U.S. AND RUSSIAN INNOVATIVE TECHNOLOGIES TO PROCESS LOW-LEVEL LIQUID RADIOACTIVE WASTES: THE MURMANSK INITIATIVE

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ABSTRACT

This paper documents the status of the technical design for the upgrade and expansion to the existing Low-level Liquid Radioactive Waste (LLLRW) treatment facility in Murmansk, the Russian Federation. This facility, owned by the Ministry of Transportation and operated by the Russian company RTP Atomflot in Murmansk, Russia, has been used by the Murmansk Shipping Company (MSCo) to process low-level liquid radioactive waste generated by the operation of its civilian icebreaker fleet. The purpose of the new design is to enable Russia to permanently cease the disposal at sea of LLLRW in the Arctic, and to treat liquid waste and high saline solutions from both the Civil and North Navy Fleet operations and decommissioning activities. Innovative treatments are to be used in the plant which are discussed in this paper.

INTRODUCTION

In the past, liquid waste from the nuclear icebreaker fleet operated by MSCo, the Russian Navy's Northern Fleet, and Atomflot's shipyard operations was dumped into Arctic seas. This practice was discontinued in late 1993; however, since there is limited capacity to treat this waste, much of the waste must be stored. According to Atomflot, capacity to store additional liquid waste has dwindled rapidly to less than 5% of its original capacity and, if the LLLRW treatment facility is not expanded and upgraded, some ocean dumping will have to be resumed.

The three countries of Russia, Norway and the United States have a mutual interest in assuring the safe treatment and storage of wastes, and in avoiding sea disposal.

DESIGN REQUIREMENTS

The facility will treat up to 5000 cubic meters per year of liquid waste, which will include:

(a) Primary Coolant (called "Drainage Circuit Waters") which is drained from the primary loops of the icebreaker reactors during refueling operations.

(b) Spent Fuel Storage water that has been used as coolant and shielding in atomic icebreaker spent fuel storage pools.

(c) Decontamination waters that have been used in the decontamination of equipment and tools in Atomflot's shops at the shipyard, and laundry waste waters produced from operation of Atomflot's facility for cleaning and laundry.
decontamination of anti-contamination and protective clothing at the shipyard laundry.

(d) Saline waters that come from ships of the Russian Navy's Northern Fleet as the result of the mixing of sea water with primary coolant, either when sea water is used in the regeneration of ion-exchange resins, or produced by dilution of wastes to enable transportation in tankers.

The LLLRW Facility is essentially a concentrator for the wastes, except for tritium which remains in solution. The waste streams are filtered to remove particulates, undergo ion-exchange for both softening and solids precipitation, and electro-separation and concentration, before final fine filtering. The activity reduction in the waste water is many orders of magnitude. Thus, the purified waters can be safely discharged, and the solids and residues from the treatment bled off for solidification with cements for storage.

Pretreatment provided is intended to reduce the water hardness by removing primarily calcium (Ca), magnesium (Mg), and non-radioactive strontium (Sr). Removal of radioactive strontium occurs as a beneficial secondary result of the process, and the decontamination factor (DF) for removal of radioactive strontium is estimated to be about 100.

There are two primary reasons why hardness must be reduced. First, some of the sorbents are intended to remove radioactive strontium selectively. However, because of its relative abundance compared to the radioactive strontium, if non-radioactive strontium is not removed first, it would be trapped on the selective absorbents too, significantly reducing their useful lifetime. Reducing the hardness of the High-salt Waters is necessary also to ensure proper operation of the electrodialysis and electroosmosis components of the Electromembrane Desalinator (Unit 6) which is also used to treat this stream. If calcium, magnesium, and non-radioactive strontium ions were allowed to enter the desalination unit, they would quickly foul the unit's membranes. This would cause premature failure and increased maintenance and calcium oxalate fouling would also be a problem for Unit 6.

