

## **Nuclear Steam Generator Chemical Cleaning Waste Treatment Using Membrane Technology**

**D. Holme, E. Przybylowski and J. Slade**  
**Ontario Power Generation**  
**Nuclear Waste Management Division**  
**PO Box 7000, RR #3**  
**Tiverton, Ontario N0H 2T0**

### **ABSTRACT**

The chemical cleaning of Ontario Power Generation's Pickering nuclear steam generators using Framatome's high temperature process generates a significant volume of spent solvent and rinse waste that requires treatment. Since 1996, these wastes have been sent off-site to a commercial facility for incineration after interim storage and radiological characterization at OPG's Spent Solvent Treatment Facility (SSTF) Tank Farm. In 2002, with the objective of reducing overall treatment costs, OPG's Nuclear Waste Management Division made the decision to investigate a simplified on-site treatment process utilizing ultrafiltration (UF) and reverse osmosis (RO) systems to volume reduce the spent steam generator cleaning wastes prior to off-site incineration. Bench scale membrane treatability tests, performed on actual waste, indicated significant volume reductions and excellent effluent quality could be achieved with membrane processes. Based on these results, re-commissioning of the SSTF UF and RO systems began in 2002 followed by full scale processing in May 2003. To date, approximately 2200 m<sup>3</sup> of steam generator chemical cleaning waste rinse water and approximately 70 m<sup>3</sup> of copper solvent has been treated in the SSTF using a combination of ultrafiltration and two-pass reverse osmosis. The overall volumetric recoveries on rinse water have been between about 90% for the RO system and about 95% for the UF system. There has been no significant degradation of system performance from the standpoint of permeate quality or membrane permeability. The influent criteria for discharge of permeate to the site sewage treatment plant have been easily met with and the facility operates at a fraction of the deminimus unity factor established by the approved radiological pathway analysis.

### **1.0 INTRODUCTION AND BACKGROUND**

The potential need to clean the secondary side of Ontario Power Generation's (formerly Ontario Hydro) nuclear steam generators was first identified in the mid 1980's [1]. A program to evaluate options to treat the contaminated aqueous wastes arising from steam generator cleaning was undertaken by in 1988. This program was accelerated when the need for full-height chemical cleaning of the Bruce NGS-A steam generators was identified in 1989, as a result of corrosion product blockage of the broach plate flow holes. A number of corrosion related tube leaks developed at Bruce NGS-A, further increasing the urgency of the tube and tubesheet cleaning program. The Bruce Unit 4 and Unit 3 steam generators were water lanced and chemically cleaned in 1993 and 1994, respectively. Bruce Unit 1 was subsequently cleaned in 1995 and Unit 3 was cleaned again in 1996.

Similarly, the Pickering steam generators experienced under deposit pitting corrosion in the vicinity of the tubesheet and lower support structures. To arrest this damage, the steam generators in Pickering Units 5, 6, 1 and 2 were cleaned in 1992, 1993, 1994 and 1995, respectively. Pickering Units 5 and 6 were again cleaned in 2001 and Units 8 and 7 were cleaned in 2002 and 2003, respectively.

The corrosion products present in the steam generator secondary side deposits are comprised of both copper and magnetite. For this reason, the cleaning process requires the use of separate copper and iron dissolution steps. The cleaning process used at both Bruce and Pickering in the 1990's utilized EDTA-based solvents similar to those developed by the Steam Generator Owners Group (SCOG) of the Electric Power Research Institute (EPRI). Due to the extended outage duration required, the relatively low temperature EPRI/SCOG process was replaced by Framatome's EDTA/EDA based high temperature chemical (HTCC) process for the last four Pickering cleans. Both the EPRI/SCOG and HTCC processes require demineralized water rinses between the dissolution steps as well as final demineralized water flushes. Table 1 provides the typical volume and composition of HTCC cleaning solvents [7]. Low levels of radionuclide contamination are found in the spent solvents and rinse water as a result of prior steam generator tube leaks and from solvent ingress into the exposed primary side of tubes remaining following removal of tube sections for metallographic analysis. The predominant nuclides are H-3, Co-60, Fe-55 and Cs-137.

In the early 1990's, a spent solvent treatment facility (SSTF) was constructed at the Bruce Site to store and process the aqueous waste produced from the on-going steam generator chemical cleaning campaigns. The facility utilized wet air oxidation technology and included a tank farm consisting of six 650 m<sup>3</sup> stainless steel holding tanks (3,900 m<sup>3</sup> total capacity). The facility started operation in 1993 producing metal oxide sludge suitable for disposal in the on-site landfill and oxidized liquor that was discharged to the adjacent sewage processing plant (SPP). Due to difficulties associated with nickel removal, a membrane-based system was installed to polish the oxidized liquor in October 1983. The membrane system employed ultrafiltration (UF) and reverse osmosis (RO) technology. Despite some good success, the SSTF treatment option was abandoned in the mid 1990's due, in part, to operability and maintenance issues created by metal oxide precipitation requiring frequent equipment shutdown and cleaning. Following interim storage at the SSTF tank farm and detailed radiological characterization, subsequent steam generator spent chemical cleaning waste was sent for off-site incineration at the Clean Harbors (formerly Laidlaw) facility in Lampton. A detailed radiological pathway analysis for this disposal option is in place and approved by the CNSC. This approved pathway establishes the upper boundary for off-site disposal of spent steam generator chemical cleaning wastes at the Clean Harbors facility each year to ensure that the de minimus dose criterion of 10 µS (1 mrem) per year is met.

In 2002, with the objective of reducing overall treatment costs, OPG's Nuclear Waste Management Division made the decision to investigate a simplified on-site treatment process utilizing only the UF and RO systems to volume reduce the spent steam generator cleaning wastes prior to shipment to Clean Harbors for incineration. Bench scale membrane treatability tests were performed using actual spent HTCC wastes. The results of the bench tests indicated that both significant volume reductions and excellent effluent quality could be achieved with membrane processes. Based on these results, re-commissioning of the SSTF UF and RO systems began in 2002. The re-commissioning activities included repair and replacement of some piping spools affected by pitting corrosion, and replacement of the UF and RO membranes. Full scale processing commenced in May 2003.

This paper deals with the experience gained to date on treating primarily rinse wastewater and some copper solvent generated from the chemical HTCC cleaning of Pickering steam generators.

