ABSTRACT

Two different reverse osmosis systems were investigated in this work. The first was a 50-element plant-scale system that is used to treat 2200 cubic metres of AECL (low to intermediate level) liquid radwastes annually. It uses thin film composite (TFC) membranes and operates at an applied pressure of 2760 kPa, with a fixed crossflow of about 40 L/min. The other system uses the same thin film composite membranes for waste processing, but is a 2-element pilot-scale system. It is operated at pressures ranging between 1500 kPa and 7000 kPa, at a fixed crossflow of 55 L/min.

The average lifetime of the thin film composite membranes in the plant-scale processing application at AECL is about 3000 hours. After this service life has expired the rejection efficiency (for bulk conductivity) declines rapidly from 99.5% to about 95% as the membranes become impaired from chemical cleaning procedures that are required after each hundred cubic metres of waste are treated. The permeation flux for the plant-scale system decreases from about 2.2 L/min/element to below 0.5 L/min/element at the end of the membrane's useful service life.

The plant-scale membrane elements, fouled by an assortment of chemicals including calcium phosphate, ferric oxide, and various organics, were successfully regenerated by exposing them to a three-step chemical cleaning procedure (in the pilot-scale system), using detergent, HCl, and an alkaline-based cleaning with EDTA respectively. The 3-step procedure was successful in elevating the flux from 0.5 L/min for the spent membrane, to 1.2 L/min after the three step cleaning procedure. The 1.2 L/min post-cleaning flux could be maintained at a crossflow velocity of 55 L/min/vessel.

The decontamination factor (DF), which is the feed to permeate concentration ratio, was determined for cesium and strontium. For the plant-scale system (at the operating pressure of 2760 kPa), the DF of cesium decreased from about 100 when the membranes were new, to about 30 after they were replaced. After cleaning the fouled membranes with the pilot-scale system, the DF for cesium increased from about 30 to 50, as the applied pressure to the system was increased from 1500 kPa to 5500 kPa. By comparison, the strontium DF increased for the fouled membranes at the operating pressure of 2760 kPa, from about 1000 (when they were new), to about 4000 for the spent membranes. The strontium DF was unaffected by the applied pressure, however. The increase of strontium DF is believed to be due to the exchange of strontium with deposited calcium on the fouled membrane.

INTRODUCTION

In the mid 1970's, AECL, at the Chalk River Laboratories (CRL) site, built a Waste Treatment Centre (WTC) for treating low-level aqueous liquid wastes. The objective was to demonstrate processes for converting Canadian Deuterium Uranium (CANDU) wastes to a form suitable for disposal. The liquid waste streams are effectively volume reduced by a combination of continuous
crossflow microfiltration (MF), spiral wound reverse osmosis (SWRO), and tubular reverse osmosis (TRO) membrane technologies (Fig. 1).

Fig. 1

Integrated Plant-scale System for Aqueous Radwaste Processing.

Backwash and chemical cleaning wastes from the membrane plant are further volume reduced by evaporation. The concentrate from the membrane plant is ultimately immobilized with bitumen using a thin-film evaporator in a shielded cell. The ability of the MF/SWRO technology to remove impurities non-selectively makes it suitable for the treatment of radioactive effluents from operating nuclear plants, with proper membrane selection, feed characterization, system configuration, and system chemistry control.

Currently, there are two streams routinely treated at CRL. One originates from the Decontamination Centre (DC waste) and the other collects waste from the Chemical Drain (CD waste) system. A total of about 2200 m$^3$ of blended liquid (low to intermediate-level) waste are currently treated by the membrane plant annually. The current overall volumetric recovery of the two stage (concentrate-staged) reverse osmosis train employing SWRO and TRO is 96.6%. For a 35 m$^3$ batch of waste treated there is 0.7 m$^3$ of backwash concentrate and 1.17 m$^3$ of TRO concentrate sent to the evaporator for further volume reduction in a small evaporator, and subsequent immobilization with emulsified bitumen in a thin-film evaporator. The bituminized product from the facility occupies 0.175 m$^3$ based on the 35 m$^3$ feed volume. The overall volume reduction of the fresh feed through the integrated plant (employing both membranes and thin-film evaporation) is about 250.
SPIRAL WOUND REVERSE OSMOSIS SYSTEM

Reverse osmosis (RO) is a technology which is well established for the production of potable water from brackish water or seawater. It has been successfully used to produce high-purity water for the electronics, pharmaceutical, and power industries. Because of its versatility to remove ionic impurities, particulates and colloids, organics, microorganisms and pyrogenic material from water, RO has attained a prominent role in water purification [1].

