REMOVAL OF BULK CONTAMINANTS FROM RADIOACTIVE WASTE WATER AT BRUCE A USING A CLAY BASED FLOCCULENT SYSTEM

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ABSTRACT

Bruce Power's Bruce Nuclear Generating Station "A", located on Lake Huron, has a treatment system that processes all aqueous radioactive waste water originating from the station. This Active Liquid Waste Treatment System (ALWTS) consists of collection tanks for the collection of radioactive waste water, a Pre-Treatment System (PTS) for the removal of bulk contaminants and suspended solids, a Reverse Osmosis System (ROS) to remove dissolved solids, an Evaporation and Solidification System (ESS) to concentrate and immobilize solids contained in concentrated waste streams from the ROS, and discharge tanks for the dispersal of the treated water. The ALWTS has been in continuous service since 1999 and is used to treat approximately 100,000 litres of Active Liquid Waste (ALW) each day. With the exception of tritium, it discharges waste water containing near zero concentrations of radioactive and conventional contaminants to the lake.

The original design of the Bruce A ALWTS used a Backwashable Filtration System (BFS) to provide solids free water to the ROS, as measured by the Silt Density Index (SDI). During commissioning, the BFS was not successful in backwashing the solids from the filter elements. For approximately one year, a temporary solution was implemented using a Disposable Filtration System (DFS). A cationic polymer was added upstream of the DFS to agglomerate the solids. The system proved to be highly unreliable. It was difficult to agglomerate solids in the waste stream containing high amounts of detergent. As a result, DFS consumption was high and very costly. The SDI specification for the RO membrane was not always met, resulting in a quick decline of performance of the first stage ROS membranes in the treatment process. In addition, the excess cationic polymer in the RO feed caused the membranes to become fouled.

In-house station staff, together with personnel from Colloid Environmental Technologies (CETCO) Company, worked to develop and implement a clay-based flocculation Pre-Treatment System. In-service since late 2000, the system has been able to reliably treat a broad range of contaminants in the waste water before being sent to the downstream ROS. This clay-based system is unique in its application; it is able to remove bulk oil and grease, suspended solids, and metal contaminants in a waste stream that contains a high amount of surfactants originating from the laundering of plastic suits (personal protective equipment for working in radioactive environments) and other waste waters from the station. The treated water from the PTS consistently meets the strict requirements for subsequent treatment by the system RO membranes.

This paper describes the laboratory and pilot scale testing that led to the development of the process, as well as the full scale implementation of this unique Pre-Treatment System.

1. INTRODUCTION

The Bruce A Active Liquid Waste Treatment System (ALWTS) is a complex, multi-stage treatment system designed to process waste water containing radioactive and conventional contaminants and produce a treated effluent that meets all regulatory limits for discharge [1].

Figure 1 provides an overview of the major systems in the ALWTS [2]. 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 Pre-Treatment System (PTS) that removes contaminants such as oils, greases, and heavy metals and produces an effluent that is free of suspended solids.