## **2.0 PROCESS DESCRIPTION**

### **2.1 Overall Waste Processing Strategy**

Based on the results of the bench scale membrane tests [2] conducted in December 2001 on actual spent solvent and rinse samples collected from the SSTF tank farm, it was estimated that the following volume reduction factors were achievable with the RO system:

- VRF for rinse: 90% to 95% of the original volume;
- VRF for copper solvent: 60% to 75% of the original volume; and
- VRF for iron solvent: 50% of the original volume.

The bench scale tests also revealed that the contaminant rejections with RO were sufficiently high to allow the influent criteria for the Bruce SPP to be easily met. It was also recognized that the quality (i.e., concentration of contaminants) of the processed rinse water at 90% VRF was approximately equal to the spent iron and copper solvents. This provides the opportunity to add the rinse concentrates to the solvent in storage for future additional volume reduction with no fear of compromising the solvent treatability.

In order to optimize the treated water throughput so that the largest volume of waste could be processed without risk of serious membrane fouling, it was decided to treat the large volume relatively clean rinse waste first [3]. The copper solvent would be treated next followed lastly by the more concentrated iron solvent. Late in 2004, given the relatively low expected VRF, potentially high membrane fouling potential and fiscal reasons, it was decided to ship the iron solvent directly to Clean Harbors for incineration.

## **2.2 Tank Farm**

Spent solvent and rinse water wastes are transported as non-radioactive shipments to the SSTF tank farm in stainless steel 35m<sup>3</sup> to 45 m<sup>3</sup> road tankers. The tank farm consists of six 650 m<sup>3</sup> stainless steel holding tanks. The tank farm is equipped with tanker loading and unloading pumps as well as piping and pumps to allow recirculation, sampling and transfer of tank contents. Both the tank farm and the tanker loading and unloading island have engineered containment to contain any potential spills or leaks. The tanks, pumps and piping are insulated and heated for freeze protection in the winter.

To the extent possible, spent iron solvent, copper solvent and rinse waste are kept segregated in the tank farm. Given that the primary goal of the UF/RO system is volume reduction, it is important to avoid diluting the solvent wastes with rinse waste.

## **2.3 Ultrafiltration and Reverse Osmosis System**

A simplified schematic of the SSTF UF and RO process is shown in Figure 1. The ultrafiltration system employs four parallel banks of ten Zenon ZPF-12 tubular membrane modules in series. The UF system is a pretreatment system for the downstream RO system which has a limited tolerance for suspended solids. The UF system operates in a modified batch mode. Fresh feed from the tank farm is transferred automatically to the UF feed tank and circulated through the membrane tubes. The suspended solids free permeate is recovered continuously from the system and directed to the 1<sup>st</sup> Pass RO feed tank. The concentrate stream is returned to the UF feed tank. The UF feed tank is level controlled so that the fresh feed make-up is equal to the permeate removed. The UF system utilizes high concentrate flow rates (greater than 3500 L/min) to minimize solids deposition and hence fouling on the membrane surface. In order to maintain high concentrate flow throughout the entire length of the membrane tubes, only a small percentage (2% to 5%) of the feed flow is recovered as permeate (instantaneous volumetric recovery). The concentration of suspended solids gradually increases in the UF process loop until such time that the system must be “batched out” to a solvent storage tank for further volume reduction at a later date. Chemical cleaning is typically required following batch out to recover lost permeate flow. Table 2 provides the operating parameters for the UF system.

The RO system is used to separate and concentrate organic and inorganic dissolved contaminants in the waste feed. The RO system is a two pass system where the permeate generated from the 1<sup>st</sup> pass system is polished in the 2<sup>nd</sup> pass system. The 1<sup>st</sup> Pass RO system has two parallel banks of two vessels in series. Each vessel houses six 20 cm by 100 cm Filmtec seawater spiral wound reverse osmosis membranes. The 1<sup>st</sup> Pass RO system also operates in a modified batch mode. UF permeate is pumped to the level controlled 1<sup>st</sup> Pass RO feed tank, as feed to the system. Permeate is continuously sent to the 2<sup>nd</sup> Pass RO feed tank. The concentrate is circulated back to the 1<sup>st</sup> Pass RO feed tank. As clean permeate is continuously removed from the system and more dissolved contaminants are added via the fresh UF permeate, the contaminant concentration in the feed increases to the point where the osmotic pressure effectively limits further permeate recovery. System batch out is required at this point and the system is filled with fresh UF permeate to begin another cycle. Chemical cleaning may also be required following batch out. The membrane inlet feed pressure is maintained at about 6000 kPa. As with the UF system, high feed/concentrate flow rates are maintained to minimize membrane fouling. The instantaneous volumetric

recovery (% of feed flow recovered continuously as permeate) of the system is typically about 40%. See Table 3 for the 1<sup>st</sup> Pass RO operating parameters.

As mentioned above, the permeate from the 1<sup>st</sup> Pass RO system is further polished in the 2<sup>nd</sup> Pass RO system to produce a high quality permeate for discharge to the SPP. This system operates at an inlet membrane pressure of about 3500 kPa and consists of eight vessels, arranged with three parallel pairs of vessels in series, followed by two individual vessels in series. The vessels each contain six 10 cm by 100 cm Filmtec seawater high rejection spiral wound reverse osmosis membranes. The 2<sup>nd</sup> Pass RO system operates in a feed and bleed mode where the concentrate from the 2<sup>nd</sup> Pass RO system is directed back to the 1<sup>st</sup> Pass RO system feed tank and the permeate is discharged continuously to the sewage processing plant. By not sending the concentrate stream back to the 2<sup>nd</sup> Pass feed tank, the 2<sup>nd</sup> Pass feed contaminant concentrations are kept relatively uniform and as low as possible in order to maximize discharge permeate quality. The high initial pH of the spent solvent and rinse waste shifts the ammonia chemical balance to the molecular form (NH<sub>3</sub>) which is not well rejected by the RO membrane. The resulting ammonia concentration in the permeate can drive the pH above the influent limit to the SPP of 9.5. To ensure compliance with both the SPP ammonia and pH influent criteria, the pH of the 2<sup>nd</sup> Pass RO system is adjusted automatically with sulphuric acid to between 7.5 and 8. The permeate is routinely monitored for radioactivity, metals, chemical oxygen demand (COD), ammonia, and pH. Due to the extremely low contaminant concentrations and, therefore, low fouling potential, the instantaneous volumetric recovery (% of feed flow recovered continuously as permeate) of the 2<sup>nd</sup> Pass RO system is as high as 80%. Refer to Table 4 for the 2<sup>nd</sup> Pass RO operating parameters.

