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Processing Macrobatch 2 at the Savannah River Site Integrated Salt Disposition Process (ISDP)

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The Savannah River Site (SRS) is currently removing liquid radioactive waste from the tanks in its Tank Farm. To treat waste streams that are high in ^{137}Cs, ^{90}Sr, and/or actinides, SRS developed the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction (CSSX) Unit. Collectively, these two processes make up the Integrated Salt Disposition Process (ISDP). The ARP part is responsible for the removal of strontium and actinides, while the MCU part is responsible for removing cesium. This paper discusses the qualification testing of the second batch of caustic waste that is being processed through ISDP currently. This paper also describes the tests conducted and compares results with current facility performance.

The ARP contacts the 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. In order to predict waste behavior, the Savannah River National Laboratory (SRNL) personnel performed tests using actual radioactive samples of the second waste batch – Macrobatch 2 – for processing prior to the start of the 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. Our work indicates that the bench scale tests are a conservative predictor of actual waste performance.

Keywords actinide; ARP; BOBCalixC6®; cesium; MCU; MST

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 oxide 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 (BOBCalixC6®) dissolved in an inert hydrocarbon matrix (Isopar 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 in 2002 (5,6). In February 2004, DOE commissioned the construction of a smaller version (i.e., 11.4 – 34.1 L/min or 3–9 gpm processing rate for the salt solution) of the final process for the interim treatment of waste until the construction of the full-scale Salt Waste Processing Facility is completed. This smaller facility is known as the Modular Caustic Side Solvent Extraction (CSSX) Unit, or MCU. Figure 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

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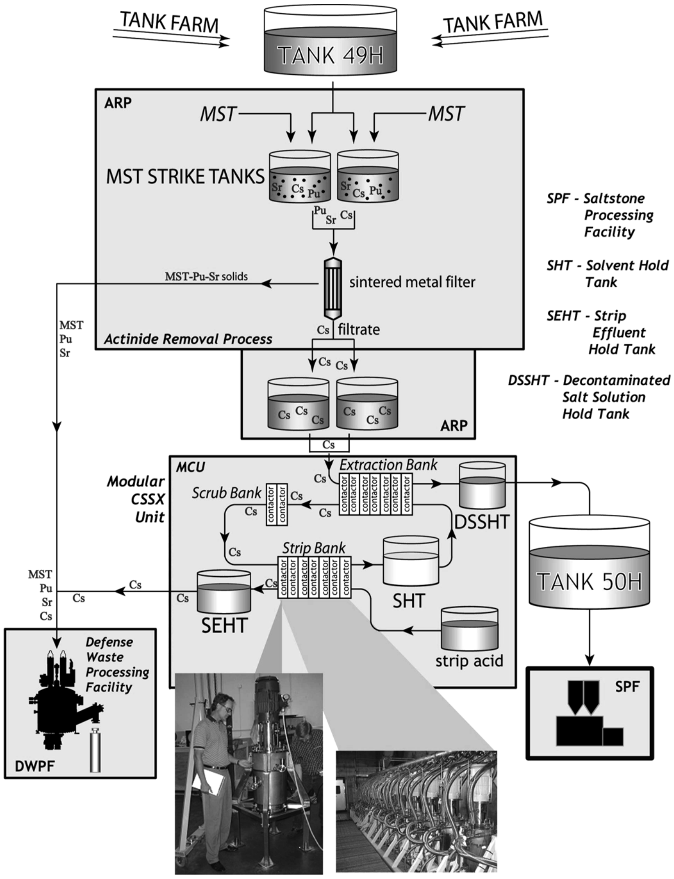

FIG. 1. Schematic of integrated salt disposition processing operations within the overall waste treatment system.

to qualify the material for processing. After being qualified, this first batch of material (Macrobatch 1) was processed from May, 2008 to September, 2008.

A second macrobatch of material was qualified in early 2009 in the same fashion as in Macrobatch 1. This material began processing in February 2009 and will have been completely processed by the time of this article.

LABORATORY TESTING

Upon receipt of the three Tank 22H and three Tank 41H samples at SRNL (July and August 2008), personnel measured the density of each tank's samples. The results indicated that each tank's samples were effectively identical, and so the samples from each tank were combined into their respective composites, and filtered through a 0.45 μm filter. The researchers then pulled aliquots of the composites for an extensive suite of chemical and radionuclide analyses.

The as-received tank samples had very few visual 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).

