

A High Recovery Membrane Process for Purification of Low-Level Radioactive Liquid Waste

Riad Al-Samadi¹, Ram Davloor², Bill Harper³

¹Ontario Power Generation, Pickering, Ontario

²Bruce Power, Tiverton, Ontario, Canada (ram.davloor@brucepower.com)

³Bruce Power, Tiverton, Ontario, Canada

Abstract

An advanced Active Liquid Waste Treatment System (ALWTS) was designed and placed in-service at the Bruce Nuclear Generating Station “A” in 1999. As part of this unique system, an innovative high recovery reverse osmosis system (ROS) was installed to concentrate the contaminants into a small retentate stream that can be processed on-site or sent off-site for disposal. The permeate is discharged to the lake. The overall permeate recovery of the system is greater than 98%. This patented system, which saw its first commercial application at the station, has now operated continuously for over thirteen years. It has enabled the ALWTS to consistently produce high quality effluent that exceeds environmental discharge limits. This paper discusses the high recovery membrane process, its unique design features aimed at minimizing the volume of rejects, its separation performance and operating history.

1. Introduction

Bruce Nuclear Generating Station “A” (Bruce A), operated by Bruce Power, is located on the shore of Lake Huron approximately 250 kilometers northwest of Toronto. Bruce A is a 4-unit CANDU generating station with a combined generating capacity of 3,200 megawatts. All four units were originally placed into commercial service between 1977 and 1979. Bruce A generating units were placed in a “lay-up” state in the latter half of 1997 and early 1998. Two of the four Bruce A units were restarted in 2004, and the remaining two units were restarted in 2012. The Active Liquid Waste Treatment System (ALWTS) at Bruce A processes low-level radioactive wastewater generated from the various station systems and the “Plastic Suits” laundry facility. The Plastics Laundry facility at Bruce A was expanded in early 2000 in order to clean plastic suits from the two other Ontario Power Generation Nuclear Stations (Pickering and Darlington), in addition to those from the Bruce site.

The Bruce A ALWTS is a complex, multi-stage membrane-based system designed to treat and purify wastewater containing radioactive and conventional contaminants and produce a treated effluent that can be discharged safely to the environment. The ALWTS system was built in response to the stringent limits for conventional chemicals in effluent streams that were set by the Province of Ontario under the Municipal-Industrial Strategy for Abatement (MISA) Regulation 215/95. The six chemistry parameters for which stringent discharge limits must be met are the pH, Total Suspended Solids (TSS), Phosphorus, Iron, Zinc and Total Oil and Grease (TOG). A more restrictive MISA criterion that must be met, however, is that the treated effluent must be non-toxic, as determined by regulatory aquatic toxicity testing (viz. 4-day Rainbow Trout and 2-day *Daphnia magna*). Prior to commitment to the

project, extensive testing was performed to determine the chemical and radiological characteristics of the ALW, and to determine which parameters might cause toxicity in the receiving waters. No single cause of toxicity could be found. The concentration of contaminants in the ALW effluent was found to vary significantly. For this reason, it was decided that an “end-of-pipe” full treatment solution would be implemented; all contaminants (with the exception of tritium) would be removed from the ALW effluent before discharge.

Two constraints imposed on the project were that only existing, available building floor space could be used, and that the treatment process would not require utilities that exceeded the capacity of the existing station services. There was insufficient floor space to accommodate conventional process solutions, which would require several large evaporators, combined with other unit operations such as chemical precipitators and low recovery membrane-based systems. The proposed solution was to implement a membrane process that used a very high recovery Reverse Osmosis System (ROS) [1]. Within the ROS system, contaminants would be successively concentrated as the wastewater progressed through the process. The “small volume” solids-rich concentrated stream would then be processed through a single evaporator that encapsulated the solids in bitumen. The final solidified waste form would be acceptable for storage at on-site radioactive waste storage facilities.

The high-recovery membrane-based ROS system was built by an external vendor beginning in 1995. The system was installed at Bruce A and commissioned in 1998-1999. This paper provides a detailed review of the features and benefits of this advanced ALW treatment process, its evolution at Bruce A, the operating and maintenance experience and challenges encountered during the past 13 years of operation.

2.0 Patented High Recovery ALWTS Process Description

2.1 Introduction

The collection and discharge tanks of the ALWTS process are located in the main powerhouse. The treatment process, consisting of the Pre-treatment System, the ROS system and the wiped film Evaporator-Solidification System (ESS) is located in a separate building, the Ancillary Services Building (ASB). A pipeline to and from the ASB connects the collection and discharge tanks to the treatment system. Figure 1 provides an overview of the main systems in the ALWTS process [2]. Wastewater is collected in the station’s collection tanks. The collection tanks are part of the Collection and Discharge System. The wastewater is then pumped to a Pre-treatment System, which removes contaminants such as suspended solids, oils, greases, and insoluble heavy metals and produces an effluent that meets the feed specification of ROS. Effluent from the Pre-treatment System is processed through the ROS.

The ROS treats and purifies the active liquid waste (ALW) by removing > 95% of the soluble organic and inorganic contaminants, including heavy metals that exhibit aquatic toxicity (e.g. copper, zinc, iron, aluminum), radionuclide (cobalt, cesium, if present), hardness ions (calcium and magnesium), silica, nitrogen compounds and sulphur compounds. These compounds are separated by passage through the RO membranes, producing purified effluent that meets all of the MISA chemistry and

toxicity criteria listed in Table 1. The ROS combines a 2-stage RO membrane system with chemical precipitation and clarification and an ultrafiltration membrane system. The entire ROS achieves a high recovery of 99%. It was developed by the main author of this paper in the mid 90's [3]. The high recovery process design concept was previously demonstrated only on a pilot-scale, so the Bruce installation was the first full-scale implementation of this process.

The concentrated reject stream from the ROS is processed through the Evaporation - Solidification System (ESS). A wiped film evaporator combines bitumen with the concentrated reject stream to encapsulate solids while the water is boiled from the reject stream inside the evaporator. This process has been used at various commercial nuclear facilities in the world, including the evaporation system installed and operated at Virginia Power's Surry Power Station [4].

