COMMERCIAL IMPLEMENTATION OF AN INNOVATIVE MULTI-STAGE TREATMENT SYSTEM FOR REMOVAL OF RADIOLOGICAL AND CHEMICAL CONTAMINANTS TO NEAR-ZERO LEVELS

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Abstract

The Bruce A Active Liquid Waste Treatment System (ALWTS) is a unique and innovative multi-stage treatment system whose function is to treat waste water containing low-level radioactive and conventional contaminants to meet stringent federal and provincial regulations. With the exception of tritium, there are near-zero waterborne emissions of radioactive and conventional contaminants to the environment. In a recent assessment, the World Association of Nuclear Operators (WANO) identified the ALWTS as an industry leading strength. A description of the system is provided, as well as a review of operating history, including a summary of achievements and operational challenges.

1. Introduction

The Bruce A Active Liquid Waste Treatment System (ALWTS) is a complex, multi-stage treatment system whose purpose is to process waste water containing radioactive and conventional contaminants and produce a treated effluent that meets all regulatory limits for discharge. With the exception of tritium, there are near-zero waterborne emissions of contaminants to the environment. Funding was released in 1991 to design and construct a treatment system that would process all waste water collected in the Active Liquid Waste (ALW) system at Bruce A. This was in response to anticipated stringent limits for conventional chemicals in waterborne waste water streams that were to be set by the Province of Ontario under the Municipal-Industrial Strategy for Abatement (MISA) program.

The most restrictive MISA parameter was that the treated waste water must be non-toxic, as determined by regulatory aquatic toxicity testing (rainbow trout, Daphnia Magna). Prior to the release of funds, the station performed extensive testing to determine characteristics of the ALW, and to determine what chemical and/or radiological parameters caused toxicity of the water. No single cause of toxicity could be found. The waste water was also found to vary significantly in composition of contaminants and their concentrations. 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 waste water before discharge.

Two constraints imposed on the project were that only existing building floor space could be used, and that the treatment process would not require utilities that exceed the capacity of the existing station services. There was not sufficient space to accommodate standard solutions that use 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 system that used a very high recovery Reverse Osmosis System (ROS) [1]. Within the ROS system, contaminants would be successively concentrated as the waste water progressed through the system. The 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.

Figure 1 provides an overview of the major systems in the ALWTS. Waste water is collected in the station's collection tanks. The collection tanks are part of the Collection and Discharge System. The waste water is then pumped to a Pretreatment System that removes contaminants such as oils, greases, and heavy metals and produces an effluent that is free of suspended solids. This clay-based flocculation process, unique in its application for ROS pretreatment, was developed by station staff in response to the difficulties encountered in achieving the required feed specification for the ROS system [2]. The high concentration of surfactants in the waste water from the Plastics Laundry operation resulted in an excessive use of cartridge filters during treatment (both uneconomical, and impractical for operation). In addition, the 0.45 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 ROS membrane performance.

