

## **Testing and Startup of the Savannah River Site Integrated Salt Disposition Process - 9193**

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### **ABSTRACT**

The Savannah River Site (SRS) is removing liquid radioactive waste from the tanks in its Tank Farm. To treat waste streams to remove Cs-137, Sr-90, and actinides, SRS developed the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU). The ARP contacts salt solution with monosodium titanate (MST) to sorb strontium and select actinides. After MST contact, the resulting slurry is filtered to remove the MST (and sorbed strontium and actinides) and entrained sludge. The filtrate is transferred to the MCU for further treatment to remove cesium. The solid particulates removed by the filter are concentrated to ~ 5 wt %, washed to reduce the sodium concentration, and transferred to the Defense Waste Processing Facility (DWPF) for vitrification. The CSSX process extracts the cesium from the radioactive waste using a customized solvent to produce a Decontaminated Salt Solution (DSS), then strips and concentrates the cesium from the solvent with dilute nitric acid. The DSS is incorporated in grout while the strip acid solution is transferred to DWPF for vitrification.

Savannah River National Laboratory (SRNL) personnel performed tests using actual radioactive samples of the first waste batch – Salt Batch 1 – for processing prior to start of operation. Testing included MST sorption to remove strontium and actinides followed by CSSX batch contact tests to verify expected cesium mass removal and concentration. This paper describes the tests conducted and compares results from MCU facility operations. The results include strontium, plutonium, and cesium removal, cesium concentration, and organic entrainment and recovery data. Additionally, the paper describes lessons learned during commissioning of the MCU facility.

### **INTRODUCTION**

In 2001, the Department of Energy (DOE) identified the CSSX process as the preferred processing option for removing cesium from SRS wastes. The first step of the process, housed within the Actinide Removal Process, involves sorption of radioactive strontium and alpha-emitting actinides onto MST (1). These solids, as well as entrained metal hydroxides (also known as “sludge”) are removed from the liquid using ultrafiltration in a conventional cross-flow filter. (2) The treated liquid is then processed to remove cesium. The CSSX process for removal of cesium from alkaline solutions uses a novel solvent invented at the Oak Ridge National Laboratory. (3, 4) This solvent consists of a calix[4]arene-crown-6 extractant (BOBCalix<sup>®</sup>) dissolved in an inert hydrocarbon matrix (Isopar<sup>®</sup> L). An alkylphenoxy alcohol modifier (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, also known as Cs-7SB) added to the solvent enhances the extraction power of the calixarene and prevents the formation of a third phase. An additional additive, trioctylamine (TOA), improves stripping performance and mitigates the effects of any

surfactants present in the feed stream. The solvent extraction process was successfully demonstrated with actual SRS high level waste supernate during testing performed at SRNL by 2002. (5, 6) In February 2004, DOE commissioned construction of a smaller version (i.e., 11.4 – 34.1 L/min (3-9 gpm) processing rate for salt solution) of the final process for interim treatment of waste until construction of the full-scale Salt Waste Demonstration Facility completes. This smaller facility is known as the Modular Caustic Side Solvent Extraction (CSSX) Unit, or MCU.

Fig. 1 shows a schematic of the combined operations, known as the Integrated Salt Disposition Project.



By June 2007, the integrated operations began using simulated salt solutions procured from vendors. By December of 2007, the first waste for processing was transferred and blended into Tank 49H. During December and into early January 2008, Operations personnel collected samples of waste from Tank 49H and transported them to SRNL for chemical analyses and process demonstrations to qualify the material for processing.

## LABORATORY TESTING

Upon receipt of the 6 nominally 200-mL samples at SRNL, personnel combined and pulled aliquots of the various tank samples for an extensive suite of chemical and radionuclide analyses. Table I shows the measured data for key constituents for the composite of samples arriving in December and also shows data from performing a lab-scale demonstration of the ARP process on the composite sample. A second composite, arriving in January after ~30 days of settling in the tank, showed only minor variance and is not reported here. For the key radionuclides, the concentrations reflect values before and after combining with MST and process water in replicate tests. Values for all other constituents represent the measurement on the as-received, combined sample.