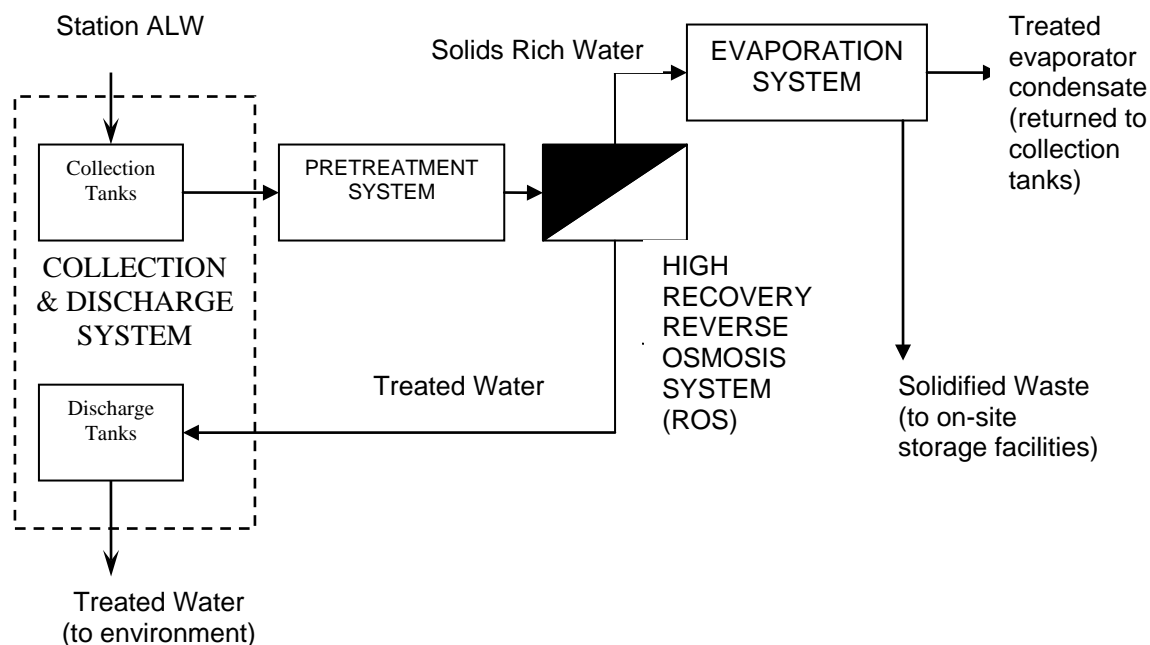


Figure 1: Schematic of Bruce A ALWTS Process

The treated wastewater is sent to the discharge tanks, which are part of the Collection and Discharge System. The wastewater is sampled and analyzed before being discharged to the environment.

2.2 Detailed Description of the ALWTS Process

2.2.1 Collection and Discharge System

As shown in Figure 2, four collection tanks, each with 100m³ working capacity, receive station liquid wastes. After a collection tank is full, it is recirculated and sampled to verify treatability by the ALWTS. Pre-treatment, including chlorine addition to reduce hydrazine levels, pH adjustment, and blending of batches between tanks, may be necessary. In some cases, process adjustments to the ALWTS may be required, e.g. adjusting the pretreatment system chemical addition dose rate. If tank

contents are acceptable for treatment, the tank is lined up to the ALWTS and the contents are pumped from the station to the ASB where it is processed by the ROS System.

The treated water is then returned to one of two discharge tanks, each with 100 m³ working capacity. The discharge tank contents are recirculated, sampled and analyzed before discharge to the lake. Using this process, approximately one discharge tank is normally treated and discharged every 24 hrs.

Table 1: Typical Discharge Water Parameters

Parameter	Typical	MISA Limit
pH	7.6	6.0 – 9.5
Total Suspended Solids	< 0.44 mg/kg	21 mg/L
Phosphorus	0.015 mg/kg	1 mg/L
Iron	0.01 mg/kg	3.0 mg/L
Zinc	0.004 mg/kg	0.5 mg/L
Oil & Grease	< 1 mg/L	13 mg/L
Toxicity (% Mortality, 48-hr <i>Daphnia</i>)	0	< 50
Toxicity (% Mortality, 96-hr Rainbow Trout)	0	< 50
Radiological Parameters	Typical	Admin Limit
Tritium (Ci/month)	350	1.06E+03
Gross Gamma (Ci/month)	1.6E-03	3.37E-03
Cs-137 (Ci/week)	8.6E-05	3.80E-04
C-14 (Ci/month)	1.4E-03	1.40E-01

2.2.2 Pre-treatment System

An innovative pre-treatment process was developed by Bruce A station staff together with Colloid Environmental Technologies Company (CETCO) to deal with the challenges encountered in achieving the required feed specification for the ROS membrane system [5]. The high concentration of surfactants in the wastewater from the Plastics Laundry operation resulted in excessive use of originally installed cartridge filters, which was very costly to the station. In addition, the 2-micron filters used could not produce filtrate that met the feed specifications of the ROS membranes. As a result, a rapid decline was observed in the ROS system performance.

The new process was installed in 1999 and has been in operation ever since. A schematic of this pre-treatment process is shown in Figure 2. The CETCO process is a 2-stage process that involves the addition of a proprietary chemical (bentonite clay, caustic soda and a cationic polymer), to the ALW feed stream. The chemical is added to the ALW stream under controlled mixing conditions to produce a large floc, which can be readily retained on the filter media. The clean water passes to a second stage where excess polymer is removed via the addition of a second, negatively charged clay-based

chemical. As shown in Table 2, filtered water from this second stage has a “15-minute Silt Density Index” (SDI₁₅) < 5 and turbidity < 0.2 NTU. The pre-treated ALW is then passed through a final 6-micron polishing cartridge filter before introducing it into the ROS membrane system.

