420	6.89	0.459	7.1	0.786	0.805	0.601	23.5
16	4690	7.03	0.478	6.9	0.786	0.797	0.6	23.7
17	5250	5.65	0.467	5.2	0.786	0.802	0.6	23.7
18	5520	6.00	0.468	5.8	0.786	0.807	0.599	23.8
19	5745	6.31	0.483	6.1	0.786	0.801	0.597	24.0
20	6125	6.89	0.460	7.1	0.786	0.793	0.601	23.5
21	6740	6.21	0.471	6.0	0.786	0.8	0.602	23.4
22	6975	5.72	0.376	5.8	0.786	0.799	0.605	23.0
23	7205	6.48	0.480	6.8	0.786	0.794	0.605	23.0

Table 19. Cross-flow results of experiment P60C10.

No	Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate Percent flow (%)	Solute rejection of Cl^-			
					Feed (M)	Concentrate (M)	Permeate (M)	Rejection (%)
1	450	6.41	0.461	6.4	0.981	0.895	0.640	0.347
2	910	6.48	0.470	6.0	0.981	0.987	0.734	0.252
3	1246	7.03	0.473	6.7	0.981	0.988	0.754	0.232
4	1555	6.45	0.465	6.3	0.981	0.989	0.757	0.229
5	1800	6.76	0.462	6.7	0.981	0.989	0.765	0.221
6	2360	6.45	0.463	6.7	0.981	0.989	0.765	0.220
7	2600	6.48	0.454	6.6	0.981	0.987	0.765	0.220
8	2905	6.55	0.455	6.9	0.981	0.990	0.768	0.217
9	3280	7.10	0.462	7.4	0.981	0.992	0.767	0.219
10	3800	7.41	0.467	7.5	0.964	0.990	0.762	0.210
11	4060	6.72	0.465	7.0	0.964	0.990	0.771	0.200
12	4360	6.79	0.462	7.4	0.964	1.008	0.768	0.203
13	4685	7.14	0.460	7.8	0.964	0.996	0.770	0.201
14	5240	7.58	0.451	8.4	0.964	0.990	0.776	0.195
15	5480	6.48	0.360	7.7	0.964	0.983	0.773	0.198
16	5850	6.89	0.452	8.4	0.964	0.987	0.791	0.179
17	6405	7.93	0.320	8.0	0.964	0.983	0.796	0.174
18	6690	6.14	0.445	6.6	0.964	0.981	0.793	0.177
19	7010	6.89	0.401	8.0	0.964	0.988	0.781	0.190
20	7310	6.03	0.451	9.2	0.964	0.983	0.787	0.183
21	7565	6.65	0.431	7.4	0.964	0.987	0.778	0.192

Table 20. Cross-flow results of experiment P5002Co.

