Nanofiltration Membranes for Agricultural Drainage Water Reclamation

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ABSTRACT

Optimization of membrane systems for treatment of agricultural drainage (AD) water involves careful consideration of feed water quality, suitable membrane selection and operating conditions. In order to evaluate the potential applicability of membrane nanofiltration (NF)/low pressure reverse osmosis (RO) to the treatment of AD water, a diagnostic approach to membrane and process evaluation was undertaken. This study was in support of the design and operation of a pilot field study of nanofiltration treatment of high salinity AD water in the California San Joaquin Valley. This AD water is a complex mixture of dissolved and suspended chemical species in addition to a wide variety of micro-organisms. An important element in the field study design involves membrane selection, establishing operating conditions and evaluating the potential for biofouling and mineral scaling. In the present study, five candidate nanofiltration and low pressure reverse osmosis membranes were evaluated using a diagnostic laboratory membrane system. Criteria for selection involved performance profiles with model salt solutions of univalent and divalent ions, biofouling potential analysis and studies involving gypsum formation and control.

KEYWORDS

Agricultural drainage water; reverse osmosis; antiscalants; nanofiltration; biofouling.

INTRODUCTION

Tile drainage of irrigated lands is practiced in many semi-arid agricultural regions. Adverse geological conditions in such areas often involve impervious layers underlying fertile land (Raveendran and Madany, 1991; Sorour et al., 1992; Smith, 1992). This form of artificial drainage is practiced in order to prevent water-logging and salinity buildup in the root zone of crops. The hydrologic and environmental impacts of artificial drainage have been extensively reviewed by Skaggs *et al.* (1994).

The fertile semi-arid California San Joaquin Valley was one of the first regions to install artificial drainage, which has proved most effective for controlling root zone salinity. Since the early 1970's, serious consideration has been given to systems for reclamation and reuse of agricultural drainage water. Motivation for application of this technology arose from two major issues. First, a successful reclamation facility would help to augment diminishing supplies of imported irrigation water. Secondly, a significant volume reduction of environmentally hazardous drainage water could also be achieved. The first installation which was designed for the above mission was built by the pilot plant group at the UCLA School of Engineering and Applied Science in 1971 (McCutchan, 1972, 1975). This historic facility at Firebaugh, California used hand-cast tubular cellulose acetate membranes. Successful results at Firebaugh demonstrated the feasibility of reverse osmosis (RO) technology for reclamation of agricultural drainage water. A larger and considerably more sophisticated treatment plant was then developed in the nearby town of Los Baños (Smith et al., 1981; Molseeed et al., 1987; Marinas and Slleck, 1987). The Los Baños plant, completed in the mid 1980's, was designed to study a variety of operating parameters and to assess the economic feasibility of drainage water reclamation using "state of the art" RO membranes available at that time. Economic data were never completely developed since an untimely shut-down of the plant was ordered by the U.S. Environmental Protection Agency in 1987. This action was taken as a result of high concentrations of selenium in the form of SeO_4^{2-} ion found at Kesterson - the site of a low-lying basin for all tile drainage in that region. This hazardous contaminant can enter the food chain and at concentrations measured in the evaporation pond it was found to be toxic to water foul. As a result, drainage in various parts of the San Joaquin valley have been since reduced or terminated.

Interruption of drainage has created a severe hardship for the farming community. If not resumed, a gradual salinity build-up will necessitate the "retirement" of large areas of fertile agricultural land. A search for solutions to the drainage problem is presently underway and again membrane desalination has been given serious consideration. This resurgence of interest arises primarily from a new generation of high performance membranes developed during the last decade (Rautenbach and Groschl, 1990; Petersen, 1993). These unique membranes, known as nanofiltration (NF), operate at remarkably low pressures with excellent product water flux and reasonably high levels of salt rejection. However, selection of the membrane for AD water desalination must involve careful consideration of feed water quality.

Consideration of water quality in relation to optimization of the desalination process is especially critical with AD water, which is a complex mixture of dissolved and suspended organic and inorganic components as well as a wide variety of micro-organisms. The TDS of this water, from the San Joaquin Valley, varies between 3,000 and 15,000 mg/L and most samples are close to saturation with respect to gypsum ($CaSO_4 \cdot 2H_2O$). As a result, the control of gypsum scale formation is critical. A series of improved chemical additives, known as antiscalants that consist primarily of polyelectrolytes, are now available from chemical industry. These antisclanats have met with some success in inhibiting membrane surface scaling by gypsum. Other approaches that make use of cation exchangers have also been proposed, but have proved to be expensive to install and operate. The problem of calcium sulfate scaling remains and must be solved before membrane desalination of AD water becomes a practical reality. Other important aspects affecting membrane performance are colloidal particles and potential microbiological growth. Prefiltration can be effective in reducing the problem of colloidal and biofouling. Design of such pretreatment systems is as important as proper choice of the membrane itself.