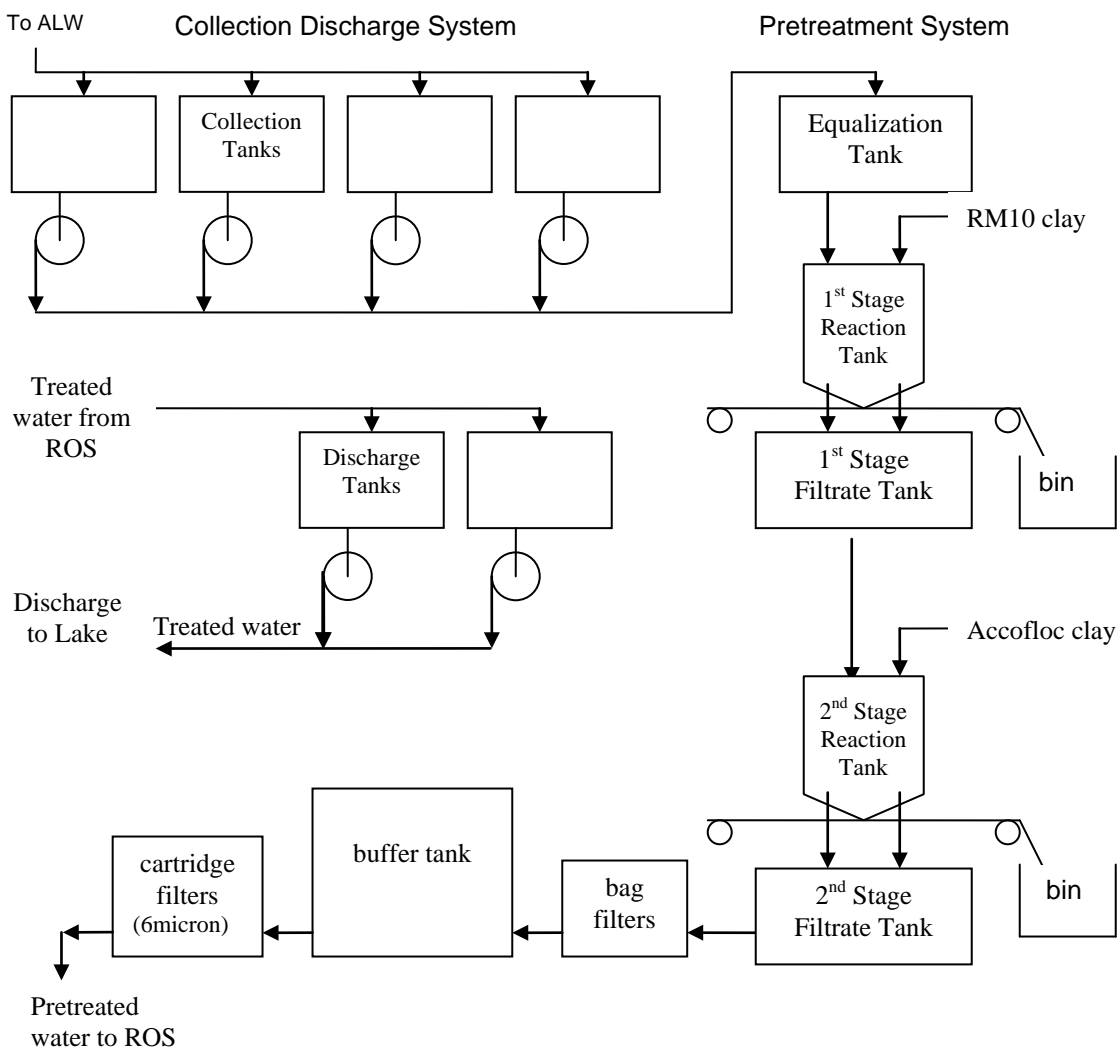


Figure 2: ALW Collection and Discharge System and Pre-treatment System

2.2.3 High Recovery Reverse Osmosis Process (ROS)

As shown in Figure 3, the membrane-based ALW purification process integrates the following four main subsystems in order to achieve its unique high permeate recovery objective:

- Primary (first stage) Low Pressure Reverse Osmosis membrane unit (RO1);
- Second Stage High Pressure Reverse Osmosis unit (RO2);
- Chemical Precipitation Softening Reaction / Clarifier Systems;

- Ultrafiltration membrane system (UF) to separate residual suspended solids from the clarifier supernatant.

100% redundancy is provided for the first stage (RO1), second stage (RO2) and UF membrane systems.

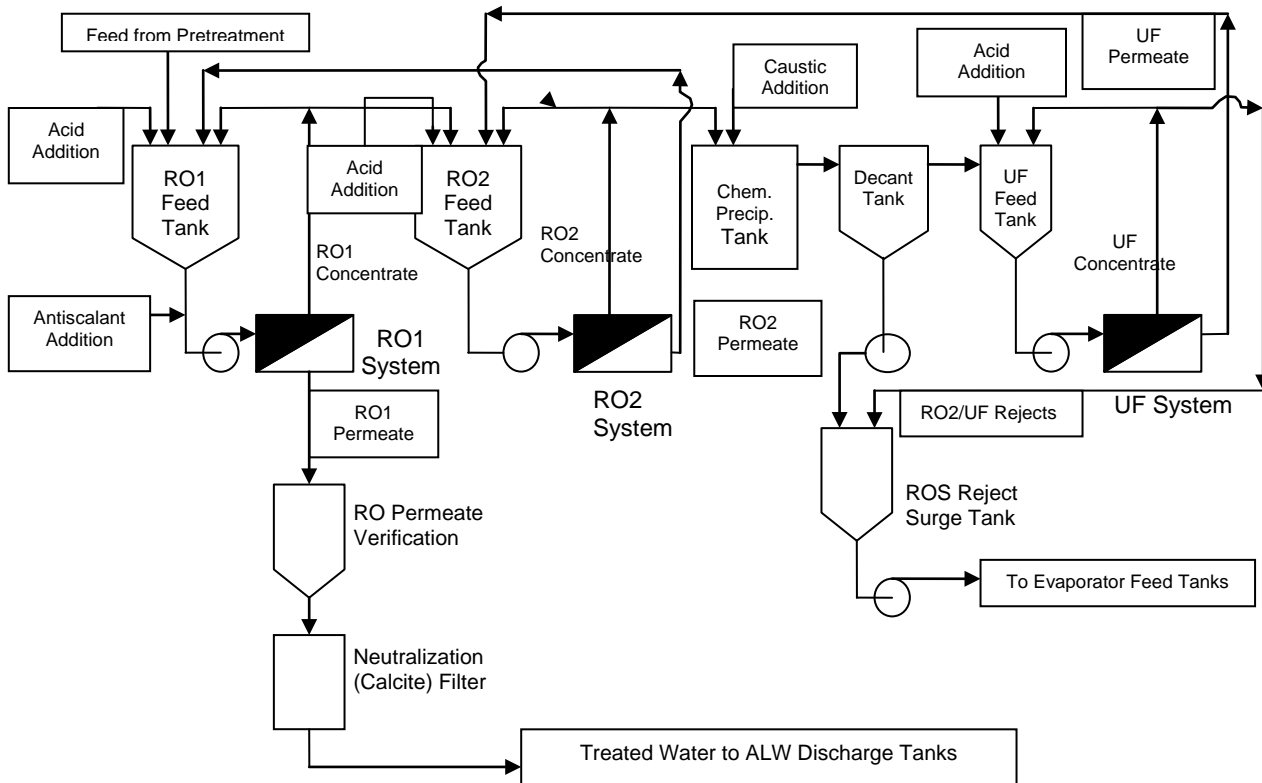


Figure 3: Simplified Diagram of Bruce A ALWTS ROS

Primary (First Stage) Reverse Osmosis Membrane Systems (RO1)