No.	Time (min)	Solute concentration in feed solution						Solute concentration in permeate solution					
		Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)
1	160	0.61	7.88	0.59	3.15	4.98	19.26	0.03	1.04	0.03	0.77	0.41	2.50
2	290	0.61	7.88	0.59	3.15	4.98	19.26	0.02	1.04	0.02	0.77	0.41	2.50
3	455	0.61	7.88	0.59	3.15	4.98	19.26	0.04	1.04	0.05	0.77	0.41	2.50
4	650	0.61	7.88	0.59	3.15	4.98	19.26	0.15	1.74	0.16	1.00	0.41	3.49
5	1205	0.61	7.88	0.59	3.15	4.98	19.26	0.32	3.74	0.31	1.56	2.30	7.86
6	1370	0.61	7.88	0.59	3.15	4.98	19.26	0.39	4.32	0.38	1.92	2.80	9.88
7	1520	0.61	7.88	0.59	3.15	4.98	19.26	0.41	4.53	0.40	2.05	2.96	10.53
8	1720	0.61	7.88	0.59	3.15	4.98	19.26	0.41	4.62	0.38	1.94	3.00	10.65
9	1845	0.61	7.88	0.59	3.15	4.98	19.26	0.44	4.79	0.42	2.15	3.29	11.68
10	1980	0.61	7.88	0.59	3.15	4.98	19.26	0.47	5.23	0.45	2.13	3.50	13.37
11	2175	0.61	7.88	0.59	3.15	4.98	19.26	0.47	5.34	0.44	2.16	3.46	12.97
12	2635	0.61	7.88	0.59	3.15	4.98	19.26	0.46	5.11	0.43	2.12	3.66	13.12
13	2805	0.61	7.88	0.59	3.15	4.98	19.26	0.46	5.26	0.44	2.05	3.70	13.07
14	2925	0.61	7.88	0.59	3.15	4.98	19.26	0.45	5.02	0.43	2.10	3.50	12.50
15	3045	0.61	7.88	0.59	3.15	4.98	19.26	0.43	4.81	0.43	1.94	3.50	12.80
16	3165	0.61	7.84	0.59	3.12	5.02	19.36	0.44	5.04	0.42	2.07	3.66	13.12
17	3340	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.01	0.42	2.15	3.50	13.02
18	3530	0.61	7.84	0.59	3.12	5.02	19.36	0.45	4.99	0.43	2.23	3.70	13.10
19	3670	0.61	7.84	0.59	3.12	5.02	19.36	0.44	4.92	0.44	2.10	3.62	12.95
20	4095	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.05	0.44	2.07	3.41	12.38
21	4220	0.61	7.84	0.59	3.12	5.02	19.36	0.44	4.95	0.43	2.20	3.66	12.20
22	4375	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.08	0.43	2.10	3.50	12.10
23	4555	0.61	7.84	0.59	3.12	5.02	19.36	0.45	4.95	0.44	2.15	3.54	12.65
24	4750	0.61	7.84	0.59	3.12	5.02	19.36	0.45	4.99	0.44	2.15	3.62	11.80
25	4895	0.61	7.84	0.59	3.12	5.02	19.36	0.45	4.88	0.44	2.15	3.54	11.73
26	5030	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.03	0.44	2.15	3.62	12.18
27	5540	0.61	7.84	0.59	3.12	5.02	19.36	0.46	5.04	0.43	2.12	3.79	12.18
28	5635	0.61	7.84	0.59	3.12	5.02	19.36	0.44	5.12	0.43	2.07	3.70	12.03
29	5825	0.61	7.84	0.59	3.12	5.02	19.36	0.44	5.01	0.42	2.15	3.70	12.13
30	5965	0.61	7.84	0.59	3.12	5.02	19.36	0.43	4.98	0.42	2.12	3.58	12.40
31	6055	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.11	0.43	2.05	3.79	12.85
32	6195	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.20	0.44	2.10	3.79	12.87
33	6650	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.07	0.43	2.07	3.83	12.75
34	7050	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.20	0.44	2.05	3.95	12.63
35	7355	0.61	7.84	0.59	3.12	5.02	19.36	0.46	5.13	0.43	2.18	3.87	12.80
36	7430	0.61	7.84	0.59	3.12	5.02	19.36	0.45	5.11	0.44	2.02	3.87	13.30

Table 21. Solute rejection of 80% diluted produced water.

Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate percent flow (%)	Solute rejection (%)					
				Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
160	5.52	0.177	13.9	95.7	86.8	95.6	75.6	91.7	87.0
290	5.79	0.263	11.0	97.1	86.8	96.5	75.6	91.7	87.0
455	5.79	0.302	9.3	93.1	86.8	92.2	75.6	91.7	87.0
650	6.21	0.155	11.6	74.8	77.9	73.5	68.3	91.7	81.9
1205	5.72	0.244	7.1	47.4	52.6	47.1	50.4	53.7	59.2
1370	5.52	0.205	6.7	36.8	45.2	36.5	39.0	43.8	48.7
1520	5.38	0.234	10.8	32.7	42.5	32.8	35.0	40.5	45.3
1720	5.45	0.181	5.4	32.5	41.3	35.2	38.2	39.7	44.7
1845	5.52	0.447	2.5	28.3	39.2	29.5	31.7	33.9	39.4
1980	5.79	0.505	4.7	23.4	33.7	24.6	32.2	29.8	30.6
2175	5.79	0.516	4.8	22.6	32.2	26.3	31.2	30.6	32.6
2635	6.21	0.522	5.0	24.9	35.1	27.7	32.7	26.4	31.9
2805	5.72	0.526	4.6	25.0	33.3	26.5	35.0	25.6	32.1
2925	5.52	0.536	4.5	27.1	36.3	27.7	33.2	29.8	35.1
3045	5.38	0.561	4.4	29.2	39.0	27.7	38.2	29.8	33.5
3165	5.45	0.510	4.4	27.9	35.7	28.4	33.6	27.0	32.2
3340	5.52	0.536	4.5	27.2	36.1	28.8	31.1	30.3	32.7
3530	5.52	0.541	4.7	26.6	36.4	28.1	28.7	26.2	32.3
3670	5.52	0.495	4.7	28.1	37.2	26.1	32.8	27.9	33.1
4095	5.52	0.534	4.7	27.2	35.6	26.5	33.6	32.0	36.1
4220	5.38	0.578	4.5	27.7	36.8	28.1	29.5	27.0	37.0
4375	5.58	0.326	5.7	27.5	35.2	27.1	32.8	30.3	37.5
4555	5.03	0.507	4.4	27.2	36.8	25.5	31.1	29.5	34.7
4750	5.55	0.527	4.8	26.0	36.4	26.4	31.1	27.9	39.0
4895	5.69	0.527	4.9	26.9	37.7	26.4	31.1	29.5	39.4
5030	5.79	0.527	5.0	26.3	35.9	26.2	31.1	27.9	37.1
5540	6.21	0.523	5.2	25.8	35.7	26.8	32.0	24.6	37.1
5635	6.07	0.484	5.1	28.0	34.7	27.3	33.6	26.2	37.9
5825	5.72	0.528	4.9	28.4	36.1	28.3	31.1	26.2	37.4
5965	5.52	0.527	4.7	29.6	36.5	29.3	32.0	28.7	36.0
6055	5.62	0.506	4.8	27.0	34.8	27.7	34.4	24.6	33.6
6195	5.79	0.527	4.8	26.4	33.6	25.7	32.8	24.6	33.5
6650	6.14	0.535	5.0	26.5	35.3	27.4	33.6	23.8	34.1
7050	5.65	0.517	5.1	26.0	33.6	26.4	34.4	21.3	34.8
7355	5.65	0.527	4.7	25.6	34.5	26.9	30.1	23.0	33.9
7430	5.52	0.390	4.8	26.2	34.8	25.2	35.2	23.0	31.3

Table 22. Cross-flow results of experiment P5004Co.