Optimization of membrane desalination systems for AD water presents a real challenge for system designers and plant operators. Of primary concern is selection of the best membrane for this specific task. An assessment may, in part, be based on controlled laboratory experiments but overall suitability can be determined only by long-term operation in the field. This is especially applicable to waste waters containing a wide and complex variety of dissolved and suspended chemical species as well as micro-organisms. In addition to membrane selection, the designer must be concerned with operating parameters and feed water pretreatment systems.

Research described in this paper deals with three basic objectives designed to assist in the selection of suitable membranes for AD water desalination and optimization of process operating conditions. First, a diagnostic performance protocol of leading commercial NF membranes is presented. These evaluations were conducted with model solutions of univalent and divalent cations. Secondly, an experimental protocol was developed for ranking antiscalants with respect to their ability to inhibit gypsum crystallization. Thirdly, the biofouling potential of candidate membranes has been evaluated under carefully controlled laboratory conditions. Results reported in this paper provide the necessary laboratory support for the design and operation of a membrane pilot plant recently installed in the California San Joaquin Valley.

EXPERIMENTAL

Membranes and Materials

Five aromatic polyamide composite nanofiltration membranes (NF-A to E) were selected from three major manufacturers based on their reported ion rejections and flux at a specific applied pressure. A total of four commercial antiscalants (AS-A to D) were also selected and evaluated with respect to their ability to retard calcium sulfate precipitation.

Ultra-pure de-ionized water was obtained by filtering distilled water through a Milli-Q Water System (Millipore Corp., San Jose, CA). Calcium chloride dihydrate (certified A.C.S), magnesium sulfate (certified A.C.S), sodium chloride (USP/FCC granular), sodium sulfate (certified A.C.S Anhydrous), sodium bicarbonate (certified A.C.S), and sodium meta-bisulfite (certified A.C.S) were obtained from Fisher Scientific (Pittsburgh, PA).

Membrane Test Unit

A small laboratory plate-and-frame recirculation unit (Figure 1) was used as a diagnostic membrane performance evaluation system. This unit consists of two test cells (Industrial Research Machine Products Co., El Cajon, CA) arranged in parallel. The membrane area in each cell is 3.1 in^2 (20 cm^2, 7.6 by 2.6). The magnetically stirred polyethylene reservoir accommodates up to 18 liters of feed water. A refrigerated recirculator (model 625, Fisher Scientific, Pittsburgh, PA) maintained constant reservoir temperature. A positive displacement pump (Hydra-Cell, Wanner Engineering, Minneapolis, MN) delivers up to 0.55 gpm of feed water to each cell. This flow arrangements results in a cross-flow velocity up to about 40 cm/s and a Reynolds number (with hydraulic radius as the characteristic length) of up to 2100. A back-pressure regulator (US Paraplate, Auburn, CA) controls the applied pressure. A digital flow meter (model 1000, Fisher Scientific, Pittsburgh, PA), interfaced with a PC, provides for continuous monitoring of permeate flux and accumulated volume. Permeate conductivity, at different times during operation of the unit, is measured using a conductivity meter (model WD-35607-30, Oakton Research, Vernon Hills, IL).

Membrane Rejection, Flux, and Biofouling Potential

A comprehensive performance testing protocol for each of the pre-selected membranes was carried out at a fixed temperature of 20^{o}C and applied pressure of 100 psi. Feed solutions used in these experiments consisted of aqueous solutions of 0.05, 0.10, and 0.15 M sodium chloride and 0.01, 0.02, and 0.05 M calcium chloride, respectively. Concentrations of sodium and calcium chloride were chosen based on water analysis (Table 1 and 2) of drainage water at the Buena Vista Site in the San Joaquin Valley.

Prior to each experiment, the membrane was first stabilized using DI water for a period of 2-6 hours which was found to be sufficient for the system to reach a steady-state flux condition. However, the 0.15 M sodium chloride solution required a six-hour stabilization period. All other solutions reached steady-state flux within 2 hours. The conductivity of feed water was measured before and after each experiment to ensure constant feed concentrations. Permeate samples were collected at various intervals and returned to the reservoir following the completion of conductivity or ion-specific measurements.