In spiral wound reverse osmosis treatment, feedwater containing dissolved and suspended solids is pumped into the system at a desired feed pressure greater than the osmotic pressure of the solution. The feed stream is pumped into a pressure vessel containing one or more membrane elements connected in series. The feedwater then flows into the channels between the membrane sheets. These feed channels are composed of a plastic netting which breaks up the flow into small turbulent areas above the membrane surface.

Immediately above the membrane surface a concentration boundary layer forms whose thickness depends on feedwater ionic strength, particulate level, and flow in these small turbulent areas. The water and ions are transported by a solubility-diffusion process to the permeate water carrier. The purified water or permeate is recovered at atmospheric pressure. The remaining water, dissolved solids and particulates form the reject stream. The pressurized concentrate or retentate is dropped to atmospheric pressure through a back pressure regulating valve, immediately downstream of the system.

The performance of an RO membrane is usually described in terms of permeate flux, or "flux", contaminant rejection efficiency, and volumetric recovery. Permeate flux refers to the amount of flow across the membrane per unit area, at a particular operating pressure and dissolved solids concentration. The flow of water across the membrane is proportional to the effective pressure (applied pressure minus pressure drop minus the osmotic pressure of the solution). Increasing the applied pressure should increase the permeate flow without increasing the solute flow.

Rejection is the relative change in contaminant concentration from the feed stream to the permeate stream. RO membranes are not absolute barriers, and some small percentage of the solute (typically about 0.5%) does pass through the membrane. The amount of solute transport is a function of the membrane type and is proportional to the differential concentration across the membrane.

Spiral wound RO membrane types can be broadly classified as cellulosic or noncellulosic. Cellulose acetate membranes are still widely used because of their resistance to fouling, and their low cost. They are, however, easily damaged by bacterial attack and have relatively low rejection efficiencies. Noncellulosic membranes, such as the thin film composite membranes used at CRL, can operate over a wider pH range and exhibit high solute rejection efficiencies. The SWRO configuration achieves a large specific surface area per unit volume, which is typically 1000 m²/m³. This can be compared to 165 m²/m³ for plate modules and 335 m²/m³ for tubular modules.

The ratio of permeate to feed in a RO system is referred to as volumetric recovery, or simply, "recovery". To achieve high recoveries (up to 85% currently employed at CRL), it is necessary to stage the concentrate stream or recycle the concentrate for reprocessing. This is normally accomplished in a tapered system design. For instance, a two-stage system may have four pressure vessels in the first stage, feeding two vessels in the second stage.
The tapered configuration compensates for feed flow loss by permeation, therefore maintaining optimum cross-flows in both stages.

Plant-Scale SWRO System Description

The CRL plant-system is a three-stage 5:3:1 tapered system with 10 cm diameter by 6 m long pressure vessels. Each pressure vessel contains six membrane elements. The system is fed with a Goulds 3333 multi-stage centrifugal booster pump. Typical feed crossflows are maintained at about 40 L/min, with an inlet pressure of 2760 kPa. This system is used for the routine liquid processing of about 2200 m³ per year of CRL wastes.

Pilot-Scale SWRO System Description

The pilot-scale (experimental) system is equipped with a 5 μm cartridge filter upstream of the two high pressure pumps, both of which can deliver a maximum of 7000 kPa. The pressurized feed flowing at about 55 L/min is directed to one of two membrane pressure vessels, each containing two 10 cm diameter by 100 cm long membrane elements. The purified permeate stream exits the vessel, then passes through a flowmeter, and can be rejected from the system or recycled back to the feed tank.