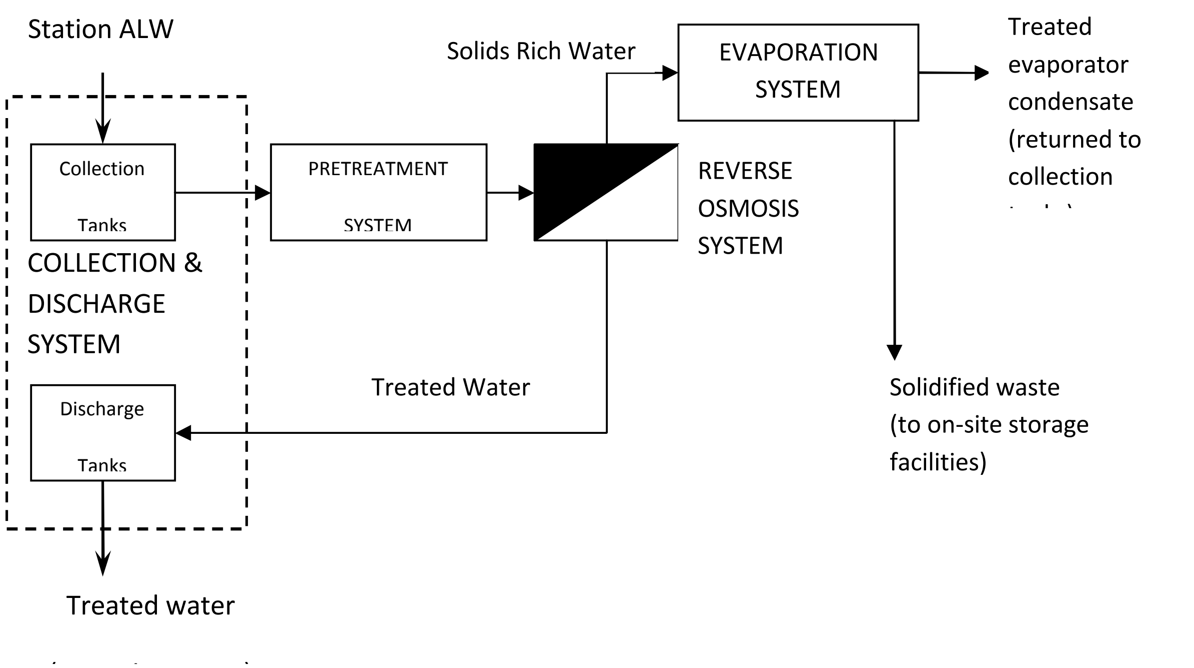

Figure 1: Overview of Bruce A ALWTS

Effluent from the PTS is processed through the ROS to remove dissolved impurities from the waste stream. The ROS is a three stage membrane-based system, with an intermediate chemical precipitation process. The concentrated waste stream from the ROS is processed through the Evaporation and Solidification System (ESS). The thin film evaporator, either further concentrates the solids in the concentrated waste water for volume reduction and disposal using a waste contractor, or utilizes bitumen to encapsulate solids.

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.

The original design of the Bruce A ALWTS used a Backwashable Filtration System (BFS). During commissioning, the BFS was not successful in backwashing the solids from the filter elements. The cause of the failure was determined to be impregnation of fine solids into the filter media. In addition, the wastewater effluent from the newly installed plastic suit laundry facility presented high amounts of solids that were problematic to filtration. A temporary solution was implemented using a Disposable Filter System (DFS), consisting of filter housings containing 6 µm filter cartridges. A cationic polymer was added upstream of the DFS to agglomerate the solids. The system proved to be highly unreliable as it was difficult to agglomerate the solids in the waste stream containing high amounts of detergent. As a result, DFS consumption was found to be high and very costly. The Silt Density Index (SDI) specification for the downstream reverse osmosis membranes was not always met, causing a quick decline in performance of the membranes. In addition, the excess cationic polymer in the reverse osmosis feed caused the membranes to become fouled [3].

Due to the poor performance with the BFS and DFS processes, in house station staff, working together with CETCO staff, began testing alternative treatments using clay flocculants. This method of treatment had been used successfully at Bruce A in the Chemical Waste Management System for the treatment of waste water from floor washing machines [4]. The water also contained high amounts of oils, and solids in a detergent environment. Tests were first conducted using different clays in a laboratory environment.

Based on screening tests of different clays from initial jar tests, a cationic clay, RM10H, followed by addition of a sodium bentonite-based clay, Accofloc 350, proved to be the most promising. When the RM10H clay is added and mixed to the waste water, it releases chemicals to raise the pH, then releases a cationic polymer and attracts charged particles. The clay hydrates and agglomerates into a floc to entrap particles. Oil and grease are also encapsulated. This method of pre-treatment is effective even in the presence of laundry detergents, which otherwise make it difficult to remove the contaminants. The purpose of the application of the bentonite clay, Accofloc 350, is to remove any excess cationic polymer that was released by the RM10H during the first treatment stage. This serves to remove any excess cationic polymer that can foul the downstream RO membranes.

