

Caustic Side Solvent Extraction At the Savannah River Site: Operating Experience and Lessons Learned - 10105

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Abstract

The Modular Caustic-Side Solvent Extraction Unit (MCU) is the first, production-scale Caustic-Side Solvent Extraction process for cesium separation to be constructed. The process utilizes an engineered solvent to remove cesium from waste alkaline salt solution resulting from nuclear processes. While the application of this solvent extraction process is unique, the process uses commercially available centrifugal contactors for the primary unit operation as well as other common methods of physical separation of immiscible liquids. The fission product, cesium-137, is the primary focus of the process due to the hazards associated with its decay. The cesium is extracted from the waste, concentrated, and stripped out of the solvent resulting in a low-level waste salt solution and a concentrated cesium nitrate stream. The concentrated cesium stream can be vitrified into borosilicate glass with almost no increase in glass volume, and the salt solution can be dispositioned as a low-level grout. The unit is deployed as an interim process to disposition waste prior to start-up of the Salt Waste Processing Facility. The Salt Waste Processing Facility utilizes the same cesium removal technology, but will treat more contaminated waste. The MCU is not only fulfilling a critical need, it is the first demonstration of the process at production-scale.

INTRODUCTION

The Savannah River Site (SRS) needs to separate high activity fission products from the salt waste stream in order to process the bulk of the waste into grout in the Saltstone Facility rather than through the Defense Waste Processing Facility (DWPF) vitrification process which is a more expensive and time consuming process. The principle high activity nuclides in the salt are the plutonium, uranium, strontium and cesium. The In-Tank- Precipitation (ITP) process was implemented using Monosodium Titinate (MST) and filters for plutonium, uranium, and strontium removal and Monosodium Tetraphenyl Borate (STPB) and filters for cesium removal. This process was deemed unsafe by the Defense Nuclear Facility Safety Board (DNFSB) and the State of South Carolina (DHEC) because of the benzene generated from the STPB and was subsequently shut down. SRS was left to obtain a technology that could safely address actinide and cesium removal.

After evaluating several ITP replacement technologies, SRS decided to continue with the MST and filter process for actinide and strontium removal but selected the relatively new caustic side solvent extraction (CSSX) process for cesium removal in the Salt Waste Processing Facility. This facility is scheduled to be constructed and in operation by 2012. Since there is a large inventory of salt waste in the tank farms and there is a shortage of tank space that impacts the ability to operate DWPF, interim facilities were required to allow for actinide and cesium removal until SWPF could be placed in service. Actinide removal technology using MST and

filtering has been established in the 96H and the 512S Buildings. CSSX technology has been established in the Modular Caustic Side Solvent Extraction Unit (MCU).

The CSSX process uses an engineered solvent developed by Oak Ridge National Laboratories to extract the cesium from the salt waste [1]. The solvent is made up of 4 parts: 0.007M Calix[4]arene-bis(tert-octylbenzo-crown-6) "**BoBCalixC6**" (Extractant); 0.75M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol "**Cs-7SB**" (Modifier); 0.003M Tri-n-octylamine "**TOA**" (Suppressor); and the remainder Isopar L[®]. The flowsheet for the CSSX process was developed by Argonne National Laboratories [2]. In the CSSX process, the solvent mixture is contacted counter-currently with the salt solution in 7 V-10 centrifugal contactors at a temperature of $23 \pm 3^\circ\text{C}$ at an Organic to Aqueous (O/A) ratio of 1/3. Figure 1 shows a cross section of a centrifugal contactor.