Pretreated ALW wastewater from the CETCO pre-treatment system is introduced into the RO1 system feed tank where it is further preconditioned by adding sulphuric acid to adjust the pH to achieve the pre-treatment criteria specified in Table 2. A polymeric antiscalant is also added to further reduce the scale potential and prevent formation of calcium sulphate and silica scale on the RO1 membrane surface.

The first stage RO1 membranes reject (i.e. separate) the soluble ionic and non-ionic contaminants with ion separation efficiency of 99.0% - 99.5% at standard temperature, to produce a ‘clean’ permeate stream that is suitable for discharge, and a concentrate stream that is concentrated further in the downstream, second stage RO2 system, Reaction/Decant Tank and UF systems.

The RO1 system is comprised of five (5) 8-inch diameter (i.e. 0.2 m dia) membrane pressure vessels, each containing two (2) 8-inch dia x 40-inch long (i.e. 0.2 m x 1.0 m) spirally wound ‘Brackish Water’ type RO membrane elements (i.e. a total of ten (10) 8-inch BW RO elements). The RO1 system’s BW RO membranes are thin film composite, chemically stable polymeric membranes which can be operated over a wide range of pH in the range 3 - 10, and at pressures of up to 600 psig or 4,140 kPa. The normal operating pressure is in the range 300 - 400 psig (i.e. 2,070 – 2,480 kPa). As shown in Figures 5, the RO1 membrane system is operated at a permeate recovery in the range 80% - 90%, i.e. producing RO1 concentrate having a flow rate in the range 10% - 20% of the influent raw ALW flow rate, to be processed by the second stage RO system.

Table 2: Typical ALW Wastewater & Pre-treated ALW Parameters

Parameter	Units	Raw ALW	Typical	Desired
Temperature	° C	13 - 22	13 – 22	< 25
pH		7.1 – 9.3	6.5 – 7.5	6.0 – 7.0
Turbidity	NTU	10 – 50	0.08 – 0.5	< 0.1
Suspended Solids (TSS)	mg/L	3.0 - 114	< 5	< 2
Silt Density Index		3.7 – 7.9	2.8 – 4.1	< 3
Conductivity	µS/cm	200 – 1000	< 1000	< 500
Total Dissolved Solids	mg/L	100 - 818	100 - 818	< 300
Iron	mg/L	1.0 – 23.0	0.02 - 0.4	< 0.1
Manganese	mg/L	0.08 – 0.18	< 0.1	< 0.1
Total Hardness	mg/L	30 – 120	30 - 120	< 150
Total Residual	mg/L	< 0.05	< 0.05	< 0.05
Total Organic Carbon	mg/L	2 – 32	2 – 32	< 10
Total Oil & Grease	mg/L	< 1	< 1	< 1
Dissolved Oxygen (DO)	mg/L	> 4.5	> 4.5	> 4.5

Second Stage Reverse Osmosis Membrane Systems (RO2)

The two 100% second stage high pressure RO systems (RO2) consist of a set of seven (7) 4-inch diameter membrane pressure vessels, each containing two (2) 4-inch dia x 40-inch long (i.e. 0.1 m x 1.0 m) spirally wound seawater (SW) type membrane elements (i.e. a total of fourteen (14) 4-inch SW RO elements). The RO2 membrane system is designed to operate at a pressure of up to 1,000 psig (i.e. 6,900 kPa), with a typical operating pressure range of 500 – 850 psig (i.e. 3,450 to 5,860 kPa).

The RO2 membranes reject soluble ionic and non-ionic contaminants from a combined stream consisting of the concentrate stream of RO1 system and the recycled concentrate from the RO2 system after removal of hardness, silica and other sparingly soluble compounds via chemical precipitation

softening, clarification and filtration. The SW RO membranes provide higher ion rejection efficiencies than the BW RO membranes (i.e. > 99.5%). Combined with RO1 permeate, the RO2 membrane system achieves an overall ROS process permeate recovery $\geq 98\%$ (Design Value: 99.1%), corresponding to an overall volume reduction factor ≥ 50 . In order to prevent calcium carbonate scale formation on the surface of the RO2 membranes, the blended feed to these membranes is conditioned further by adding acid to reduce the pH to 6 – 6.5. The RO2 membrane system is typically operated at a permeate recovery of approximately 60%, based on the combined feed flow which includes RO1 concentrate and softened RO2 concentrate recycle flow. As a result of the high overall ROS system product water recovery, the total concentration of soluble ionic and non-ionic compounds (i.e. Total Dissolved Solids, TDS) in the RO2 concentrate will be in the range 30,000 – 50,000 mg/L or 3% – 5%, depending on the TDS of the influent ALW.

Chemical Precipitation Softening System

The chemical precipitation softening step in Figure 3 continuously precipitates scale precursors including calcium and magnesium hardness, silica, iron oxides and other sparingly soluble compounds externally, downstream from the second stage RO membranes, as these compounds concentrate within the two RO systems.

As shown in Figure 3, the chemical precipitation tank is a fully mixed tank wherein the RO2 concentrate is blended with an alkali solution (e.g. sodium hydroxide) to achieve a precipitation pH of 10 - 11. The tank is sized to provide a sufficiently large retention time to affect the hardness, silica and iron oxide precipitation reactions.