No.	Time (min)	Solute concentration in feed solution						Solute concentration in permeate solution					
		Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)
1	195	1.22	17.38	1.20	6.65	10.66	28.69	0.45	5.65	0.45	2.25	4.16	9.98
2	335	1.22	17.38	1.20	6.65	10.66	28.69	0.47	5.75	0.45	2.48	4.36	10.45
3	480	1.22	17.38	1.20	6.65	10.66	28.69	0.62	7.74	0.60	3.38	5.72	14.22
4	1020	1.22	17.38	1.20	6.65	10.66	28.69	0.84	10.62	0.81	4.53	7.61	19.21
5	1185	1.22	17.38	1.20	6.65	10.66	28.69	0.91	11.35	0.84	4.83	7.82	21.11
6	1340	1.22	17.38	1.20	6.65	10.66	28.69	0.94	11.76	0.88	4.94	8.02	21.91
7	1520	1.22	17.38	1.20	6.65	10.66	28.69	0.94	11.96	0.88	5.02	8.43	22.26
8	1700	1.22	17.38	1.20	6.65	10.66	28.69	0.97	12.08	0.88	4.94	8.02	21.13
9	1840	1.22	17.38	1.20	6.65	10.66	28.69	0.95	11.97	0.89	4.76	8.11	21.28
10	1970	1.22	17.38	1.20	6.65	10.66	28.69	0.95	11.75	0.90	4.88	8.32	20.81
11	2495	1.22	17.38	1.20	6.65	10.66	28.69	0.96	12.08	0.91	5.01	8.56	21.81
12	2665	1.22	17.38	1.20	6.65	10.66	28.69	0.97	12.39	0.88	4.89	8.93	22.16
13	2855	1.22	17.38	1.20	6.65	10.66	28.69	0.97	12.28	0.89	4.91	8.97	23.13
14	2975	1.22	17.70	1.20	6.60	10.53	29.44	0.98	12.28	0.91	5.06	8.93	22.63
15	3100	1.22	17.70	1.20	6.60	10.53	29.44	0.99	12.39	0.91	4.94	8.85	22.58
16	3210	1.22	17.70	1.20	6.60	10.53	29.44	0.98	12.08	0.92	5.09	9.01	22.28
17	3380	1.22	17.70	1.20	6.60	10.53	29.44	1.00	12.39	0.95	4.86	8.72	22.71
18	3980	1.22	17.70	1.20	6.60	10.53	29.44	0.99	12.28	0.92	4.83	8.64	22.46
19	4165	1.22	17.70	1.20	6.60	10.53	29.44	1.00	12.36	0.91	4.73	8.59	22.06
20	4345	1.22	17.70	1.20	6.60	10.53	29.44	1.00	12.49	0.91	4.86	8.72	21.96
21	4580	1.22	17.70	1.20	6.60	10.53	29.44	0.99	12.28	0.97	4.96	8.60	22.01
22	4730	1.22	17.70	1.20	6.60	10.53	29.44	1.01	12.49	0.99	4.89	8.72	22.06
23	4895	1.22	17.70	1.20	6.60	10.53	29.44	1.01	12.60	0.98	4.94	8.85	23.03
24	5385	1.22	17.70	1.20	6.60	10.53	29.44	1.00	12.49	0.96	5.09	8.68	22.21
25	5745	1.22	17.70	1.20	6.60	10.53	29.44	1.04	13.43	1.00	5.35	9.09	23.68
26	5925	1.22	17.70	1.20	6.60	10.53	29.44	1.06	13.32	1.05	5.42	9.13	24.00
27	6170	1.22	17.70	1.20	6.60	10.53	29.44	1.05	13.22	1.03	5.42	9.22	23.78
28	6410	1.22	17.70	1.20	6.60	10.53	29.44	1.05	12.80	1.03	5.45	9.13	23.85

Table 23. Solute rejection of 60% diluted produced water.

Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate percent flow (%)	Solute rejection (%)					
				Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
195	5.86	0.340	4.8	63.0	67.5	62.5	66.2	61.0	65.2
335	6.00	0.529	4.3	61.9	66.9	62.5	62.7	59.1	63.6
480	6.24	0.534	4.5	49.2	55.4	49.6	49.2	46.3	50.4
1020	5.83	0.544	4.3	31.2	38.9	32.2	31.9	28.6	33.0
1185	5.65	0.534	4.1	25.5	34.7	30.0	27.3	26.6	26.4
1340	5.58	0.541	4.1	23.2	32.3	26.2	25.8	24.7	23.7
1520	5.52	0.555	4.0	23.1	31.2	26.5	24.5	20.8	22.4
1700	5.69	0.533	4.2	20.9	30.5	26.4	25.8	24.7	26.3
1840	5.83	0.548	4.3	21.9	31.1	25.6	28.5	23.9	25.8
1970	5.90	0.531	4.4	22.1	32.4	25.0	26.7	22.0	27.5
2495	5.93	0.546	4.4	21.2	30.5	24.3	24.6	19.7	24.0
2665	5.62	0.542	4.2	20.6	28.7	26.4	26.5	16.2	22.8
2855	5.52	0.532	4.1	20.5	29.3	25.5	26.2	15.8	19.4
2975	5.52	0.532	4.0	19.2	30.6	21.3	23.3	15.2	23.1
3100	5.62	0.541	4.1	19.0	30.0	21.6	25.2	16.0	23.3
3210	5.62	0.568	4.3	19.3	31.8	20.8	22.9	14.5	24.3
3380	5.79	0.533	4.3	18.0	30.0	18.1	26.4	17.2	22.9
3980	5.90	0.492	4.5	18.6	30.6	20.7	26.7	18.0	23.7
4165	5.62	0.542	4.2	17.8	30.2	21.3	28.3	18.5	25.1
4345	5.41	0.549	4.0	18.0	29.4	21.8	26.4	17.2	25.4
4580	5.45	0.546	4.1	18.5	30.6	16.5	24.8	18.4	25.3
4730	5.48	0.532	4.2	17.4	29.4	14.5	26.0	17.2	25.1
4895	5.41	0.553	4.2	16.8	28.8	15.1	25.2	16.0	21.8
5385	5.55	0.544	4.3	17.5	29.4	17.0	22.9	17.6	24.6
5745	5.52	0.527	4.1	14.8	24.1	13.9	19.0	13.7	19.6
5925	5.03	0.518	4.0	12.5	24.7	9.1	17.8	13.3	18.5
6170	4.90	0.506	3.7	13.4	25.3	10.8	17.8	12.5	19.2
6410	5.38	0.509	3.8	13.8	27.6	11.1	17.4	13.3	19.0

Table 24. Cross-flow results of experiment P5006Co.