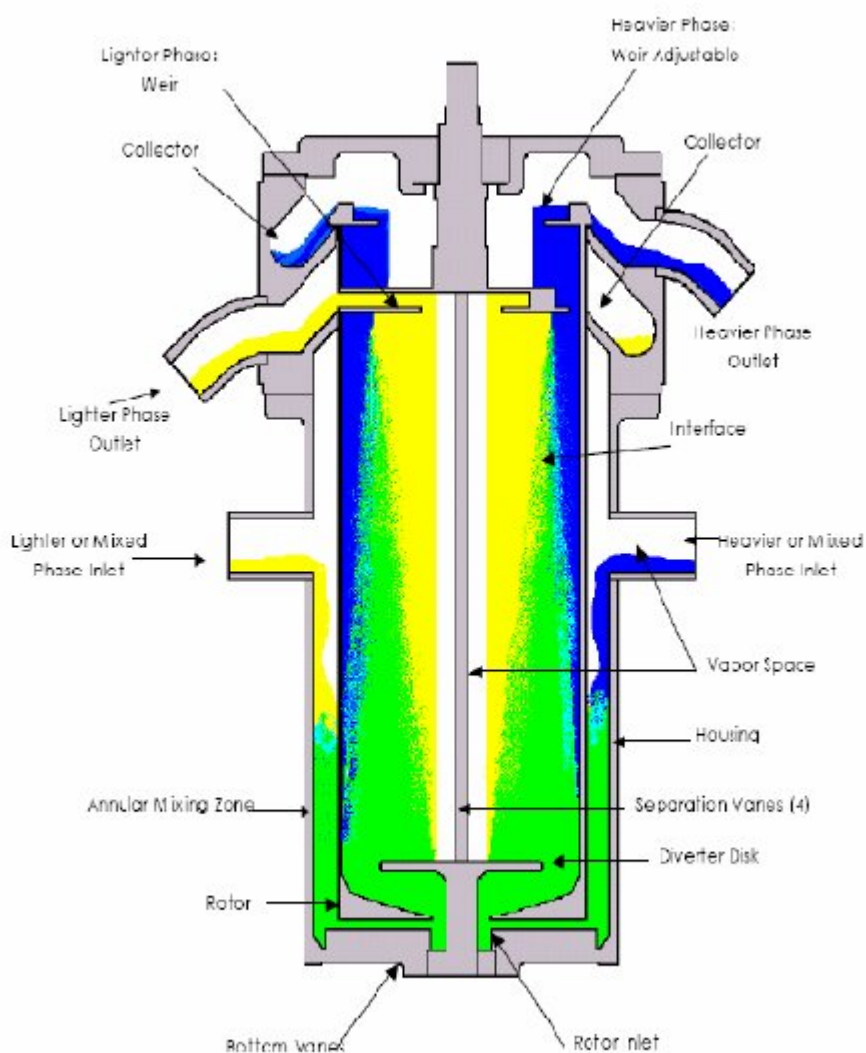


Figure 1 Centrifugal Contactor

Preliminary hydraulic testing of the V-10 contactors with solvent and simulated salt solution indicated that there could be up to 1000 mg/L carryover of the solvent in aqueous stream with the majority of the droplets being less than 10 μ in diameter. This level of carryover could potentially lead to flammability concerns in the Saltstone facility, as well as rapidly deplete the inventory of solvent in the MCU facility. To recover the solvent a coalescer and decanter are installed downstream of the extraction contactors. The coalescer media is a 102 cm (40 in.) long, 20 micron Ryton[®] filter element. The decanter is sized to serve a dual purpose to remove the organic carryover and to provide decay time for barium to allow for accurate inline measurement of the gamma activity of the decontaminated salt solution (DSS).

The solvent leaving the extraction contactors enters a set of 2 V-05 contactors where it is contacted with scrub acid (0.05 M nitric acid) solution at an O/A of 1/5 to remove other soluble salts (Na⁺, K⁺, etc) from the solvent stream and neutralize any hydroxide carryover from the extraction bank, which is necessary for adequate performance of the strip portion of the process. The scrub solution is combined with the salt waste processed through the V-10 contactors.

The solvent exiting the scrub contactors is then heated to 33 \pm 3^oC and enters a set of 7 V-05 contactors where it is contacted with a strip acid solution (0.001 M Nitric Acid) at an O/A of 1/5 to strip the cesium from the solvent. Preliminary hydraulic testing of the V-05 contactors indicated that there could be up to 400 mg/L carryover of the solvent in aqueous stream with the majority of the droplets being less than 10 μ in diameter. This would again potentially cause a flammability concern in the DWPF facility, so a coalescer and decanter are installed downstream of the Strip contactors. The strip effluent coalescer media is a 26 cm (10 in.) long, 10 micron Ryton[®] filter element.

The stripped solvent is finally contacted with a wash solution (0.01 M Sodium Hydroxide) at an O/A of 1/5 to remove any solvent degradation products or organic contaminants that may have accumulated in the solvent. The solvent is then recycled back through the process. As the wash solution depletes it is continually replenished, with the spent wash being processed through the DSS decanter. Figure 2 is a process schematic of the MCU process and Figure 3 shows the solvent recovery system in MCU.