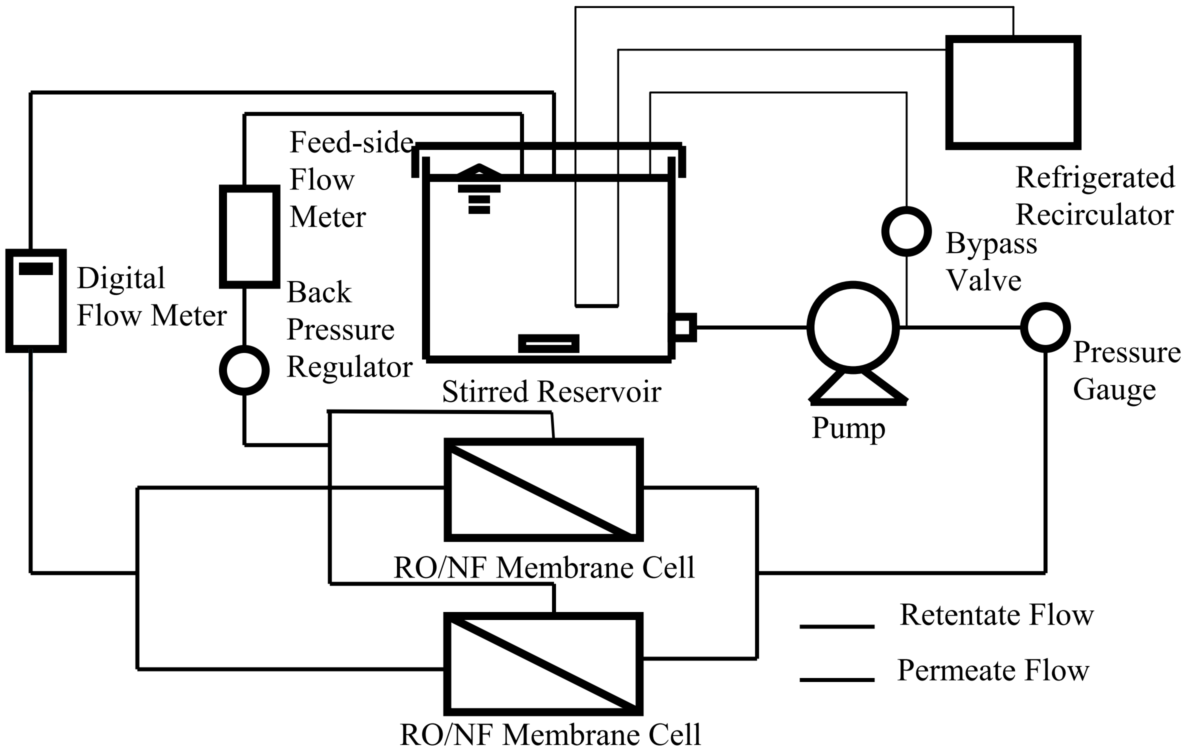

Figure 1. Laboratory-scale RO/NF membrane diagnostic system.

Table 1. Basic properties of typical Buena Vista drainage water

Property	Results
pH	7.7
Total Dissovled Solids (TDS)	5250 mg/L
Total Ogranic Carbon (TOC)	2.77 mg/L
Hardness	1630 mg/L
Turbidity	0.8 NTU

Table 2. Concentrations of major ions in Buena Vista drainage water

Substance	**Concentration**	
Cations	(mg/L)	(mol/L)
Na^+	1150	0.0500
Ca^+	555	0.0139
Mg^+	60.7	0.0025
Anions		
Cl^-	2010	0.0567
SO_4^{-2}	1020	0.0106
HCO_3^-	291	0.0048

Membrane biofouling potential was evaluated, using the biofouling assay developed by Ridgway and co-workers (Knoell et al., 1999; Ridgway et al., 1999), at the Orange County Water District Biotechnology Laboratory. Bacterial attachment assays were performed on each membrane, along with three control membranes with ten trials conducted for each membrane. The three controls consisted of the new and old versions of FT-30 from The Dow Chemical Company (Midland, MI), and a low-pressure cellulose acetate membrane from Applied Membranes, Inc. (San Marcos, CA). The test bacteria for the biofouling attachment assays were a hydrophobic strain of Mycobacterium (BT12-100) and a hydrophilic strain of Flavobacterium (PA-6) both radio-labeled with $Na_2{}^{35}SO_4$. Two sets of biofouling assays were performed. In the first set, the membranes were contacted with a NPM (sodium phosphate + magnesium chloride) buffer containing the test bacteria for 5 hours at 28°C on a rotary shaker at 200 rpm. In the second set, the NPM buffer was replaced by actual AD water. For each set of experiment, ten trials were conducted for each membrane. In each trial, a 1-in.-diameter coupon of the test membrane was placed inside a sterile 16 x 125 mm plastic tube containing 5 mL solution (buffer or AD water) and 100 µL radiolabeled cell suspension.The bacterial attachment count (i.e., number of bacteria/cm^2) was determined by a liquid scintillation counter. Biofouling assays were performed on all but the NF-D membrane, which was considered only in the final stages of the study.

Based on the above, a candidate membrane was selected for initial performance testing with a model aqueous solution composed of all major ions present in the AD water (Table 3). For each run, the membrane was first stabilized for 14 hours using a solution containing all the above major ions except calcium. The conductivity of the feed solution was measured before and after the experiment and the permeate concentrations of sodium and calcium were monitored throughout the experimental runs which were carried out for a period of five days.

