

Evaluation of reverse osmosis and nanofiltration for *in situ* persulfate remediated groundwater

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Abstract

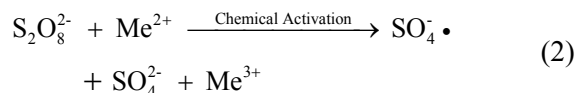
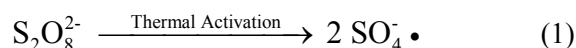
Sodium persulfate is a common oxidant used for *in situ* chemical oxidation (ISCO) remediation of ground water contaminants (e.g., trichloroethylene (TCE)). Following ISCO unused persulfate and oxidation by-products such as sulfates remain within the groundwater at elevated levels. In this laboratory study the performance of three membranes: one nanofiltration (NF) membrane (designated DK) and two reverse osmosis (RO) membranes (designated AE and AG), manufactured by GE Osmonics, Inc., were evaluated for the removal of total dissolved solids (TDS), mainly persulfate and sulfates, and other associated by-products from a simulated groundwater. Experiments consisted of short-term sheet membrane evaluations, long-term spiral wound membrane evaluations and membrane compatibility tests. The general order of membrane performance was AE > AG > DK. SEM analysis of membrane surfaces clearly showed that both the DK and AG membranes experienced degradation and cracking after exposure to elevated sodium persulfate solutions for 30 days while the AE membrane appeared unchanged. This finding is in agreement with the membrane performance test results, again confirming that the AE membrane was the best membrane of this group.

Keywords: *In situ* chemical oxidatin (ISCO); Trichloroethylene; Sulfate free radical; Groundwater

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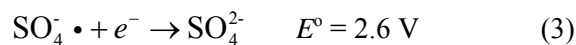
1. Introduction

In situ chemical oxidation (ISCO) is a treatment method used to remediate soil and groundwater contamination caused by organic contaminants (e.g., trichloroethylene (TCE)). This technology is based on the delivery of oxidizing agents to a contaminated source zone in order to convert the contaminants into harmless end products within the soil mass. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is a popular oxidant that is commonly used for ISCO [1–4]. The persulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant with a redox potential of 2.01 V. For the purposes of ISCO the persulfate anion can be thermally or chemically activated to produce a stronger oxidant known as the sulfate free radical ($\text{SO}_4^{\cdot-}$) ($E^\circ = 2.6$ V). The production of the sulfate free radical ($\text{SO}_4^{\cdot-}$) can be described by the following reactions [5]:



where Me^{2+} represents divalent transition metals (e.g., Fe^{2+}).

When $\text{SO}_4^{\cdot-}$ enters into an oxidation reaction, the reduction of $\text{SO}_4^{\cdot-}$ results in the production of sulfate (SO_4^{2-}) as follows:



The reaction between $\text{SO}_4^{\cdot-}$ and transition metals would also result in the production of sulfate as follows:



Following ISCO residual sodium persulfate or elevated sulfate concentrations in groundwater resulting as end-products when persulfate anions are used to oxidize organic contaminants or when

persulfate is decomposed to form sulfate in accordance with the above mentioned reactions could pose environmental concerns. The US National Secondary Drinking Water Standard Regulations for sulfate is 250 mg/L [6]. This is a non-enforceable guideline that is recommended by the USEPA. However, if sulfate is associated with hydrogen ion under acidic condition, the formation of sulfuric acid would cause corrosive conditions within the groundwater. Also, drinking of groundwater containing high sulfate concentrations can result in illnesses such as diarrhea [7].

A common issue pertaining to ISCO remediation of contaminated soil and groundwater is that this treatment might increase metal mobility due to reaction mechanisms such as the oxidation destruction of natural organic matter and mineral linkages [8]. Also, oxidation induced by low pH can result in increases in dissolved metal concentrations in groundwater. For example, experiments conducted by Liang et al. [3] revealed that ferrous ion activated persulfate oxidation of the common groundwater contaminant trichloroethylene (TCE) in an aqueous phase usually resulted in pH changes from an initial value of approximately 5 that dropped to around 3 as the reaction proceeded. The form of persulfate salt selected could contribute significant amounts of dissociated metal cations. For example, sodium persulfate is commonly used for *in situ* remediation due to its high water solubility. Therefore, elevated sodium concentrations would be expected in sodium persulfate treated groundwater.

During ISCO the oxidant is often injected on one side of a contaminated area while extracting groundwater on the other side. This method is used to induce the migration of oxidant through the target subsurface area and is known as *in situ* chemical oxidation with recirculation (ISCOR). In practice it is anticipated that the groundwater extraction system portion of the ISCOR would collect more water than is injected. The excess groundwater may contain high concentrations of

total dissolved solids (TDS) (mainly sulfate and residual persulfate) and these must be removed from the system prior to reinjection or discharge. In order to reduce the environmental impact of ISCO remediation with persulfate, it is necessary to explore a method for removing elevated sulfate or residual persulfate from the remediated groundwater.

Membrane separation processes such as reverse osmosis (RO) and nanofiltration (NF) have been widely used to purify water including removal of hardness [9–11], metals such as: iron (Fe), manganese (Mn), calcium (Ca), silicon (Si) [12–14] and natural organic matter (NOM) [11, 15]. Visser et al. [7] successfully applied NF membranes for the removal of sulfate and other ions (e.g., Ca^{2+} , Na^+ , Cl^-) which existed in water contaminated by mining activity. Barr [16] developed a sulfur removal system (SRS) incorporating NF membrane technology and demonstrated that a NF membrane can effectively separate sulfate from chloralkali brine at NF pressures of 20.7–41.4 bar and achieve sulfate rejection levels above 92% from a solution containing a sodium sulfate concentration of 180 g/L. Note that for general purposes NF systems are typically operated at pressures of 5–10 bar [17]. In addition, Visser et al. [7] also found that the performance of sulfate removal decreased in a low pH solution ($< \text{pH } 2$) due to the high fraction of bisulfate ion (HSO_4^-) present. Note that a pKa value for the system of bisulfate and sulfate ions is 2.0 [18], which indicates that at a pH less than 2 the HSO_4^- prevails over the SO_4^{2-} . The application of ISCO using persulfate usually results in acidic pH conditions somewhat greater than 2 [2–4] unless an extremely high persulfate concentration (e.g., 1 M) is used. Therefore, SO_4^{2-} would be the dominant species when persulfate is decomposed in general applications.

This study was conducted to evaluate the feasibility of using selected commercial RO and NF membranes for the removal of TDS (e.g., sulfates and persulfate) and other ions from

synthetic groundwater. The synthetic ground water was designed to mimic groundwater that would result from ISCO with sodium persulfate. Many membrane materials are effective in removing impurities (e.g., sulfate), however, concerns pertaining to the treatment of ISCO remediated groundwater which also contains residual oxidant (e.g., persulfate) needed to be resolved. Therefore, it was necessary to investigate membrane sensitivity to ISCO oxidants (i.e., persulfate or sulfate free radicals) while simultaneously evaluating membrane performance. Also, the materials compatibilities of the solutions and the membranes tested were examined.

2. Experimental

2.1. Materials

Barium chloride (BaCl_2 , 98.0% min.), potassium sulfate, (K_2SO_4 , 99.0% min.), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 99.0–102.0%), boron (B, 1000 mg/mL), silica gel (SiO_2 , 60–200 Mesh), sodium bicarbonate (NaHCO_3 , 99.7–100.3%), trichloroethylene (C_2HCl_3 , 99.5 min.), and sodium sulfate (Na_2SO_4 , 99.0% min.) were purchased from J.T.Baker. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%) and sodium chloride (NaCl , 99.0 min.) were purchased from Alfa Aesar and VWR International, respectively. Calcium chloride (CaCl_2 , 96% min.), sodium carbonate (Na_2CO_3 , 99.5%), and sodium nitrate (NaNO_3 , 99.0% min.) were purchased from EMD Chemical Inc. The NF membrane tested designated as DK is one of the GE Osmonics D-series. The two types of RO membrane tested designated as AG and AE tested are of the GE Osmonics A-series designed for desalination of brackish water and seawater families, respectively. The specifications of the three membranes are provided in Table 1. Water (deionized water (DI)) was produced from a Barnstead B-pure™ system equipped with a pretreatment deionization cartridge and an ultrapure deionization cartridge.

Table 1
Membrane characteristics (GE Osmonics, Inc.)

Membrane	DK nanofiltration membrane	AE reverse osmosis membrane	AG reverse osmosis membrane
Descriptions	Proprietary nanofiltration thin-film membrane (TFM _®)	Thin-film membrane (TFM _®)	Thin-film membrane (TFM _®)
Applications	Dye removal/concentration, heavy metal removal, acid purification	Seawater desalination	Brackish water desalination, reactive silica removal
Rejection characteristics	Molecular weight cut-off of 150-300 daltons for uncharged organic molecules	NaCl rejection ^a : 99.2% average	NaCl rejection ^b : 99% average
Operating pH range	2.0–11.0	4.0–11.0	4.0–11.0

^aNaCl 32,000 ppm at 55.1 bar and 25°C.

^bNaCl 500 ppm at 7.9 bar and 25°C.