Table 1 shows the critical parameters for the ROS influent [5]. The objective of the laboratory testing was to develop a reliable PTS that could consistently meet these parameters.

Table 1: Critical Reverse Osmosis System Influent Parameters

Parameter	Limit	Target
Free oil and grease, mg/kg	<3	<0.5
Turbidity, NTU	<0.5	<0.2
Total iron, mg/kg	<0.5	<0.1
Silt Density Index (SDI)	<5	<3

2. LABORATORY SCALE TESTS

Laboratory jar tests were performed in May – July 1999 on samples taken from 9 separate ALW collection tanks [6]. Two tests were performed to clarify the water samples: one using a liquid cationic polymer; another using RM10H followed by Accofloc 350 clay-based products.

The laboratory test procedure is summarized as follows:

1. A representative sample was obtained from a collection tank and a suite of chemical analyses were performed.

2. To simulate the full scale cationic polymer addition/DFS pre-treatment system that was being used at the time, the following was performed:

    a. An optimum dose of the liquid cationic polymer was determined by existing procedures [7].

    b. The liquid in a 5 gallon pail was then clarified using the predetermined dose of polymer. After solids settling, the supernatant was filtered through a course 100 micron filter cloth into another pail. The water was then filtered through a 6 micron, 2 inch diameter x 1 inch depth polypropylene cartridge filter. The filtrate was analyzed for iron, turbidity, and SDI.

3. For the tests using clay-based chemicals,

    a. RM10H dose corresponding to 2g per 1,000 ml was first added to the sample, and mixed for 1 minute in a 5 gallon pail. The mixer was stopped and the solids were allowed to settle for 1 minute. The mixer was restarted for 1 minute. The solids then settled for 5 minutes, and were filtered through a course 100 micron filter cloth from one pail to another. The filtrate was analyzed for iron and turbidity.

    b. A measured amount of 5 wt% Accofloc 350 solution, corresponding to 500 mg per 1,000 ml, was added to the filtrate. The liquid was stirred for one minute and allowed to settle for one minute. The mixer was then restarted for one minute, and the solids were allowed to settle for 5 minutes. The water was passed through a 100 micron filter cloth and into another pail. The water was then filtered through a 6 micron, 2 inch diameter x 1 inch depth polypropylene cartridge filter. The filtrate was analyzed for iron, turbidity, and SDI. A qualitative test [8], consisting of adding a liquid anionic polymer corresponding to 1 mg/kg in the filtrate was performed to check for residual cationic polymer. If the solution became cloudy after anionic polymer addition, then residual cationic polymer was left in the filtrate after Accofloc 350 treatment.

The results of these tests are shown in Table 2 below.