The mixed slurry from the Chemical Precipitation Tank overflows into the conical bottom Decant Tank/Clarifier where sufficient retention time is provided to allow settling of the precipitated solids to the bottom of the conical bottom tank. Solids contacting in the Decant Tank/Clarifier is enhanced by recirculating the slurry externally around the bottom of the Decant Tank using an air-driven diaphragm pump. This also serves as a means to continue moving the inorganic slurry in order to prevent plugging of the bottom discharge lines. The air-driven diaphragm pump is also used to continuously transfer a small solids reject stream (i.e. 1% - 2% by volume based on raw ALW feed volume), from the bottom of the Clarifier/Decant Tank to the Evaporator-Solidification System for final volume reduction and disposal.

Ultrafiltration Membrane System

Before further permeate recovery can be achieved from the chemically softened RO2 concentrate, the softened, high TDS concentrate/supernatant from the Decant Tank/Clarifier must be filtered efficiently to remove all remaining suspended solids and fines that are carried over from the clarifier. As shown in Figure 3, the pH of the clarifier supernatant must first be lowered by adding acid to the ultrafiltration membrane system (UF) feed tank to “extinguish” the calcium carbonate precipitation reactions and reduce the scale potential of the supernatant.

The two 100% Ultrafiltration Membrane Systems include a set of eight (8) tubular membrane housings (4" dia. x 154" long, i.e. 0.1 m dia x 3.9 m long). Each of the eight membrane housings contains ZENON's 8-tube double ZPF-8 tubular membrane elements (12 feet or 3.66 m long). The UF membranes are operated at a pressure of up to 100 psig (700 kPa). The UF membranes provide complete separation of fine suspended solids down to < 0.05 microns, as well as removal of emulsified oils and other colloidal compounds (e.g. silica and iron oxides) in the Clarifier supernatant. The recycle flow through the chemical precipitation /clarifier train and UF membranes is typically similar in magnitude to the RO1 system concentrate and can be adjusted depending on the concentration of scale precursors in the raw (influent) ALW stream.

The UF membranes safely and efficiently separate any precipitated amorphous scale compounds and prevent them from accumulating on the RO2 membranes.

Auxiliary Equipment and pH Adjustment

The High Recovery Membrane Process requires adjustment of pH in a number of stages. A chemical feeder skid, designated Reaction and UF Chemical Feeder Skid is equipped with a day tank that has 93% sulphuric acid and a tank for 50% sodium hydroxide. These chemical feeding skids include metering pumps, valves and piping to allow the transfer of sulphuric acid to the RO1 and the UF systems and the transfer of sodium hydroxide to the Reaction Tank.

The RO1 feed pH is lowered to about 6.0 to 6.5 by adding sulphuric acid, in order to reduce calcium carbonate precipitation potential and prevent scale formation on RO1 membranes. Similarly, the RO2 feed pH is adjustment to 6.0 - 6.5 by adding sulphuric acid.

As pointed out earlier, the pH of RO2 retentate is raised to 10.0 - 11 using a 50% sodium hydroxide solution in order to precipitate CaCO_3 , $\text{Mg}(\text{OH})_2$, CaF_2 , SiO_2 , CaSO_4 , heavy metal oxides, etc., in the Reaction Tank.

After decanting the settled solids, the supernatant is pH adjusted to a neutral pH, in the range of 7-7.5 before the UF membranes using acid, in order to "extinguish" the scale forming reactions, thus completely preventing fouling and/or scale formation on the UF and RO2 membranes.

As discussed in section 1, the absence of aquatic toxicity from the treated ALW effluents must be verified before discharge, as part of MISA Ontario Regulation 215/95. To meet the toxicity criteria, the effluent must be non-toxic (i.e. < 50% mortality) to Rainbow Trout during a standard 96-hr toxicity test. The ALW effluent must also be non-toxic to *Daphnia magna* organisms (i.e. water flees) during a 48-hr test.

Following installation of the ROS-based waste treatment system, initial toxicity test results were not successful despite the high purity of the effluent (i.e. absence of contaminants). Subsequent laboratory-based toxicity testing showed that the ROS effluent water quality was too pure to support marine life, but this could be remedied by the re-introduction of low hardness (i.e. > 10 mg/kg as CaCO_3) into the water. As a result of this testing, a neutralization filter column was installed. This

unit contains a 2 – 3 ft layer of limestone, supported over a bed of gravel and fine sand, through which the RO permeate percolates, picking up hardness and alkalinity. Using this filter, hardness in the effluent is maintained at 20-50 mg/kg and has the additional benefit of buffering the pH of the effluent to meet the provincial discharge limits, as shown in Table 1.

After the Neutralizing Filter, the ALW is transferred to the final ALW Discharge Tank where its quality is monitored via detailed analyses to ensure complete compliance with the MISA chemistry and toxicity criteria before discharge.

Special Design Features of the ROS High Recovery Process

As the soluble organic and inorganic (ionic) compounds in the ALW become concentrated over the first stage RO and the second stage RO membranes, where concentration factors > 50 are encountered, the scale formation potential of calcium compounds (e.g. carbonate, sulphate, phosphate, fluoride, etc) is increased. Similarly, the silica scale potential and insoluble iron and other heavy metal oxide fouling potential are also increased. Any soluble, biodegradable organic compounds will also increase in concentration and in the absence of sufficient dissolved oxygen, will support anoxic/anaerobic biological activity which can be detrimental to the RO membranes. Furthermore, as the concentration of soluble ionic compounds increase, e.g. over RO2 membranes, there is more breakthrough of ions into the permeate streams. The following special design features have been incorporated into the ROS process to address these technical challenges:

- a. Addition of an effective polymeric antiscalant compound upstream of the RO1 membranes at low dosage in order to provide a safeguard against the possibility of crystalline scale formation on the RO1 and RO2 membranes. The antiscalant compound is rejected by the RO membranes and therefore it concentrates over the 2-stage membrane system and acts to prevent formation of “hard”, crystalline scale in the equipment downstream, and thereby facilitating acid cleaning of the reaction tank, clarifier, slurry pumps, piping and valves.
- b. The ROS process includes a unique feature involving the recycle of the low-scale UF permeate to the RO2 feed stream at a rate sufficiently high to prevent fouling and scaling of the high recovery RO2 membranes (i.e., by blending with RO1 concentrate and lowering the average concentration of the sparingly soluble salts to well below their saturation values). This continuous softening and recycle of RO2 concentrate enables the safe operation of the RO2 membranes at the highest available recovery, limited only by the osmotic pressure exerted by the completely soluble inorganic compounds (e.g. sodium chloride, sodium sulphate etc.).
- c. Furthermore, by placing the chemical precipitation softening step downstream from the RO2 membrane system, the precipitation equipment and UF membrane system will process a much smaller volume than if this equipment is placed upstream, at the front end, thus resulting in significantly lower capital cost. In addition, since the hardness, silica and other fouling/scaling compounds have been highly preconcentrated over RO1 and RO2 membranes, their chemical precipitation potential is enhanced.