The as-received waste had very few solids. The design assumption for ARP is a concentration of ~600 mg/L of entrained solids; the measured value is only ~2% of the design assumption. The 600 mg/L design assumption equates to nearly equal amounts as the MST added for each portion of waste treated. The facility treats multiple portions (or batches) of waste until reaching a calculated inventory of ~5 wt % solids in the MST strike tank. At that time, the solids are washed to reduce the sodium concentration in the liquid and the accumulated solids transferred to the DWPF for vitrification. Since the waste contains very little sludge, the facility will process nearly twice the nominal amount of waste prior to requiring a transfer of the solids. A full description of the laboratory testing and chemical analysis of the waste is available in a separate report. (7)

Approximately three weeks elapsed between the replicate MST tests. The Sr concentration dropped appreciably over this period suggesting the suspended solids may contain appreciable Sr. The Pu concentration did not vary appreciably over this period. The Cs concentration varied more than expected based on analytical uncertainty. The cause of this variance is unknown and is indicative of the overall experimental uncertainty for the replicate experiments.

Table I. Concentrations of key constituents in first waste feed samples.

Density (g/mL)	1.251 ± 0.0078	
Turbidity (NTU) <sup>b</sup>	31.0 ± 0.52	
Solids (mg/L) estimated <sup>a</sup>	12.5	
Na (M)	5.05 ± 0.17	
K (mM)	6.1 ± 0.1 (0.0061 M)	
	Feed Sample for 1 <sup>st</sup> MST Test	Feed Sample for 2 <sup>nd</sup> MST Test
Cs-137 (Bq/L)	(2.34 ± 0.056)E+09	(2.58 ± 0.036)E+09
Sr-90 (Bq/L)	(8.99 ± 1.52)E+06	(5.25 ± 0.977)E+06
Pu-238 (Bq/L)	(1.13 ± 0.055)E+06	(1.10 ± 0.059)E+06
	24 Hours After MST Addition	

Cs-137 (Bq/L)	$(2.77 \pm 0.061)E+09$	$(2.28 \pm 0.033)E+09$
Sr-90 (Bq/L)	$(1.52 \pm 0.277)E+05$	$<9.66E+04$
Pu-238 (Bq/L)	$(8.07 \pm 0.636)E+04$	$(5.18 \pm 0.311)E+04$

<sup>a</sup> Solids content is estimated using a correlation (see equation 1 and Figure 4) for simulated SRS sludge in a typical salt solution developed in a prior study (C. J. Martino, M. R. Poirier, F. F. Fondeur and S. D. Fink, "Flocculating, Settling, and Decanting for the Removal of Monosodium Titanate and Simulated High-Level Waste Sludge from Simulated Salt Solution," WSRC-TR-2001-00413, October 16, 2001).

<sup>b</sup> NTU = nephelometric turbidity units

Personnel added water and MST (at 0.4 g/L of composite) to the combined salt solution in proportions emulating facility operating conditions. The resulting solution measured 4.7 M in sodium, on the low side of the nominal operating range. Researchers filtered the solution at various time intervals (i.e., 6, 12 and 24 hours after MST addition) and analyzed for plutonium (Pu) and strontium (Sr) concentrations in the liquid. The experiment occurred in duplicate. After 24 hours, plutonium decontamination factor (DF; i.e., ratio of starting feed concentration versus concentration in the filtered liquid) measured  $17.5 \pm 5.0$ . For strontium, the DF measured  $59 \pm 11$ . Personnel also measured cesium (Cs) concentration as a control. The Pu and Sr DF values agree reasonably well with predictions, 11 for Pu and 63 for Sr, using a previously published model and the measured concentrations of the feed. (8)

The MST has no affinity for sorption of Cs and hence one expects a DF value of 1. The measured value equals  $0.99 \pm 0.20$ . The Sr and Cs variance falls within the analytical method uncertainty. The Pu variance is likely the result of cross-contamination and higher experimental uncertainty at the low average final Pu concentrations of  $6.62 (\pm 2.03) E+04$  Bq/L.

Personnel used the filtered liquid from the MST test to examine the cesium mass transfer behavior with the solvent. They performed sequential batch contacts for the extraction, (two) acid scrubs, and (three) acid strip stages of the process. Table II contains the measured cesium distribution values, values from a prior test with a chemically-similar salt solution performed while qualifying the same solvent for facility operations, and the acceptable ranges assumed for the design of the facility. An empirical model exists for predicting the extraction distribution value as a function of solution composition. (9) The prediction for this waste (9.5) agrees well with the measured value of 9.07. The data shows acceptable cesium mass transfer.