Table 2: Summary of Laboratory Scale Tests

	TK1	TK3	TK7	TK1	TK3	TK7	TK2	TK3	TK7
Date	99-05-30	99-06-01	99-06-08	99-06-22	99-06-26	99-06-27	99-06-28	99-07-14	99-07-16
RAW WATER									
pH	7.3	7.1	6.8	7.0	6.4	7.0	6.9	7.6	7.3
Conductivity, µS/cm	310	1033	508	388	874	484	375	983	795
Turbidity, NTU	15.3	22	36	12.5	20	13.7	52	35	40
Iron, mg/kg	4.4	5.9	8.0	4.1	23.0	3.5	10.7	9.3	12.0
Colour	pale yellow	grey brown	pale yellow	pale yellow	pale yellow	grey	grey brown	pale yellow	pale yellow
Foaminess	foamy	no foam	foamy	foamy	no foam	no foam	no foam	foamy	foamy
TREATMENT BY CATIONIC POLYMER ADDITION									
Polymer concentration, mg/kg	64	64	32	16	24	8	64	16	48
Turbidity after polymer addition, and 6µm filtration, NTU	0.20	0.14	0.50	0.30	0.50	0.36	0.18	0.32	0.33
Iron, after polymer addition, and 6µm filtration, mg/kg	1.20	0.86	0.80	0.19	7.90	0.16	1.70	0.20	0.13
Silt Density Index	7.9	5.8	6.0	3.7	5.1	3.2	3.8	5.2	5.5
TREATMENT BY CLAY ADDITION									
Step 1: Add RM10H Clay									
Amount of RM10H clay added, g/1000ml	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Turbidity after 100 µm cloth filtration, NTU	1.0	0.87	1.2	1.3	4.6	1.7	2.2	2.2	2.1
Iron, after polymer addition, and 100 µm filtration, mg/kg	0.53	0.52	0.53	not done	0.60	0.06	0.19	0.13	0.11
Step 2: Add Accofloc 350 Clay									
Accofloc concentration, mg/kg	500	500	500	500	500	500	500	500	500
Turbidity after 100 µm cloth filtration, NTU	0.66	0.45	0.98	1.1	2.3	1.7	1.3	1.0	0.42
Iron, after polymer addition, and 100 µm filtration, mg/kg	0.52	0.43	0.53	not done	0.53	0.17	0.08	0.12	0.03
Step 3: Filtration by 6 µm Filter									
Filtrate turbidity (= turbidity ROS influent)	0.23	0.11	0.50	0.22	0.24	0.08	0.30	0.10	0.12
Filtrate iron (= iron ROS inlet), mg/Kg	0.36	0.40	0.43	0.08	0.44	0.13	0.07	0.08	0.02
Silt Density Index	3.3	4.1	3.7	2.8	3.9	3.1	3.1	2.7	2.2
Residual polymer (qualitative test), residual or none	none	none	none	none	none	none	none	none	none
Colour	clear	clear	clear	clear	clear	clear	clear	clear	clear

Note: TK1, TK2, TK3 and TK7 are ALW collection tanks

For tests involving the liquid cationic polymer, the iron limit was not achieved in 5 of 9 tests, the turbidity specification was always met, and the SDI limit was not achieved in 6 of 9 tests. These tests verified the field operating experience where high consumption of DFS filters and low operating life of first stage RO membranes had been observed.

From the results for the clay addition tests, the iron specification was met in the final product for all tests. The RM10H flocculent resembled 2-3 mm cotton balls, resulting in excellent filterability properties. The Accofloc 350 flocculent was less than 1 mm and did not enlarge as much as the RM10H flocculent. The RM10H clay alone removed bulk solids to produce a product, after course filtration, with turbidity in the 1 – 5 NTU range. The final product, after Accofloc 350 addition followed by 6 micron filtration, had turbidity less than 0.5 NTU. The qualitative test showed no residual cationic polymer. More significantly, SDI was consistently less than 5. These results inferred that the more time consuming SDI analysis did not have to be performed if it could be shown that there is less than 0.5 NTU product water going to the ROS and DFS filter consumption was acceptable.

The success of the laboratory tests using the clay-based products led to the subsequent pilot scale tests.

3. PILOT SCALE TESTS

Pilot scale tests were performed in September 1999 on two ALW collection tanks during a period of high solids excursion in the waste stream going to the ALW collection tanks [9]. The wastewater had high iron and turbidity values and was also chronically foamy due to the high percentage of laundry water in the waste stream. The detergent and high pH (from the booster chemical used in laundry) combined with the high suspended solids and iron concentrations presented a significant challenge to pre-treat the stream and meet the ROS influent specifications.

The pilot scale test equipment consisted of 4 open top epoxy lined carbon steel drums, 2 low shear mixers, 3 portable diaphragm pumps with pumping maximum capacity 5 USGPM, two portable filter housings containing 50 micron polypropylene bag filters, and a portable filter housing containing a 2 inch diameter x 10 inch length, 6 micron polypropylene filter.

The pilot test procedure can be summarized as follows:

1. The first drum was filled three quarters full with collection tank water and sampled and analyzed.

2. The mixer was started, and 330g of RM10H was added to the liquid. A mix, settle, mix and settle sequence followed to make sure a large flocculent was formed. The entire drum was then pumped through the bag filter into a second empty drum. A sample of liquid taken from the second drum was analyzed for iron and turbidity.