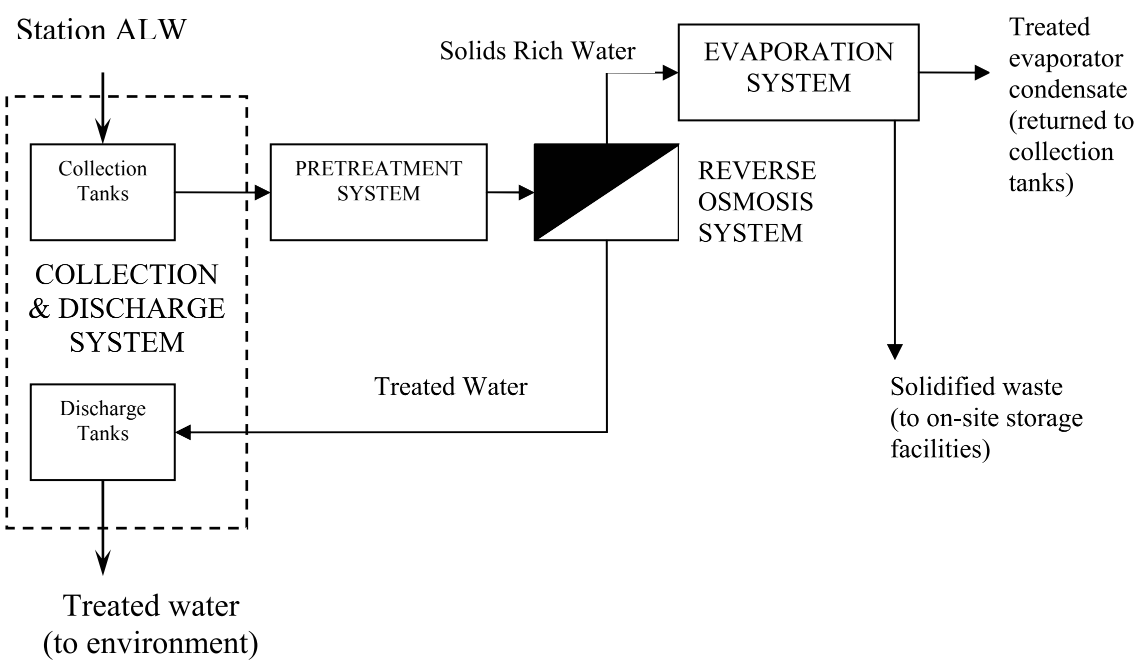

Figure 1: <u>Overview of Bruce A ALWTS</u>

Effluent from the Pretreatment System is processed through the ROS to remove dissolved impurities from the waste stream. The ROS is a three stage membrane system, with an intermediate chemical precipitation process, developed by Zenon Environmental [3]. The concept was previously demonstrated only on a pilot-scale level. Hence, the Bruce A installation was the first full-scale implementation of this process.

The concentrated waste stream from the ROS is processed through the Evaporation and Solidification System (ESS). Thin film evaporators, utilizing bitumen to encapsulate solids, have been used at commercial nuclear facilities in the world. A similar evaporation system is installed and operated at Virginia Power's Surry Power Station [4]. A later development at Bruce A allowed the use of an alternative cement-based solidification agent. The treated waste water is returned to discharge tanks, which are part of the Collection and Discharge System. The waste water is sampled and analyzed before being discharged to the environment.

Since 1998, the ALWTS has processed approximately 90,000 litres/day of a difficult-to-treat waste stream. With the exception of tritium, the system consistently produces near-zero discharges of radiological and conventional pollutants. Bruce A is the only CANDU commercial nuclear facility with such an "end of pipe" solution. In addition to the development, implementation and integration of several unique operations into a complex process, the station staff had to do significant troubleshooting and modifications, and develop operating and maintenance procedures and strategies to make this "first-of-a-kind" system work. In its 2007 assessment of Bruce Power nuclear facilities, WANO identified the Bruce A ALWTS as an industry-leading strength.

2. Active Liquid Waste Treatment System (ALWTS) Description

The collection and discharge tanks of the ALWTS are located in the main powerhouse. The treatment system, consisting of the Pretreatment, ROS and ESS systems, 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. Each major system in the Bruce A ALWTS is controlled by Programmable Logic Controllers (PLCs). The PLCs are integrated, and a single operator control area, with human-machine interface (HMI) displays and panels, allows operation of the various systems from one location.

2.1 Collection and Discharge System

A simplified diagram of the Bruce A ALWTS Collection and Discharge and Pretreatment systems is provided in Figure 2. Four collection tanks, each with $100m^3$ working capacity, receive station liquid wastes. After a collection tank is full, it is recirculated and sampled to verify treatability by the ALWTS. Pretreatment, including chlorine addition to reduce hydrazine levels, pH adjustment, and combining batches between tanks, may be necessary. In some cases, process adjustments to the ALWTS (e.g. pretreatment system chemical addition dose rate) may be required. 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. The treated water from the ALWTS is returned to one of two discharge tanks ($100m^3$ working capacity, each). The discharge tank contents are then recirculated and sampled/analyzed before discharge to the lake. Using this process, one discharge tank is normally treated and discharged each 24 hr period.

2.2 Pretreatment System

The ALWTS Pretreatment System incorporates the unique application of a commercial system to treat waste water before processing through reverse osmosis. The application, which was developed by station staff, deals with the problem of high amounts of surfactants in the Plastics Laundry effluent that would otherwise be difficult to pretreat for the ROS using traditional pre-treatment by chemical addition and filtration. The purpose of the Pretreatment System is to remove gross contaminants, such as oil and grease, total suspended solids, and iron from the waste water. The system consists of a 2-stage clarification process, followed by filtration through bag filters. Final polishing is by filtration through 6-micron cartridge filters to meet reverse osmosis feed specifications.