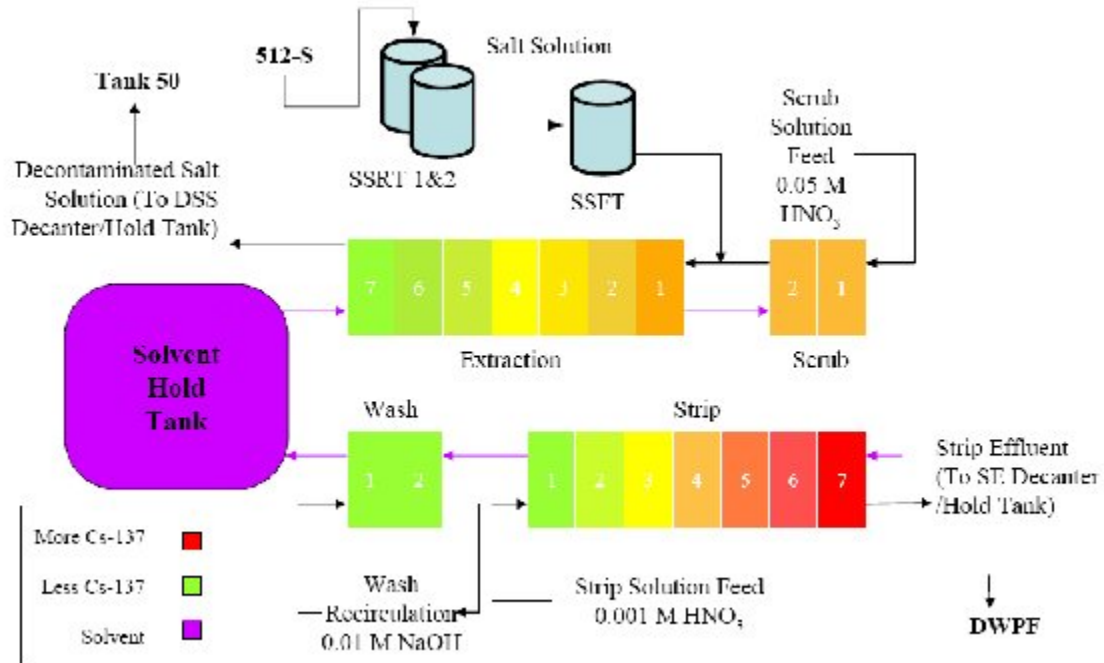


Figure 2 MCU Process Schematic

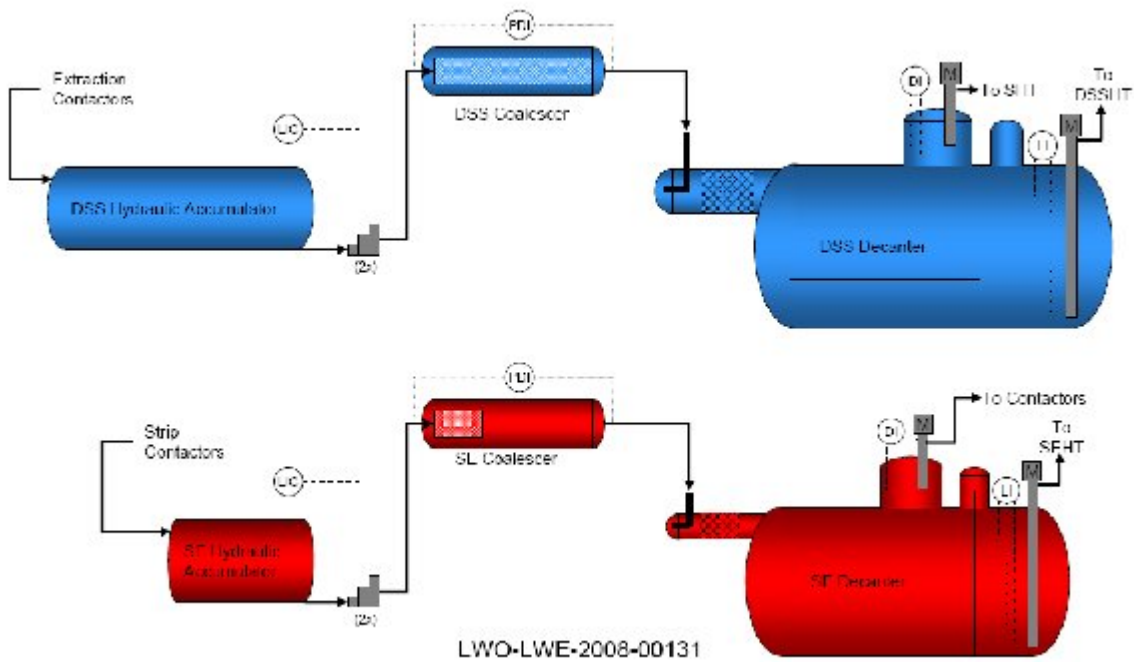


Figure 3 MCU Solvent Recovery Systems

OPERATIONS

The first salt batch was processed through MCU between May 2008 and September 2008. A total of 523,000 liters (138,000 gallons) of salt was processed. As shown in Figure 1, the decontamination factor for cesium removal averaged 167 over the course of the batch.