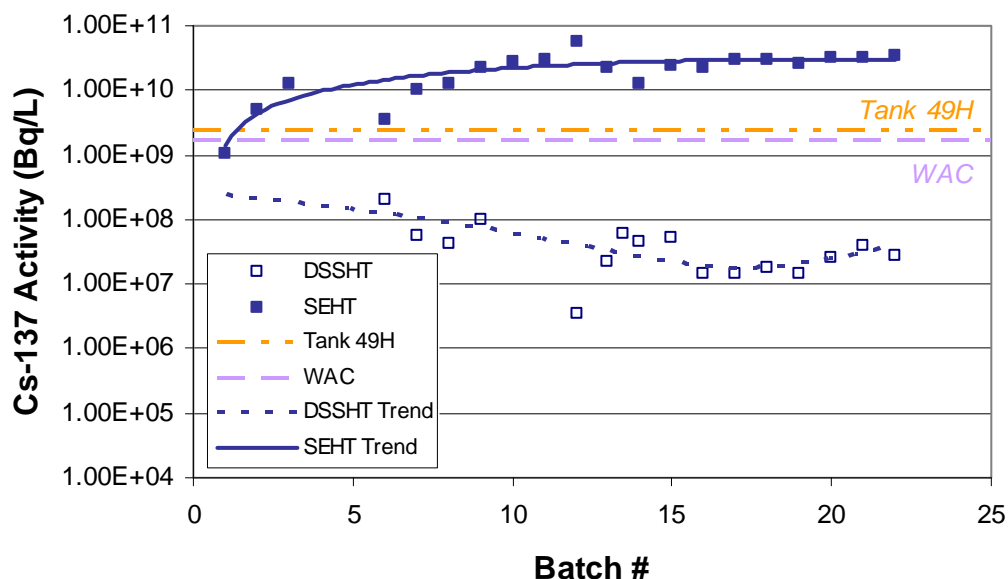
Table II. Cesium distribution values measured in sequential batch contacts for extraction, acid scrub, and acid strip stages of process.

Stage	Extraction	Scrub #1	Scrub #2	Strip #1	Strip #2	Strip #3
Acceptable Range	>8	>0.6, <2	>0.6, <2	<0.2	<0.16	<0.16
Prior test with solvent (10)	9.53	2.54	1.72	0.147	0.0607	0.0615
Current Test	9.07	1.60	1.29	0.070	0.046	0.042

Personnel also observed the stability of the filtrate from the MST treatment over time. The amount of silicon and aluminum in the waste are such that the solution is supersaturated with respect to precipitation of aluminum hydroxide and sodium-aluminosilicates. The turbidity of the filtrate increased gradually over 72 days reaching ~8.5 NTU which corresponds to an estimated 3.5 mg/L of solids in the solution.