Waste water from the ALW collection tanks is transferred in batches to a feed equalizing tank. From this tank, water is pumped to a 4,500 L reaction vessel. A measured quantity (1 to 4 grams/L) of bentonite clay mixture (RM10) is metered into the reaction vessel. The clay is mixed, settled, remixed and resettled according to timed sequences. During this period, the clay releases chemicals to change the pH, release a cationic polymer, and attract charged particles. The clay hydrates and agglomerates into a floc to entrap particles. Oil and grease are also encapsulated. This method of pretreatment is effective even in the presence of laundry detergents, which otherwise make it difficult to remove the contaminants. The settled floc is separated by a 30-micron moving paper filter. The sludge on the paper is dewatered using press rollers, before being conveyed into a 2.5 cubic metre, rectangular, solid waste bin. A water-binding polymer is added to the bins to ensure there is no free standing water.

The filtrate is collected in the first stage filtrate collection tank. Water from this tank is pumped to the second stage reaction tank, where between 0.1 to 0.5 grams/L of bentonite clay (Accofloc) is metered into this tank while the tank contents are being mixed. The bentonite clay is formulated so that it removes excess cationic polymers from the RM10 clay material introduced in the first stage. Cationic polymers will foul the downstream reverse osmosis membranes. As in the first stage, a moving paper filter on a conveyor separates the settled floc from the water. The waste paper containing sludge is again discharged to a waste bin and a polymer is added to bind excess water in the sludge. The solid waste in the bins from the first and second stages has been tested and has been approved for storage at on-site radioactive storage facilities operated by Ontario Power Generation (OPG).

The water collected in the second stage filtrate collection tank is passed through 50-micron bag filters and transferred to an intermediary buffer tank. The buffer tank contents are pumped through pleated cartridge filters which have removal efficiency of 6-microns (absolute). The filtrate typically has a Silt Density Index (SDI) of less than 5 which meets the influent particulate specification for the reverse osmosis system. Alternately, testing has shown that a turbidity of less than 0.2 NTU consistently meets this SDI limit.