2.2. Synthetic groundwater preparation

The water was spiked with variety of inorganic chemicals and TCE in accordance with the design concentrations presented in Table 2. The synthetic groundwater was prepared in a 275 liter high-density polyethylene tank at room temperature and allowed to sit overnight. The total volume of solution prepared was 265 liters. The water was then analyzed for metals, sulfates, persulfate, pH, alkalinity, total dissolved solids, carbonate species, and hardness before the testing started.

2.3. Short-term evaluation of membrane performance

The schematic diagram of a high pressure cell test unit (GE Osmonics, Inc.) is shown in Fig. 1. The sample membrane sheets were placed over 2 stainless test cells, each cell with an area of 81.03 cm². The test unit was operated according to the following sequence: fully open the backpressure regulator, turn on power switch to start pump, allow system to run for a couple of minutes, slowly close both backpressure regulators simultaneously, while monitoring the pressure gauge until the desired pressure is reached.

Table 2
Composition of synthetic groundwater

Component	Design concentration (mg/L)	Chemicals
Barium (Ba)	0.11	BaCl
Calcium (Ca)	77.66	CaCl ₂
Potassium (K)	27.93	K ₂ SO ₄
Sodium (Na)	5,151 ^a 20,219 ^c 16,273 ^b	
Magnesium (Mg)	51.06	MgSO ₄ ·7H ₂ O
Boron (B)	0.05	B standard, (1 mg/mL)
Silicon (Si)	28.34	SiO ₂
Alkalinity as CaCO ₃	138.00	NaHCO ₃ / Na ₂ CO ₃
Nitrate/Nitrite as N ₂	27.00	NaNO ₃
Chloride (Cl ⁻)	183.72	NaCl
Trichloroethylene	1.00	TCE
Sulfate (SO ₄ ²⁻)	10,270.39	Na ₂ SO ₄
Sodium persulfate (Na ₂ S ₂ O ₈)	2,000 ⁽¹⁾ 10,000 ⁽²⁾ 80,000 ⁽³⁾	Na ₂ S ₂ O ₈

^aShort-term evaluation of membrane performance tests. ^bLong-term evaluation of spiral wound membrane element performance tests. ^cCompatibility tests. Note: sodium contents are not produced from a specific chemical (e.g., NaCl), but are the sum of all associated sodium ions resulting from the addition of all chemicals used. Chloride and sulfate contents included the associated Cl⁻ and SO₄²⁻ ions from the addition of chemicals used.

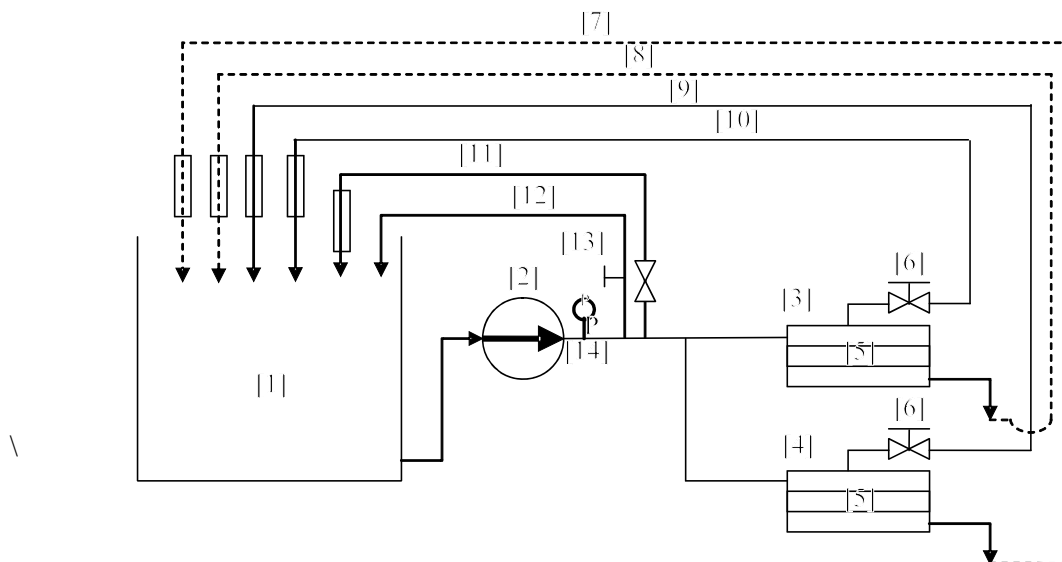


Fig. 1. Schematic representation of a high pressure cell test unit (modified from a figure provided by DesalTM Membrane Products). [1] Feed tank, [2] P.D., Pump 800 psig 1.1 gpm, [3] Test cell 1, [4] Test cell 2, [5] Membrane (12 sq. in.), [6] Back pressure regulator, [7] Test cell 2 permeate, [8] Test cell 1 permeate, [9] Test cell 2 concentrate, [10] Test cell 1 concentrate, [11] Bypass flow, [12] Relief, [13] Pressure relief valve, [14] Operating pressure monitor, [15] Flow meters. Dashed lines are subject to removal depending on design experimental conditions.

reached. Since two test cells were assembled and run in parallel, a relatively high pressure applied to one test cell would cause higher feed water flow rates to the other test cell. Therefore, both backpressure regulators were opened to promote equal pressurization at the beginning of the experiments by monitoring concentrate and permeate flows through the in-line flow meters. The operating pressure was applied when both permeate flow rates were approximately equal and the sum of both flow rates reached a maximum value. All tests were run in a recycle mode (both concentrate and permeate were recycled back to the feed tank) for 4 days, and thereafter, permeate was collected and removed from the feed for the remainder of the test period (2 days) similar to the work of [19]. It was anticipated that the removal of permeate water would result in more concentrated feed water and eventually lead to membrane clogging.

2.4. Long-term evaluation of spiral wound membrane element performance

In these long-term tests a high pressure stainless steel 1812 spiral wound membrane element test unit (GE Osmonics, Inc.) equipped with spiral wound membrane elements was used to replace the two flat square membrane sheet cells used in previous tests. In the test unit the spiral wound membrane element is positioned around a central stainless steel permeate collection tube. For brevity these spiral wound membrane elements will often be referred to as simply “DK membrane, AG membrane or AE membrane”. The synthetic feed groundwater used in these tests was prepared as described in Table 2, with exception that elevated sodium persulfate and sulfate ion concentrations of 10,000 and 30,000 mg/L were used. The system was run in a recycle mode throughout the duration of operation and the operating pressure was set in

accordance with procedures previously described for the membrane tests.

2.5. Membrane compatibility tests

The water prepared for this test was prepared as described in Table 1 with the exception that the sodium persulfate concentration was increased to 80,000 mg/L and no TCE was added. The membrane was soaked in the spiked groundwater for 30 days. After removing membranes from solution, the membrane was rinsed with fresh DI water. Before and after the test, the membrane surface was examined using a scanning electron microscope (SEM) and an energy dispersive X-ray spectrometer (EDXS).

2.6. Analysis

TCE standards were prepared to determine a GC response factor and linear nature of calibration data. An HP Model 5890 GC/FID equipped with an HP7673 autosampler was used for sample analysis. Samples were analyzed following solvent extraction of samples with pentane. Analytical parameters were in accordance with those detailed in Liang et al. [2].

The metals Ba, K, B, Ca, Mg and Si were analyzed with a direct current plasma (DCP) atomic emission spectrometer model IIIB manufactured by Spectrametrics, Inc. Na was analyzed via flame atomic absorption (FAA) spectrometry.

The pH was measured using a pH probe (Fisher Accumet AR15) and chloride ions were measured using a benchtop pH/ISE meter (Orion model EA™ 940 expandable ionanalyzer) equipped with a Fisher chloride ion selective electrode and a double junction reference Ag/AgCl electrode. In accordance with analytical procedures described in Standard Methods for the Examination of Water and Wastewater [20], hardness was measured using an EDTA titrimetric method; TDS were determined by drying at 180°C; carbonate and bicarbonate species were

measured using a titration method; sulfate ion was measured with a turbidimetric method. Langelier Saturation Index (LSI) was determined in accordance with the calculation for concentrate stream of a reverse osmosis device [21].

To examine membrane materials with a SEM, the membrane samples were initially carbon evaporated in a Denton Vacuum DV-502A to improve conductivity. The samples were pumped down to a vacuum of $1.33 \times (10^{-3} \text{ to } 10^{-4})$ Pa. Under these conditions the coating thickness is between 5 to 15 nm. The samples were then placed in the chamber of an Amray 1820I SEM with EDXS and pumped to a vacuum of $1.33 \times (10^{-4} \text{ to } 10^{-5})$ Pa, depending on how much the samples out-gassed. The samples were then imaged under the SEM and digitally photographed.

3. Results and discussion

3.1. Short-term evaluation of membrane performance

Fig. 2 shows the permeate flow rate and recovery percentage as a function of operating time and also variation of operating pressure is shown in insert. The initial starting pressures were between 34.5 and 37.9 bar for all membrane tests. The AE membrane exhibited a quick increase in operational pressure shortly after the test unit was started (e.g., 35.8 bar at time = 0 increased to 57.2 bar at time = 36 hrs). Pressures for the other two membrane tests appeared to slowly increase to levels ~47.5 bar and ~48.9 bar on day 6 for DK and AG, respectively, which are lower than the observed pressure for AE at the same time period.