## SUMMARY OF COMBINED ARP/MCU FACILITY PERFORMANCE

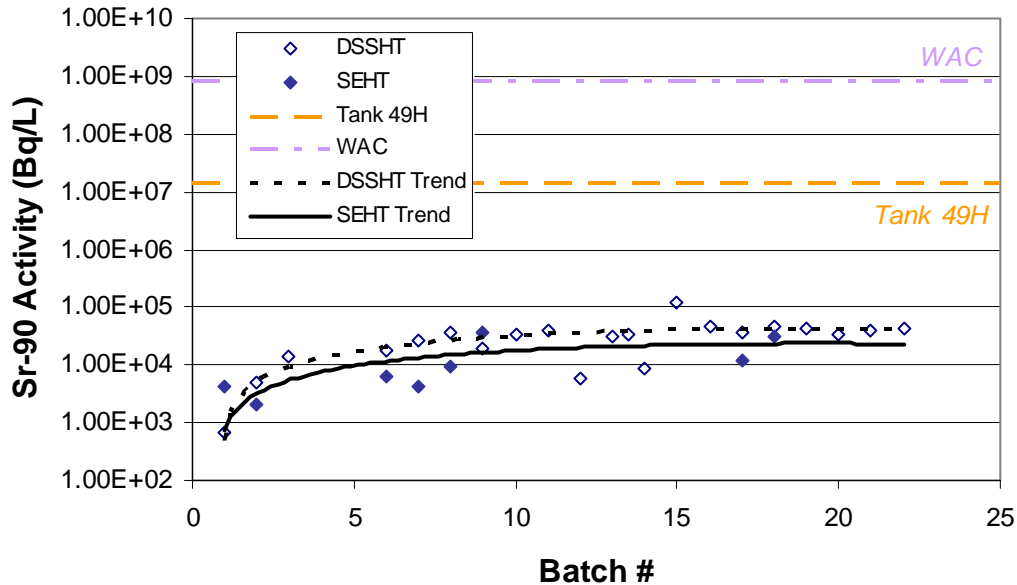
Facility operations began in early May 2008. For each batch of product streams from MCU, personnel collected samples from the Decontaminated Salt Solution Hold Tank (DSSHT, which holds the treated waste after radionuclide removal) and the Strip Effluent Hold Tank (SEHT, which holds the cesium-enriched acid stream for transfer to vitrification) – See Fig. 1. SRNL analyzed these samples for cesium, strontium and plutonium concentrations. Fig. 2 shows the cesium decontamination performance for approximately the first ~380,000 L (~100,000 gal) of treated waste, or the first 22 sets of samples from either the DSSHT or SEHT. The blue “Tank 49H” line represents the initial values for Tank 49H. The red “WAC” line represents the Waste Acceptance Criteria (WAC) limits for the receiving Saltstone Production Facility. The cesium concentration in the DSSHT samples decreases steadily over sequential batches reflecting the improvement in reaching near steady-state operations. The cesium concentration in the strip effluent acid correspondingly increases asymptotically over time as expected. The ratio of the Cs in the SEHT to that of the feed is known as the Concentration Factor. This ratio reaches a value of ~14 compared to design expectations of 12-15. Performance is well within facility operational limits.



**Fig. 2. Cesium concentrations in samples from decontaminated salt solution hold tank and strip effluent hold tank.**

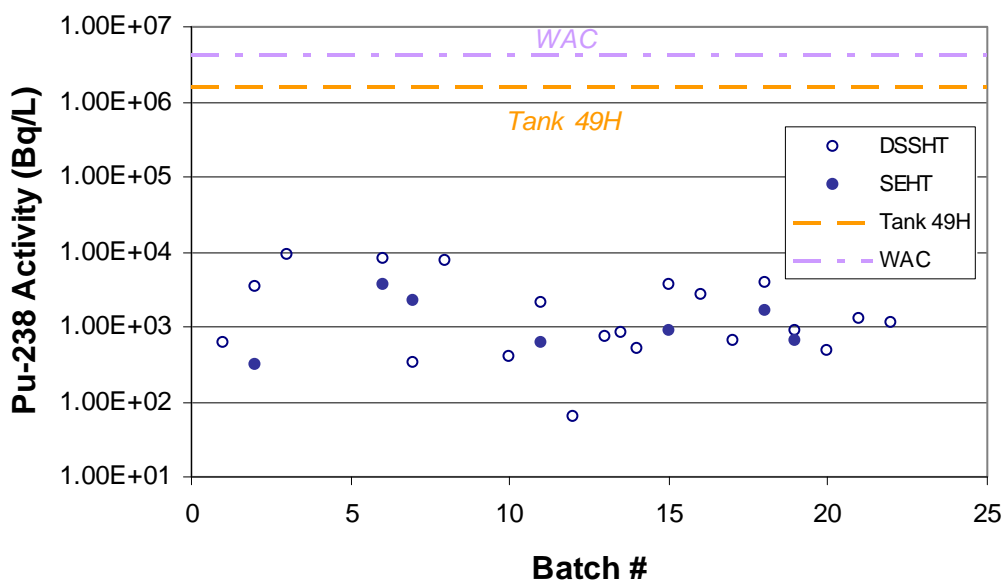
Fig. 3 displays the strontium concentration data per batch number for the SEHT and DSSHT during processing of the first ~380,000 L of the salt solution. This data is also compared to the concentration of the original waste in Tank 49H and to the Saltstone WAC limit. Most of the measurements for the SEHT samples fell below analytical method detection limits. The solvent has no significant affinity for Sr and hence this species only transfers to the strip acid due to aqueous entrained in the solvent from the final extraction stage and persisting through the two scrub acid stages. The instances of measurable Sr concentration in the SEHT samples appear to correlate with known periods of deviation from normal

operations in the facility. Hence, some of these values may represent contamination of the SEHT due to direct transfer of unprocessed waste through those tanks or due to solvent hydraulic excursions. Each of these causes are discussed in limited form later within this paper.