Table 3. Concentrations of major ions in model solutions

Substance	**Concentration (Experimental)**		
	(mg/L)	(mol/L)	(Equiv/L)
Na^+	1150.0	0.050	0.050
Ca^{+2}	561.1	0.014	0.028
Mg^{+2}	72.9	0.003	0.006
Cl^-	2020.7	0.057	0.057
SO_4^{-2}	1056.7	0.011	0.011
HCO_3^-	305.0	0.005	0.005

Gypsum Scaling Thresholds and Evaluation of Antiscalants

The suitability of antiscalant inhibition of gypsum ($CaCl_2 \bullet 2H_2O$) scale formation was evaluated using model solutions composed of the major ions (Table 3) expected in field AD water. Chemical equilibrium analysis using the MINTEQ software (Allison et al., 1991) predicted that gypsum saturation at a concentration factor CF=2 (i.e., twice that of the AD water; Table 3). However, comparison of the antiscalants, in a stirred beaker precipitation experiment, could be more conveniently carried out at a higher CF value. Under these conditions, the onset of calcium sulfate precipitation could be observed in a reasonably short period of time. For the present study, the antiscalants were compared at a CF=5. At this concentration precipitation was observed, in the absence of antiscalant additives, within a period of about thirty minutes. This experimental protocol was designed to evaluate the onset of precipitation for different solution chemistries. The protocol consisted of mixing a 50 ml solution of CF=10 (0.03 M $MgSO_4$, 0.08 M

Na_2SO_4, and 0.34 M NaCl) with a 50 mL solution of CF=10 $CaCl_2$ (0.14 M) resulting in a final solution concentration at CF=5 (0.07 M $CaCl_2$, 0.015 M $MgSO_4$, 0.04 M Na_2SO_4, 0.17 M NaCl). For this preliminary study of antiscalant, a dosage of 3 ppm of each antiscalant was applied to the CF 5 model solution. Each test solution was continuously stirred using a magnetic bar and the free calcium ion concentration was monitored with a calcium specific electrode (Orion 97-20 BN; Beverly, MA) connected to an Accumet model 15 pH meter (Fisher Scientific, Pittsburgh, PA). The analog signal was amplified and processed using a signal conditioner module (Dataforth SCM5830-02; Tucson, AZ), and recorded via a computerized data acquisition system (5500 MF; American Data Acquisition Corporation, Woburn, MA). The experimental set-up is shown in (Figure 2).

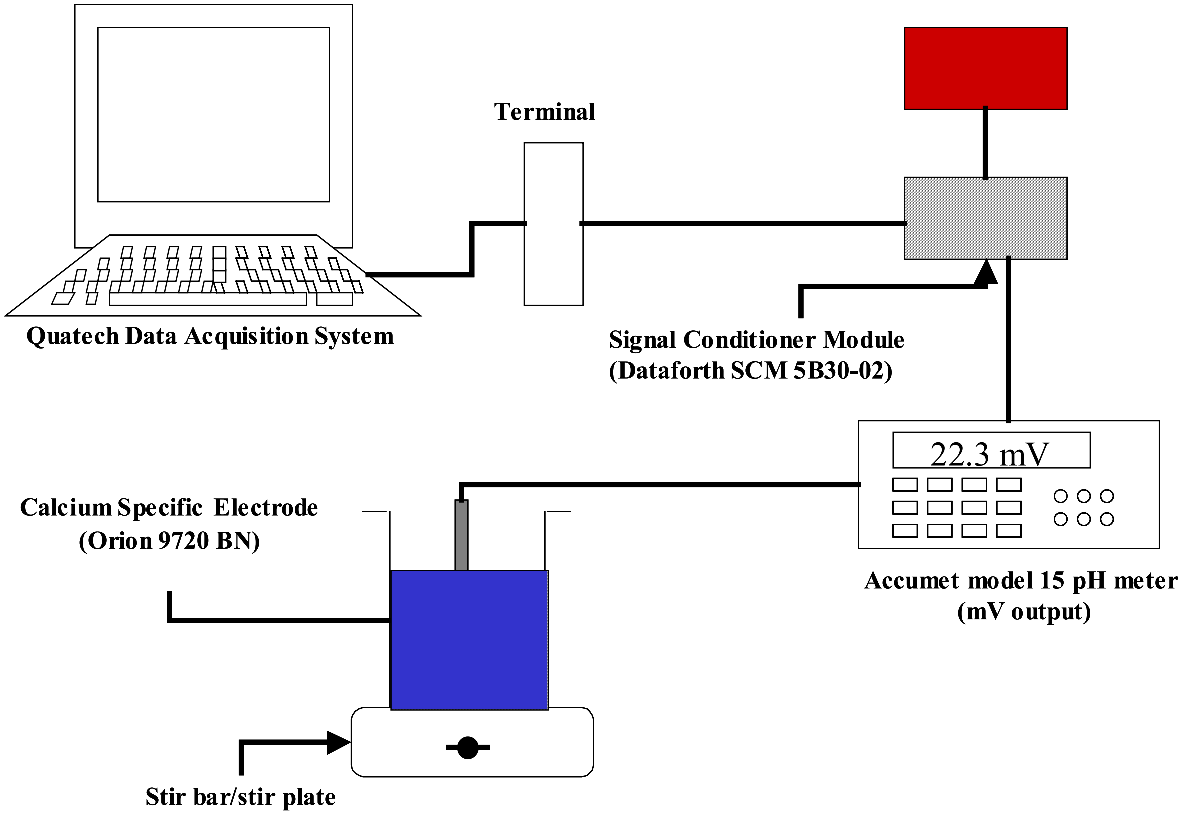

Figure 2. Laboratory system for evaluation of calcium precipitation and antiscalant ranking.