The permeate recovery of the membranes tested is calculated by the following equation:

$$R = (Q_p/Q_i) \times 100\% \quad (5)$$

where R represents the percentage of permeate

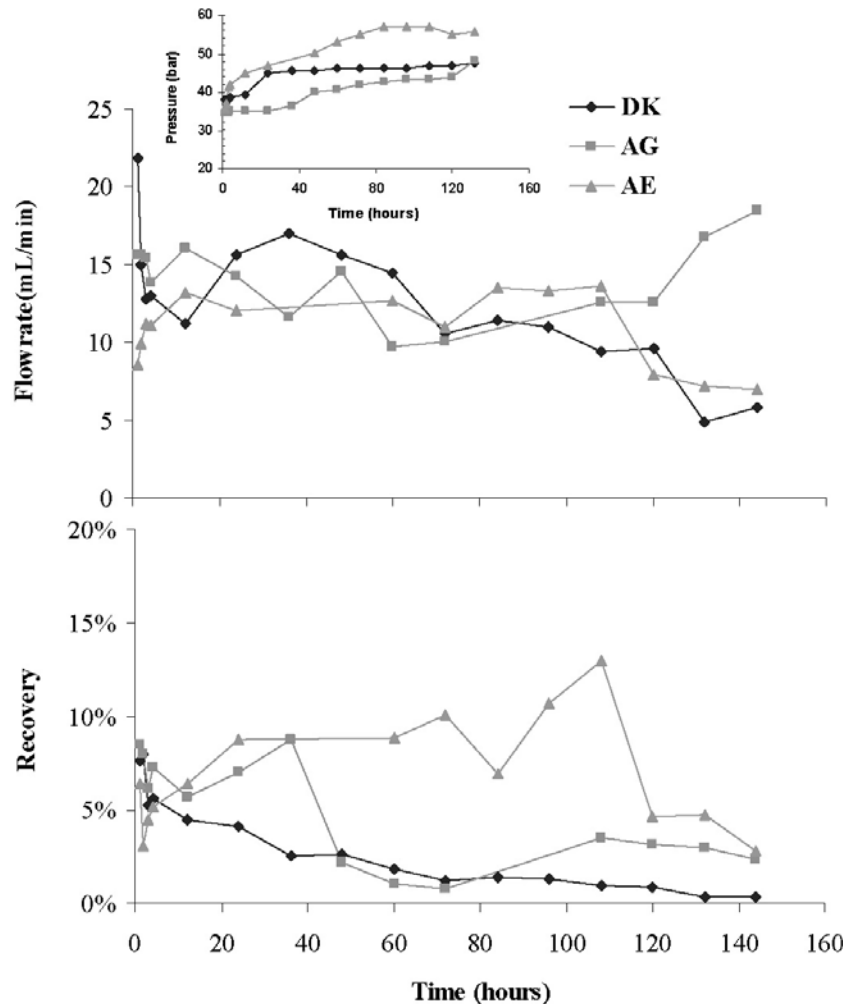


Fig. 2. Variation of permeate flowrate and percentage recovery rate as a function of operating time. Insert shows operating pressure vs. time.

water recovered (i.e., produced), and Q_p is the permeate flow rate, and Q_i is the inlet flow rate which equals the sum of concentrate and permeate flow rates (excluding bypass flow rate).

In general, the permeate production for AE and AG RO membranes is more stable than the DK NF membrane which exhibited declines in recovery and permeate flow rates with time. However, there was also a fluctuation of the percentage recovery for two RO membranes (AE and AG). Particle size ranges removed by RO

membranes (AE and AG) are from 0.1–1 nm and the NF membrane (DK) has a range of 0.4–6 nm [17]. Fouling of membranes could increase resistance to flow and cause a decrease in the permeate flow rate. This was observed as increases of bypass flow rates and decreased recoveries with respect to time.

The TDS levels in all streams (i.e., feed, concentrate and permeate) are shown in Fig. 3. It was observed that all three membranes could significantly reduce TDS in the permeate water.

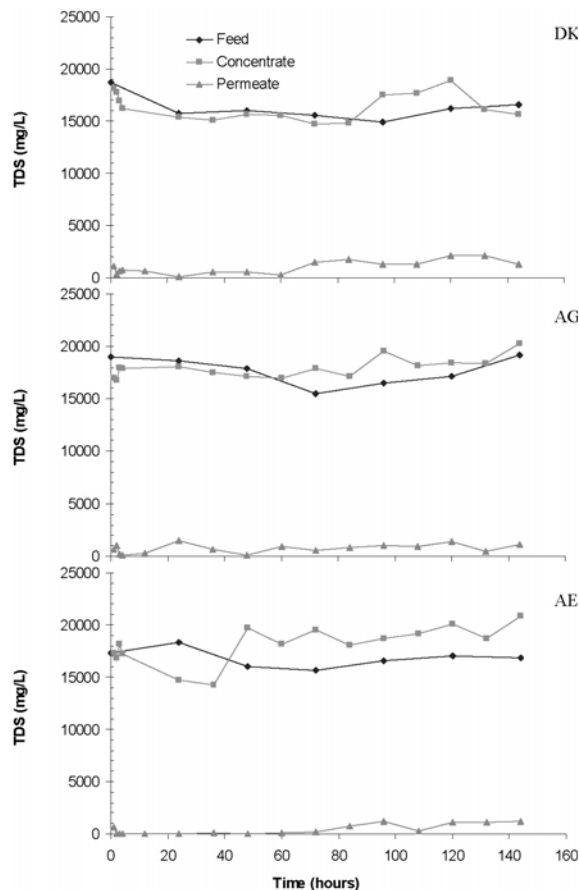


Fig. 3. Variation of TDS concentrations in all streams, i.e., feed, concentrate, and permeate, as a function of operating time.

Among them, the AE membrane exhibited the best performance (e.g., TDS removal: 99% for AE versus 91% for AG and 90% for DK at $t = 72$ h). However, TDS concentrations for all three membranes increased after 4 days when the permeate water was removed from the feed water. It was also observed that the TDS in the DK permeate water increased at a greater rate in comparison to other membrane tests.

Fig. 4 shows the removal of persulfate results. Only the AE membrane exhibited no persulfate anion in permeate water. The DK permeate exhibited a higher persulfate concentration level than

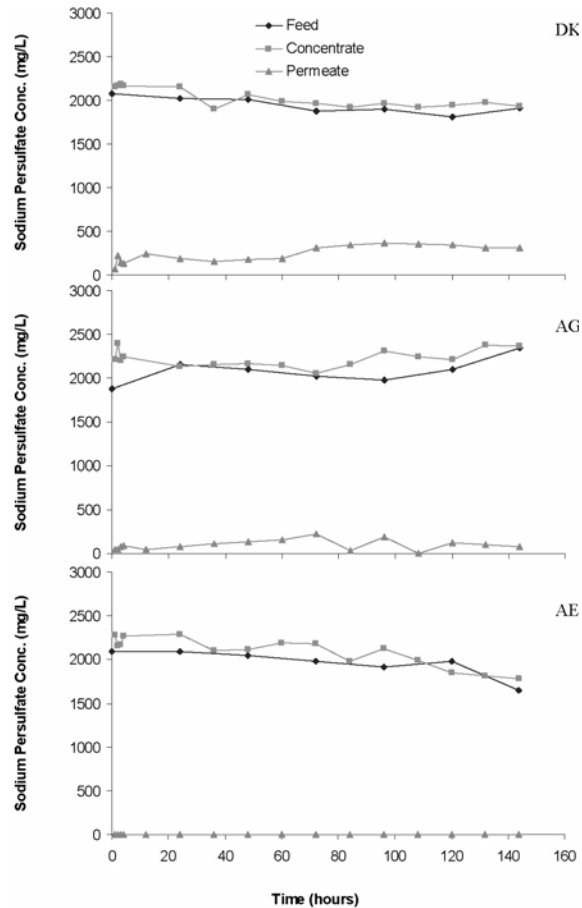


Fig. 4. Variation of sodium persulfate concentrations in all streams, i.e., feed, concentrate, and permeate, as a function of operating time.

the level observed in AG membrane. Fig. 5 shows the removal of sulfate results. The AE membrane exhibited the best performance for removal of sulfate ions (e.g., <100 mg/L SO_4^{2-} in the permeate during the duration of the test) while the others maintained less than 200 mg/L in the permeate within the first or two days of test run and then SO_4^{2-} levels gradually increased.