No.	Time (min)	Solute concentration in feed solution						Solute concentration in permeate solution					
		Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)
1	105	1.89	24.57	1.83	9.51	15.06	54.39	0.77	8.54	0.74	4.04	6.42	21.81
2	775	1.89	24.57	1.83	9.51	15.06	54.39	1.42	16.24	1.38	7.47	11.85	40.42
3	1190	1.89	24.57	1.83	9.51	15.06	54.39	1.56	17.90	1.59	7.88	12.92	44.91
4	2075	1.89	24.57	1.83	9.51	15.06	54.39	1.59	18.11	1.63	8.03	13.08	44.91
5	2525	1.89	24.57	1.83	9.51	15.06	54.39	1.62	18.74	1.58	8.18	13.50	46.21
6	2955	1.89	24.57	1.83	9.51	15.06	54.39	1.64	18.74	1.59	8.39	13.50	47.21
7	3665	1.91	25.19	1.83	9.67	15.39	53.89	1.66	18.95	1.60	8.49	13.50	47.26
8	4085	1.91	25.19	1.83	9.67	15.39	53.89	1.61	18.53	1.63	8.18	13.58	48.75
9	4915	1.91	25.19	1.83	9.67	15.39	53.89	1.63	18.95	1.57	8.29	13.74	48.61
10	5415	1.91	25.19	1.83	9.67	15.39	53.89	1.61	18.74	1.54	7.88	13.00	47.56
11	6395	1.91	25.19	1.83	9.67	15.39	53.89	1.64	18.95	1.56	8.18	13.25	49.10
12	6875	1.91	25.19	1.83	9.67	15.39	53.89	1.65	18.74	1.58	8.44	13.17	49.55
13	7800	1.91	25.19	1.83	9.67	15.39	53.89	1.63	18.53	1.59	7.93	13.17	49.45

Table 25. Solute rejection of 40% diluted produced water.

Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate percent flow (%)	Solute rejection (%)					
				Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
105	5.41	0.177	13.9	59.5	65.3	59.6	57.5	57.4	59.9
775	5.65	0.263	11.0	24.9	33.9	24.4	21.5	21.3	25.7
1190	5.58	0.302	9.3	17.6	27.1	13.3	17.2	14.2	17.4
2075	5.90	0.155	11.6	15.9	26.3	10.7	15.6	13.1	17.4
2525	5.58	0.244	7.1	14.4	23.7	13.7	14.0	10.4	15.0
2955	5.79	0.205	6.7	13.2	23.7	13.1	11.8	10.4	13.2
3665	5.62	0.234	10.8	12.7	24.8	8.1	12.2	12.3	12.3
4085	5.38	0.181	5.4	15.4	26.4	6.8	15.3	11.8	9.5
4915	6.03	0.447	2.5	14.3	24.8	10.2	14.3	10.7	9.8
5415	5.45	0.505	4.7	15.4	25.6	11.8	18.5	15.5	11.8
6395	5.76	0.516	4.8	14.0	24.8	10.3	15.3	13.9	8.9
6875	5.48	0.522	5.0	13.2	25.6	9.6	12.7	14.4	8.1
7800	5.76	0.526	4.6	14.4	26.4	8.8	18.0	14.4	8.2

Table 26. Cross-flow result of experiment P5008Co.