RESULTS AND DISCUSSION

Selection of a suitable membrane for AD water was based on membrane salt rejection, recovery, and bio-fouling potential. Membrane percent rejection, R, for the target solute is defined as $R = 100 (1- C_p/C_f)$, where C_p and C_f are the solute concentrations in the permeate and feed streams, respectively. Comparison of the rejection of sodium and calcium cations by the five membranes is shown in Figure 3a. As expected, these NF membranes consistently demonstrate a higher rejection for the divalent calcium ion than for the univalent sodium ion. This behavior is consistent with published studies for multivalent electrolytes (Voros et al., 1996; Hanra and Ramachandhran, 1996).

Rejection results at different feed NaCl and $CaCl_2$ concentrations are shown in Figures 4a and 4b for all but the NF-E membrane. The NF-E membrane exhibited relatively low rejection compared to other membranes tested. Therefore, additional testing at different feed concentrations of calcium chloride and sodium chloride for NF-E was not performed. The results for the different membranes (Figure 4a and 4b) demonstrate greater than 90% rejection for both the 0.05 N sodium chloride and 0.02 N calcium chloride feed solutions, which correspond to calcium levels in the AD water. However, for 0.15 N sodium chloride feed solution only the NF-D membrane displayed a rejection higher than 90%. The above results provide a reasonable performance comparison of the different membranes over a range of concentrations expected during the drainage season.

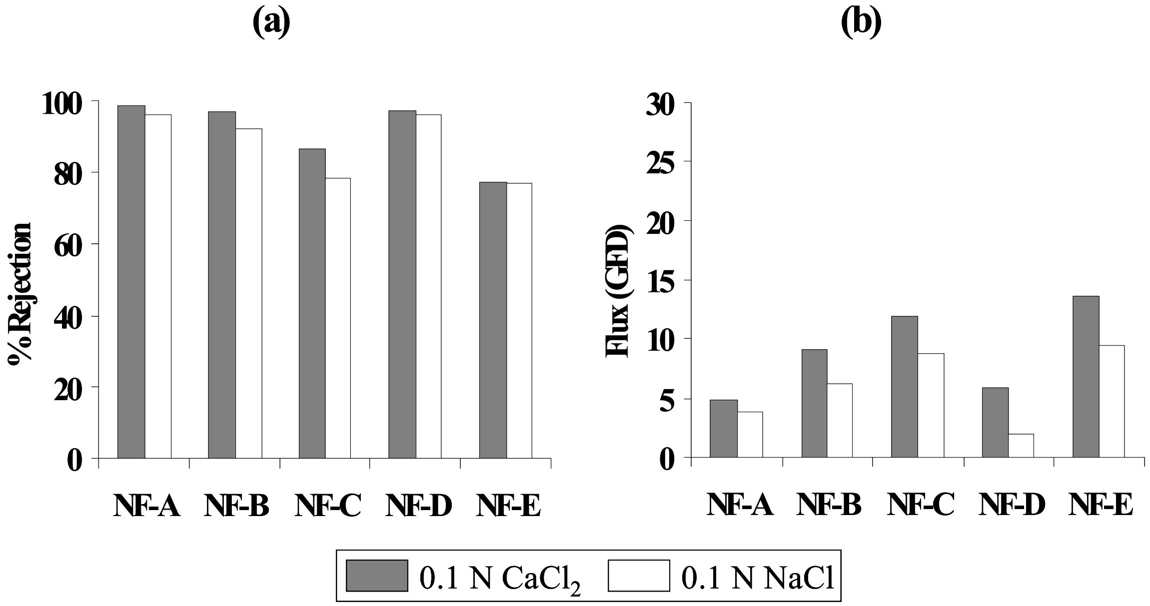

Figure 3. Comparison of rejection (a) and permeate flux (b) for five commercial nanofiltration membranes (transmembrane pressure= 100 psi, T= 20^{o}C).