The initial pH in all feed water was around 9. Upon the decomposition of the persulfate anion, it could react with water to produce hydrogen ions resulting in decreases in pH according to the following reactions [5]:

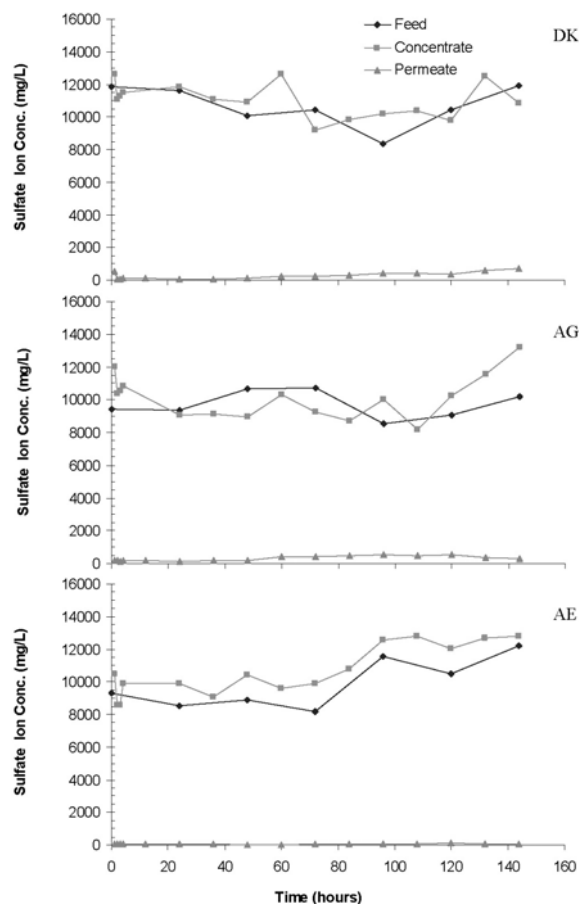
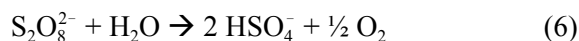


Fig. 5. Variation of sulfate ion concentrations in all streams, i.e., feed, concentrate, and permeate, as a function of operating time.



Use of DK and AE membranes resulted in greater pH decreases (e.g., pH 9 gradually decreased to 3–4 in all streams) in comparison to use of the AG membrane (e.g., pH 9 decreased to ~7). As a result of the high pressures produced within the pumping/separation system, after just 1 day for all membrane testing, feed and concentrate stream temperatures were increased from room temperature (~25°C) to around 38°C where they remained for the duration of the test run.

Both AG and AE membranes produced significant reductions in alkalinity in the permeate water. Alkalinity in the DK permeate water was slightly high (e.g., 100 mg/L as CaCO_3) for the first 4 days in comparison with other two membranes (data not shown). However, alkalinity in the feed and concentrate gradually decreased with increased operation time (e.g., after 4 days). Decreases in alkalinity for DK and AE membranes are possibly due to the decreases of pH (from pH 9 to 3–4) in solution, therefore converting carbonate species to carbonic acid (H_2CO_3) or dissolved carbon dioxide (CO_2) [18].

All membranes demonstrated excellent performance in removing hardness (no hardness concentrations were measured in the permeate for all 3 membrane tests) (data not shown). This is due to the removal of divalent metal cations. However, after about 4 days of running, DK and AE tests exhibited significant increases in measured hardness concentrations in both feed and concentrate water. The measurement of increased hardness may be unreliable and possibly related to a decrease in pH in feed and concentrate water. In the determination of hardness with EDTA, there are several competing equilibria involved and the sample solution needs to be buffered at pH 10 to increase EDTA/chelate stability. However, it was determined that upon the addition of ammonia buffer that the desired sample solution pH was not obtained. Therefore, the results obtained when using an EDTA titrimetric method under these conditions are not necessarily reliable.

In an ISCOR system, extracted groundwater might contain untreated target contaminants. To evaluate the effect of ISCOR on target contaminant removal the synthetic groundwater was prepared to contain untreated target organic contaminant (i.e., TCE) and oxidant. Test results indicated that the permeate for the DK membrane test contained TCE at concentrations of 141 and 32 $\mu\text{g/L}$ at 1 hour and 32 hours respectively and thereafter there was no TCE detected in the

permeate (data not shown). In NF, the rejection of organics is usually for those compounds with a molecular weight above 200–500 [22], while TCE has a molecular weight of 131.35 g/mole. AG and AE membranes contained low levels of TCE (e.g., ~ 5 $\mu\text{g/L}$) in the permeate water at times less than 12 hours. TCE was reduced to a non-detection level in all streams (i.e., feed, concentrate and permeate) for all membrane tests after about 2 days run. The possible fate of TCE could have been evaporation due to elevated system temperatures, oxidation by persulfate during the course of test run, or absorption by the materials used in the test apparatus such as the tank or tubing.

The AE membrane exhibited the best performance for the removal of chloride ions, e.g., initial levels of ~ 200 mg/L Cl^- in feed water were reduced to 3–8 mg/L in the permeate water during the course of test run (data not shown). Use of the AG membrane also resulted in a significant removal of Cl^- (i.e., to levels of less than 20 mg/L during the course of test run). However, the DK membrane exhibited no Cl^- removal. Since RO is a commonly used for desalination of brackish water and seawater, it is expected that the membranes would retain small organic compounds as well as ions (e.g., chloride) better than the NF [22].

The LSI index is usually applicable for concentrate streams containing more than 10,000 ppm of TDS to determine the need for calcium carbonate scale control in the operation and the design of reverse osmosis installations [21]. The analysis of LSI results presented in Figure 6 shows that the permeate water for the three membranes exhibited no tendency to form calcium carbonate scale. It should be noted that the concentrations of all species prepared in the feed water were already pre-calculated by a computer program (i.e., Minteqa2/Prodefa2, a geochemical assessment model) for complete dissolution of metals and to reduce any possible precipitation. However, due to water quality

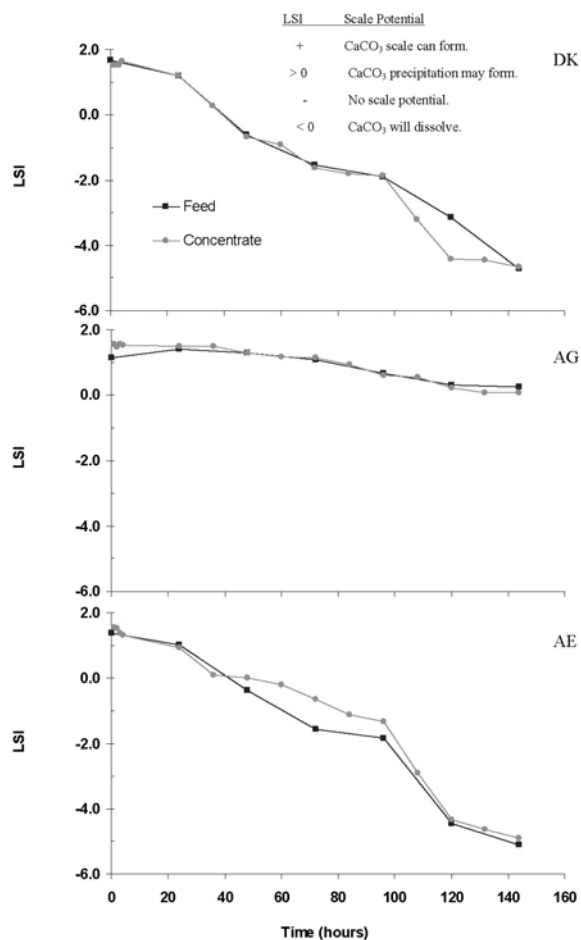


Fig. 6. LSI as a function of operating time for the feed and concentrate streams.

change during the course of operation, the possibility of scaling (i.e., the precipitation of calcium carbonate or calcium sulfate) existed. The variation of LSI data can indicate the presence of a driving force and the tendency to form calcium carbonate scaling, which could be damaging to separation performance [21]. The AG feed and concentrate presented a greater driving force to form calcium carbonate precipitates during the course of the test run than the DK and AE membranes, which exhibited no tendency for the feed and concentrate to form precipitate after running 48 hours.

Table 3

Inorganic removal percentage in the permeate water of each membrane in the short-term evaluation of membrane performance tests

Membrane	Operation period	Removal percentage (%) ^a						
		Ba	Ca	K	Mg	B	Si	Na
DK	1–4 days	88	95	96	98	61	23	95
	5–6 days	69	95	95	76	33	10	94
AG	1–4 days	74	97	97	98	70	94	97
	5–6 days	69	98	94	94	55	87	94
AE	1–4 days	93	96	98	96	83	89	98
	5–6 days	90	N.A.	97	94	93	92	98

^aMean of percentage removal is an averaged value of triplicate sample analysis.

N.A. = not applicable.

Metal removal data for the three membranes are summarized in Table 3. All membranes exhibited good metals removal performance with the exception of the DK membrane that exhibited a poor Si removal efficiency. The EDXS analysis of the three membranes surfaces conducted before and after the test run indicated that all original membranes exhibited the presence of a sulfur component (note: sulfur was the only component detected) and after separation silica appeared to deposit on all membrane surfaces (i.e., silica-scaling). Sodium was also retained on both AG and AE membranes.

The membrane surfaces were examined before and after each run by SEM analysis (e.g., 5000 \times for original membrane, and 1000 \times for tested membrane). The original AE membrane has noticeable texture in comparison with DK and AG membranes which appeared to have smooth surfaces (see Fig. 13). The SEM images of the tested membranes showed that a variety of foulants were evenly distributed over the entire membrane surface. AG membranes exhibited more pits or foulant accumulated on its surface than the other two membranes. According to EDXS analysis, Si was the major component found on the membrane surface. It has been

reported that a silica level of less than 10 mg/L in the RO feed water will not result in a scaling problem and the associated significant reduction of water recovery rate [23]. However, the silica level (28 mg/L) in feed water in this study was greater than the recommended silica level. It should be noted that at lower pH and higher solution temperatures the solubility of silica is generally reduced. Hence, the major foulants could be inorganic and organic combined Si. In addition, since no Si existed in the permeate of AE and AG, it was evident that the foulants retained on the membrane surfaces were possibly caused by Si or Si species.