### **3.0 RESULTS AND DISCUSSION**

#### **3.1 Contaminant Rejection and Effluent Quality**

As stated earlier, a primary goal of restarting the SSTF UF and RO systems was to volume reduce and concentrate the spent solvent and rinse waste in order to lower off-site incineration costs thereby lowering the overall treatment costs. To achieve this goal it is also necessary to produce a permeate stream that is of sufficient quality for discharge to the site sewage processing plant. Unfortunately these two goals compete with one another to some extent. As described in Section 2.3, both the SSTF UF and 1<sup>st</sup> Pass RO systems behave essentially as semi-batch concentrators. That is, permeate is continuously removed as fresh feed is introduced to maintain a constant system volume. The contaminant-laden concentrate is continuously returned to the feed tank. The concentration of contaminants in the loop increases with time. For the UF system this is primarily a fouling concern and has little effect on the UF permeate quality. The reason is because the UF system is a physical filter and its ability to remove solids is primarily a function of the pore size of the membrane and size of the solids. This is not the case for the RO system. In addition to fouling concerns, increasing dissolved contaminant concentrations also have negative effect on permeate quality. At a given temperature and pressure, the RO membrane has a fixed contaminant removal efficiency. The mass transfer of contaminants across the membrane into the permeate is by diffusion and is directly proportional to the feed concentration. Consequently, as the RO loop becomes more concentrated, the permeate quality deteriorates. This effect is evidenced by the permeate conductivity data for the 1<sup>st</sup> Pass RO in Table 3. The data ranges from 12 µS/cm to 1401 µS/cm. The corresponding concentrate conductivities were 1900 and 45000 µS/cm, respectively. When operating RO systems, one has to balance the desire to achieve high overall volume reduction factors with the requirement to maintain good permeate quality and low membrane fouling.

The two-pass RO system employed at the SSTF ensures good permeate quality while achieving a high overall VRF. Consistent with the bench scale tests that were performed, the overall VRFs (% of feed volume recovered as permeate) obtained on spent steam generator rinse with the SSTF RO system have been between about 90%. Table 5 shows typical feed and permeate contaminant concentrations and calculated rejection efficiencies. Excellent rejection efficiencies for metals are achieved in the 1<sup>st</sup> Pass RO with values ranging from 99.31% for copper to 99.38% for zinc. Similarly the 1<sup>st</sup> Pass RO rejection for chemical oxygen demand (COD) was 99.83%. The rejection of ammonia in the 1<sup>st</sup> Pass RO is significantly lower at just over 90%. This is expected, as molecular ammonia is not well rejected by the RO membrane. The lower rejection efficiency for total dissolved solids (TDS), 97.35%, is partially a result of relatively

poor ammonia rejection. The metal rejection efficiencies in the 2<sup>nd</sup> Pass RO are slightly lower than those attained in the 1<sup>st</sup> Pass RO ranging from 92.97% for zinc to 94.17% for copper. This is attributed to the fact that two of the eight 2<sup>nd</sup> Pass RO pressure vessels have end-cap O-ring leaks that allow a small bypass of feed to the permeate. Exhaustive efforts to correct this problem failed, and, given the overall system was delivering excellent effluent quality, it was decided to operate the system with the defect. With the exception of ammonia and TDS, the combined overall RO rejection of contaminants is in excess of 99.9%. It is interesting to note that the overall system (UF and RO) contaminant rejections are slightly lower than the overall RO rejection. This is a result of the feed contaminant concentration increase in the 1st Pass RO loop as discussed in the start of this section.

Note that precise rejection efficiencies could not be calculated for the radionuclides Cs-137 and Co-60 for both the 1<sup>st</sup> and 2<sup>nd</sup> Pass RO systems due to the fact that the permeate concentrations were below the minimum detection limit. This is also the case for COD rejection in the 2<sup>nd</sup> Pass RO. The overall system rejection efficiency for Co-60 should be the same as that achieved for iron and the other metals (>99.5% overall system) while the Cs-137 rejection will be slightly less (~99%) as the membrane is less effective at removing small monovalent anions. The Co-60 and Cs-137 rejection assumptions are supported by work performed by AECL on treating radioactive wastewater with RO [4, 5]. Of course, there is no rejection of H-3 in the process.

Table 6 compares the contaminant concentrations in 2<sup>nd</sup> Pass RO discharge to the influent criteria limits for the Bruce Site SPP. The data reported in this table is typical from a weekly composite sample. As can be seen, all the SPP influent criteria are easily met. The one discharge parameter that requires the most attention is pH. Sulphuric acid injection is required upstream of the 2<sup>nd</sup> Pass RO in order to shift the ammonia/ammonium balance in the feed more to the ammonium (ionic) form which is better rejected by the RO membrane. Acid injection sufficient to yield a pH of about 7.5 seems to work best in this application. If the feed pH is too high (> 8) the pH of the permeate for discharge will rise to about pH 10. This is due to the higher levels of ammonia passing into the permeate and forming ammonium hydroxide. Conversely, just the opposite problem occurs if the feed pH is adjusted too low (<7). In this case, essentially all the ammonia is rejected but carbon dioxide (produced when the small amount of carbonate/bicarbonate passing through the 1<sup>st</sup> Pass RO converts to CO<sub>2</sub> at the lower pH) passes freely through the membrane depressing the 2<sup>nd</sup> Pass permeate to below pH 6. Consequently, reliable and accurate pH measurement and control are essential in order to meet the SPP influent pH criteria.