Composite Ratios

Tank Farm personnel derived the proper mixing ratios between the Tank 22H, 41H, and 49H (the heel from the previous macrobatch) samples (8). Furthermore, the Tank Farm decided to add 50 wt% caustic in order to reach a free hydroxide to 2.0 M in order to inhibit aluminum compound precipitation. Table 1 lists the components and volumes of the materials to comprise the ISDP Composite.

After analysis of the Tank 22H and 41H samples was complete and the proper volumes of tank material (and sodium hydroxide) were combined and mixed in Tank 49H, a confirmatory sample was pulled and analyzed in the same manner as the Tank 22H and 41H samples (see Table 2, furthest right column).

Actinide Removal Demonstration

For the ARP Demonstration Tests, technicians generated 200 mL of the ISDP Composite (without filtration), placing half into each of the two 250-mL polyethylene bottles. We did not observe gross formation of solids and did not measure the turbidity. We used one of the bottles to conduct the MST addition experiment, while one bottle served as a control. We added 0.4 g/L of MST solids (from an archived batch of material from Blue Grass Chemical Specialties, lot # MST-2753) to the experiment bottle at time = 0 hours. During the experiment, personnel collected samples from each of the two bottles at 0, 12, and 24 hours. For the sample at 0 hours, sampling occurred immediately prior to MST addition.

TABLE 1
Constituents of the ISDP macrobatch 2 composite

Component	Volume ratio
Tank 22H	2.47
Tank 41H	1.74
Tank 49H$^{\Sigma}$	7.77
50 wt% NaOH	1

$^{\Sigma}$This is material left over from the previous macrobatch processing (heel).

TABLE 2
Results of the tank sample analyses

Analyte	Tank 22H	Tank 41H	22–41–49 Composite
Density (g/mL)	1.024 (0.74%)	1.412 (1.07%)	not measured
Na (M)	0.409 (0.18%)	8.19 (1.65%)	5.55 (2.48%)
Al (M)	0.000597 (1.79%)	0.657 (1.85%)	0.262 (2.47%)
K (M)	0.000212 (10%)[ℑ]	0.0136 (3.87%)	0.00621 (2.49%)
Si (M)	0.00404 (1.02%)	<0.00489	0.00172 (2.56%)
Free OH (M)	0.141 (0.71%)	1.05 (1.46%)	2.14 (10%)
NO_3^- (mg/L)	0.0724 (0.059%)	5.69 (9.68%)	2.13 (5.72%)
NO_2^- (mg/L)	0.160 (0.48%)	0.221 (7.10%)	0.222 (1.81%)
^{238}Pu (pCi/mL)[ϒ]	3.90×10^{1} (119%)	3.46×10^{4} (4.08%)	2.65×10^{4} (14.0%)
^{235}U (pCi/mL)	2.99×10^{-1} (8.93%)	2.12×10^{-1} (7.00%)	2.50×10^{-1} (10.1%)
^{238}U (pCi/mL)	7.51×10^{0} (1.70%)	5.70×10^{-1} (2.18%)	1.67×10^{0} (1.30%)
^{137}Cs (pCi/mL)	2.31×10^{5} (7.70%)	9.56×10^{7} (4.01%)	5.34×10^{7} (2.12%)
^{90}Sr (pCi/mL)	2.18×10^{5} (7.32%)	5.79×10^{3} (2.50%)	2.93×10^{5} (1.78%)
Total Alpha (pCi/mL)[ƒ]	$<9.81 \times 10^{2}$	3.71×10^{4} (2.06%)	$<2.86 \times 10^{4}$

[ℑ] This is a single analytical result, with the value in parenthesis being the analytical uncertainty.
[ϒ] soluble ^{238}Pu, not total ^{238}Pu.
[ƒ] Cs-removed.

Throughout the course of the experiment, the bottles were agitated using a magnetic stir plate and stir bars. Temperature control (to 25°C) was initially provided by an actively controlled water bath. Unfortunately, the water bath temperature controller failed (integrated circuit electronic components have a limited and unpredictable lifespan in the Shielded Cells). However, records of the measured temperature over the duration of the experiment showed that the temperature stayed at 22–23°C, which was within the desired operating range.

Technicians filtered the samples using 0.45 μm Versapor™ syringe filters, diluted them with acid where necessary (to reduce personnel exposure to radiation during sample handling), removed them from the cells for analysis, and analyzed for plutonium (PuTTA), ^{90}Sr (beta scintillation), ^{137}Cs (gamma scan), and ^{237}Np (ICPMS).