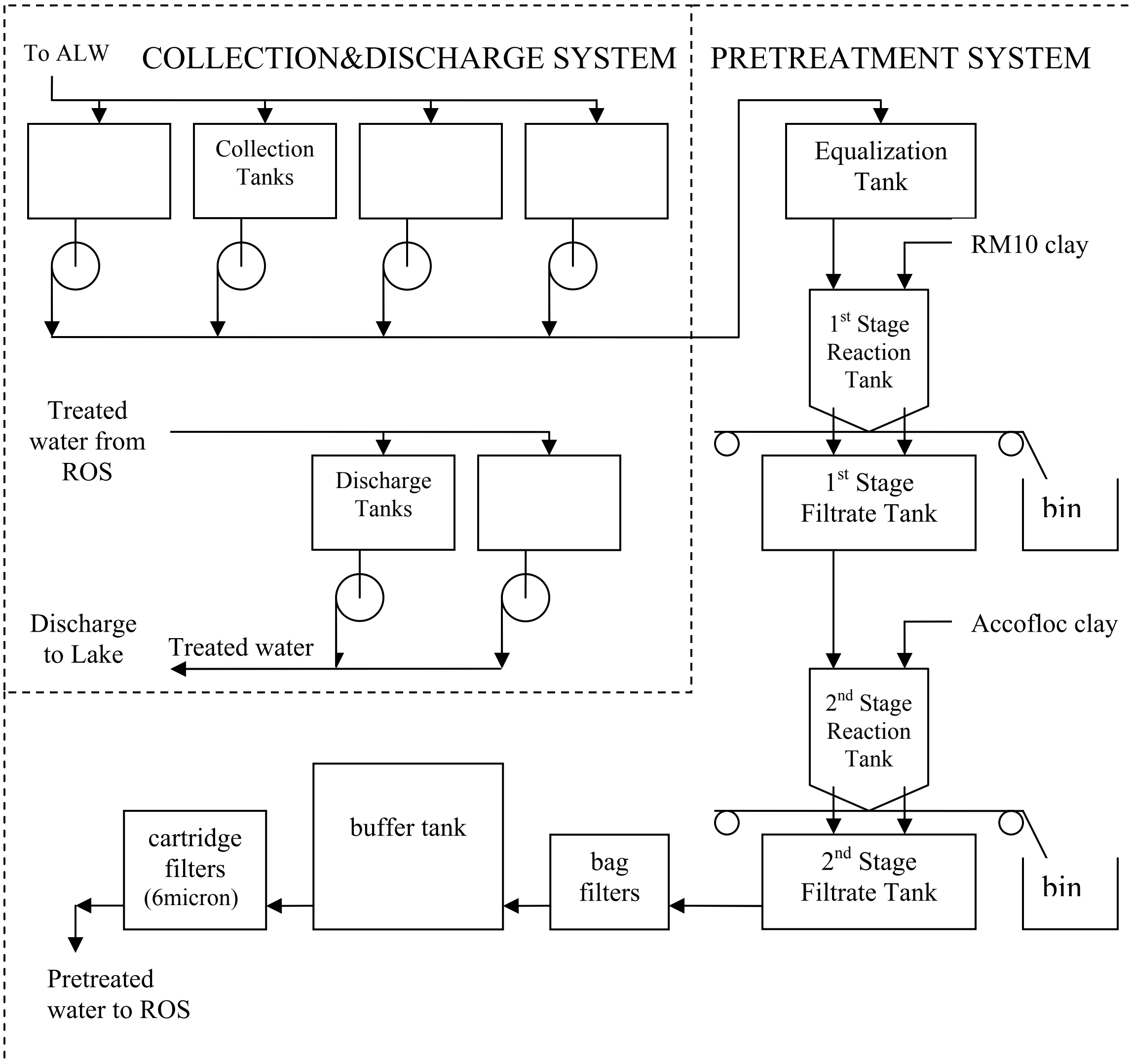

Figure 2: ALW Collection and Discharge System and Pretreatment System

2.3 Reverse Osmosis System (ROS)

The ROS is a unique system developed by Zenon Environmental. It is characterized by three membrane stages and an intermediate precipitation stage that produces a waste stream having high solids content suitable for further treatment by a single, relatively small capacity evaporator. The high recovery is accomplished within a small space footprint, and avoids the need for multiple evaporators. A simplified diagram of the ROS is provided in Figure 3.

The ROS removes dissolved solids from the influent received from the pretreatment system. It produces a treated water stream that eventually gets discharged to the environment via discharge tanks, and a solids-rich stream that goes to the evaporation system for further treatment. The ROS consists of the following subsystems: primary reverse osmosis units (RO-1); crystallizer ROS units (RO-2); reaction/decant (R/D) tanks; crystallizer ultrafiltration units (UF); a permeate verification tank; and a limestone softening bed. Each of RO-1, RO-2, R/D and UF have 2 x 100% capacity for redundancy. RO-1, RO-2, UF are also equipped with clean-in-place (CIP) tanks for cleaning membranes. The entire ROS processes water at approximately 3 L/s with an overall recovery of 99.0 to 99.2%. The very high recovery allows the feed solids, with typical Total Dissolved Solids (TDS) of 400 mg/kg, to be concentrated to 50,000 mg/kg.