- d. The design enables the operators to implement field adjustments of the low-hardness UF permeate flowrates to reduce the scale potential, should the hardness, iron and silica concentrations in the raw ALW feed increase beyond design.
- e. Since the TDS of the RO2 concentrate is high (i.e. 20,000 – 30,000 mg/L) due to the very high overall ROS permeate recovery of 98 - 99%, the RO2 permeate TDS will also be relatively high, i.e. 150 – 250 mg/L in spite of the high conductivity rejection of the seawater membranes used (viz. > 99.5%). This TDS is mostly due to passage of monovalent ions (i.e. sodium, potassium, chloride, etc), as well as small, unionized organic molecules. Although this ALW water quality is quite suitable for discharge, the permeate quality from RO2 is improved further by recycling to the first stage RO1 membrane system, to effect further purification, resulting in an overall RO1 (product) permeate TDS in the range 9 – 27 mg/L.

3. ROS System Performance and Operating Experience

3.1 Wastewater and Discharge Water Characteristics

Wastewater feed to the Bruce A ALW Collection and Handling system comes from a number of sources in the station. These sources include the active sumps located in the station, the vacuum building sump, the unit turbine area building sumps (Units 1-4), the Plastic Suit Laundry Facility sump (Unit 0), the Chemistry Laboratory, Fuel Handling Operations (including decontamination facilities) and the tanker unloading facility which provides a location for unloading of active liquid waste tankers transferred from various locations on site, into the Bruce A ALW system.

The relative amounts of water from each source can vary considerably, depending primarily on the number of process leaks on the reactor and turbine sides of the plant and the amount of Plastics Laundry being processed during outages. Wastewater collection rates must be carefully monitored and controlled to avoid stressing the capacity of the treatment system. Annual waste volumes collected and processed by the ROS for the period 2001 to 2011 are shown below in Figure 4.

Typical or average chemistry and radiological parameters for the water produced from the Bruce A ALWTS are summarized with their respective limits for discharge in Table 1. Removal efficiencies of 95% or greater are typical for the system. The MISA limits shown refer to the provincial regulatory limits for conventional parameters in discharges while the administrative limits for radiological parameters are derived from federal discharge regulations and are set internally to be well below the legal limits. As shown, the ROS system consistently produces water that meets all regulatory and Bruce Power administrative limits.

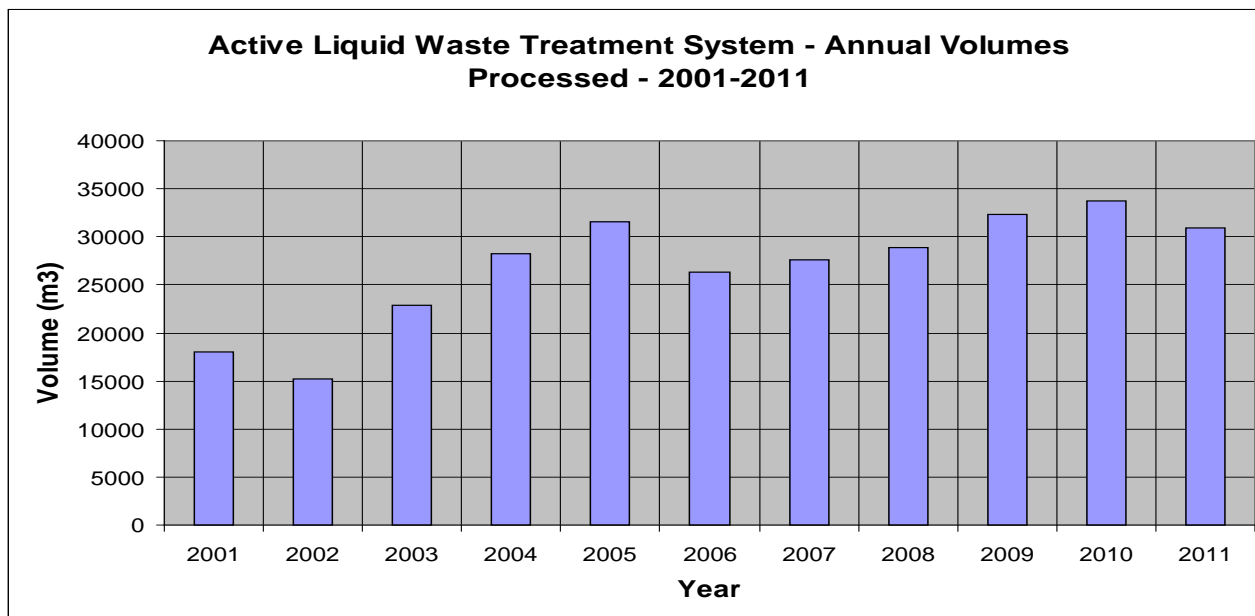


Figure 4: Annual Waste Volumes (m³) Processed through Bruce A ALWTS ROS

3.2 ROS System Performance Review

In any membrane application, the system’s throughput, i.e. the overall system’s permeate (or purified water) flowrate depends on the quality of the pretreated feedwater which is represented primarily by the feedwater’s turbidity, SDI₁₅ index and its TDS. Low turbidity (i.e. < 0.1 NTU) and low SDI₁₅ (i.e. < 3) ensure minimal surface fouling. Elevated turbidity and SDI on the other hand are indicative of colloidal and/or biological fouling, resulting in increased fouling of the membranes.

3.2.1 ROS System Permeate Recovery Profile

Based on a detailed assessment, the ROS system achieves an overall permeate recovery in the range 93% - 100%, with an average annual recovery of 98.0%. Table 3 shows the individual membrane system recoveries (i.e. RO1A, RO1B, RO2A, RO2B, UFA and UFB). The average annual RO1 system recovery was 87.5%, RO2 59.2% and the UF 97.0%. This means only 1% - 2% of the raw Influent ALW volume must be disposed of safely via ESS or offsite. While most of the ALW is treated by RO1, the RO2 system adds approximately 10% to the overall recovery.