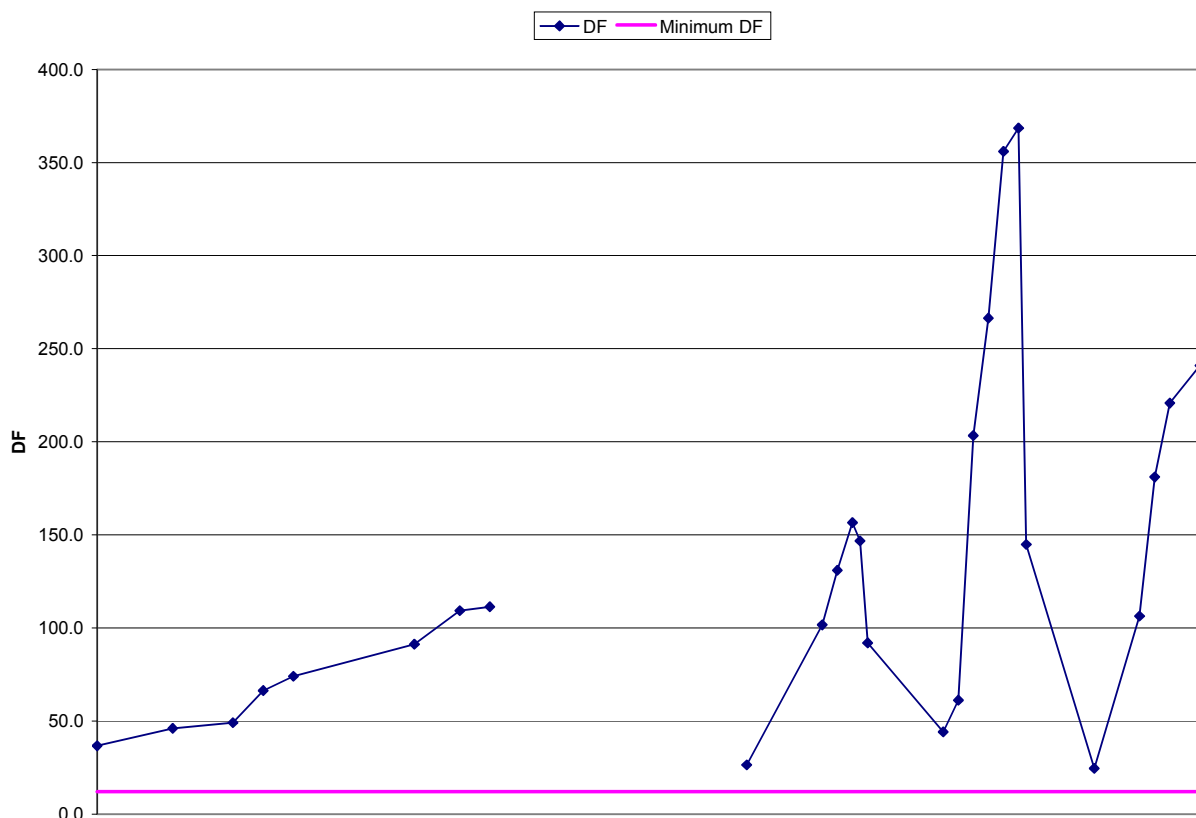


Figure 4 Salt Batch 1 Decontamination Factor

The concentration factor for cesium during periods of extended operations averaged around 12.6 (Target between 12 and 15).

Extended operations during salt batch 1 was difficult to achieve. After processing the first 49,000 liters (13,000 gallons) of DSS material, the decontaminated salt solution coalescer media differential pressure reached the alarm limit of 172 kPa (25 PSID). Attempts to clean the media with nitric acid and deionized water as originally planned failed. As a result the media needed to be replaced. The second media lasted approximately 144,000 liters (38,000 gallons) before it too needed to be replaced. A third media was installed. This media lasted for 329,000 liters (87,000 gallons). When the third media plugged, salt batch 1 operations were ended and the facility went into an outage period for equipment upgrades and preparation of Salt Batch 2. Figure 5 shows the differential pressure rise in each of the three media versus the gallons of decontaminated salt solution process through the media.