**Fig. 3. Strontium concentrations in samples from decontaminated salt solution hold tank and strip effluent hold tank.**

Fig. 4 shows the plutonium concentration per batch number for the SEHT and DSSHT during processing of the first ~380,000 L of the salt solution. These data are compared to the original waste from Tank 49H and to the Waste Acceptance Criteria (WAC) for the Saltstone Production Facility. The starting plutonium concentration in Tank 49H was less than the WAC limits. These data contain appreciable scatter. While many measurements of plutonium in the SEHT samples fell below the method detection limit, the data is much less consistent than that for Sr. The cause of this variation is still under investigation.



**Fig. 4. Plutonium concentrations in samples from decontaminated salt solution hold tank and strip effluent hold tank.**

For both Sr and Pu, decontamination performance significantly exceeds the values observed in laboratory tests. The strontium DF values, as measured through both ARP and MCU, exceed 300 while Pu DF values are 400 – 2000 or greater. One contributor to the improved performance is linked to facility throughput rate. Due to various interruptions or delays, the average contact time with MST for waste exceeded the nominal 24 hours in many cases. Longer contact time will lead to an increase in sorption. For strontium, the laboratory data suggested possible precipitation from the feed over time. Hence, as the waste sits in Tank 49H for an extended period, Sr feed concentrations may decline leading to an apparent increase in DF values. Another possible explanation for the scatter in the data could be linked to chemical cleaning of the ARP secondary guard filter which restricted flow during periods of operation. To alleviate the ARP flow restriction, personnel conducted cleaning cycles that ultimately resulted in diluting some waste feed with portions of 50 wt % sodium hydroxide. The net result of such additions is a slight dilution of Pu and Sr and a possibility of precipitation of Pu and Sr. Finally, bayerite solids did form and collect on the coalescers before the DSSHT during operations. (11) These solids may also contribute to precipitation of Pu and Sr from solution.

Despite the increased scatter in the measured Sr and Pu measurements, all the values fall well below the operational limits for the facility.

#### SOLVENT QUALITY AND RECOVERY AT MCU

During operations, the Isopar<sup>®</sup> L evaporates from the solvent due to its volatility and the process ventilation flow. Operations personnel continuously monitor the density of the solvent to prevent the value drifting outside acceptable ranges for hydraulic operation of the centrifugal contactors. Also, samples are periodically collected and transported to SRNL for analyses. Despite these steps, after processing ~190,000 L (~50,000 gal) on waste, the solvent density drifted high enough to cause hydraulic



upsets and carryover of caustic wash solution into the Solvent Hold Tank (SHT, see Fig. 1, this tank holds the working inventory of solvent as it recycles through the process). This event resulted in an interruption of operations during which personnel added Isopar<sup>®</sup> L to return the solvent composition to within acceptable ranges. Facility personnel revised the density alarm limits and no additional hydraulic upsets occurred during processing.

On a later occasion, personnel added an additional 50 gal of solvent (freshly prepared by SRNL) to the inventory. Over time, solvent accumulated in the decanter tanks for the strip effluent acid and for the decontaminated salt solution as expected. Collection of solvent in those locations depleted the inventory in the Solvent Hold Tank requiring addition of fresh solvent to maintain the desired operating volume of the tank. The addition of solvent to the Solvent Hold Tank brought the operating volume back to within desired range.

The strip effluent acid and the decontaminated salt solution each pass through organic recovery equipment prior to exiting the facility. The recovery equipment consists of a single stage coalescer flowed by a decanter tank with an included coalescer entrance stage. The equipment recovers the valuable solvent for use in the process and also minimizes transfer of Isopar<sup>®</sup> L to facilities receiving the aqueous effluents. Isopar<sup>®</sup> L if present in sufficient quantities can pose a flammability risk in downstream facility process vessels.

Samples from the SEHT and DSSHT for each batch are sent to another process support laboratory on site and analyzed to determine amount of entrained Isopar<sup>®</sup> L. Only five samples from each tank contained Isopar<sup>®</sup> L above the minimum measurable limit for the analytical method. The maximum measured value approached 25 mg/L. Each of the cases of measured carryover correlates with known periods of deviation from routine operations in MCU. During all periods of normal operation, the entrained concentration of solvent in the aqueous effluent streams fell below measurable concentrations (e.g., < 13 mg/L).