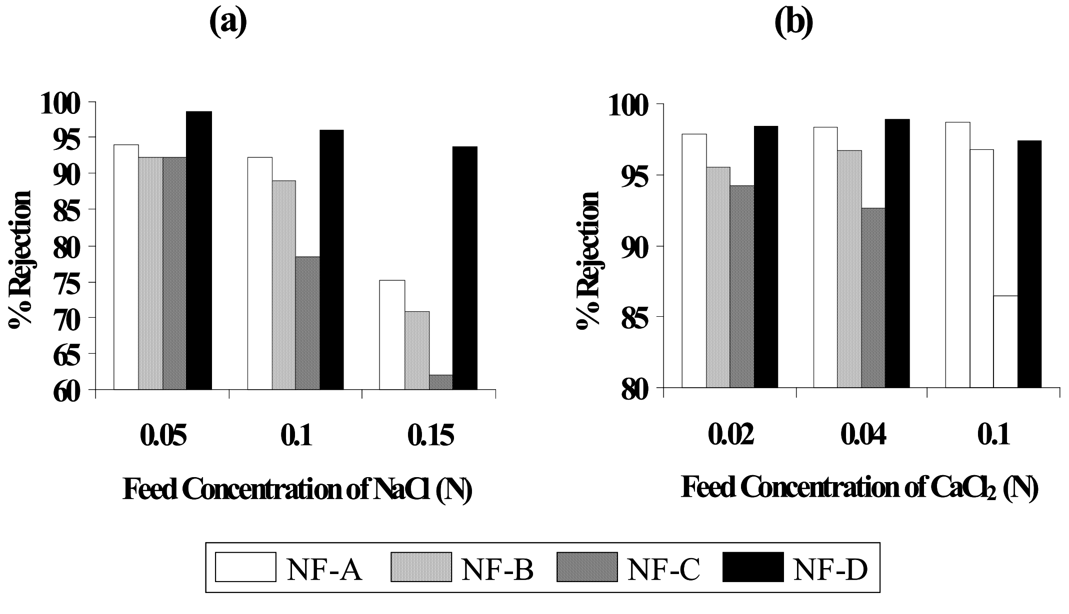

Figure 4. Flux comparison for four candidate membranes using different (a) $CaCl_2$ feed concentrations; and (b) $CaCl_2$ feed concentrations. (Transmembrane pressure= 100 psi, Temperature= 20^{o}C).

Permeate flux for the calcium chloride solutions was consistently higher (Figure 3b), validating that the performance of the NF membranes is better for divalent ions. Since the comparison was done on an equivalent charge basis, the higher permeate flux for the calcium feed solutions might be attributed to the lower number of calcium ions present in the feed, relative to sodium, at the same normality. The higher flux for calcium chloride solutions was evident for all the membranes (Figures 5a and 5b). It is interesting to note that although the NF-C membrane had the lowest rejection, it did exhibit the highest permeate flux for all feed solutions. The above results clearly suggest that membrane selection must involve a trade-off between solute rejection and permeate flux. We note that in the present diagnostic membrane system, recovery could not be evaluated due to the small membrane surface area; however, flux and rejection results can be used to estimate recovery for full-scale process analysis.

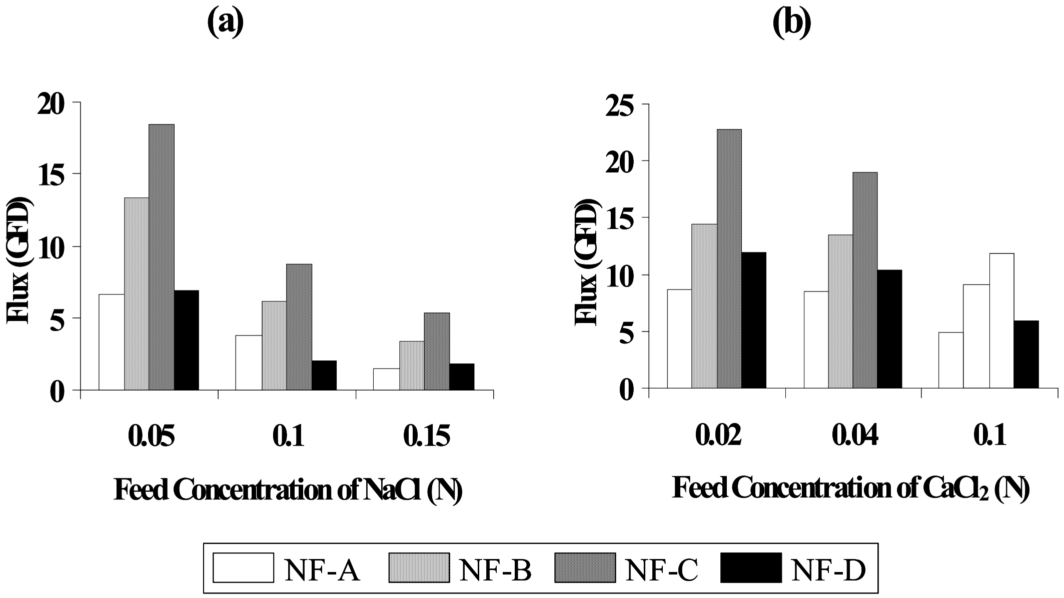

Figure 5. Flux comparison for four candidate membranes using different (a) NaCl feed concentrations; and (b) $CaCl_2$ feed concentrations. (Transmembrane pressure= 100 psi, Temperature= 20^{o}C).