No.	Time (min)	Solute concentration in feed solution						Solute concentration in permeate solution					
		Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl^- (M)	SO_4^{2-} (mM)	Na^+ (M)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)
1	329	2.61	32.17	2.42	11.43	20.00	60.63	1.65	18.06	1.50	8.21	13.66	47.71
2	638	2.61	32.17	2.42	11.43	20.00	60.63	1.93	21.96	1.79	9.00	14.69	50.15
3	888	2.61	32.17	2.42	11.43	20.00	60.63	2.13	23.58	2.09	9.34	15.35	51.15
4	1303	2.61	32.17	2.42	11.43	20.00	60.63	2.22	24.72	2.09	9.41	15.76	51.90
5	1608	2.61	32.17	2.42	11.43	20.00	60.63	2.32	26.44	2.06	9.85	16.21	54.39
6	2098	2.61	32.17	2.42	11.43	20.00	60.63	2.30	25.71	2.15	9.74	15.76	52.90
7	2623	2.61	32.17	2.42	11.43	20.00	60.63	2.32	26.80	2.29	9.72	15.96	51.90
8	2883	2.61	32.17	2.42	11.43	20.00	60.63	2.31	25.82	2.05	9.82	15.59	52.65
9	3183	2.61	32.17	2.42	11.43	20.00	60.63	2.32	25.97	2.13	9.95	15.47	55.39
10	3508	2.62	32.95	2.36	11.71	18.72	60.63	2.29	26.08	2.30	9.85	16.87	54.89
11	4063	2.62	32.95	2.36	11.71	18.72	60.63	2.24	26.44	2.27	10.18	17.03	54.89
12	4303	2.62	32.95	2.36	11.71	18.72	60.63	2.28	26.44	2.27	10.21	16.70	54.39
13	4643	2.62	32.95	2.36	11.71	18.72	60.63	2.30	26.28	2.21	9.92	16.54	52.65
14	4938	2.62	32.95	2.36	11.71	18.72	60.63	2.31	26.70	2.27	10.18	16.25	54.89
15	5483	2.62	32.95	2.36	11.71	18.72	60.63	2.31	25.92	2.11	9.97	16.66	53.40
16	5773	2.62	32.95	2.36	11.71	18.72	60.63	2.25	26.54	2.11	9.57	16.38	52.65
17	6078	2.62	32.95	2.36	11.71	18.72	60.63	2.31	26.44	2.23	9.87	16.62	55.14
18	6273	2.62	32.95	2.36	11.71	18.72	60.63	2.34	26.49	2.18	10.41	16.54	55.64

Table 27. Solute rejection of 20% diluted produced water.

Time (min)	Inlet Pressure (Mpa)	Total Flow rate (ml/min)	Permeate percent flow (%)	Solute rejection (%)					
				Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
329	6.00	0.177	13.9	36.8	43.9	38.2	28.2	31.7	21.3
638	6.03	0.263	11.0	26.1	31.7	26.1	21.3	26.5	17.3
888	6.03	0.302	9.3	18.4	26.7	13.6	18.3	23.3	15.6
1303	5.76	0.155	11.6	15.1	23.1	13.4	17.7	21.2	14.4
1608	6.17	0.244	7.1	11.1	17.8	14.7	13.9	18.9	10.3
2098	6.48	0.205	6.7	11.9	20.1	11.3	14.8	21.2	12.8
2623	6.10	0.234	10.8	11.2	16.7	5.4	15.0	20.2	14.4
2883	5.69	0.181	5.4	11.5	19.7	15.4	14.1	22.0	13.2
3183	5.65	0.447	2.5	11.1	19.3	11.9	13.0	22.6	6.6
3508	5.83	0.505	4.7	12.6	20.9	2.9	15.9	9.9	9.5
4063	6.03	0.516	4.8	14.6	19.7	3.8	13.1	9.0	9.5
4303	5.24	0.522	5.0	13.0	19.7	3.7	12.9	10.8	10.3
4643	6.10	0.526	4.6	12.3	20.2	6.6	15.3	11.6	13.2
4938	6.41	0.536	4.5	11.8	19.0	3.8	13.1	13.2	7.4
5483	6.48	0.561	4.4	11.9	21.3	10.7	14.8	11.0	11.9
5773	6.38	0.510	4.4	14.0	19.4	10.6	18.3	12.5	13.2
6078	6.48	0.536	4.5	12.0	19.7	5.8	15.7	11.2	9.1
6273	6.07	0.541	4.7	10.5	19.6	7.7	11.1	11.6	4.5