3. The mixer in the second drum was started and 1.6 liters of 4.1 wt% Accofloc 350 solution was added. A mix, settle, mix sequence followed. The liquid in the drum was pumped through the second bag filter into the third drum. A sample from the third drum was analyzed for iron and turbidly.

4. The contents in the third drum were pumped through the 6 micron cartridge filter and into a fourth drum. Iron, turbidity and SDI analyses were performed on a sample taken from the fourth drum. A qualitative test for residual cationic polymer was also performed.

The results of these tests are shown in Table 3.

As in the laboratory scale tests, the RM10 flocculent was large, and settled quickly. The Accofloc 350 flocculent was smaller and lighter than observed during the laboratory tests. The pilot scale tests on the two collection tanks showed the same favourable results as the laboratory scale tests. Despite the challenging waste stream, the turbidity was less than 0.3 NTU for both samples, iron was much less than 0.5 mg/kg and SDI was less than 4.

As a result of the successful laboratory and pilot scale tests, approval was received for the design and implementation of a full scale pre-treatment system utilizing clay based chemicals.

4. FULL SCALE IMPLEMENTATION

Design, procurement, installation and commissioning of the full scale CETCO clay-based pre-treatment system took place between October 1999 and December 2000 [10]. The system was designed to handle an average feed flow of 3.0 kg/s, with a maximum feed flow of 5.0 kg/s over a 72 hour period [11]. A schematic flow diagram is shown in Figure 2.

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 that can be input by the operator. The settled floc is separated using a 50-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 Accofloc 350 in powder form bentonite clay is metered into this tank while the tank contents are being mixed. 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 water collected in the second stage filtrate collection tank is passed through 30-micron bag filters and transferred to an intermediary buffer tank. The buffer tank contents are pumped through 6 μm pleated polypropylene cartridges contained in the DFS. The flocculent on the filter paper hardens while it is stored in the bins. To ensure there is no free standing water, a water absorbing polymer in powder form is spread in the bottom and in layers while the waste is collected. 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).

Table 4 shows the performance data obtained during system commissioning [12]. During commissioning, the influent to the Pre-Treatment System was foamy, and had elevated pH and iron values. The effluent data showed that the clay based pre-treatment system followed by 6 µm filtration produced water that met the iron and SDI specifications for ROS influent. Because SDI was consistently met when turbidity was less than 0.5 NTU, SDI was no longer measured and an effluent specification of less than 1.0 NTU was adopted [13].

Table 3 - Two Step Clay Treatment Using Drum Scale Equipment

	TK3 ALW Water	TK7 ALW Water
Date	99-09-23	99-09-30
Raw Water		
pH	8.3	9.1
Conductivity, µS/cm	983	795
Turbidity, NTU	35	41
Iron, mg/Kg	9.3	13.8
Colour	Yellow	Brown
Foaminess	Very foamy	Very foamy
RM10H Addition, 50 µm Filtration		
Volume of batch, liters	164	164
Amount of RM10H added, Kg	0.33	0.33
Mix sequence, time 1. Mix, add RM10H 2. Stop mixer, settle 3. Mix 4. Settle 5. Pump out and filtering time	 1 min-30s (good floc started) 1 min-30s 2 min-0s (large floc) 5min-0s 14min-45s	 1 min-30s (good floc started) 1 min-30s 2 min-0s (large floc) 5min-0s 16min-30s
Est. volume of filtered waste, liters	1.35 (incl. paper)	1.35 (incl. paper)
Turbidity of filtrate, NTU	1.0	0.80
Iron in filtrate, mg/Kg	0.16	0.15
Accofloc 350 Addition, 50 µm Filtration		
Volume of batch, liters	134	137
Concentration of stock Accofloc 350 solution, wt%	4.1	4.1
Volume of stock Accofloc 350 solution added, liters	1.63	1.67
Concentration of Accofloc 350 in batch, mg/Kg	500	500
Mix sequence, time 1. Mix, add RM10H 2. Stop mixer, settle 3. Mix 4. Pump out and filtering time	 1 min-30s (full floc already formed) 1 min-0s 1 min-30s (large floc) 23min-30s	 1 min-30s (full floc already formed) 1 min-0s 1 min-30s (large floc) 27min-30s
Est. volume of filtered waste, liters	0.5 (incl. paper)	0.5 (incl. paper)
Turbidity of filtrate, NTU	1.0	0.80
Iron in filtrate, mg/Kg	0.90	0.42
6 µm Filtration		
Pump out and filtration time	17min-15s	18min-30s
pH of filtrate	7.2	7.3
Conductivity, µS/cm	966	823
Turbidity, NTU	0.38	0.4
Iron, mg/Kg	0.15	0.06
Silt Density Index	3.4	3.9
Residual polymer test (qualitative)	None	None
Colour	Clear	Clear