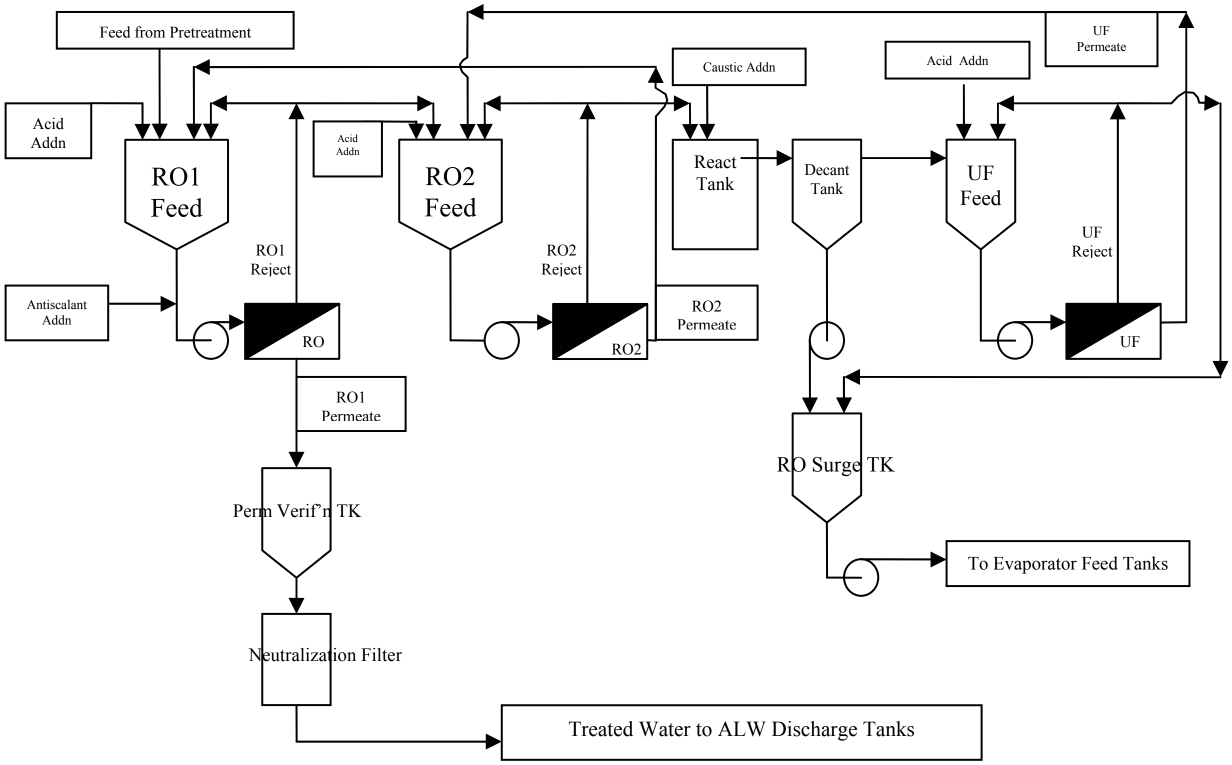

Figure 3: <u>Simplified Diagram of Bruce A ALWTS ROS</u>

Prior to entering RO-1, the feed stream is pH adjusted (sulphuric acid), followed by addition of antiscalant. The feed passes through a series arrangement of membrane housings, with permeate from each membrane housing collected in a common header. The reject stream becomes concentrated as it sequentially passes through each membrane housing. The permeate stream goes to the permeate verification tank. Approximately one half of the reject stream goes to RO-2; the other half is returned back to the RO-1 feed tank. This enriches the solids content within the entire ROS system, and results in overall high recovery.

RO-1 operates at 1500 to 2400 kPa, with a flow rate of approximately 280 L/min, and has a recovery of 60 to 65%. The RO-1 membranes are 8" diameter, thin film composite, spiral-wound membranes. Feed to RO-2 is first pH adjusted (sulphuric acid) in the RO-2 feed tank and then passes through membranes in parallel and series arrangements. RO-2 operates at 3,300 to 6600 kPa, with a flow rate of approximately 90 L/min, and recovery of 40 to 50%. The RO-2 membranes are 4" diameter, thin film composite, spiral-wound membranes. The RO-2 permeate stream is returned to the RO-1 feed tank. Approximately half of the reject stream goes to the reaction/decant system, while the other half is returned to the RO-2 feed tank. This configuration helps to increase the overall system recovery.

The reaction tank receives the reject stream from the RO-2 system. Sodium hydroxide added to this tank raises the pH to between 11 and 12. As the tank contents are mixed, the reaction tank contents are sent to the decant tank through an overflow line. The large residence time in the decant tank allows solids to precipitate and settle at the bottom of the conical tank, from which they are pumped to the RO surge tank. RO surge tank contents are eventually pumped to the evaporator feed tanks for further processing. The solids content from the bottom of the decant tank is between 50,000 and 100,000 mg/kg.

The final major unit operation of the ROS is the Ultrafiltration (UF) system. The supernatant from the decant tank must first be brought down to a pH of approximately 7.5 by the addition of sulphuric acid to the UF feed tank. The UF feed tank contents are then pumped through a parallel arrangement of UF membrane housings which operate at a pressure between 480 and 690kPa and a flow-rate of approx 12 L/min. The solids content in the retentate is between 25,000 and 35,000 mg/kg and the system has an average recovery of 95%. Membranes are 4" in diameter by 12 foot long, thin film composite, tubular type. The UF permeate is returned to the RO-2 feed tank. Approximately half of the retentate is directed to the ROS surge tank, while the other half is returned to the UF feed tank. After collecting the solids-rich stream from the decant tank and UF system, the ROS surge tank contents are pumped to the evaporator feed tanks. The solids concentration in the surge tank range as high as 50,000 mg/kg.