Extraction, Scrub, Strip (ESS) Experimental Demonstration

An ESS test is a series of aqueous-solvent contacts designed to approximately mimic the MCU process, and to test the ability of the solvent to complex and release cesium. Using a 125-mL Teflon™ separatory funnel, the test starts by contacting 90 mL of aqueous phase (in this case, the ISDP Composite material after contact with MST and consequent filtration) with 30 mL of fresh, unused CSSX solvent. After mixing and contacting for ~24 hours, the phases are separated and sampled. The organic phase is transferred back into the funnel, and ~5 mL of scrub acid (0.05 M HNO_3) is added. After mixing and contacting for ~24 hours, the phases are separated and sampled. This general procedure is repeated one more time with scrub acid, followed by three cycles of ~5 mL of strip acid (0.001 M HNO_3). SRNL measured cesium distribution coefficients (see Table 5) of the batch of solvent that most closely matched that is in the MCU facility ("S2-D1-YESBOB-T-WI"). In previous documents, (9,10) we measured the D values from this same batch of solvent.

EXPERIMENTAL RESULTS

Generally, sample results are the average of triplicate samples. The results are shown in Table 2, with the % residual standard deviation given in parentheses. The results of the tank analyses were as predicted.

ARP Test Results

For the MST strike, researchers analyzed the filtered samples for ^{238}Pu. Table 3 shows the plutonium results for ^{238}Pu. The ^{238}Pu data is more useful than the $^{239/40}$Pu as the former is not limited by detection limit values.

The uncertainty in Table 3 is the analytical uncertainty associated with the measurement and does not include any contribution to uncertainty due to experimental and sampling methods.

Researchers also analyzed the filtered samples for ^{90}Sr. Table 4 shows the results for ^{90}Sr. The uncertainty in Table 4 is the analytical uncertainty associated with the measurement and does not include any contribution to uncertainty due to experimental and sampling methods.

TABLE 3
^{238}Pu concentrations in the MST strike filtrates

Time	Control activity (pCi/mL)	Control DF	Experimental activity (pCi/mL)	Experimental DF
0▽	$2.46(\pm0.143) \times 10^4$	N/A	$2.46(\pm0.143) \times 10^4$	N/A
12	$2.93(\pm0.218) \times 10^4$	0.84	$4.30(\pm0.223) \times 10^3$	5.73
24	$2.82(\pm0.169) \times 10^4$	0.87	$4.36(\pm0.257) \times 10^3$	5.64

▽The Time = 0 Control and Experimental values are calculated from a single value taken before the addition of MST and thus are the same.

TABLE 4
^{90}Sr concentrations in the MST strike filtrates

Time	Control activity (pCi/mL)	Control DF	Experimental activity (pCi/mL)	Experimental DF
0▽	$1.91(\pm0.160) \times 10^5$	N/A	$1.91(\pm0.160) \times 10^5$	N/A
12	$1.76(\pm0.142) \times 10^5$	1.09	$2.15(\pm0.193) \times 10^3$	88.9
24	$1.71(\pm0.135) \times 10^5$	1.11	$2.70(\pm0.262) \times 10^3$	70.9

▽The Time = 0 Control and Experimental values are calculated from a single value taken before the addition of MST and thus are the same.

TABLE 5
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
Expected Range	>8	>0.6, <2	>0.6, <2	<0.2	<0.16	<0.16
Prior test with solvent (11)	9.53	2.54	1.72	0.147	0.0607	0.0615
Current Test	14.6	1.51	2.13	0.742	0.0879	0.0312

ESS Test Results

Material from the ARP (MST strike) test was used in an ESS test. For this test, we used a nominal starting volume of 90 mL of aqueous feed, and 30 mL of fresh, unused CSSX solvent (S2-D1-YESBOB-T-WI).

Table 5 shows the test results from the ESS test, corrected to the normal process operating temperatures (23°C for extraction, and 33°C for scrubbing and stripping). As a comparison, the results from an ESS test (using the same solvent) in August, 2007 are displayed.

The current test shows values within the expected ranges except for the Scrub #2 and Strip #1 results. These two values, while outside the range of what was expected, are not far enough from expectations to warrant concern.