Because each waste stream is different (in salinity, particulates and activity) the exact treatment path is unique. Thus, the plant is designed in a modular fashion, within designated functional Units, which allows for some degree of standardization in the layout and for the manufacturing replication of filters, pumps and fittings wherever possible.

The system provides three trains of processing for the High-salt Waters, Decontamination Waters, and Low-salt Waters respectively. Laundry Waters are processed using some of the equipment provided for the first two processing trains. At the inlet of each train, there is a large Accumulation Tank for receiving the waste water. All but the Decontamination Waters are pumped from ships at dockside to these tanks. The Decontamination Waters come from the Atomflot repair facility on site. Flow block diagrams illustrating the process flow for each type of waste stream are shown in the Figures. On these diagrams, ASPECT's module and unit designations are shown; however, only the Unit designations will be used throughout this paper.

INNOVATIONS IN PLANT DESIGN AND PERFORMANCE

Unit 1 is designed for the pretreatment of High-salt Waters, to precipitate several of these constituents which would interfere with processing in subsequent units, and provides rough mechanical filtration and electrochemical processing to reduce the hardness of the incoming water. This is required so that the sorbent columns in Unit 4 and the membranes in Unit 6 are not quickly loaded. As a side benefit, the hardness reduction process removes also some of the radioactive strontium present in the waste stream.

Unit 2 provides for the destruction and disassociation of organic compounds; using electrochemical means, and to avoid problems with these residual solvents Unit 3 is a subsequent treatment step. The Electrocatalytic Destructor is a vessel fitted with titanium cathodes, and either platinum coated titanium or ruthenium dioxide coated titanium anodes. Passage of current (electrical power required is in the range of 1 to 3 kw) through the unit generates active forms of chlorine, e.g., hypochlorite. The source of chlorine for the electrochemical decomposition is salt (NaCl) present in the decontamination solution. Active chlorine attacks and destroys organics due to its high oxidizing potential. The ultimate end products resulting from the destruction of the organics are carbon dioxide and water.

Although the Unit was not designed expressly for radionuclide removal, some precipitation is expected. As the organics are destroyed, the solution will lose some of its ability to retain dissolved solids and thus some of the solids will precipitate. A small amount (several percent of the input to the ElectrocatalyticDestructor) of radionuclides will be electro-deposited on the unit's cathodes. However, continuous dissolution of this material is expected to occur. Hence, significant permanent
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deposition of radioactivity on the cathodes should not be a problem. Small amounts of chlorine and hydrogen gas are produced as byproducts of the electrolysis. These potentially hazardous gases will be managed by venting from the system.

The liquid leaving the Electrocatalytic Destructor is highly corrosive due to the active chlorine. The Destructor and downstream equipment which come in contact with the liquid must be made of titanium. A titanium column containing either sulphocarbon and/or manganese dioxide will be provided in the final design. The column will be inserted at the back end of Unit 2. The columns will scavenge residual active chlorine. Reducing the corrosivity of the liquid will allow subsequent processing units to be fabricated from stainless steel.

Unit 3 is to provide further mechanical filtration. The sand filters for each stream are dedicated to those streams and thus, from a functional standpoint, Unit 3 could be considered to be comprised of two independent sub-units. Thus, Unit 3 is a bank of six columns filled with quartz sand which are designed to act as mechanical filters. In actuality, although Unit 3 is considered to be a single module, it has two distinct and separable functions. The first three sand columns are dedicated to processing Decontamination Waters from Unit 2; the other three columns process High-salt Waters from Unit 1. Replacement of sand is done by slurrying the old sand to a waste container, and slurrying the new sand into the empty column.

The quartz sand is layered so that the waste passes through sand of decreasing particle size. The result is that the columns are able to remove particulate down to about 100 microns in size.