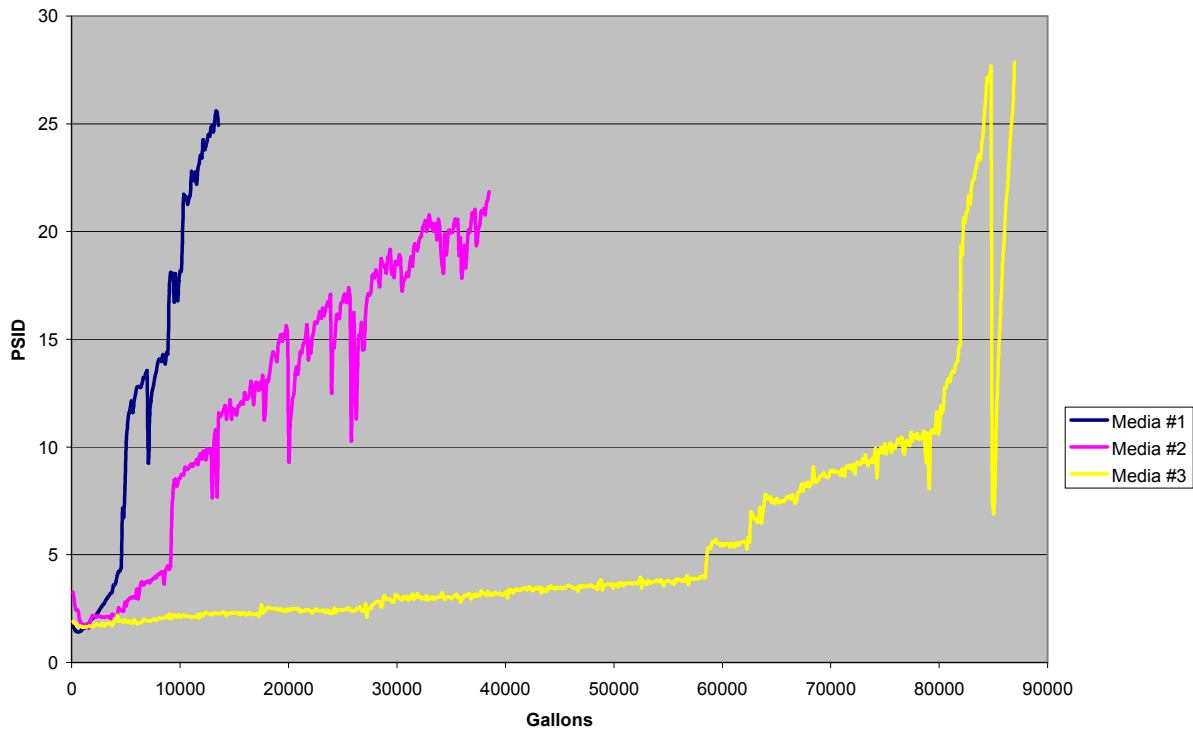


Figure 5 DSS Coalescer Media Differential Pressures

In spite of the problems with pluggage of the DSS coalescer media, solvent removal met or exceeded expectations for the facility. Figure 6 shows the Isopar carryover results for the DSS and Strip Effluent (SE) streams. The procedural limit for transferring to downstream facilities is 50 mg/L.