It is also worth looking at the bulk conductivity rejection of the RO system since startup. This data is calculated from on-line conductivity readings. On-line conductivity measurement is essential as it can provide early indication of a mechanical leak (i.e., membrane rupture or O-ring failure), membrane degradation or membrane fouling. The calculated conductivity rejection data is presented in Figures 6 and 7. As can be seen, the rejection efficiency for bulk conductivity is considerably lower than the rejections reported in Table 5. The Table 5 data samples were taken on Run Day 36 (about mid-way on the x-axis of Figures 6 and 7. At this point, for example, the 1<sup>st</sup> Pass metal rejections are greater than 99% compared to about 97.5% for conductivity, whereas, the rejection for TDS compares well at 97.35%. Obviously there are other ionic species in the feed water contributing to conductivity that are not as well rejected as those reported in Table 5. These species likely include carbonate, bicarbonate, carbon dioxide and sodium. Regardless, the calculation and trending of bulk conductivity rejection remains a valuable diagnostic tool for the RO systems. The logarithmic decline in conductivity rejection for both RO systems could be indicative of slight membrane degradation or fouling causing increased solute passage across the membrane. This trend warrants attention but is not considered serious because, as stated above, the rejection for the species of main concern remains very high.

With respect to the SSTF discharges, the Bruce Site SPP does not have specific influent criteria for radionuclides. Rather, a detailed radiological pathway exists for the treatment of spent steam generator boiler cleaning waste at the SSTF. This pathway defines the maximum inventory for individual nuclides that can be processed in a year at the SSTF. The pathway assumes a very conservative rejection efficiency for radionuclides (excluding tritium) of 98% with 2% of the radionuclides discharged to the SPP with the permeate stream. There is no rejection of tritium in the system and none is assumed in the pathway analysis. Representative samples of the waste feed stored in the tank farm undergo detailed radiological

characterization prior to treatment. The characterization includes determination of gamma emitting nuclides as well as pure beta emitters and transuranics. The inventory of individual nuclides treated in the system is recorded and the ratio of the individual nuclide to its maximum inventory is calculated. The fractional summation of the individual nuclide ratios must be less than 1.0 (unity factor) to ensure that the de minimus dose to the most exposed individual is not exceeded. The year-to-date unity factor is reported to the CNSC on a monthly basis. The unity factor in 2004 was less than 0.05, and as stated above, no gamma activity has been detected in the permeate discharge to the SPP. Tritium discharges were typically around 0.02 MBq/L.

As shown in Figure 5, the UF system is producing excellent permeate for the RO system. The UF permeate turbidity is consistently below 0.1 NTU which is well below the minimum value of 2 NTU for spiral wound RO feed water recommended by Filmtec.

### 3.2 Membrane Permeability

Permeate flux is defined as the flowrate of permeate through the membrane, per unit area of membrane surface. In this report it is expressed as litres per m<sup>2</sup> per day or LMD. Permeate flux is highly dependent on feed temperature so it is typical for the permeate flux to be compensated for temperature by calculating the temperature normalized flux. This is done by multiplying the actual membrane permeate flux applying a temperature correction factor. In this report the permeate flux values are normalized to 20°C.

In addition to temperature, the flowrate of permeate through the membrane is also a function of the driving force pressure across the membrane. The units of permeability used in this report are LMD/kPa. The advantage of calculating the membrane permeability is it provides a temperature and pressure corrected permeate flux parameter that can be used to assess the hydrodynamic performance of the membrane system and determine if fouling or osmotic pressure effects are significant.

Plots of temperature normalized permeate versus run days are shown for the UF, 1<sup>st</sup> Pass and 2<sup>nd</sup> Pass RO systems in Figures 2, 3 and 4, respectively. Also shown on these plots are when system batch out and chemical cleans occurred. For the cleans CA is citric acid and D is a high pH detergent clean.

The permeability of the UF system ranged from 2.6 LMD/kPa to 12.9 LMD/kPa with an average of 7.5 LMD/kPa. This corresponds to actual permeate flow rates of 75 L/min to 189 L/min (average of 128 L/min). The Figure 2 data clearly shows a dramatic drop in permeability as the UF feed loop concentrates over time. Typically the UF system required concentrate batch out followed by chemical cleaning every 500 m<sup>3</sup> to 600 m<sup>3</sup> of rinse waste treated resulting in an overall volume reduction of about 95%. It was not possible to recover the UF membrane permeability by simply batching out the concentrate thereby indicating actual membrane fouling. It should be noted that the fouling deposits were not significant enough to result in serious pressure drop increases and concentrate flows remained steady. The average crossflow pressure drop was 268 kPa at a concentrate flow of 3744 L/min. The typical cleaning regime for the UF system was a citric acid wash followed by a high pH detergent wash. In all cases cleaning was able to restore membrane permeability.

The permeability of the 1<sup>st</sup> Pass RO system ranged from 0.03 LMD/kPa to 0.089 LMD/kPa with an average of 0.051 LMD/kPa. The actual (not normalized) permeate flows ranged from 137 L/min to 247 L/min with an average of 183 L/min. The permeability of the 2<sup>nd</sup> Pass RO system ranged from 0.12 LMD/kPa to 0.213 LMD/kPa with an average of 0.169 LMD/kPa. The actual (not normalized) permeate flows ranged from 98 L/min to 148 L/min with an average of 129 L/min. The permeability of the 2<sup>nd</sup> Pass RO is greater than the 1<sup>st</sup> Pass RO because of the very low osmotic pressure of its feed. Figure 3 and Figure 4 show a logarithmic decrease in membrane permeability with run days. This is typical of membrane systems and is attributed to membrane compaction [6]. Compaction is caused by creep deformation of the polymeric membrane material over time and is caused by the applied feed pressure. The result of compaction is a tightening of the membrane's rejecting layer reducing its permeability. Typically, compaction is taken into account in system design resulting in initial excess permeate flow at lower than design pressures. This is the case with both the 1<sup>st</sup> and 2<sup>nd</sup> Pass RO systems that still permeate more than the design rates. Over time the system "breaks in" to design conditions. The decline could also be attributed to membrane fouling but this is not

the case as simply batching out the system was usually sufficient to restore permeability. Obviously, permeability decreased as a result of increasing osmotic pressure as the contaminant concentrations in the loop increased. This is most evident from the “saw tooth” pattern of the curve for the 1<sup>st</sup> Pass RO presented in Figure 3. Chemical cleaning did not seem to have a significant additional effect on restoring permeability. Typically the 1<sup>st</sup> Pass RO system was batched out after processing approximately 350 m<sup>3</sup> of rinse waste for an overall volumetric recovery of about 90%. The overall volumetric recovery could probably be pushed to 95% without fear of membrane fouling, but given that the concentrates are blended with copper solvent for further volume reduction, it was decided to keep to the more conservative value.