A comparison of the performance of tested membranes is presented in Table 4. In summary the AE membrane exhibited superior performance with respect to the removal of typical target species such as TDS, persulfate, and sulfate ions over the six-day period of evaluation. The order of performance for membranes tested in general was AE > AG > DK. However, the superior performance of AE membrane required a higher pressure (i.e., approximate 57.2 bar) while the DK and AG membranes were operated at approximately 47.5 and 48.9 bar, respectively. In all of these cases, the associated energy required

Table 4
Summary of the performance of tested membranes (AG, DK, and AE)

	DK		AG		AE	
	1–4	5–6	1–4	5–6	1–4	5–6
Operation period, days	1–4	5–6	1–4	5–6	1–4	5–6
TDS	E	G	E	G	E	G
Hardness	E	E	E	E	E	E
Persulfate	G	G	E	G	E	E
Sulfate	E	E	E	G	E	E
Chloride	P	P	G	G	E	E
Ba	G	F	F	F	G	G
Ca	E	E	E	E	E	N.A.
K	E	E	E	G	E	E
Mg	E	F	E	G	E	G
B	F	P	F	P	F	G
Si	P	P	G	G	G	G
Na	E	G	E	G	E	E

Guide to results: Poor (P): <60% Removal; Fair (F): 60–85% Removal; Good (G): 85–95% Removal; Excellent (E): >95% Removal.

N.A.: Not Applicable.

to produce these pressures would be very costly. Moreover, it should be advised that the relatively low permeate recoveries observed in these tests could make this process uneconomical in practice.

3.2. Long-term evaluation of spiral wound membrane element performance

To better understand the rationale, for the sequence of experiments utilized within the long-term evaluation of spiral-wound membrane element experiments, the following explanation is provided. The cost of the DK NF membrane is significantly less than either of the RO membranes (AG or AE). Based on its acceptable performance with the short-term membrane testing and its relative cost it was initially selected for further evaluation. The DK NF membrane was initially selected for testing. After a 7 day run it was observed that the DK membrane was not

able to effectively remove dissolved ions (e.g., sulfate and persulfate). Similar results have been observed and explained in the previous short-term DK membrane evaluation section. It should also be noted that an elevated sodium persulfate concentration was used in the long-term evaluation when evaluating the spiral-wound membrane. Therefore, the DK test was stopped and subsequently the AG RO membrane was chosen and the testing continued using the same feed water. During the course of the AG membrane test, at day 6 the pump failed and a replacement pump was then used to continue the test. The AG membrane test was stopped after a total of 14 days run due to observations of significant increases in persulfate and sulfate concentrations in the permeate. The evaluation of the AE RO membrane was then conducted using freshly prepared feed water.

Fig. 7 shows the flow rate versus time for DK/AG and AE membrane tests and their

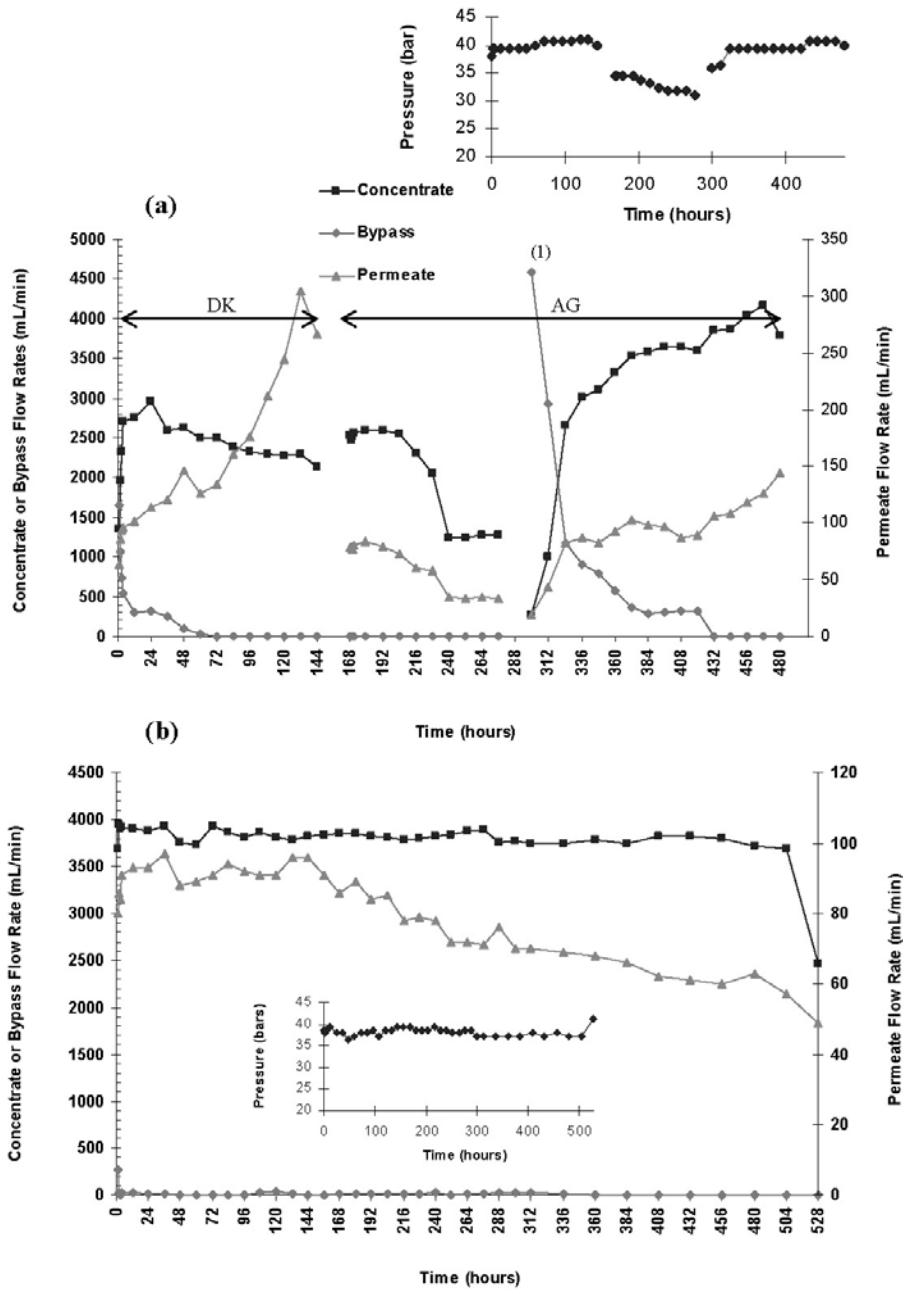


Fig. 7. Flowrate and pressure versus operating time for (a) the DK and AG spiral wound membrane elements and (b) the AE spiral wound membrane element. Note: ⁽¹⁾Installation of a new replacement pump.

operating pressures have been inserted. It was seen that the relatively strong resistance of the AG membrane significantly reduced the flow of

water through the membrane in comparison to the DK membrane. It was also seen that when the DK membrane test was running, the bypass flow rate

gradually decreased, while both concentrate and permeate flow rates gradually increased and then bypass flow rate finally decreased to zero. It was suspected that with time the small openings in the membrane active layer (i.e., nano size) of the DK membrane might have become altered or even developed surface cracks leading to an increase in effective pore size, resulting in a diminished ability to trap dissolved ions under these operating conditions and therefore resulting in increased outputs (i.e., the permeate). For the first 7 day run of the AG membrane test (before the pump broke), the bypass flow rate was zero and both concentrate and permeate flow rates gradually decreased from their initial rates. A slight decrease in operating pressure (i.e., ~3.4 bar) was also observed. These observations indicated that the pump was failing and membrane clogging had possibly occurred. Before the replacement pump was turned on the bypass flow valve was fully opened and the back pressure regulator was kept in the same position where it was when using the original pump. Thereafter, only the bypass flow valve was adjusted to increase the operating pressure. The bypass flow valve was only slightly closed and this resulted in a 34.4 bar operating pressure. Under these conditions, concentrate and permeate flow started at very low rates (e.g., 19 mL/min) and thereafter they gradually increased as operation time increased. However, bypass flow rate decreased to zero after a few days run. Operating pressure for the AE membrane was within a range of 37–39 bar during the test period with exception that on day 22 (528 hours) when the pressure suddenly increased to 42 bar and serious leaking was observed near the inlet connector and at this time the AE test was terminated. All streams in the AE test exhibited more stable flow rates than those observed in the DK and AG test. However, the permeate revealed a gradual decrease to about 40% of flow rate during the test period.

Because both persulfate and sulfate concentrations were significantly increased in these tests

in comparison to the previous test, the resulting TDS in the initial feed water was around 55,000 mg/L which is much greater than the level of ~20,000 mg/L previously used. Fig. 8 shows the TDS data in all streams. After the DK membrane test started, TDS of the permeate rapidly increased to near 50,000 mg/L within 7 days. This indicated a failure in TDS removal. As for the AG membrane test, TDS in the permeate water also gradually increased during the first 5 days run to a level near 10,000 mg/L. After the replacement pump was started, TDS was still maintained below 10,000 mg/L until later when TDS rapidly increased (e.g., 30,000 mg/L observed at day 14 (480 hours)). This condition is indicative of a possible failure of the AG membrane in removing TDS. For the AE membrane test generally 90% removal of TDS was obtained during the test run. It was evident that RO membranes (AG and AE) presented far better performance than the NF membrane (DK). This result is not surprising because reverse osmosis membranes are commonly used for desalination of seawater (note: seawater typically contains 36,000 ppm of TDS) and brackish water (note: brackish water typically contains 50 to 10,000 ppm of TDS) [24].