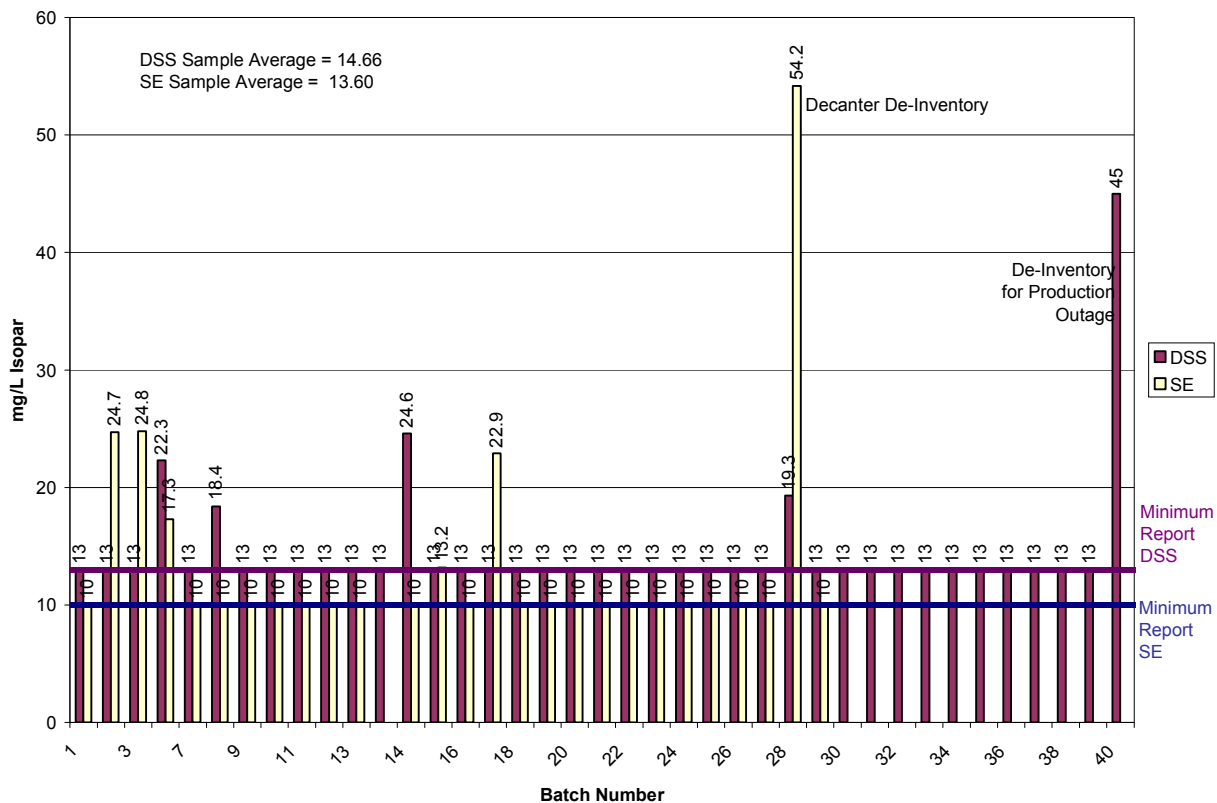


Figure 6 Isopar Carryover in Decontaminated Salt Solution and Strip Effluent

Analysis of the media removed from the DSS coalescer was performed at Savannah River National Laboratories (SRNL). The primary contaminants on the media were found to be Aluminum Hydroxide compounds. Review of the sample data from the process showed the increased life in the third media was during a period of increased free hydroxide concentration in the feed due to cleaning evolutions in the cross flow filter in the 512-S facility upstream of MCU. Computer modeling of the salt solution determined that increasing the free hydroxide concentration in the salt batch would reduce formation of solids during the MCU process. Salt Batch 2 was adjusted to 2.2 M free hydroxide during the batch preparation process. To improve process performance in the 512-S facility, the concentration is increased to 2.6 M before it enters the MCU process.

In addition to raising the free hydroxide concentration in the feed, several changes were made in the MCU facility. The first was the addition of a pre-filter upstream of the DSS coalescer. The DSS coalescer is installed in the main process cell and is difficult to get access to. Replacing the media requires de-inventorying of all of the process cell tanks to reduce the exposure to the mechanics performing the replacement. The prefilter installed upstream of the coalescer is designed with three filter elements. These elements are the same element as used in the coalescer itself, only the flow is outside to in versus inside to out in the coalescer media. This gives the filter media a 30X greater initial surface area than the coalescer media. The prefilter is also installed to be removable, allowing for removal without cell entry.

Also, the ability to flush the coalescer with sodium hydroxide was added to the facility through changes to procedures and the authorization basis documents.

Salt Batch 2 operations commenced in February 2009 and to date has processed over 2,350,000 liters (622,000 gallons) of salt from the feed tank. The facility rapidly began experiencing a high differential pressure on the Strip Effluent Coalescer Media. The scrub flow rate was adjusted to an O/A ration of 2/5 to reduce the impact of the increased hydroxide concentration in the carryover from the extraction contactors. This reduced the rate of rise of the differential pressure, but the media still needed to be replaced after processing only 14,000 liters (3700 gallons) of strip effluent solution. In comparison, the media in Salt Batch 1 (which was replaced during the outage), never exceeded 83 kPa (12 PSID) and processed over 34,000 liters (9000 gallons) of strip effluent. The new media installed for salt batch 2 has now processed over 163,000 liters (43,000 gallons) with the differential pressure holding at less than 69 kPa (10 PSID).

The DSS coalescer media processed over 2,270,000 liters (600,000 gallons) of decontaminated salt solution before reaching the high differential pressure limit. The prefilter has not shown any appreciable increase over the entire batch. Caustic flushing of the DSS coalescer media with 30% sodium hydroxide has shown a limited ability to clean the media to allow for continued operation. Figure 7 shows the DSS coalescer and pre-filter differential pressures for Salt Batch 2.