### 3.3 Summary

In summary, to date approximately 2200 m<sup>3</sup> of steam generator chemical cleaning waste rinse water and approximately 70 m<sup>3</sup> of copper solvent has been treated in the SSTF using a combination of ultrafiltration and two-pass reverse osmosis. The overall volumetric recoveries on rinse water have been between about 90% for the RO system and about 95% for the UF system. There has been no significant degradation of system performance from the standpoint of permeate quality or membrane permeability. The influent criteria for discharge of permeate to the site sewage treatment plant have been easily met and the facility operates at a fraction of the de minimus unity factor established by the approved radiological pathway analysis.

### ACKNOWLEDGEMENTS

The authors would like to thank the operators of the facility, Brad Slater and Sheldon Speedie, for their methodical approach to running the equipment and collection of data. The authors would also like to recognize the efforts of Riad Al-Samadi and Gabe Nicolaides from OPG’s Chemistry, Metallurgy & Welding Department, and Joe Green from Zenon Environmental, for their invaluable assistance during re-commissioning of the facility.

### REFERENCES

1. Evans, D.W., Solaimani, H.M., Garamszeghy and Stott, J.B., “Treatment of Steam Generator Chemical Cleaning Wastes: Development and Operation of the Bruce Spent Solvent Treatment Facility”, Proceedings of the Fifth International Symposium on Chemical Oxidation: Technology for the Nineties, Nashville, Tennessee, February 15-17, 1995.
2. Al-Samadi, R., “Reverse Osmosis Membrane Treatability Tests on Pickering’s Unit 6 Hot Boiler Chemical Cleaning Wastes, Final Report”, OPG Report 06116-REP-79590-00001-R00, September 2002.
3. Al-Samadi, R., “Effluent Treatment Strategy and Supporting Technical Documents for Recommissioning of SSTF’s UF/RO System”, OPG Report 06116-REP-79550-00001-R00, August 2002.
4. Sen Gupta, S., Slade, J.A., “Membrane Treatment of Radioactive Waste Liquids”, Ultrapure Water, Tall Oaks Publishing Inc., November 1993.
5. Sen Gupta, S., Slade, J.A. and Tulk, W.S., “Integrated Plant for Treatment of Liquid Radwaste”, Ultrapure Water, Tall Oaks Publishing Inc., November 1995.
6. Amjad, Z., “Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications”, pp. 5, 1993.
7. Smee, J.L., “Chemical Cleaning of the Pickering Unit 8 Boilers Using the Framatome ANP High Temperature Process – Final Report”, OPG Report NK30-REP-36330-00013-R00, 2002.

**Table 1. Typical Solvent Parameters at the End of the HTCC Process  
(Pickering Unit 8, 2002)**

<b>Parameter</b>	<b>Iron Solvent</b>	<b>Copper Solvent</b>
Total EDTA, g/L	80-100	N/A
Free EDTA, g/L	2-5	N/A
Hydrazine, g/L	0.01	N/A
pH	8	10
Copper, g/L	-	3
Iron, g/L	12	N/A
Nickel, g/L	4	0.2
Zinc, g/L	1	N/A
Hydrogen Peroxide	N/A	-
Total EDA, g/L	N/A	12
Free EDA, g/L	N/A	5
Guanidine, g/L	N/A	20
Iron Solvent Volume, m <sup>3</sup>	174	
Copper Solvent Volume, m <sup>3</sup>	181	
Rinse Volume, m <sup>3</sup>	1005	
Total Volume, m <sup>3</sup>	1360	

**Table 2. UF System Operating Parameters**

<b>Parameter</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Average</b>	<b>Standard Deviation</b>
Feed Temperature, °C	10	27	19	3
Membrane Inlet Pressure, kPa	344	595	406	66
Differential Pressure, kPa	197	298	268	16
Permeate Flow, L/min	75	189	128	26
Permeate Flux – Temperature Normalized to 20 °C, LMD <sup>1</sup>	847	2233	1608	365
Membrane Permeability – Temperature Normalized to 20 °C, LMD/kPa	2.6	12.9	7.5	3.0
Concentrate Flow, L/min	3114	3976	3744	149
Permeate Turbidity, NTU	0.02	0.16	0.06	0.03
Instantaneous Volumetric Recovery, %	1.9	4.8	3.3	0.6

Notes:

1. LMD – L per m<sup>2</sup> of membrane surface area per day.



**Table 3. 1<sup>st</sup> Pass RO Operating Parameters**

<b>Parameter</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Average</b>	<b>Standard Deviation</b>
Feed Temperature, °C	21	31	26	2.5
Membrane Inlet Pressure, kPa	4314	6894	5601	632
Differential Pressure, kPa	116	515	294	62
Permeate Flow, L/min	137	247	183	30
Permeate Flux – Temperature Normalized to 20 °C, LMD <sup>1</sup>	194	391	270	50
Membrane Permeability – Temperature Normalized to 20 °C, LMD/kPa	0.030	0.089	0.051	0.014
Concentrate Flow, L/min	253	341	289	17
Permeate Conductivity, µS/cm	12	1401	430	346
Conductivity Rejection, %	96	99	98	1
Instantaneous Volumetric Recovery, %	29	49	39	5

Notes:

1. LMD – L per m<sup>2</sup> of membrane surface area per day.

**Table 4. 2<sup>nd</sup> Pass RO Operating Parameters**

<b>Parameter</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Average</b>	<b>Standard Deviation</b>
Feed Temperature, °C	23	35	28	2.5
Membrane Inlet Pressure, kPa	2675	3661	3212	259
Differential Pressure, kPa	792	1353	1159	133
Permeate Flow, L/min	98	148	129	13
Permeate Flux – Temperature Normalized to 20 °C, LMD <sup>1</sup>	295	550	433	60
Membrane Permeability – Temperature Normalized to 20 °C, LMD/kPa	0.120	0.213	0.169	0.021
Concentrate Flow, L/min	33	40	37	2
Permeate Conductivity, µS/cm	1	324	99	83
Conductivity Rejection, %	82	100	93	4
Instantaneous Volumetric Recovery, %	72	81	78	2

Notes:

1. LMD – L per m<sup>2</sup> of membrane surface area per day.

**Table 5. Typical Contaminant Feed and Permeate Parameters and Contaminant Rejection Efficiencies**

<b>Parameter</b>	<b>UF Feed</b>	<b>UF Permeate</b>	<b>1<sup>st</sup> Pass RO Feed</b>	<b>1<sup>st</sup> Pass RO Permeate / 2<sup>nd</sup> Pass RO Feed</b>	<b>2<sup>nd</sup> Pass RO Permeate</b>	<b>UF Rejection (%)</b>	<b>1<sup>st</sup> Pass RO Rejection (%)</b>	<b>2<sup>nd</sup> Pass RO Rejection (%)</b>	<b>Overall RO Rejection (%)</b>	<b>Overall System (UF/RO) Rejection (%)</b>
pH	9.0	9.0	8.4	7.7	8.1	-	-	-	-	-
NH <sub>3</sub> , mg/L	565.45	560.80	3256.72	295.83	36.97	0.82	90.92	87.50	98.86	93.43
TDS, mg/L	6232	5395	33485	888	52	13.43	97.35	94.14	99.84	99.17
Turbidity, NTU	107	0.07	-	-	-	99.93	-	-	-	-
COD, mg/L	1100	1100	6100	10.3	<1.0 <sup>1</sup>	Nil	99.83	90.29 <sup>2</sup>	99.98	99.91
Cu, mg/L	171.6	143.2	942.4	6.52	0.38	16.55	99.31	94.17	99.96	99.78
Fe, mg/L	130.2	108.5	653.9	4.19	0.27	16.67	99.36	93.56	99.96	99.79
Ni, mg/L	81.92	73.27	472.8	3.16	0.20	10.56	99.33	93.67	99.96	99.76
Zn, mg/L	11.16	10.95	60.02	0.37	0.026 <sup>1</sup>	1.88	99.38	92.97	99.95	99.73
H-3, Bq/L	20000	18000	20100	20000	20000	-	-	-	-	-
Co-60, Bq/L	2.91	2.43	15.0	<0.5 <sup>1</sup>	<0.5 <sup>1</sup>	16.49	96.67 <sup>2</sup>	- <sup>3</sup>	96.67 <sup>2</sup>	82.82 <sup>2</sup>
Cs-137, Bq/L	0.59	0.57	3.75	<0.5 <sup>1</sup>	<0.5 <sup>1</sup>	3.39	86.67 <sup>2</sup>	- <sup>3</sup>	86.67 <sup>2</sup>	15.25 <sup>2</sup>

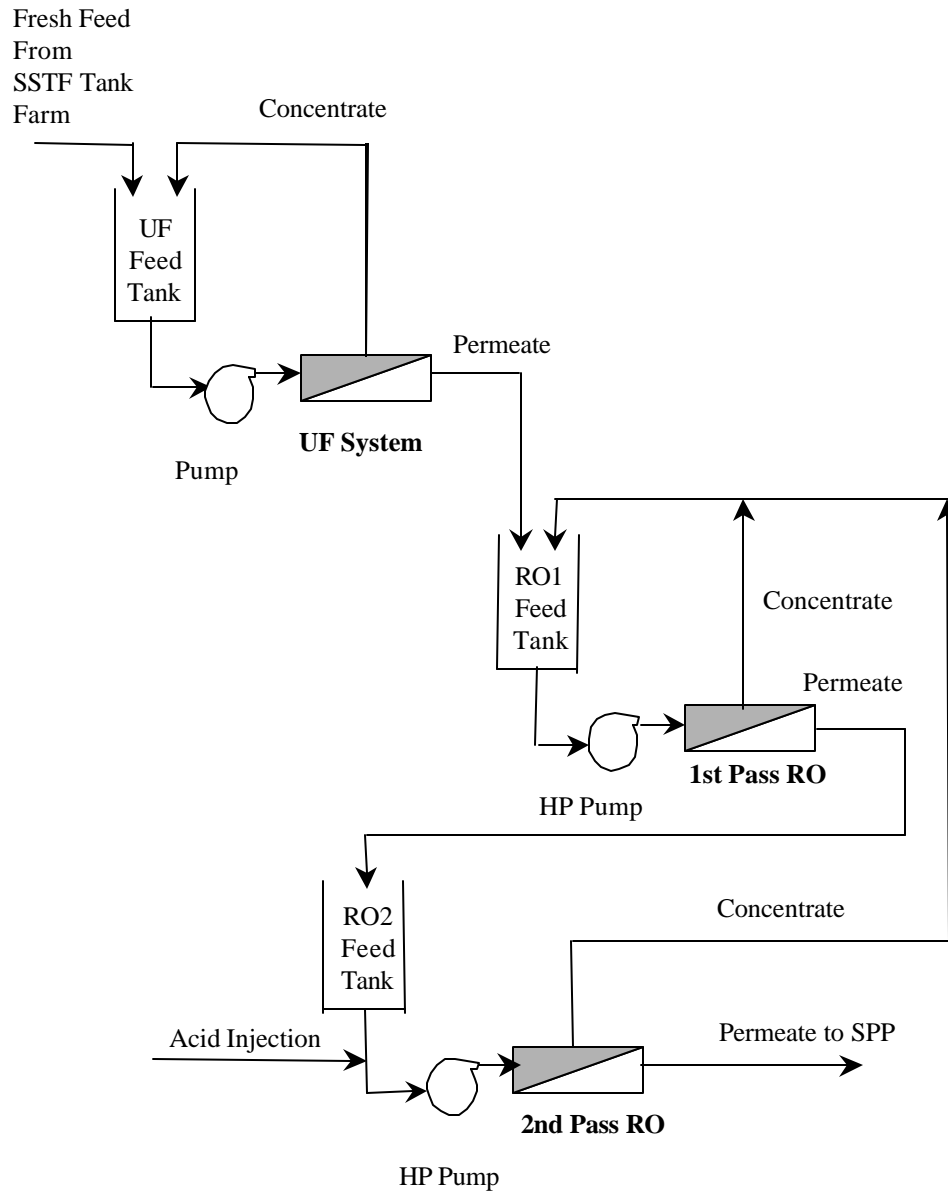
Notes:

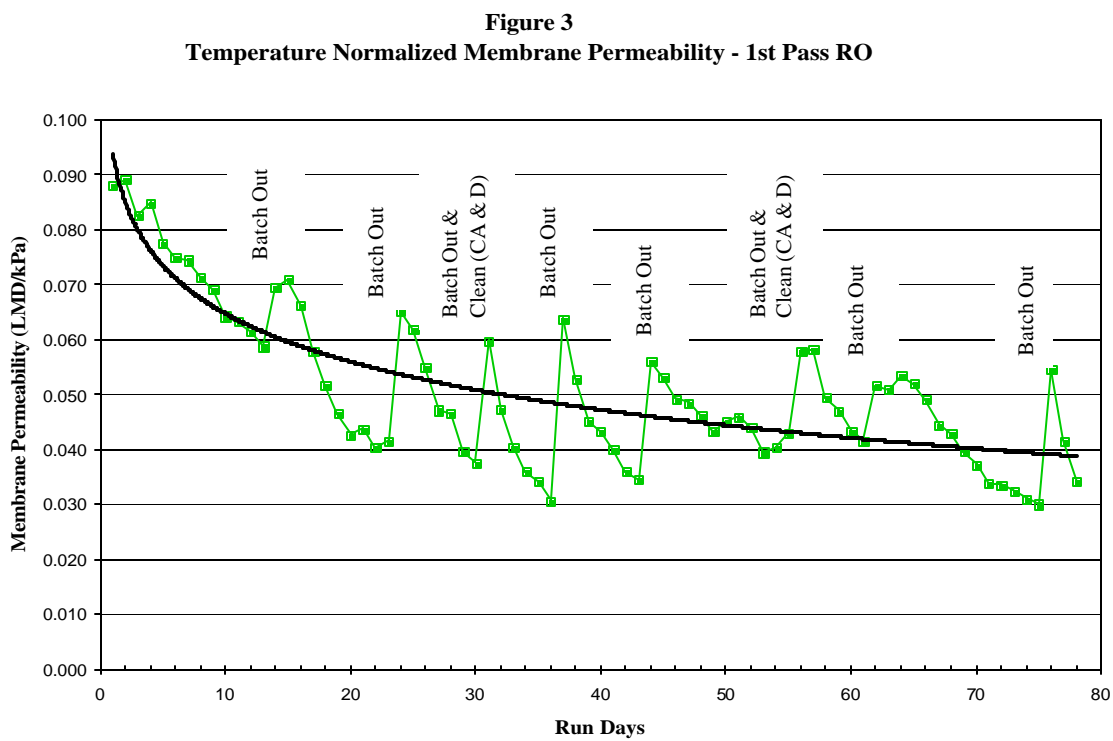
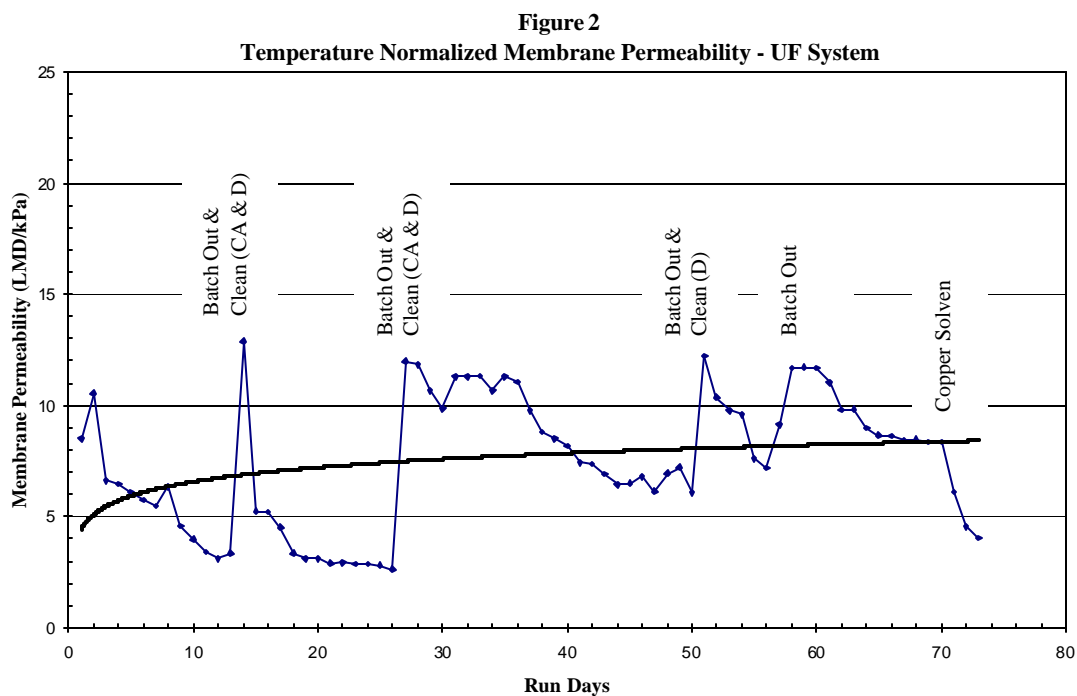
1. Approximate minimum detection limit.
2. Rejection efficiency calculated with a permeate value less than the minimum detection limit.
3. Rejection efficiency could not be meaningfully calculated as both the feed and permeate values were below detection limits.