The process configuration, with all the recycle streams, is such that the treated water from the entire ROS is the permeate from the RO-1 system. This permeate has Total Dissolved Solids of less than 10 mg/kg and is remineralized slightly to ensure that the product will pass regulatory toxicity testing (MISA). To accomplish this, the contents of the permeate verification tank are passed through a Neutralization Filter, containing a bed of calcium carbonate, to bring the calcium level to between 10 to 20 mg/kg. The outlet stream from the calcium carbonate vessel is directed to the ALW discharge tanks.

2.4 Evaporation Solidification System (ESS)

A simplified diagram of the Bruce A ALWTS Evaporation and Solidification System is provided in Figure 4, below. The purpose of the ESS is to evaporate water in the stream received from the ROS, and immobilize the solids in either bitumen or a cement-based solidification media (Aquaset II). The solidified waste is transferred to on-site storage facilities. The ESS system consists of a feed system, an evaporator, a condenser, an off gas treatment system, and a polishing system.

The ESS is a batch process, as opposed to the Pretreatment and ROS systems; the ESS is only operated when the feed tanks become full. The Pretreatment and ROS systems operate every day. The evaporator can operate in concentration mode or bitumenzation mode. In concentration mode, the contents in the ESS feed tanks are raised from 0.5 wt% solids to between 8 and 15 wt%. In bituminization mode, the concentrated waste stream is combined with a bitumen emulsion stream (60 wt% bitumen, 40 wt% water). As the aqueous waste and bitumen emulsion streams travel down the evaporator, the water and volatile chemicals are driven off. Solids and molten bitumen exit from the bottom of the evaporator into 205 L drums. The bitumen and solids harden to form solidified waste. The solid waste has solids content between 20 and 35 wt%. Alternatively, concentrated waste in the ESS feed tanks can be drained by gravity from the ESS feed tanks directly into 2.5 m^3 waste bins to which a solidification agent, Aquaset II has been added, producing an approved solidification product.

There are two ESS feed tanks, each with a capacity of 17,000 L. Sulphuric acid or sodium hydroxide is added to precondition the feed. Tank contents are continuously mixed so that solids do not settle to the bottom and plug lines. A separate 36,000 L tank that holds the bitumen emulsion is outside the ASB. This tank is kept warm so that the water and bitumen components do not separate, and so that the mixture does not freeze in winter.

The evaporator is a thin film evaporator, consisting of an internal rotor with blades that sweep close to the heated surface. A thin film evaporator was chosen because of its suitability to process aqueous waste streams having high solids concentration and high foaming tendencies. Steam is fed to an annulus outside the inner evaporator surface to evaporate the waste feed. Feed rates to the evaporator are typically 350 L/hr in concentration mode, and 160 L/hr in bitumenization mode. In bitumenization mode, the bitumen and solids exit the bottom of the evaporator into a drum. The evaporator outlet valve automatically closes when a drum is full, and a new drum replaces the full drum. Handling of drums is done remotely, and is monitored by surveillance cameras. Contact gamma dose rate from drums are generally less than 50 mR.

A condenser and off gas system consists of a condenser, condensate holding tank, and off gas system. The condenser condenses the overhead vapour from the evaporator. The condensate passes through a bulk oil-water separator before being collected in the condensate holding tank. The oil originates from light fractions in the bitumen emulsion which are driven off during bitumenization. The exhaust from the condensate holding tank, vapours from the drum being filled, and other vented equipment in the system, are passed through the off gas system to remove non-condensable volatile contaminants and particles entrained in the vapour. The main components in the off gas system are the blowers and the particulate and activated carbon filters. The particulate filters are designed to remove entrained particles and the carbon filters to retain radioactive iodines and reduce emissions of volatile organic carbons. The treated gaseous effluent exhausts to the ASB active ventilation system and eventually discharges to the environment.

The condensate in the condensate holding tank is further treated to remove contaminants in the evaporator condensate. Two methods of treatment are available: centrifuge/UV-oxidation, and carbon/particulate filtration. With the centrifuge/UV-oxidation equipment, the centrifuge first separates oil droplets from the bulk aqueous stream before processing through the UV-oxidation equipment. Hydrogen peroxide is added to the influent stream, and the mixture is then exposed to a high intensity UV light stream inside a chamber. Organic contaminants are broken down to carbon dioxide and water.