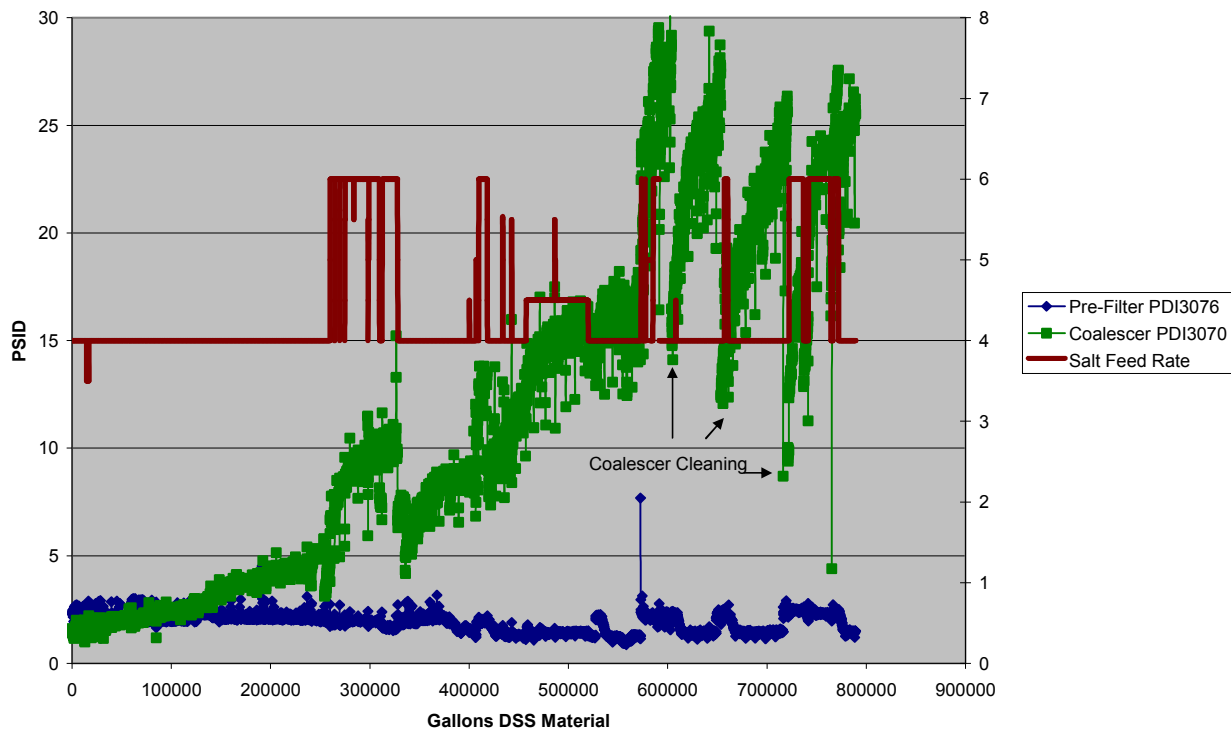


Figure 7 DSS Coalescer and Pre-Filter Differential Pressure for Salt Batch 2

The decontamination factor for Salt Batch 2 continues to well exceed the required minimum of 12. The values are averaging over 311 with some results during extended run operations exceeding 600. DF values for Salt Batch 2 are shown in Figure 8.