The majority of the retentate (concentrate stream with 99% of the contaminants in the feed), recirculates back to the suction side of the high pressure pump to maintain the high crossflow rate. The remainder of the retentate is directed back to the feed tank. The operating pressure of the system is manually controlled by adjusting the backpressure control valves on both retentate streams leaving the vessel. A system is provided to flush the vessel and piping with clean water after an experiment. An onboard cleaning tank is also provided if chemical cleaning of the membranes is required.

The primary difference between operations of the pilot-scale and the plant-scale system was the effective crossflow rate through each vessel; for the pilot-scale system it was 55 L/min/vessel, while for the plant-scale system it was about 40 L/min/vessel. A more subtle difference between the units is the actual processing method to achieve the desired volumetric recovery of between 85 - 95%. For the plant-scale system retentate was recirculated to the feed tank, and a small bleed fraction was continuously removed. Filtrate was continuously added to the feed tank from the MF system, and so the operation was continuous. By comparison, the pilot-scale rig was operated in a batch mode of operation where a given volume of fresh filtrate (from the plant-scale MF system) was volume reduced to the predetermined volumetric recovery.

PERFORMANCE OF THIN FILM COMPOSITE MEMBRANES FOR LIQUID WASTE PROCESSING

Normalised Permeation Flux

The permeation flux from an RO system is a function of several variables including temperature, pressure, and pH. The plant-scale system used 50, 40-inch elements in nine pressure vessels, which were staged as 5:3:1. The permeation flux data obtained was normalised to an applied pressure of 2.76 MPa and a feed temperature of 25°C using a method given by Bukay [2]. The observed permeation flux (OBF) was normalised for temperature using a temperature correction factor (TCF) obtained from the membrane manufacturer,
\[ NPF = \frac{I}{TCF} \left[ \frac{2.76(MPa)}{\text{FEED PRESSURE} - \text{PERMEATE BACK} - \text{OSMOTIC}} \right] \times \frac{OBF}{\text{No. Elements}} \] (1)

an effective pressure, and for the total number of elements using equation (1).

From a processing perspective it is desirable to maintain a permeation rate of between 0.80 and 1.0 L/min/element at all times, so that the throughput of the 50-element plant-scale system matches the filtrate production rate of about 42 L/min from the MF system situated upstream. In the continuous mode of operation, downtime of equipment is minimized and maximum utility is made of the equipment.

Fig. 2 shows the normalised permeation flux for the plant-scale system after the first full-scale membrane change at 3800 cumulative hours of operation. Membranes were changed again after 7000 hours of operation, when the NPF decreased below 0.25 L/min/element. By comparison, the NPF for the pilot-scale system, which is operated at higher crossflow velocity, is consistently at 2.2 L/min/element. The scatter of the data in Fig. 2 is not due to errors in measurement; rather, it is the result of permeation flux declines during a given run, and the subsequent recovery after a chemical cleaning with an appropriate solvent. After a chemical cleaning it was possible to have up to a 100% improvement of normalized permeation flux or more, although this improvement of performance could not be maintained.

When the membranes were replaced after 7000 hours of operation (Fig. 2), several precautions were taken to minimize the large flux loss observed at 3800 hours. These included: i) operating at a volumetric recovery 5% lower than for the previous set which was processing to 85%; ii) using recommended anti-scalant chemicals in the feed solutions and; iii) cleaning at more regular intervals. Yet, none of these preventative measures appeared to be of much benefit in the resulting loss of throughput that was observed. Regular chemical cleaning cycles appeared to decrease the pressure drop across the membrane plant, but had less impact on improving permeation flux than similar chemical cleanings performed on the previous membrane set. After about 7000 hours of cumulative service the membranes were replaced due to i) the deterioration of membrane rejection efficiency, and ii) inefficient plant operation due to the frequency of equipment shut-downs from excessive chemical cleaning requirements.
Rejection Efficiency of TFC Plant-Scale Membranes

Another performance indicator that can be used to assess the RO membranes is the overall removal efficiency of conductive ions. The many aggressive chemical cleanings that were required to restore the permeation flux (Fig. 2) may have had a detrimental effect on the membrane integrity, resulting in the considerable loss of membrane rejection performance. Physical abrasion of the polyamide rejecting layer over time may also have been a contributing factor.