SUMMARY OF COMBINED ARP/MCU FACILITY PERFORMANCE

Facility operations on Macrobatch 2 began in February, 2009. Material was processed through ARP and MCU in a series of "microbatches" of ~20,000 L each. For each microbatch, 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). SRNL analyzed these samples for cesium, strontium, and plutonium concentrations.

During the processing of Macrobatch 2, the operators made several changes to the system. First, on March 6, 2009 the rate of scrub acid flow (0.05 M nitric acid) was doubled in an effort to reduce the pressure drop across the Strip Effluent (SE) coalescer (the coalescer is a device to separate organic carryover from the aqueous SE stream). This was successful for a time. On March 25, the SE coalescer was replaced when the pressure drop continued to increase. On May 4, the MST strike time at ARP was reduced to 12 hours in order to increase the throughput. These changes are noted in the figures below.

Figure 2 shows the cesium decontamination performance for approximately the first ~680,000 L (~180,000 gal) of treated waste, or the first 34 sets of samples from either the DSSHT or SEHT.

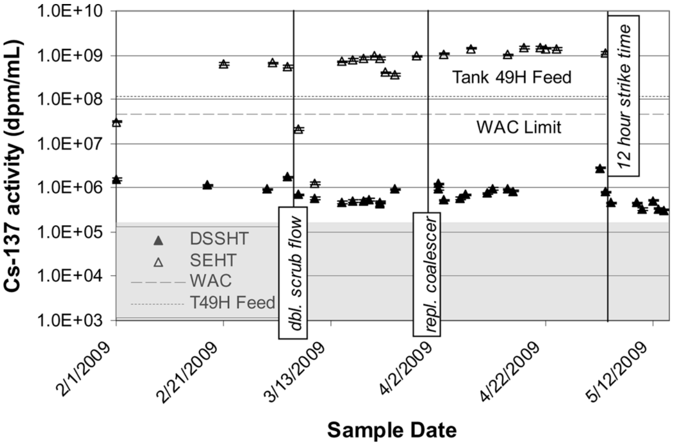

FIG. 2. Cesium processing results.

The "Tank 49H" line represents the initial values for Tank 49H (the feed for ISDP). The "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 average of the cesium DF (source material/DSSHT) across all samples is 150. Performance is well within facility operational limits. The shaded grey area represents the range of results from blank samples (activity from background contamination in the high Activity Cells).

Another way to look at the cesium removal data is to examine the concentration factor (CF), which is the ^{137}Cs activity in the SEHT divided by the ^{137}Cs in the source tank. The CF values increase over time, reaching a steady value of ~12.5 over time, compared to a theoretical maximum of 12–15.

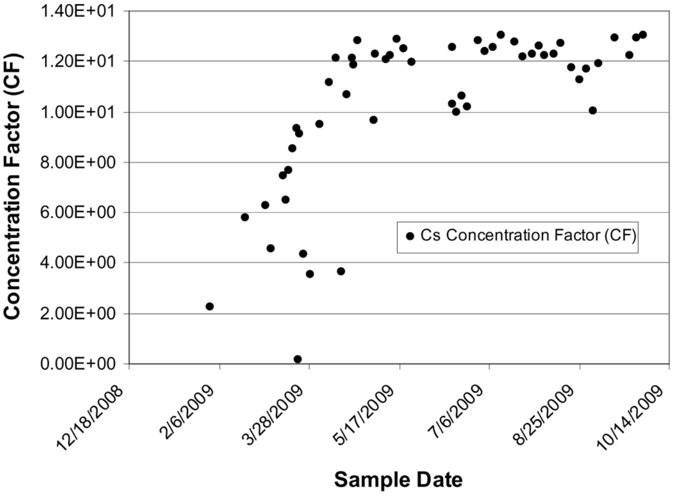

FIG. 3. CF values for ^{137}Cs over time.

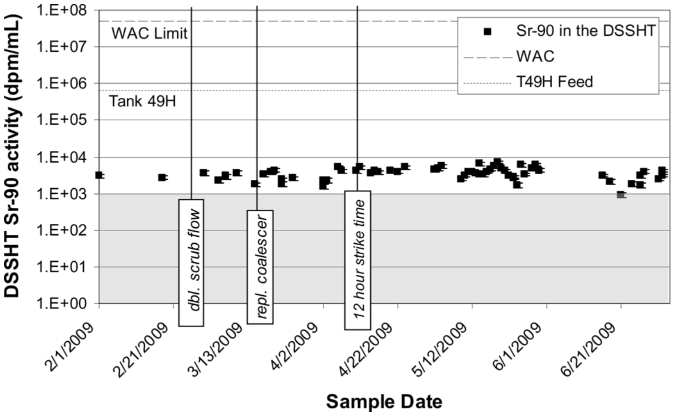

FIG. 4. Strontium processing results.