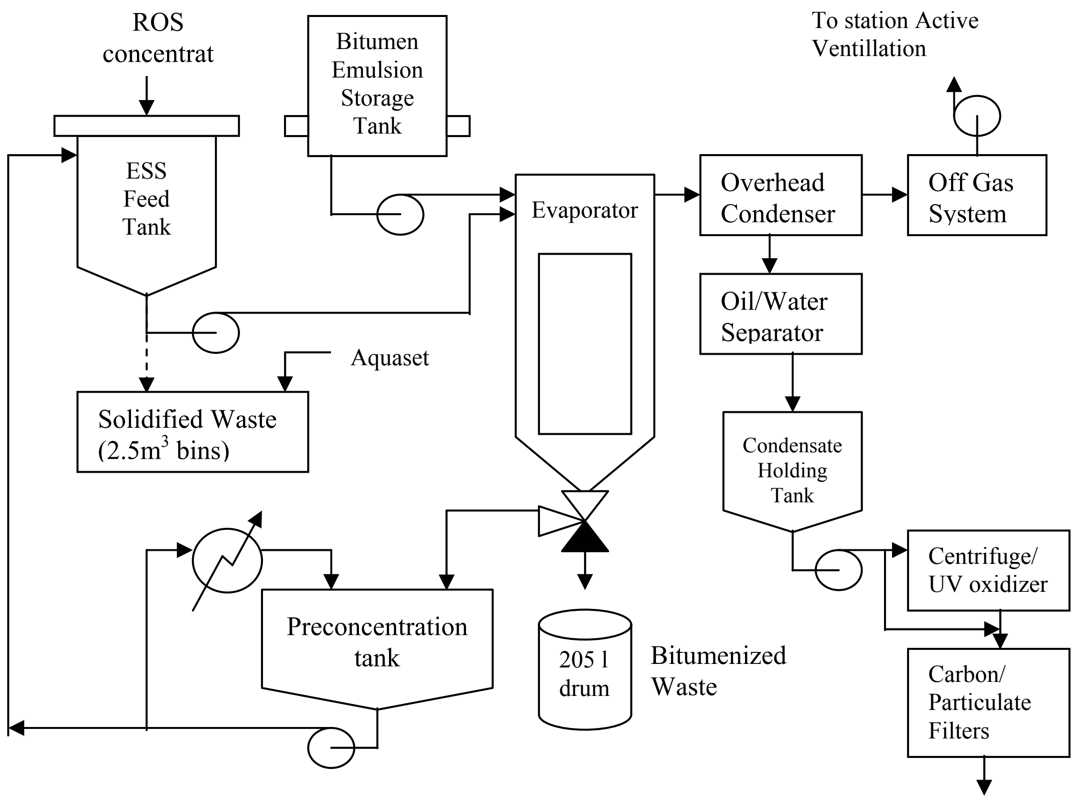

Figure 4: Simplified Diagram of Bruce ALWTS Evaporator and Solidification System

The second available polishing method is to pass the condensate through a vessel containing activated carbon and then through a particulate filter. The final treated effluent is collected in a sump and returned back to the ALW collection tanks. Both treatment methods are effective in reducing Total Organic Carbon (TOC) levels to less than 15 mg/kg.

3. Operating experience

3.1 Waste Water and Discharge Water Characteristics

Waste water feed to the Bruce A Active Liquid Waste Collection and Handling system comes from a number of sources in the station. These sources include the active sumps located in Units 0, 1, 2, 3, 4 and the East Service Area, the vacuum building sump, the unit turbine area building sumps, the Plastic Suit Laundry Facility sump (Unit 0), Chemistry Laboratory, Fuel Handling Operations (including decontamination facilities) and the tanker unloading facility which provides a location for unloading of active liquid waste tankers from various locations on site, including OPG facilities, 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. Typical key wastewater feed parameters and desired limits are provided in Table 1.