A plot of the conductivity rejection efficiency versus the elapsed processing time (after the initial membrane change at 3800 hours) is shown in Fig. 3. The feed conductivity in the present application ranged between 100 and 1000 mS/m, while the permeate conductivity varied between 0.6 and 20 mS/m. The membranes were replaced after 3800 hours because the flux decreased to very low permeation throughputs (Fig. 2), and since the rejection efficiency decreased to values below 95%. A rejection efficiency of 95% indicates that the thin film composite polyamide membranes have degraded to a point where they are no longer useful in this application.

After the membranes were replaced at 3800 hours (Fig. 3), the rejection efficiency increased back to 99.5% overall. The rejection remained at about 99.5% until about 7000 cumulative hours of operation, when the overall efficiencies again declined back to about 95%, and the membranes were subsequently replaced. For those runs between 3800 hours and 7000 hours where
the removal efficiency was lower than 99%, leakage took place of excessive nitrate and sodium ions into the permeate following a chemical cleaning. Monovalent ions have low rejection efficiencies. Since the plant feed would have been temporarily overloaded with monovalent ions, this situation resulted in a reduced overall rejection efficiency. After the cleaning chemicals were flushed from the system, the rejection efficiency was restored to about 99.3% overall.

Fig. 3
Rejection Efficiency of Filmtec Membranes in Plant-Scale System

Cause of Flux Decline in Plant-Scale System

The flux decline with time observed in Fig. 2 at 3800 hours and 7000 hours, is the result of concentration polarization and/or surface fouling [3]. Surface fouling occurs when there is deposition of submicron particles on the surface, as well as crystallization and precipitation of smaller solutes. It is manifested when rejected solids are not transported from the surface of the membrane back to the bulk stream. In general, there are five types of fouling: namely membrane scaling, fouling by metal oxides device plugging, colloidal fouling, and biological fouling [4]. The different types of fouling frequently occur at the same time and can influence each other. Unfortunately, the interactions between the types of fouling are poorly understood.
While operating, thin film composite membranes take on an anion charge on the surface. This causes cationic foulants, such as aluminum and ferric hydroxides, along with cationic coagulant polymers, to be attracted to it. Further, because of the high flux rates on thin film composite membranes, fouling occurs faster and is more noticeable than with other membranes [5]. Moreover, in the CRL plant-scale application the volumetric recovery is maintained at about 85%. This high recovery leads to increased solute concentrations at the boundary layer, leading to more concentration polarization and a higher deposition of fouling substances.

The chemical scale on the fouled plant-scale RO membranes is comprised primarily of aluminum, silica, calcium, phosphorous, and to a lesser extent iron and sulphur. Calcium hydroxyapatite and ferric oxide scale have been identified as the major fouling species from Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analyses (EDX). Clay and aluminum silicate-based scale is thought to account for the initial large flux decline associated with concentration polarization, and represents the scale which is the most difficult to remove by standard chemical cleaning procedures. Precipitates approaching 10 µm in diameter have been observed on the surface of the membrane by SEM, and these precipitates are hard to dissolve in even the most concentrated acids. This is further supported by the observation that alkaline cleaning chemicals at pH 12 are the most effective for permeate flux restoration where silica solubilizes to silicic acid [6]. The precipitates in the 50 membrane elements of all three SWRO stages are similar in chemical composition based on the results of the EDX analyses on membranes from all stages of the system.

**Performance of Pilot-Scale System**

The primary difference between operations of the pilot-scale and the plant-scale system is the effective crossflow rate through each vessel; for the pilot-scale system it was 55 L/min/vessel, whereas for the plant-scale system it was about 40 L/min/vessel. To compare the performance of the two systems, the fresh feed to the pilot plant was the same 50:50 blend of the CD/DC waste streams. The pilot-scale system was run in parallel with the plant-scale system, and both of the systems were targeted to achieve 85% volumetric recoveries overall. By comparison with the plant-scale system, which was only able to maintain 0.5 L/min/element (at the start of a processing campaign), the pilot-scale system was able to sustain a permeation rate of 2.2 L/min. During the course of a run, the flux typically decreased from 2.2 L/min to about 1.7 L/min, depending upon the final volumetric recovery that was sought. However, the loss of flux during a run was always reversible (after flushing the system with permeate), indicating it was due to concentration polarization, and not irreversible fouling. If the system was placed in total recirculation at any time during the run the permeate flows would not decrease further.