Unit 4 provides selective absorption for isotopes of cesium and strontium, and employs sorption columns to selectively remove strontium, cesium, and organics by employing sorption columns. The six columns of Unit 4 are identical to those used to hold the quartz sand but the first two columns are filled with a sulphocarbon sorbent to remove organic impurities. The following two columns are nickel ferrocyanide, primarily to remove the residual cesium-137(134). Although nickel ferrocyanide is generally known to be a good sorbent material, it has not been used to any great extent in the United States. Without a carrier material, Nickel ferrocyanide packs too tightly in a column to be of any practical use. U.S. manufacturers have not developed a process to manufacture nickel ferrocyanide in a useable form yet; however, the Russians have developed carrier particles (0.2-0.8 mm dia.) coated with nickel ferrocyanide (40 mg per gram of carrier) which have been proven in actual use. The final two columns are filled with zeolite. The zeolite removes strontium-90 (and residual cesium) selectively. As noted above, Unit 4 is dedicated to the cleanup of radioactive species, primarily cesium and strontium which remain in the High-salt Waters after pre-processing by Units 1 and 3.

Unit 5 is again a set of sorbent columns for selective removal of radioactive species and consists of four sorbent-filled columns. The first two columns are nickel ferrocyanide primarily to remove the cesium-137(134). The last two columns are filled with zeolite. The zeolite removes strontium-90 (and residual cesium) selectively. As noted above, Unit 5 is dedicated to the cleanup of radioactive species, primarily cesium and strontium, which remain in the Decontamination Waters after preprocessing in Units 2 and 3. Very little cesium and strontium are removed in pre-treatment.

Unit 6 is the next stage of treatment of waste volume reduction, which is accomplished by electrodialysis and electroosmosis; Unit 6 reduces salt content further using electromembrane technology. This is Russian developed technology, not used outside of the Former Soviet Union (FSU). Besides reducing salt content, it removes additional radioactivity along with the concentrated brine. The Electromembrane Desalinator unit will process both High-salt and Decontamination Waters. The primary purpose of desalination is waste volume reduction and Unit 6 is comprised of two types of active devices: electrodialytic desalinators (ED) and electroosmosis concentrators (EO). EDs and EOs are designed to function in different concentration regimes. Both devices employ the same cation-anion membrane technology. The electrodialysis and electroosmosis must work together in order to achieve the desired degree of waste concentration.

The technology employed in Unit 6 was selected for the following reasons. Conventional distillation (i.e., a waste evaporator) is energy intensive and should be operated continuously for best efficiency. There will not be enough wastes at this site to keep an evaporator operating continuously. In addition, special, expensive titanium equipment would be needed for evaporation of the High-salt Waters, given the associated high chloride levels. Finally, radioactive sediments would form in the interior of the evaporator. This would interfere with heat transfer, necessitating cleaning and, thereby, producing additional liquid radioactive waste.

Another option reverse osmosis (RO) has the advantage of being inexpensive. However, the output
solids content cannot approach 200 g/L. The membranes employed in RO (pore size < 0.2 m) are easily fouled by organics and biological contamination (viruses and bacteria).

Thus, electrodialysis and electroosmosis were selected over evaporation or RO primarily because less energy is needed than for evaporation. Also, a higher degree of volume reduction can be obtained than with RO and the membranes used are not as susceptible to fouling as those used in RO.

The Unit's primary function is to obtain a substantial reduction of the waste volume. This is to be accomplished in a two-stage process. First, the EDs produce two flow streams, one of relatively pure water (diluate) and the other a concentrate of the contaminants of the wastewater (brine). This brine becomes the feed for the EO units. The EO units also generate diluate and brine effluent streams. The combined ED and EO process is designed to yield brine for disposal which contains ~200 g/l solids. The overall decontamination factor for Unit 6 was stated to be 10 to 100 and the majority of the radioactivity remains in the brine. The brine will be sent to the cementation module. EO diluate will be recycled as feed to the EDs for further treatment. The diluate from the EDs is the purified stream and will be designed to contain less than about 200 mg/l solids. This will be an adequate level of desalination and will allow the diluate to be discharged to the site's industrial wastewater treatment system and ultimately to the environment.