In both DK and AG membrane tests, alkalinity was reduced to non detectable levels after approximately 3 days run when the pH was decreased to below 4.0. Therefore, the alkalinity anions, i.e., carbonate and bicarbonate species, whose presence are pH dependent would likely be present in the form of carbonic acid or dissolved carbon dioxide. Initial pHs for all streams for the DK membrane test were between 8.5 and 9.0 and gradually decreased to 3.6 at the end of test run (6 days). Therefore, initial pHs in all streams for the AG membrane test started from this level (i.e., pH = 3.6) and thereafter further decreased slightly to pH 2.6–2.8. For the AE membrane test initial pHs for all streams were also around 9.0. After the start of pumping the pHs quickly decreased in the feed/concentrate and permeate streams to 4.0

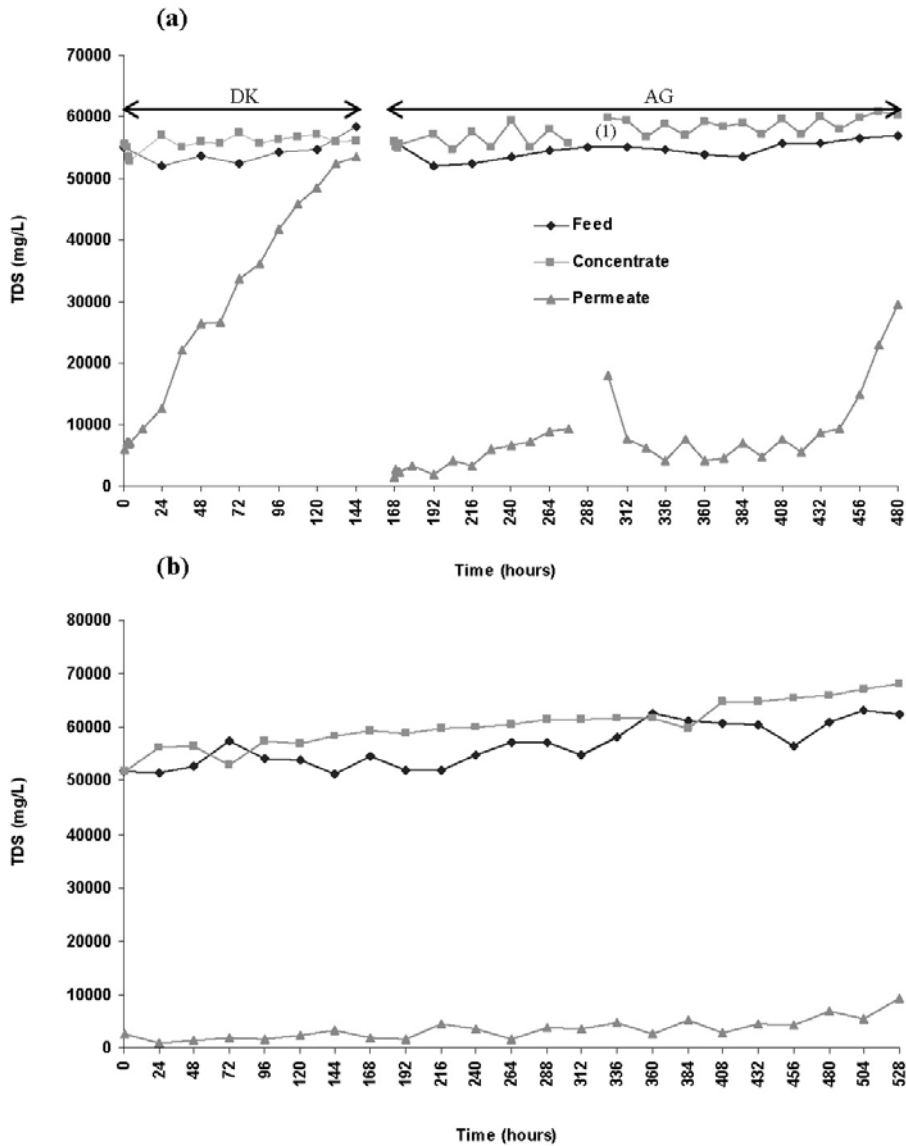


Fig. 8. Variation of TDS concentrations in all streams for (a) the DK and AG spiral wound membrane elements and (b) the AE spiral wound membrane element. Note: ⁽¹⁾Installation of a new replacement pump.

and 5.1 within 3 days and for the remaining test run (day 4–day 23) dropped further to around 2.4 and 3.0, respectively. As a result, alkalinity was not detected under those low pH conditions. The system temperature gradually increased for the DK membrane test (e.g., 25 to 38 °C) during the

first two days run and thereafter decreased (38 to 31 °C). This decrease in temperature occurred two days after the concentrate flow rate started decreasing and as permeate flow increased. The resistance of the DK membrane seemed to decrease which resulted in an increased permeate

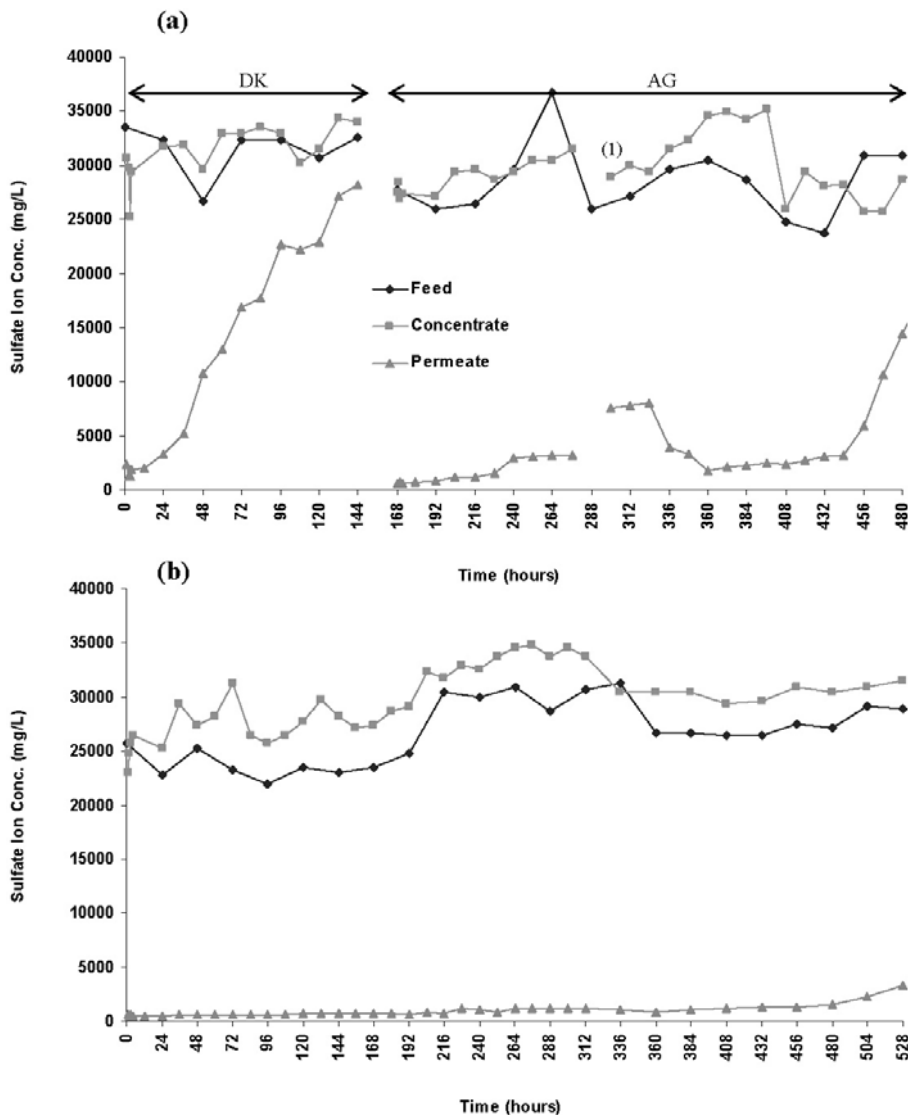


Fig. 9. Variation of sodium persulfate concentrations in all streams for (a) the DK and AG spiral wound membrane elements and (b) the AE spiral wound membrane element. Note: ⁽¹⁾ Installation of a new replacement pump.

flow rate and an associated slight decrease in temperature. However, the temperature is still higher than that observed in previous DK membrane test (“previous” data not presented). For the AG spiral membrane test, the temperature gradually increased with time (e.g., 25 to 36°C for the permeate). The temperature changes for the AE membrane are similar to that in the

previous membrane tests with exception that temperature in the permeate increased from 25°C to 32°C. Hardness removal in the spiral membrane tests appeared to be similar to observations in the previous membrane test.