Table 3. Average Monthly Membrane System Permeate Recovery (%)

Date	RO1A	RO1B	RO2A	RO2B	UFA	UFB	Overall
January 2000	N/A	83.8%	68.44%	62.96%	97.61%	96.02%	93.20%
February 2000	88.3%	83.5%	60.2%	N/A	N/A	98.1%	95.6%
March 2000	87.79%	N/A	64.89%	58.96%	98.31%	98.26%	98.96%
April 2000	87.39%	86.97%	65.14%	69.24%	97.18%	98.91%	98.79%
May 2000	89.01%	88.29%	61.93%	54.35%	95.69%	N/A	98.41%
June 2000	89.41%	83.19%	73.75%	52.19%	94.72%	N/A	98.48%
July 2000	88.01%	88.38%	59.76%	N/A	96.07%	100.00%	99.47%
August 2000	89.11%	NA	56.74%	56.47%	95.40%	NA	99.48%
September 2000	89.06%	NA	53.95%	57.06%	95.55%	97.40%	100.13%
October 2000	88.74%	88.41%	50.25%	52.67%	94.61%	97.77%	97.57%
November 2000	88.25%	NA	55.07%	49.83%	96.83%	98.28%	98.27%
Individual Membrane Train Permeate Recovery	88.5%	86.1%	60.9%	57.1%	96.2%	98.1%	98.0%
Overall Annual Average Permeate Recovery	87.5%		59.2%		97.0%		98.0%

3.2.2 ROS System Separation Performance

The concentrations of the main parameters of concern for the treated ALW are summarized in Table 1. These parameters include the MISA Chemistry parameters (i.e. pH, TSS, P, Fe, Zn and Oil & Grease). Table 1 shows that all of these parameters are well below their MISA discharge limits. This is achieved as a result of the high separation efficiencies of the ROS System’s RO membranes (typically > 95% rejections, even at the high system’s recovery of 98 - 99%). The RO membranes also form an effective barrier against all suspended matter, emulsified oil, etc. Furthermore, after passing the RO permeate through the calcite (i.e. neutralizing filter) column, the pH of the water is neutralized and its hardness increased to 30 – 50 mg/L as calcium carbonate, thus completely eliminating the toxicity of the discharged effluent and achieving 0% mortality on a consistent basis.

In addition to meeting the MISA chemistry and toxicity criteria, the ROS membrane system also achieves efficient separation of all heavy metals and radioisotopes, including aluminum, iron, copper, zinc, cobalt, cadmium, cesium, strontium, etc. Due to their higher atomic valence, these ions are rejected by the RO membranes with efficiencies > 99%, thus achieving decontamination factors on the order of 2-3 (i.e. 99.0 – 99.9%). The only radioactive parameter that cannot be separated is tritium, whose concentration is maintained well within the nuclear station’s emission guidelines.

3.2.3 ROS Scaling Issues

The greatest challenge facing the continued successful operation of the ALWTS has been the formation of scale in the membranes and sub-systems within the ROS where the wastewater contaminants are most concentrated. This condition arises from the tendency of calcium, primarily from service water entering the ALW collection tanks, to combine with the sulphate added as sulphuric acid to control pH in the ROS, to form insoluble calcium sulphate. Formation of this scale poses operational problems

with respect to fouling of instrumentation in the system (eg. pH probes), fouling of membranes, and scaling and flow reduction in system piping and heat exchangers.

The tendency for calcium sulphate fouling increased when the ROS was periodically operated in a so-called “sewering” mode. In the event that equipment downstream of the RO1 membranes is unavailable due to loss of redundancy from various maintenance issues (e.g. membrane failure/replacement, pump failure, etc.) the system can still be operated in a “sewering” mode by processing water through the RO1 membranes only. In this mode, clean effluent is produced for discharge while the RO1 concentrate is recycled back to the wastewater collection tanks. However, the pre-concentration of the dissolved contaminants in this manner ultimately results in increased osmotic loading and scaling potential in the system when this water is eventually processed.

The increased scaling potential in parts of the ROS has resulted in numerous operational issues over the years. Initially difficulties arose with level indication in the Reaction and Decant tanks due to formation of scale in the air bubbler level indication lines. Preventative maintenance routines were established to periodically remove the polyethylene liner added to the inside of tubing to more easily remove the scale and ensure accurate level indication. Significant scaling within the Reaction and Decant tanks also caused the loss the pH monitoring in the tanks due to complete fouling of the pH elements on occasion. Routines were subsequently developed to ensure regular checks were made on the condition and response of the pH probes and to perform periodic acid cleaning of the tanks to remove the excess scale.

Overall, the operational problems caused by formation of calcium sulphate in the ALWTS point to the importance of carefully monitoring and maintaining pH control in the ROS to avoid over addition of sulphuric acid, and to the importance of minimizing the amount of calcium entering the system by limiting or eliminating service water leaks at the source. The RO-2 membrane system’s operating pressure was reduced by increasing the RO1 system recovery, in order to reduce the fouling potential and the RO2 membrane replacement. The ROS System permeate recovery must also be controlled within design limits to guard against precipitation of calcium sulphate and other hardness compounds. Consideration will also be given to replacing the sulphuric acid with hydrochloric acid to eliminate the sulphate scaling problem. Alternatively, ion exchange softening of the RO2 concentrate should be considered in lieu of or in addition to the chemical precipitation softening step to reduce the scale potential and prevent fouling and scaling of downstream equipment and lines.

3.2.4 ROS pH Control Issues

As noted above, accurate pH monitoring and control in the ROS is essential to maintaining proper operation of the system. The addition of excess sulphuric acid to the system results in a higher scaling potential and probability of fouling critical components in the system, including the RO membranes. Attention is required to ensure that pH probes and acid metering pumps are checked routinely for proper operation and the Programmable Logic Controllers (PLC) are properly tuned to account for acid metering rates and the locations of the pH probes within the system.

Sulphuric acid is added as required to maintain optimum pH control at three stages in the ROS, including the RO1 feed tank, the RO2 feed tank, and UF feed tanks. The effect of excess acid added to the RO1 feed tank can be fairly minimal while the effect of excess acid on RO2 membrane performance can be severe. On occasion, RO2 membranes have been found to be completely plugged by scale as a result of an acid excursion caused by a malfunctioning of a pH probe or metering pump. In the UF sub-system, chronic pH control problems (e.g. cycling) caused by the lags between pH measurement and the acid addition location were improved by optimizing the delays time for acid pump operation.