Figure 4 displays the ^{90}Sr concentration data per batch number for the SEHT and DSSHT during processing of the first ~680,000 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, and so the SEHT data is not shown.

The average of the ^{90}Sr DF (source material/DSSHT) across all samples is 211. Performance is well within facility operational limits. The shaded grey areas represent the range of results from blank samples (activity from background contamination in the high Activity Cells).

Figure 5 shows the ^{238}Pu concentration per batch number for the DSSHT during processing of the first ~680,000 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 ^{238}Pu concentation in Tank 49H was less than the WAC limits. These data contain appreciable

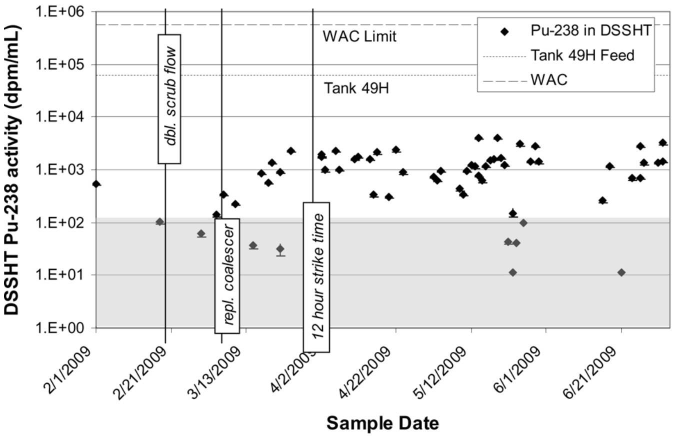

FIG. 5. Plutonium processing results.

scatter. Many measurements of ^{238}Pu in the SEHT samples fell below the method detection limit so the data is much less consistent than that for theDSSHT results. The cause of this variation is still under invesitgation, and as such, the SEHT data is not shown.

The average of the ^{238}Pu DF (source material/DSSHT) across all samples is 190. Performance is well within facility operational limits. The shaded grey areas represent the range of results from blank samples (activity from background contamination in the high Activity Cells).

For the Pu, decontamination perfomance significantly exceeds the values observed in laboratory tests. One contributor to the improved perfomance is linked to the 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 (at least until the strike time was reduced to 12 hours). Longer contact time will lead to an increase in sorption. Furthermore, the MST solids are not removed with each microbatch. Flushing and cleaning of the ARP filter occurrs irregularly, and this leaves the partially loaded MST to accumulate over time, which can remove more MST.

SOLVENT QUALITY AND RECOVERY AT MCU

During operations, the Isopar® 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. When indicated from these types of analyses, Isopar® L is added to the system to make up for evaporative losses. However, even with the occasional Isopar® L addition, the bulk solvent is still lost over time. For example, trioctylamine and Modifier both have small, but finite solubility in the strip acid. The BOBCalixC6® extractant is likely to have a small solubility in the strip acid, although this has not been measured. During Macrobatch 2, MCU added 50 gallons of solvent in April, 2009, and 100 gallons in September, 2009.

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® L. The average Isopar® L concentration in the strip acid is found to be 16 ppm, while the Isopar® L in the DSSHT is 6 ppm.

CONCLUSIONS

SRS successfully treated more than ~750,000 gallons of radioactive salt waste solution as of this writing, and completed the Macrobatch 2 processing campaign target of ~910,000 gallons in December, 2009. 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 100 curies of ^{238}Pu, 300 curies of ^{90}Sr, and 200,000 curies of ^{137}Cs from the waste during the initial operations.

Our laboratory scale testing is a conservative indicator of plant performance–acceptable laboratory scale performance seems to translate into ever better ISDP performance. In the case of cesium, the difference is mostly due to having multiple extraction stages (seven at MCU) compared to the one extraction step in the lab testing. For plutonium and strontium the superior ISDP performance is due at least in part to residual MST left in the strike tank over the lifetime of Macrobatch 2. SRNL is currently examining whether or not we can more accurately predict ISDP performance, as well as continuing to process further batches of waste.

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