Fig. 9 shows the persulfate removal results. After one day run, a rapid increase in persulfate concentration in the permeate water was observed

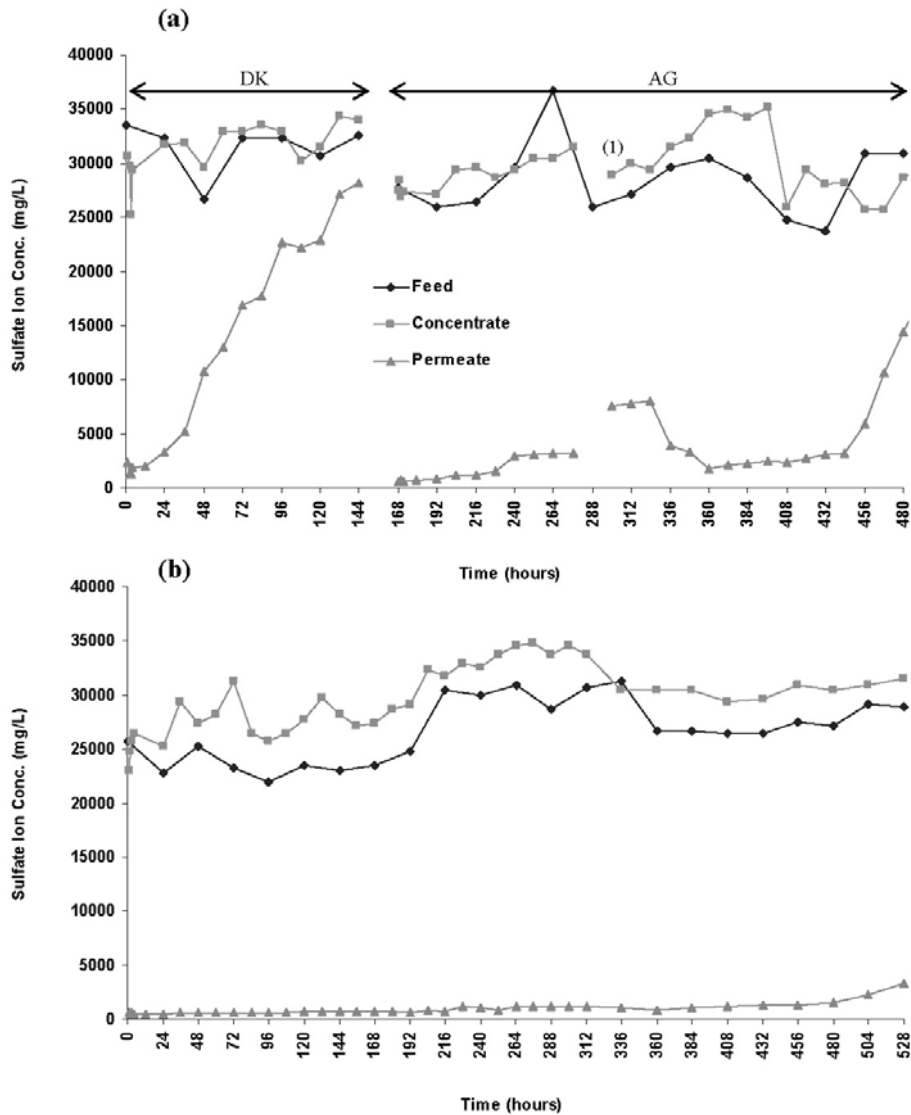


Fig. 10. Variation of sulfate ion concentrations in all streams for (a) the DK and AG spiral wound membrane elements and (b) the AE spiral wound membrane element. Note: ⁽¹⁾ Installation of a new replacement pump.

in the DK membrane test. The AG membrane test exhibited better performance than the DK membrane. For example, sodium persulfate concentration was less than 1,000 mg/L in the permeate stream except for the first day when the replacement pump was started and the last two days of the AG membrane test. The AE membrane presented the best performance in removing per-

sulfate anion (e.g., less than 300 mg/L sodium persulfate observed in the permeate for 15 days with a gradual increase to near 1,100 mg/L on the last day, i.e., day 23). Fig. 10 shows the removal of sulfate results. The DK membrane was not able to remove sulfate ion and therefore the sulfate concentration level observed in the permeate water was close to the level found in the feed

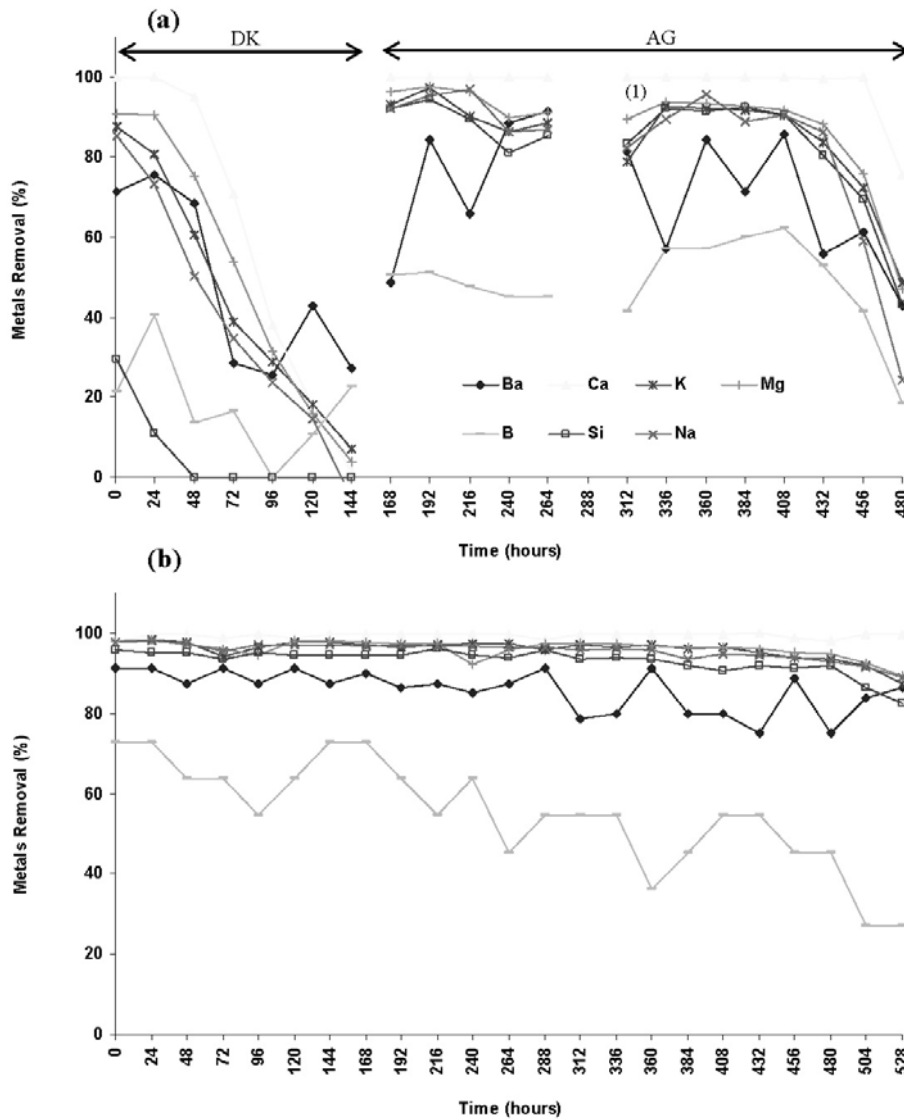


Fig. 11. Metals removal percentage for (a) the DK and AG spiral wound membrane elements and (b) the AE spiral wound membrane element. Metal removal percentage = $1 - (\text{Conc.}_{\text{permeate}} / \text{Conc.}_{\text{feed}}) (100)$. Note: ⁽¹⁾Installation of a new replacement pump.

water after 7 days of running. The AG membrane exhibited sulfate removal resulting in generally less than ~3,000 mg/L in the permeate water and the trends of removal efficiency were similar to those observed in persulfate removal. In the case of the AE membrane test sulfate concentrations in the permeate were maintained at less than

800 mg/L for the first 9 days run and then gradually increased to nearly 3,200 mg/L at the end of testing (i.e., 22 days).

TCE was present in the permeate for the DK membrane test (54 µg/L at 2 hours), however, there was no TCE observed in all streams after 3 hours. It should also be noted that no TCE was

present in all streams following the AG tests. As for the AE test, TCE was initially detected in the permeate (e.g., 17 $\mu\text{g/L}$ at 1 hour), however no TCE was detected in all streams after a few hours of running (e.g., 2 hours). Both RO membranes tested (AG and AE membranes) effectively removed chloride ion, e.g., in general $<50 \text{ mg/L}$ and 0 mg/L Cl^- was observed in the permeate for the AG and AE, tests respectively. However, the NF (DK membrane) was incapable in removing chloride ($\sim 0\%$ removal). The LSI analysis showed that all streams exhibited no tendency to form calcium carbonate scale, with the only exception being the feed and concentrate streams within the first few hours of the DK membrane test run (data not shown).