Table 1: Typical Waste Water Parameters

Parameter	Normal Range	Desired Range
pH	6.5 – 8.5	6.5 – 7.5
Turbidity	10 – 40 NTU	< 25 NTU
Conductivity	200 – 1000 µS/cm	< 1000 µS/cm
Iron	0.2 – 1.5 mg/kg	< 0.5 mg/kg
Hydrazine	0 – 10 mg/kg	< 2 mg/kg
Hardness (as CaCO3)	30 – 120 mg/kg	< 30 mg/kg

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 2. The system consistently produces water that meets all regulatory and Bruce Power administrative limits. Removal efficiencies of 95% or greater are typical for the system.

Table 2: Typical Discharge Water Parameters

Parameter	Typical	MISA Limit
pH	7.6	6.0 – 9.5
Total Suspended Solids	< 0.44 mg/kg	25 mg/L
Phosphorus	0.015 mg/kg	1 mg/L
Iron	0.01 mg/kg	1.0 mg/L
Zinc	0.004 mg/kg	0.5 mg/L
Oil & Grease	< 1 mg/L	13 mg/L
Toxicity (% Mortality)	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

3.2 ALWTS Fouling – Calcium Sulphate

From day one, the greatest challenge facing the continued successful operation of the ALWTS has been the formation of scale on the walls of the evaporator system and in the sub-systems within the ROS where the wastewater is most concentrated. This condition arises from the tendency of calcium, primarily from service water entering the ALW collection tanks, to combine with sulphate, added to control pH in the ROS, to form insoluble calcium sulphate. The formation of this scale poses operational problems with respect to fouling of instrumentation in the system (eg. pH probes), fouling of membranes, scaling and flow reduction in system piping and fouling of the heat transfer surface of the evaporator.

The likelihood of calcium sulphate precipitation is highest in the evaporation and solidification system where the most concentrated waste from the ALWTS is further concentrated by evaporation, in preparation for final disposal. The problem was initially discovered in 2000 during the first full year of ESS operation, when the scaling increased to the point where the blades of the evaporator rotor would no longer turn. Examination of the evaporator walls revealed a sufficient build-up of calcium sulphate dihydrate ($CaSO4 \cdot 2\ H_2O$) to prevent the rotor from turning. Fortunately, due to the mechanical properties of this compound, commonly referred to as gypsum, the walls of the evaporator were easily cleaned using mechanical methods. An antiscalant was tested to prevent scaling, but met with limited success. The regularity of this problem, particularly during the bitumenization process, and the costs associated with lost production and high maintenance requirements, eventually lead to the decision to eliminate the bitumenization step and solidify the concentrated waste instead. Concentrated ESS waste is now solidified for disposal in bins, using a commercially available solidifying agent, Aquaset II Granular.

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.

3.3 ROS Membrane Cleaning Versus Replacement

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.

Given the challenges faced with calcium sulphate fouling during early operation of the ESS system and the resulting low availability of the ESS due to high maintenance, it was decided that the volume of waste water generated by frequent cleaning of the membranes could not be tolerated. Waste water generated from membrane cleaning was adding to the increasing inventory in the ESS feed tanks. The choice was therefore made to replace fouled membranes rather than chemically clean them. The cost of replacing membranes corresponds closely with the extra costs associated with increased operation and maintenance of the ESS required to process the membrane cleaning wastes. This decision has been further buoyed by price decreases for ROS membranes, as availability and competition increase in the industry.

4. Conclusion

The Bruce A Active Liquid Waste Treatment System (ALWTS) consists of a complex, multi-stage treatment system whose function is to process low-level radioactive wastewater and to produce a treated effluent which meets the Municipal Industrial Strategy for Abatement (MISA) limits as set out by the Ontario Ministry of Environment. The Bruce A ALWTS has been processing waste water from Bruce A for approximately 10 years while consistently meeting all regulatory chemical and toxicity requirements. With the exception of tritium, there are near-zero waterborne radioactive emissions to the environment.

5. References

[1] Davloor, R., Higgins, R.S., “Design Description Radioactive Liquid Waste System”, Bruce Power NK21-DD-79200, Dec 1993

[2] Davloor, R., Christie, W., “Bruce 1-4 Active Liquid Waste Treatment System (ALWTS) Pre-Treatment Process Laboratory Tests”, NK21-79200-T10, Sep 17, 1999

[3] Zenon Environmental Systems, Inc, “Design Description for an Active Liquid Waste (ALW) Treatment System”, Zenon A.O. 6356, Nov 21, 1997

[4] Halverson, W.C., “An Overview of Surry Radwaste Facility Operations”, *Nuclear Plant Journal*, July – August 1992, pp.50 - 54