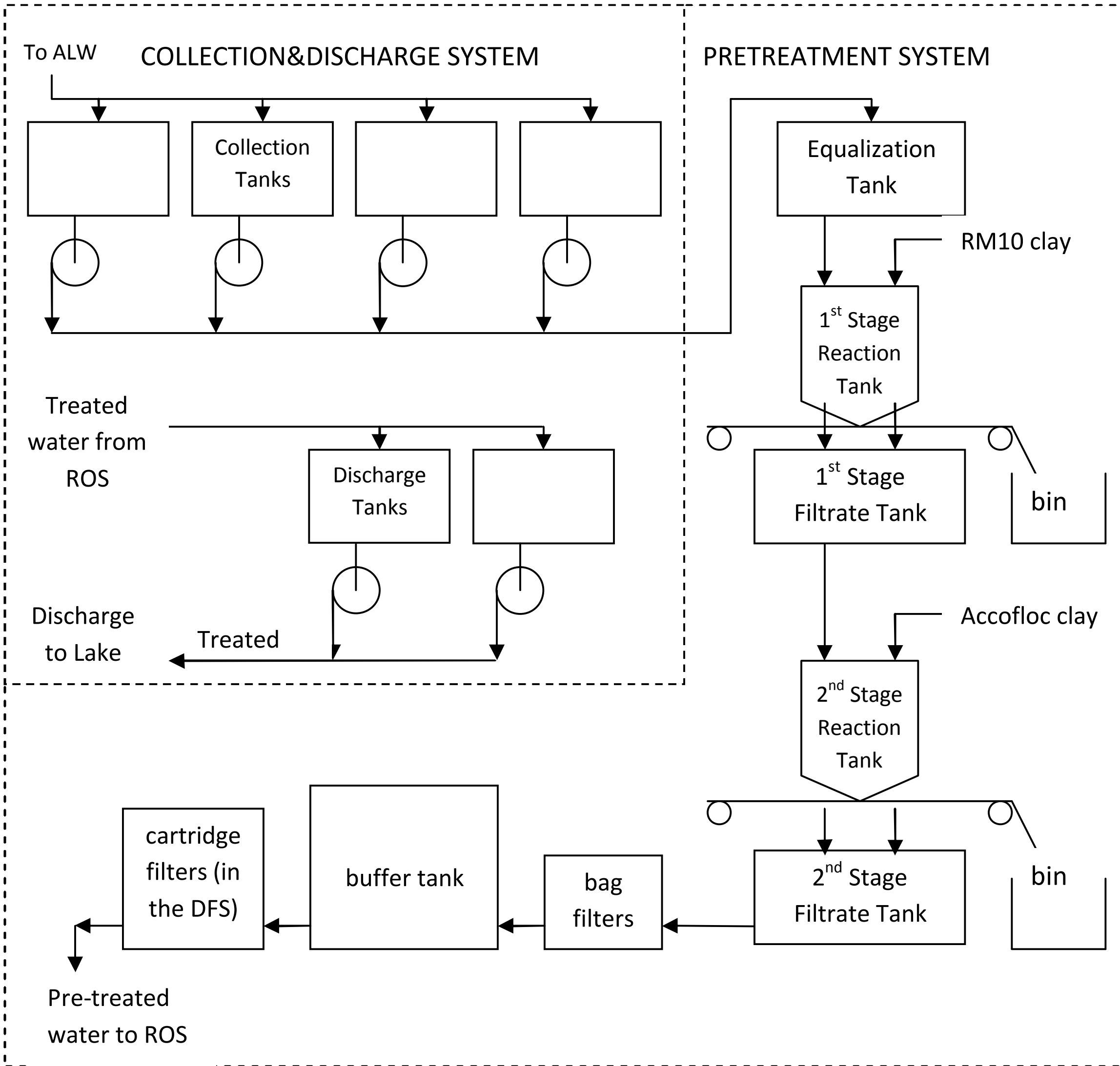

Figure 2 ALW Collection Tanks and Pre-treatment System

The Bruce A ALWTS Pre-Treatment System has now been operating successfully for over 10 years. The typical waste volume processed each day is 100,000 liters. The process generates, on average, 130m^3 of sludge waste each year for a total of approximately 40,000 metres of wastewater processed. DFS filter consumption is approximately 20 - 30 filter assemblies each year. First stage reverse osmosis membranes have typically lasted up to 3 months before replacement. This is a significant improvement to twice weekly change outs of DFS cartridges and monthly change out of first stage reverse osmosis membranes that took place before the Pre-Treatment System was installed.

Table 4: PTS Influent and Effluent Characteristics

	Design Average	Design Maximum	Measured
Influent Data			
Temperature, deg C	25	45	13 - 22
pH	6.3	8.9	7.1 - 9.3
Conductivity, µS/cm	202	1,054	454 - 1,380
Total Suspended Solids, mg/Kg	7.9	51	7.1 - 23
Total Organic Carbon, mg/Kg	12	67	5.5 - 32
Iron, mg/Kg	6	50	7.5 - 17.3
Gross gamma (as Cs-137), µCi/Kg	0.025		0.017 - 0.13
Tritium, µCi/Kg	211		83 - 512
Effluent Data (DFS Outlet)			
Conductivity, µS/cm	1,000	2,500	480 - 1,450
Iron, mg/Kg	0.1	0.5	0.13 - 0.45
Turbidity, NTU	0.2	0.5	0.15 - 0.850
Silt Density Index	3	5	2.8 - 4.4

Note: measured values taken from 13 separate treatment batches between September 2000 - December 2000

The two main performance problems observed with the PTS operation are associated with elevated pH of the influent stream and overdosing of RM10H. High pH in the influent stream is caused by high amounts of booster chemical used in the plastic suits laundry. Under these conditions, the RM10H does not form into a large floc such that the filterability is adversely affected. While the floc is deposited on the filter paper, it breaks into smaller fragments from the hydraulic force of water going through the filter paper. The small fragments result in high bag filter and DFS consumption. The use of the laundry booster chemical has been reduced so that the pH of the influent water is typically less than 9.