3.2.5 ROS Membrane Replacement versus Cleaning

The ROS system was designed with a clean-in-place (CIP) capability to chemically clean membranes in all three stages of treatment to remove inorganic and organic foulants. Typical chemical cleaning steps include an initial high-pH alkaline cleaner to emulsify oils and high molecular weight polymers, proteins and biomass, followed by use of an acidic cleaner to dissolve inorganic compounds, including calcium carbonate, iron oxide, etc., followed by a final high-pH alkaline cleaning step to remove residual or loosened organic contaminants.

The waste from membrane cleaning requires a separate process for treatment of the potentially radioactive chemical waste thus generated. Originally, it was intended that this wastewater would be treated via the Evaporation-Solidification System (ESS) designed for treatment of the ROS concentrate stream. However, due to the large volume output from operation of the ROS, the frequency of membrane cleaning required and problems encountered with operation of the ESS due to calcium sulphate scale formation, the decision was made to replace rather than clean the membranes. This decision has been facilitated by the gradual decrease in the price of membranes, due to greater competition in the industry. In general, it is more practical and cost-effective in the nuclear industry to produce and safely dispose of and store low level solid waste than low level liquid waste.

3.2.6 Treatment of High Hydrazine and Iron Concentration in Wastewater

The ALW Collection Tanks contain water from a number of plant sources including leakage from water systems dosed with hydrazine for corrosion control. While the RO membrane rejection rate for hydrazine is typically 90% or better, the small amount passing through the membranes into the discharge tanks can pose toxicity concerns. To minimize the toxicity risk, procedures have been successfully implemented to minimize the hydrazine concentration in the collection tanks by addition of sodium hypochlorite to meet a target of < 1 mg/kg of hydrazine in the feed before RO treatment. To minimize potential adverse impacts of residual hypochlorite on the RO membranes, sodium metabisulphite may also be added if required.

Routine aeration of the ALW Collection Tanks has also been implemented in order to mitigate anaerobic microbial growth and minimize fouling due to iron oxide deposition on the membranes. Aeration oxidizes the iron so that it is more easily removed by the chemicals used in the Pre-treatment system. Elevated iron levels in the ALW wastewater have been effectively reduced to suitable RO influent levels (< 1 mg/L) through a combination of aeration and the RO Pretreatment system.

4. Conclusions

The following statements summarize the performance of the ROS high recovery ALW treatment process after more than 13 years of operation at the Bruce A nuclear station:

The ROS System continues to successfully treat ALW wastewater using a two-stage RO system, chemical precipitation softening unit, clarifier and UF membrane system.

The ROS system has delivered very high permeate recoveries ranging from 97.5% to 98.5%, compared to the maximum design value of 99.1%.

The quality of treated ROS membrane permeate sent to the Neutralizing Filters is very high, having a typical conductivity in the range 15 – 20 $\mu\text{S}/\text{cm}$ and a hardness of 3-5 mg/L as CaCO_3 . The treated membrane permeate readily meets all MISA parameters including the pH, TSS, total phosphorous, zinc, iron and Total Oil and Grease (TOG). After the Neutralizing Filters, the water is completely free from toxicity to Rainbow Trout and *Daphnia magna*. The pH of the final discharge is typically in the range 7.5 – 8 and the hardness is in the range 30 - 50 mg/L as CaCO_3 .

The total gamma levels in the Discharge Tanks range from 0.002 $\mu\text{Ci}/\text{kg}$ to 0.03 $\mu\text{Ci}/\text{kg}$ which are approximately two orders of magnitude (i.e. 99%) lower than their concentration in the ALW Collection Tanks (typically 0.25 $\mu\text{Ci}/\text{kg}$ – 1.0 $\mu\text{Ci}/\text{kg}$).

The concentration of heavy metals in the treated RO permeate including iron, copper, nickel, zinc, barium, manganese, chromium, mercury, lead, arsenic, antimony, selenium, cobalt, vanadium, beryllium, cadmium, molybdenum, silver and thallium were all below detection limits, with typical rejection efficiencies > 99%. The overall concentration of organic compounds as Total Organic Carbon (TOC), including Total Oil and Grease (TOG), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) in the RO permeate were all < 1.0 mg/L, confirming the RO membranes' high separation efficiencies of > 95% for large organic molecules such as the laundry surfactant, lubricating and hydraulic oils, water treatment polymers and polymeric scale inhibitor. These compounds cannot be separated effectively and consistently by any of the conventional coagulation/filtration and ion exchange processes.

Loss of accurate and reliable pH control resulted in increased sulphuric acid addition and calcium sulphate scale formation potential, leading to RO2 membrane fouling and premature replacement, plugging of lines feeding the ESS unit and loss of evaporator system. A preventative maintenance program was instigated, aimed at routinely inspecting, cleaning and calibrating the pH probes, optimizing the set-points to improve process separation performance, reduce chemical usage, reduce the TDS and improve the overall permeate recovery, and acid cleaning of the Reaction Tank and Decant Tank to improve system's availability.

5. References

- [1] R. Davloor, and R.S. Higgins. “Design Description Radioactive Liquid Waste System”, Bruce Power NK21-DD-79200, December 1993.
- [2] R. Davloor, B. Harper, D. Bastien and J. Rapley. “Commercial Implementation of an Innovative Multi-Stage Treatment System for Removal of Radiological and Chemical Contaminants to Near-Zero Levels, Proceedings of the 23rd Annual Conference of the Canadian Nuclear Society, Toronto, Ontario, Canada, 2008 June 1-4.
- [3] Al-Samadi, R., Benedek, A., “Micro-filtration Enhanced Reverse Osmosis for Water Treatment”; U.S. Patent No. 5,501,798; March 1996.
- [4] Halverson, W.C., “An Overview of Surry Radwaste Facility Operations”, *Nuclear Plant Journal*, July – August 1992, pp.50 – 54.
- [5] R. Davloor, R. and B. Harper. “Removal of Bulk Contaminants from Radioactive Wastewater at Bruce A Using a Clay-based Flocculent System”, Proceedings of the Waste Management, Decommissioning and Environmental Restoration for Canada’s Nuclear Activities Conference, Toronto, Ontario, Canada, 2011 September.