The ED units are divided into chambers by membranes. Ordinary, common membranes are used (anion and cation exchangers in the form of films). The passage of electrical current through the system transports material across the membranes, i.e., electrical current drives the charged ions across the membranes, while the membranes retard the movement of water. Hence, in operation, the liquid in a chamber on one side of the membrane will become more concentrated with impurities, while the liquid on the opposite side of the membrane becomes more dilute. The desired concentration of solids at the output (diluate) of the EDs is 400-500 mg/L. The concentrate from the process will contain ~40 g/l solids.

Unit 6 contains a total of four EDs which will be operated as parallel pairs with the two pairs connected in series. Experience with the particular ion-exchange membranes used in the EDs indicate that they will not be susceptible to much scaling and fouling (given the intended pretreatments of the raw Decontamination Waters and High-salt Waters). The EDs are expected to operate for five years before membrane replacement is required.

The EO units are multi-chambered devices also, with separation being provided by the same types of membranes used in the ED units. The operation of the EO units is similar to that of the ED units. While the two units utilize similar membranes, they are constructed differently and, thus, the EO and ED units produce different results.

Based on previous Russian experience, membranes are not expected to foul easily, and an estimated membrane lifetime of ~1.5 years is projected for the EO units. These EO units are to be operated in parallel. The diluate from the process exits at the top of the unit, while the brine exits at the bottom. The diluate will be returned to the EDs for further treatment, while the brine is sent to the cementation unit (Unit 7). The flow rates are 50 l/hr for the concentrate going into Concentrated Brine Tank and 1 m^3/hr for the total unit. Since the brine pump has a capacity of 20 m^3/h, and the filtrate and diluate pumps both have a 2 m^3/hr capacity, the flows through the system can be varied. In fact, the salt content can be controlled by changing the flows (depending on the filtrate concentration).

Unit 7 provides for a final absorption polishing of the large volume of desalinated water from the process, prior to discharge to the industrial waters treatment plant. The final polishing in the sorption columns removes additional radioactive species so that the effluent has a gross activity of less than 10^-10 Ci/l. Then the wastewater is discharged to the "biological control station". Unit 7 is designed as a polishing unit to lower radioactive species concentrations below discharge limits. It processes all waters passing through the facility except primary coolant. Unit 7 consists of six sorbent-filled stainless steel columns where the first two columns contain nickel ferrocyanide, primarily to remove the cesium-137(134). The next two columns are filled with zeolite. The zeolite removes strontium-90 selectively. The fifth column contains activated-carbon to remove trace organics. The last column is a mixed-bed ion exchanger to remove the balance of the radioactive species.

Unit 8 treats the wastes from the above unit by cementation, packaged and stored, as appropriate.

Overall, the plant reduces the activity levels below those required by Regulations prior to discharge.
CONCLUSIONS

A cooperative initiative on avoiding discharge of LLRW has been undertaken under the U.S.-Russian Joint Commission on Economic and Technological Cooperation, with the active and key participation of Norway. New technical design of the facility in Murmansk is a considerable advance in both capacity and technology over the existing liquid waste treatment capability. The facility will enable treatment of all liquid LLRW from the operation of the Baltic icebreaker and Navy fleets.

The Plant has been designed to meet the necessary throughput and Regulatory discharge limits. There are provisions for treatment of multiple waste streams of different initial salinity and organic content.

The facility construction will take about 18 months, and operation will be preceded by training, procedure development, and acceptance testing. A full year of assessment of the operation is deemed necessary to ensure adherence to the discharge limits, which will therefore include an enhanced environmental monitoring program. Innovative technologies are to be used in the sorption columns, for electrodestruction of organics, and for electro-membrane concentration. The treatment of high-salt wastes is also a significant advance.

The proposed facility is really a prototype demonstration and utilizes technologies which were developed by the Russians, and is the only one of its kind. These technologies include absorption of radionuclides on selected inorganic resins, and desalination and concentration of saline wastes using electromembranes. In addition, some technologies from the U.S. are being utilized where possible, including back washable filters to assist in secondary waste minimization, and programmable controllers for process control optimization.