**Regeneration of Spent Plant-Scale Membrane Elements with Pilot-Scale System**

Since the performance of the pilot-scale system was so much superior to the plant-scale system for CRL liquid waste processing applications, a test was undertaken to evaluate the cleaning effectiveness for spent plant-scale membranes in the pilot-scale system. The spent membranes were removed from the plant-scale system at 7000 hours (Fig. 2), and two were chosen from the first stage for cleaning tests.
A chemical cleaning campaign of a fouled plant-scale thin film composite membranes was carried out using a three-step procedure at an applied pressure of 2760 kPa (the same operating pressure as the plant-scale system). The fouled membrane was taken from the first stage of the three-stage system. During the first cleaning step a detergent formulation (1 wt.%) was used to remove surface oil and grease. In the second step, HCl (at a pH of 2 and ambient temperature), was employed for the dissolution of metals. In the third step, NaOH (at pH of 12) and 2 wt.% EDTA was used to complex metals and remove silica deposits by dissolution.

A 73.5% improvement of permeability was observed after cleaning with the detergent. A total of 0.8 kg of oil and grease was removed from the element with the detergent cleaning process. After the second cleaning procedure with HCl, a further improvement of 14% was observed. After the third step where chemical cleaning was carried out with NaOH and EDTA, an incremental improvement of 20% was noted. The overall improvement of permeation flux for the element based on the three-step cleaning sequence was 137%; the water permeability increased from 0.48 L/min before cleaning to 1.14 L/min after cleaning. The same cleaning tests were carried out on another fouled element, and the results could be replicated.

A complete regeneration of the fouled membrane elements was not achieved. The permeation flux for a new element (after concentration polarization effects were taken into account) was about 2.2 L/min. The pilot-scale cleaning procedure was capable of restoring about 50% of the membrane's original performance. The cleaned elements could be reused in the plant-scale system at a throughput of 1 L/min, however, because this would match the filtrate production from the MF system situated upstream.

Following the 3-step cleaning procedure, a series of three further experiments were carried out in which blended CD/DC (MF-filtered) waste was processed in the pilot-scale unit to evaluate the long term benefit of the cleaning methods. Results are shown in Fig. 4, for the flux curves before cleaning and after cleaning (represented by Tests 1,2,3). In the first experiment a batch of CD/DC waste was passed through the system with a 5 micron prefilter in place. The feed was reduced to a final recovery of 90%. After flushing the system with permeate at the completion of the run, the same test was replicated (Test 2). The purpose of Test 2 was to determine if the permeate flux after a pure water flush could be restored to the same initial value (which had previously been observed for CD/DC waste processing). Finally, a third test was carried out in which the 5 micron prefilter was removed from the system to determine if a coarse filter was required upstream of the membranes at the higher crossflow velocities.
At a volumetric recovery of 90% in Test 1, the permeation flux decreased to 0.88 L/min. The flux decline curve was identical for Test 2, indicating that the performance curve was reproducible. It also provided evidence that the chemical cleaning procedures had been effective in displacing scaling materials. In Test 3, where the 5 micron prefilter was removed from the system, the permeation rates at all volumetric recoveries mimicked the previous two tests. The results of Test 3 suggest that a coarse 5 micron prefilter is not required upstream of the RO system.

**Pure Water Permeability after Spent Membrane Regeneration**

A water permeability test was carried out before and after the chemical regeneration procedures, so that comparisons of the cleaning efficiency could be made on the basis of membrane permeability. Pure deionized water was passed through the element at various applied pressures ranging between 1500 kPa and 5500 kPa, and the permeation flux was recorded as a function of the operating pressure.