Membrane selection must also be based on the fouling potential of the candidate membranes. Fouling is a general term often used to encompass flux decline resulting from colloidal particles, dissolved organics, mineral scale and bacterial adhesion. In most cases, it has been shown that a filtration pre-treatment system is likely to control most of the potential particulate fouling. However, gypsum scaling and microbiological fouling are also of concern and thus should be evaluated. Bacterial analysis of filtered AD water samples revealed a bacterial count of 1.36 x 10^6 bacteria per mL. This value indicates that, despite filtration pretreatment, biological fouling may be anticipated in the long term. Membrane bio-fouling potential analysis on the membranes was conducted at the Orange County Water District laboratories. Two sets of evaluations were conducted. The first test utilized a buffer solution (Figure 6), while the actual filtered AD water was used for the second test (Figure 7). The NF-B and NF-E membranes were ranked as having the highest bio-fouling potential while the NF-A and NF-C membranes displayed the lowest bio-fouling potential. Although the NF-D membrane was not tested for biofouling potential, the flux for this membrane was lower than for the NF-C membrane.

The above biofouling analysis suggests that if biofouling is an anticipated problem then membranes NF-C and NF-A could be the choice membranes. However, membrane NF-C had a reasonable flux and acceptable rejection and therefore, at the initial stage of the field study-support work, it was decided to evaluate the performance of the NF-C membrane with a diagnostic solution of a composition that mimics that of the AD water (Table 3). Using such a model solutions as feed, a permeate flux of 10 gfd and rejection of 89% and 92% for sodium and calcium, respectively, were obtained. The permeate flux was about 50% lower than obtained for the single ion model solutions but the rejection decreased by less than about 3.5% and 2.3% for sodium and calcium, respectively. These differences in permeate flux and rejections are attributed to the presence of other ions in the model solution.

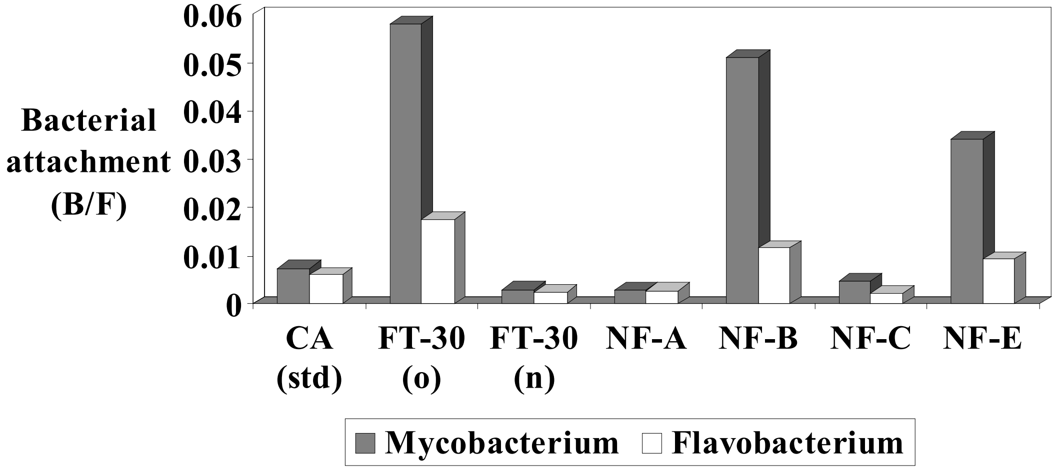

Figure 6. Comparison of biofouling potential for selected membranes. CA, FT-30 (n), and FT-30 (o) are membranes used as controls. **NPM solution** (10 mM sodium phosphate + 1mM $MgCl_2$, pH 7.0) was used as buffer. A hydrophobic strain of Mycobacterium and a hydrophilic strain of Flavobacterium were used as the test bacteria. Bacteria attachment (B/F) is the ratio of bacterial count on the membrane and the number of free bacteria in solution.

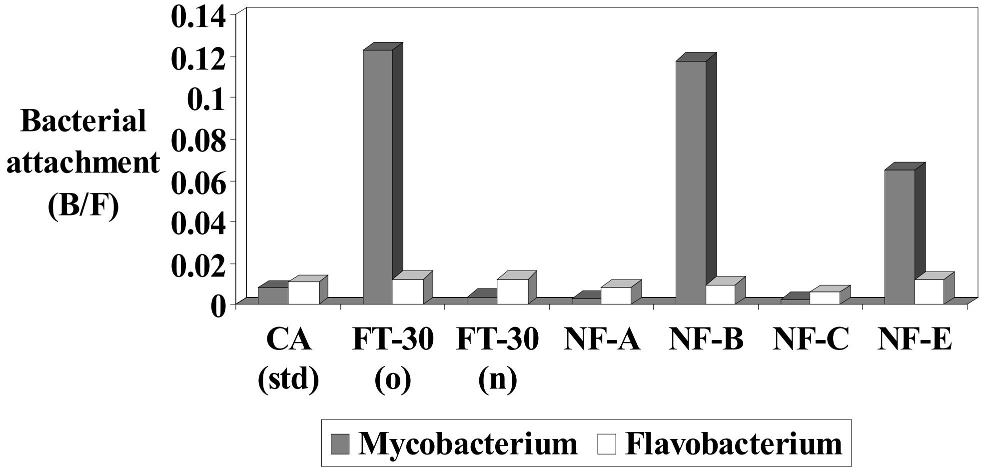

Figure 7. Comparison of biofouling potential for candidate membranes. CA, FT-30 (n), and FT-30 (o) are membranes used as controls. Note: **Buena Vista water** was used without buffer. A hydrophobic strain of Mycobacterium and a hydrophilic strain of Flavobacterium were used as the test bacteria.