Metal removals are shown in Fig. 11. The results show that the DK membrane attained significant removals of Ba, Ca, K, and Mg during initial 1 or 2 days run, then these metal concentrations in the permeate stream steadily increased in a manner similar to that observed for other anions (e.g., SO_4^{2-}), as was previously discussed. The DK membrane appeared to be incapable of removing B and Si. The AG membrane exhibited good performance in removing metals except for B which in general was less than 60% removal. However, metal removal trends followed the same pattern as the removal of other anions (e.g., SO_4^{2-}), where high concentrations of ions were observed on the first day after the replacement pump was started and on the last few days of the AG membrane test. The AE membrane exhibited more than 90% metal removal for all metals except for Ba and B on the last two days of the test. The element Boron always presented the lowest removal efficiency in all of the membrane tests. Because the pHs were usually low in all streams for all membrane tests, the major boron species would be boric acid in molecular form. Note that pK_a for boric acid is 9.14. Therefore, due to the absence of ionic charges, the non-dissociated boric acid is a molecule that is smaller than the dissociated form. This would result in

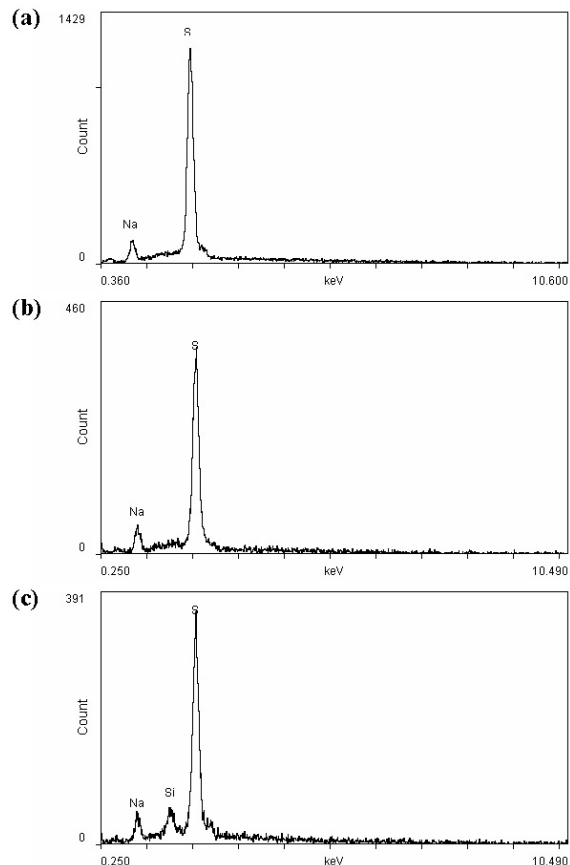


Fig. 12. The results of EDXS analysis for residual elements on the membrane surface after 30 days of being submerged in synthetic groundwater for (a) DK, (b) AG, and (c) AE membranes.

less rejection of the molecule by the membrane [25].

3.3. Membrane compatibility tests

Figs. 12a, b, and c show the results of EDXS analysis and Figs. 13a, b, and c show the results of digital image analysis by SEM of the DK, AG, and AE membranes, respectively, after being submerged in the spiking solution for 30 days. All three membranes exhibited the presence of the elements S, Si, and Na on their surfaces. It should be noted that membranes are usually made

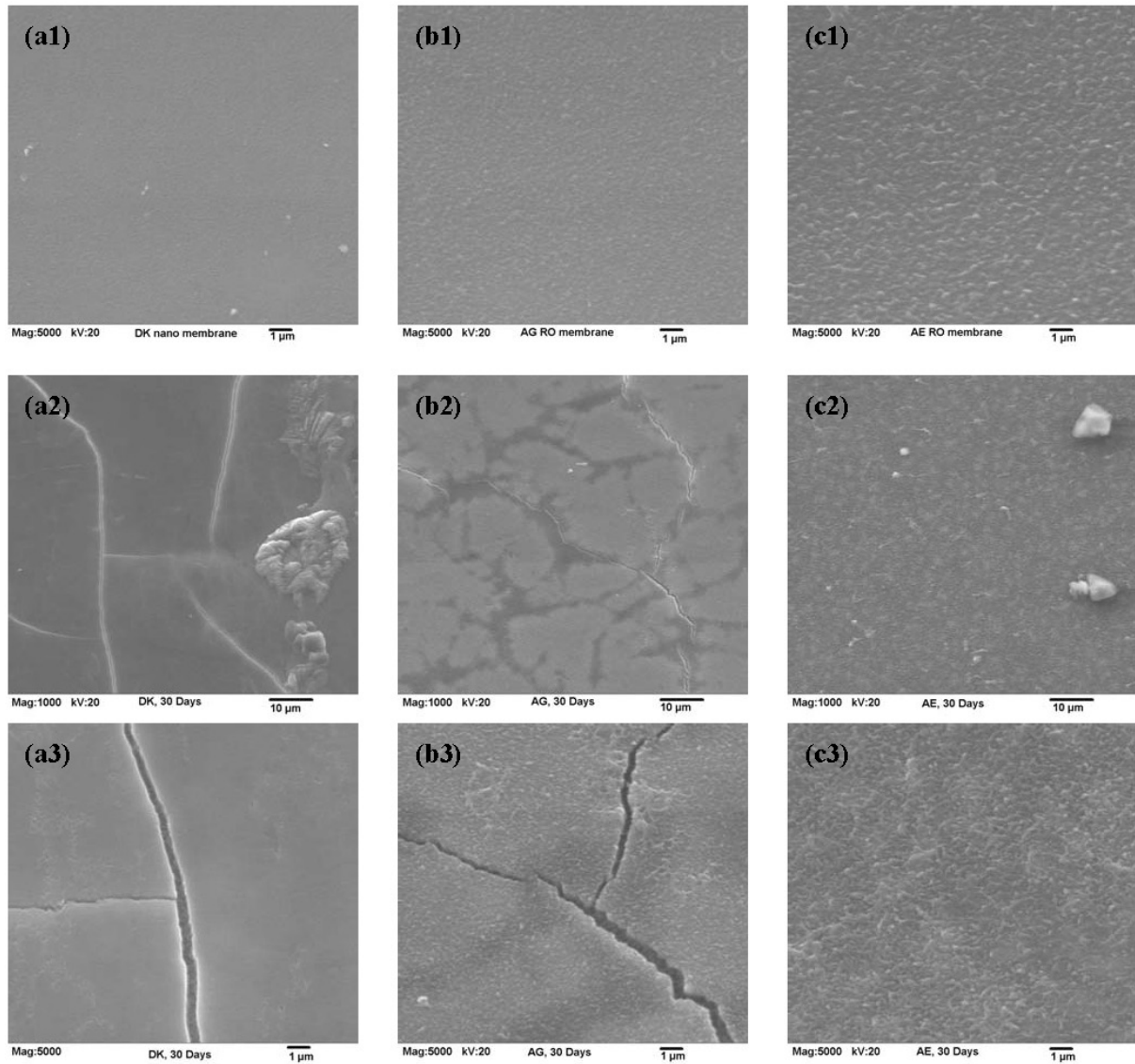


Fig. 13. SEM images of the (a) DK, (b) AG, and (c) AE membrane surfaces after 30 days of being submerged in synthetic groundwater. (1), (2), and (3) annotation represent original membrane ($\times 5000$), treated membrane ($\times 1000$) and ($\times 5000$), respectively.

from organic polymers (e.g., polysulfone) and the element S was originally present on all three new membranes as determined by EDXS analysis (data not shown). The SEM images revealed that both DK and AG membranes exhibited degradation at high levels of sodium persulfate (i.e.,

80,000 mg/L). For example, the DK and AG membranes showed cracks on the membranes (see Figs. 13(a3) and 13(b3)); moreover, the AG membrane appears to have an uneven density on the membrane surface (see Fig. 13(b2)). It appears that the original textures of DK and AG

have been altered. In the DK membrane test it was evident that the water quality drastically decreased with an increase in operation time. It is speculated that this behavior could be as a result of membrane sensitivity to persulfate and sulfate free radicals (e.g., sodium persulfate concentration of 80,000 mg/L) resulting in membrane cracking. Therefore it is speculated the membranes had suffered oxidative degradation. A study by Platt et al. [26] who tested stability of several NF membranes including the DK membrane under acidic conditions observed that DK membrane was unstable after 1 month immersed in 20% sulfuric acid. They speculated that acid-catalyzed hydrolysis was the cause of membrane degradation. They also mentioned that aggressive chemicals can irreversibly degrade the membrane by processes such as oxidation. Platt et al. [26] said that one of the key indicators of chemical degradation of membranes is surface cracking, which is similar to our observations for the DK and AG membrane surfaces. As for the AE membrane, its surface texture appeared to be intact when compared to the original. Therefore, it is believed that the AE has a relatively strong resistance to persulfate or associated sulfate free radical attack. Therefore, the AE membrane always resulted in better separation performance than other membranes tested (i.e., DK and AG).

4. Conclusion

The AE membrane proved to be the best within the group and it exhibited superior performance with respect to the removal of the target species: persulfate; sulfate ions; and TDS over the evaluation period. Additionally the AE membrane achieved more than 90% removals of metals such as Ba, Ca, K and Mg for the majority of the test period. For the membranes evaluated the general order of performance was AE > AG > DK. However, the AE membrane requires the highest operating pressure resulting in the highest energy costs.

SEM analysis of membrane surfaces was conducted in an attempt to explain membrane performance. The SEM images clearly showed that both the DK and AG membranes experienced degradation and cracking after exposure to 80,000 mg/L sodium persulfate solutions for 30 days while the AE membrane appeared unchanged. This finding is in agreement with the membrane performance test results, again confirming that the AE membrane was the best of this group.

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