The Strip Effluent Coalescer operated with maximum pressure drop of less than 110 kPa (16 psid) since initial processing of radioactive waste. The facility established an operating limit of 138 kPa (20 psid) based on a vendor recommended limit of 207 kPa (30 psid). The vendor indicates integrity of the media is risked at greater differential pressures. While the pressure drop did not exceed limitation or impose operational difficulties, the value exceeded expectations based on pilot testing. At a later date, SRNL will receive and analyze the spent coalescer to gain an understanding of the material restricting flow.

In contrast, the Decontaminated Salt Solution Coalescer pressure drop increased with progressive volumes of waste processed. After processing the first three DSSHT batches of wastes (~38,000 L or ~10,000 gal), the pressure drop exceeded 172 kPa (25 psid). Pilot scale testing, in comparison, reported a maximum pressure drop of 86.2 kPa (12.5 psid) even for the maximum liquid flow rate tested which exceeds that measured during operations.

Personnel removed the coalescer cartridge, replaced it with a fresh cartridge, and resumed operations. After processing an additional ~151,000 L (or 40,000 gal equivalent to 8 DSSHT batches) of waste, the pressure drop exceeded 138 kPa (20 psid). Personnel replaced the cartridge again and resumed operations. The pressure drop remained below 34 kPa (5 psid) for the next ~227,000 L (~60,000 gal) of waste (13 DSSHT batches) but began to increase again and exceeded 172 kPa (25 psid) after processing an additional ~95,000 L (or ~25,000 gal) of waste. Efforts to chemically clean the first and third cartridges in the facility using nitric acid proved ineffective.

SRNL performed destructive analyses of the coalescers from the first and second replacements. (The third cartridge still awaits transfer to SRNL for analyses at this time – January, 2009.) The fouling is due primarily to aluminum hydroxide solids (i.e., bayerite) that cover almost the entire flow area of the coalescer. A separate report provides a more detailed account of the studies. (**Error! Bookmark not defined.**)

## LESSONS LEARNED

During operations, the MCU facility decontaminates the incoming waste stream to well within acceptable parameters. To date, operations have treated ~510,000 L (~135,000 gallons) of salt solution. Physical upsets to plant operations occurred and can be attributed to two general causes. First, evaporation of the Isopar® L diluent slowly increases the density of the solvent causing hydraulic performance in the contactors to deteriorate. This problem can be countered by monitoring the solvent density and composition with occasional additions of Isopar® L to bring the solvent within specification.

Second, aluminum-containing solids that precipitate from pH swings or from a supersaturated feed foul the DSS coalescer. Several steps are in progress to minimize these upsets. The facility will add pre-filters prior to the DSS Coalescer to collect the solids and increase the time between required replacements of the media. Also, personnel will adjust the composition of the next waste solution for processing by addition of sodium hydroxide solution. The amount added will be selected to eliminate supersaturation of the solution as calculated by predictive thermodynamic models. In addition, ongoing research efforts continue to study the causes of fouling in the third coalescer. Similarly, personnel are testing coalescer elements or alternate designs intended to increase available surface area and decrease frequency of fouling

## CONCLUSIONS

SRS successfully treated more than ~510,000 L (~135,000 gallons) of salt solution of radioactive waste through the Actinide Removal Process and the Modular Caustic Side Solvent Extraction Unit. Removal of plutonium and strontium by sorption on monosodium titanate exceeded expectations based on laboratory testing and confirmatory demonstrations. Cesium removal efficiency through the solvent extraction operations agreed well with expectations based on laboratory studies and model predictions. Using Tank 49H as a starting feedstock, SRS separated 20 curies of plutonium-238, 200 curies of strontium-90, and 33,000 curies of cesium-137 from the waste during the initial operations.

Fouling of the coalescer cartridges that remove the entrained solvent from the effluent aqueous streams is the most significant and persistent operational challenge. Laboratory testing identified precipitation of aluminum solids from the saturated waste as the leading cause for the fouling. A design modification to install filters before the coalescer is in progress to mitigate this fouling behavior. Additionally, treatment of the next batch of waste will include addition of sodium hydroxide in sufficient quantities to reduce the aluminum concentration below the value at which precipitation is predicted by available thermodynamic models.

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