In addition to biofouling, gypsum scaling could ultimately limit the long-term performance of any membrane plant treating agricultural drainage water. It is now accepted that antiscalants are effective for gypsum scale control. Effective use of antiscalants requires selection of an antiscalant (AS) and the dose that would provide sufficient inhibition of calcium sulfate crystallization. As a first stage in evaluating suitable antiscalant additives, batch experiments were conducted with model solutions, whereby calcium ion depletion was monitored under various conditions. Gypsum precipitation kinetics and the incipient time for nucleation was evaluated with an ion-specific electrode calibrated against calcium chloride standard solutions. An illustration of a typical calcium depletion plot is shown in Figure 8. These results indicate a sharp decline in calcium ion concentration, at the incipient point at which precipitation begins. In order to investigate the suitability of the present method of antiscalant evaluation, the incipient time for precipitate formation was evaluated for the different antiscalants at 3 ppm dosage. As shown in Figure 9, antiscalants AS-B, C, and D proved effective in retarding gypsum precipitation. Clearly, in all cases, precipitation eventually occurred. Apparently, the tested antiscalants affect the kinetics of crystallization by retarding the onset of crystallization. In this context, one could regard the precipitation retardation time (or the incipient precipitation time) as an indication of the effectiveness of the antiscalant to slow-down the crystallization process. Current studies are ongoing to extend this approach and arrive at a quantitative correlation to relating the incipient time of crystallization to antiscalant dosage and CF value for the anticipated range of compositions of AD water in the Buena Vista Water Storage District.

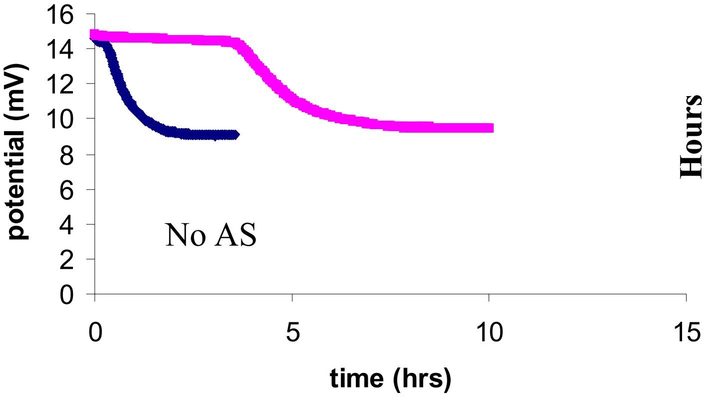

Figure 8. Calcium depletion as a function of time for an antiscalant free solution (No AS) and a solution with AS-D antiscalant. The sharp drop in the potential, as measured by a calcium-specific electrode, indicates the onset of precipitation.

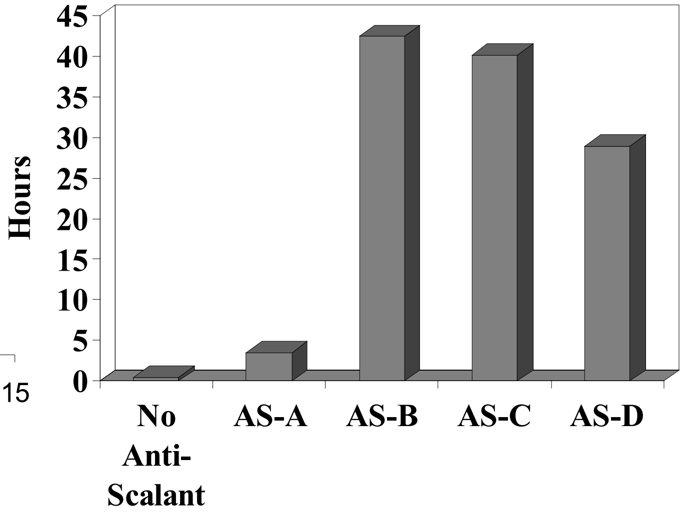

Figure 9. Calcium precipitation time for different antiscalants at a dose of 3 ppm.

CONCLUSIONS

Selection of a suitable membrane for desalination of agricultural drainage water requires membrane characterization with regards to flux, ion rejection, potential biofouling and propensity for scale formation. The choice of strategies for reduction of fouling due to both mineral scale formation and biofouling can in principle involve both suitable filtration pretreatment, use of chemical additives and membrane selection. In the present study, it was shown that when selecting a membrane one may have to consider the trade-offs between reduction in biofouling potential and membrane performance as well as between membrane rejection and permeate flux. Although the choice of suitable antiscalants can be made based on laboratory evaluation of retardation of mineral salt precipitation, long-term performance in pilot-field studies are necessary. Current work is ongoing in support of a membrane desalination field study with a focus on evaluating appropriate strategies for reducing membrane fouling via the combination of pretreatment, use of chemical additives and optimization of membrane system configuration.

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