A second performance problem is caused by high RM10H dose. RM10H greater than 2 g per kg of waste water has resulted in high DFS consumption. Under high RM10H dose conditions, the floc does not properly form and can pass through the band filter paper and bag filters. The higher than normal solids content in the DFS influent causes the cartridge filters to spend rapidly. Operating experience has shown that an RM10H dose of 1 g per kg of waste water is sufficient to clarify the waste water. Higher does are used only during solids excursions in the influent stream.

5. CONCLUSIONS

The CETCO clay-based Pre-Treatment System is a unique process that is able to pre-treat aqueous radiological liquid wastes with high solids, iron and other gross contaminants in the presence of detergent chemicals. The Bruce A system is a unique process developed by in house engineers at Ontario Power Generation / Bruce Power nuclear facilities, together with CETCO personnel. The process has enabled the complex Bruce A Active Liquid Waste Treatment System to operate continuously to achieve near zero discharge of chemical and radiological contaminants to the environment. The PTS has been demonstrated as a reliable front end treatment system for reverse osmosis systems, which require stringent specifications to be met for suspended solids, oils and greases and metals, such as iron. Because of its ability to successfully remove bulk contaminants with a high degree of varying composition and concentration, the system would have application in ground water processing, decommissioning wastes and other aspects of waste management.

6. REFERENCES

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