The results of the permeability tests for the two different membrane elements are shown in Fig. 5. Prior to the chemical cleaning procedure, the flux for element #1 varied between 0.25 and 0.9 L/min/element, as the pressure increased from 1500 kPa to 5500 kPa. After cleaning the flux for element #1 increased to between 0.6 and 2.2 L/min/element over the same pressure range. A similar improvement of pure water permeability was observed for element #2 after the cleaning procedures. The pure water permeabilities for both
elements after the chemical cleaning procedures were approximately the same (at all pressures), even though element #1 was more fouled. This would indicate that the membranes were cleaned to the maximum possible extent by the three-step cleaning procedure, which is about 50% of the new membrane's performance.

**Effect of Pressure on Decontamination Factor**

Tests were carried out to evaluate the impact of the chemical cleaning procedures on the removal efficiencies of cesium and strontium. The results are plotted in Fig. 6 in terms of a decontamination factor (DF), rather than a rejection efficiency for clarity on the figure. The decontamination factor (DF) is defined by equation (2).

\[
DF = \frac{\text{Feed Concentration}}{\text{Permeate Concentration}} = \frac{1}{1 - \text{Fraction Rejected}}
\]  

(2)

It was necessary to use stable isotopes of cesium and strontium instead of radioactive isotopes to determine the DF of each accurately. This was required since the resolution of the analytical instruments was not sufficient to detect radioactive contaminants reliably at low concentrations in the permeate. The results of these tests showed that the DF before cleaning for
cesium was 30 (at 1500 kPa), and increased to 50 (at 5500 kPa) before cleaning. However, the cesium DF for a new element was about 100, which indicated that there had been some permanent loss of rejection after its 3800 hour service life was over. There was no increase of cesium removal after the three-step cleaning procedure with the pilot-scale system. The tests demonstrated that the aggressive chemical cleaning carried out did not impair the membrane's ability to remove contaminants.

The DF for strontium increased from about 1000 for a new membrane element to roughly 4000, after the membrane had been exposed to about 3800 hours of liquid waste processing. The strontium DF was relatively independent of both the applied pressure and the chemical cleaning procedures. The increase of DF after waste processing can be rationalized by noting that the dominant scale on the plant-scale membranes is calcium phosphate. It is probable that strontium replaces the precipitated calcium on the fouled membrane (as strontium phosphate), liberating calcium in the process. Evidence of this phenomenon can be gleaned from the contact beta radiation fields on the fouled membranes. Following their removal from the plant-scale system at 7000 cumulative hours (Fig. 2), the fouled membranes had contact beta fields that sometimes approached 20 Rads/h. The high beta field is evidence of Sr-90 deposits; there are no other abundant pure beta emitters in the CRL waste streams.
CONCLUSIONS

Membrane replacements are required after approximately 4000 hours in the plant-scale liquid waste processing application at AECL. After this period, the average permeation flux for the 50-element plant-scale system decreased below 0.3 L/min/element, and the bulk conductivity rejection efficiency declined rapidly from 99.5% to 95%. By comparison, with the pilot-scale system, where there is 50% higher feed crossflow, it is possible to maintain a permeation flux of about 2.2 L/min/element.

The fouled CRL membrane elements could be regenerated by exposing them to a three-step chemical cleaning procedure (at higher crossflow in the pilot-scale system), using detergent, HCl, and an alkaline-based cleaning solution containing EDTA. The 3-step procedure was successful in boosting the flux from 0.5 L/min for the fouled membrane element, to 1.2 L/min for both elements that were cleaned.

The decontamination factors for cesium and strontium were not affected by the aggressive cleaning procedures in the pilot-scale system. The DF for cesium increased from about 30 to 50 as the applied pressure increased from 1500 kPa to 5500 kPa. However, there was no further change of the cesium DF after the cleaning procedures were completed. For strontium, the DF varied between 3000 to 4000, and was unaffected by the applied pressure or the chemical cleaning procedures. In addition, the strontium DF increased from 1000 (for the new element) to 4000 for the fouled membrane. The increase is believed to be due to the exchange of strontium from solution with deposited calcium (scaled out as calcium phosphate) on the fouled membrane surface.

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