**Table 6. Comparison of 2nd Pass RO Permeate Discharge to Site Sewage Processing Plant (SPP)  
Influent Criteria**

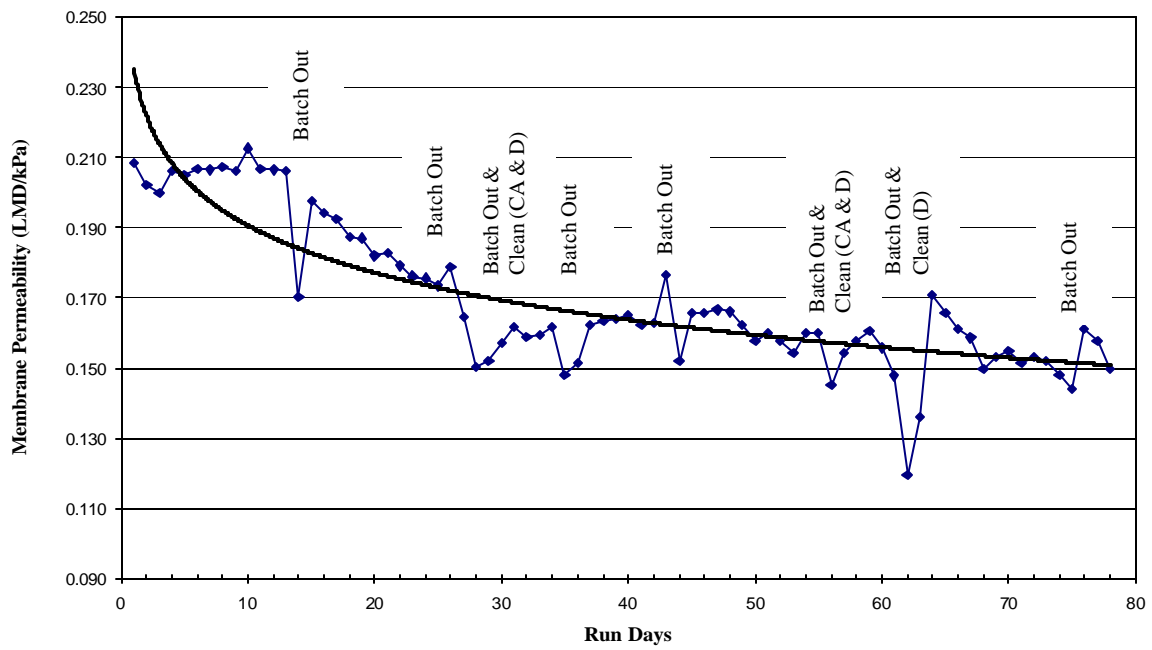
<b>Parameter</b>	<b>Units</b>	<b>Influent Criteria To SPP</b>	<b>Measured Value</b>
pH	-	6.5 – 9.5	8.1
COD	mg/L	300	0.09
Ammonia	mg/L	300	37.0
Copper	mg/L	3	0.38
Iron	mg/L	15	0.27
Nickel	mg/L	3	0.20
Zinc	mg/L	3	0.03

**Figure 1. Simplified SSTF UF/RO System Flowsheet**

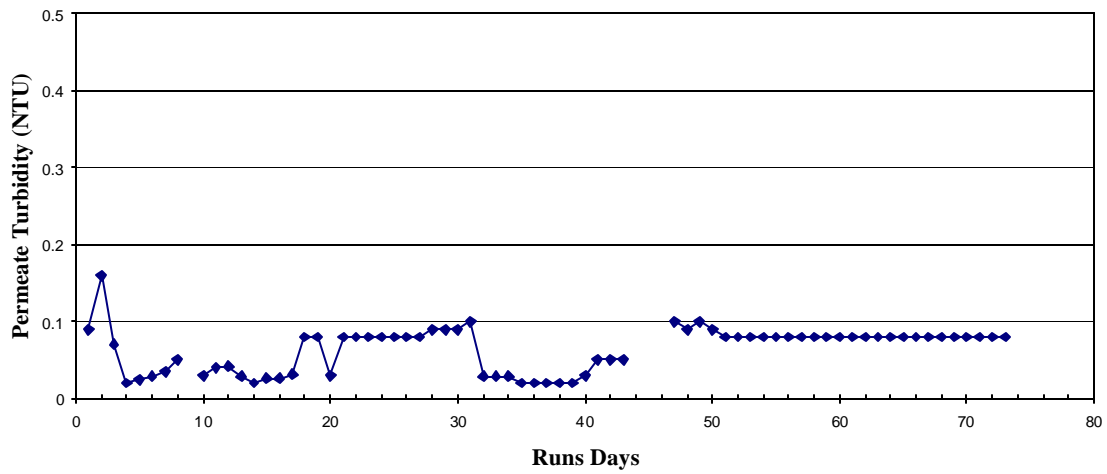




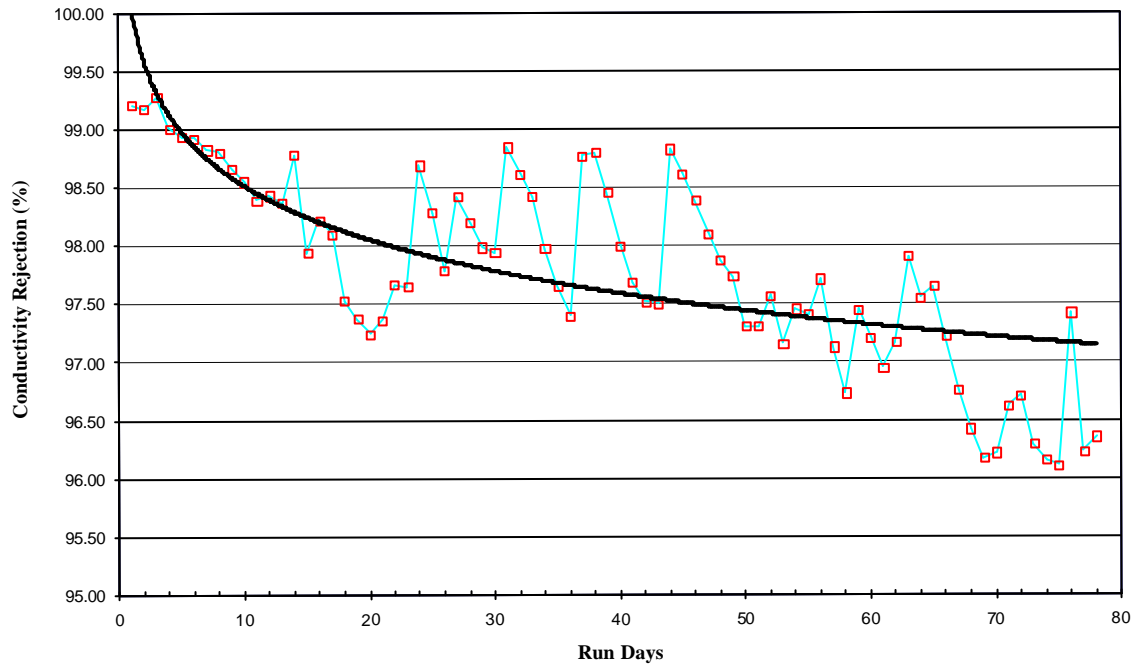
**Figure 4**  
**Temperature Normalized Membrane Permeability - 2nd Pass RO**



**Figure 5**  
**Permeate Turbidity Profile - UF System**



**Figure 6**  
**Conductivity Rejection - 1st Pass RO**



**Figure 7**  
**Conductivity Rejection - 2nd Pass RO**