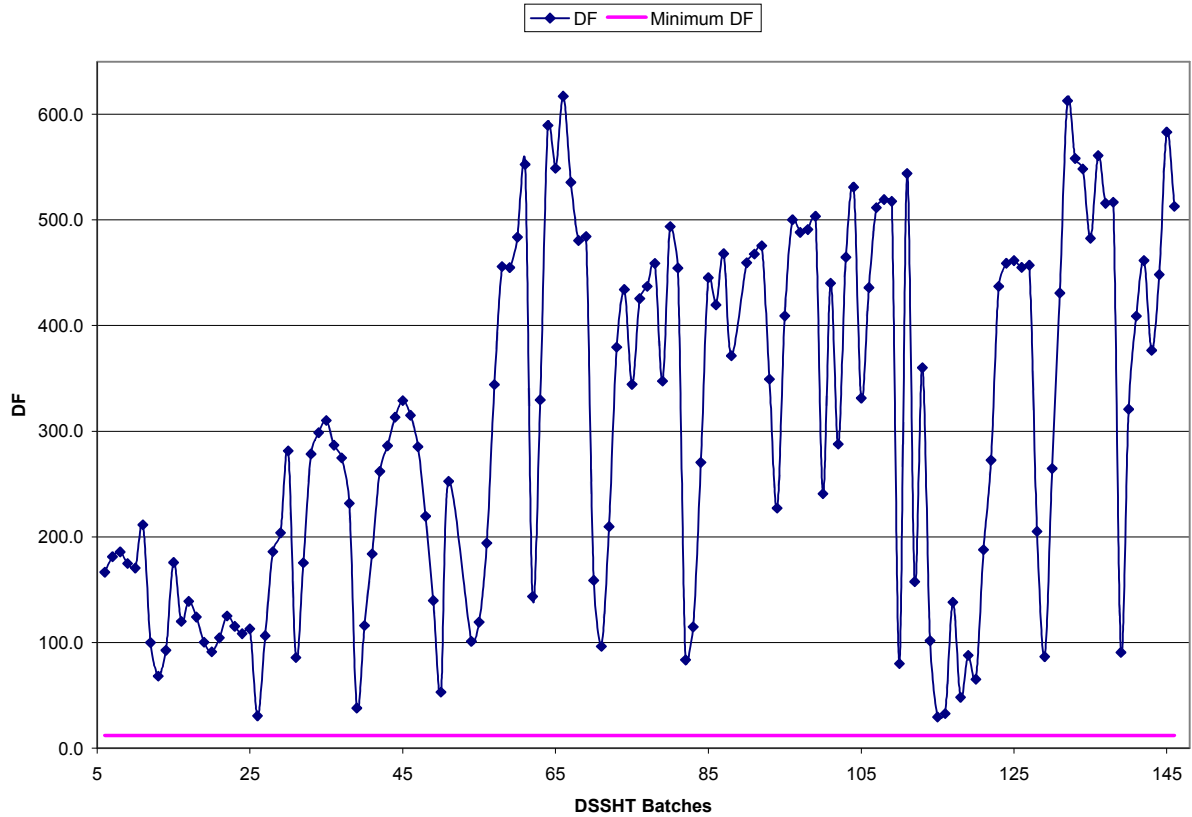


Figure 8 Salt Batch 2 Decontamination Factor

The concentration factor for Salt Batch 2 continues to average at 12 and gets higher over extended run periods up to close to 15.

DSS Isopar carryover also continues to be low as shown in Figure 9.

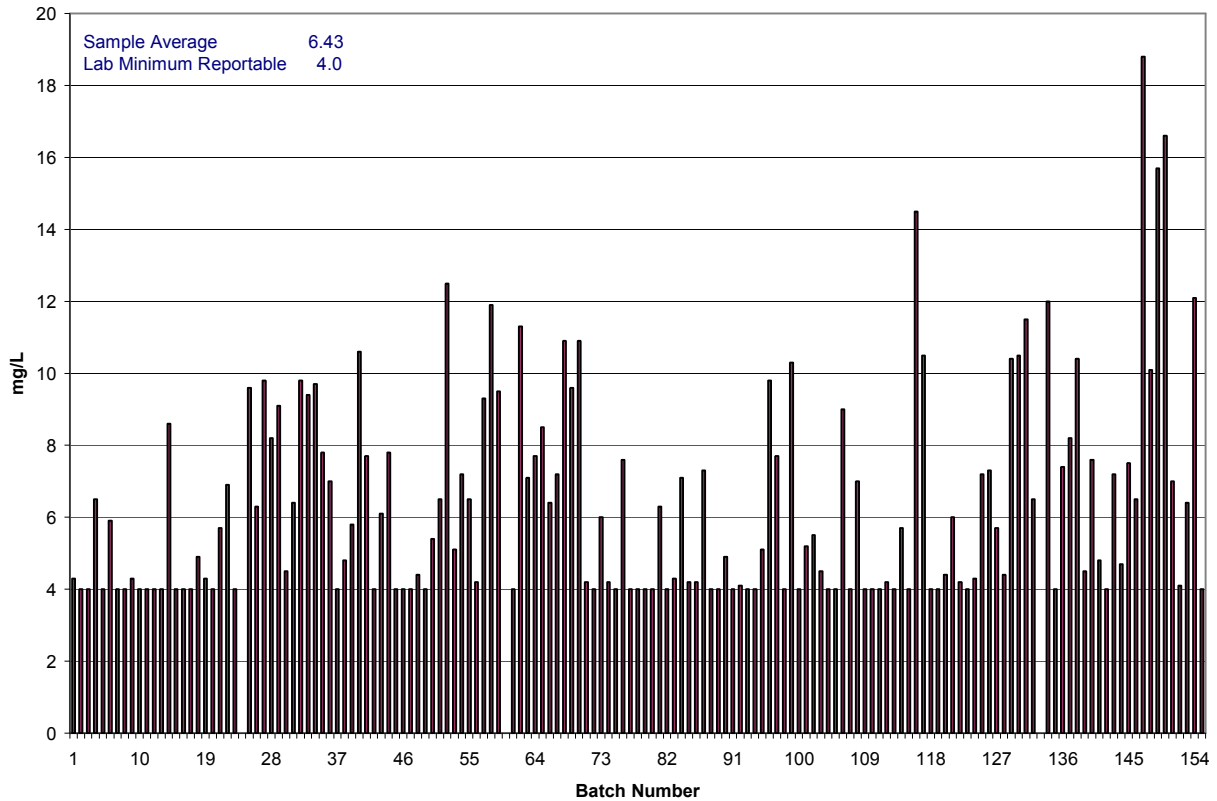


Figure 9 Salt Batch 2 DSS Isopar L Carryover Results

The Isopar carryover results for the Strip Effluent appear to show and increase in carryover, but is actually due to problems with the sampling system getting cross contaminated by samples from other tanks. Plans are in place to repair the sampler during the outage between Salt Batches 2 and 3. Overall the SE samples are still not exceeding the 50 mg/L limit and are still averaging less than 17 mg/L.

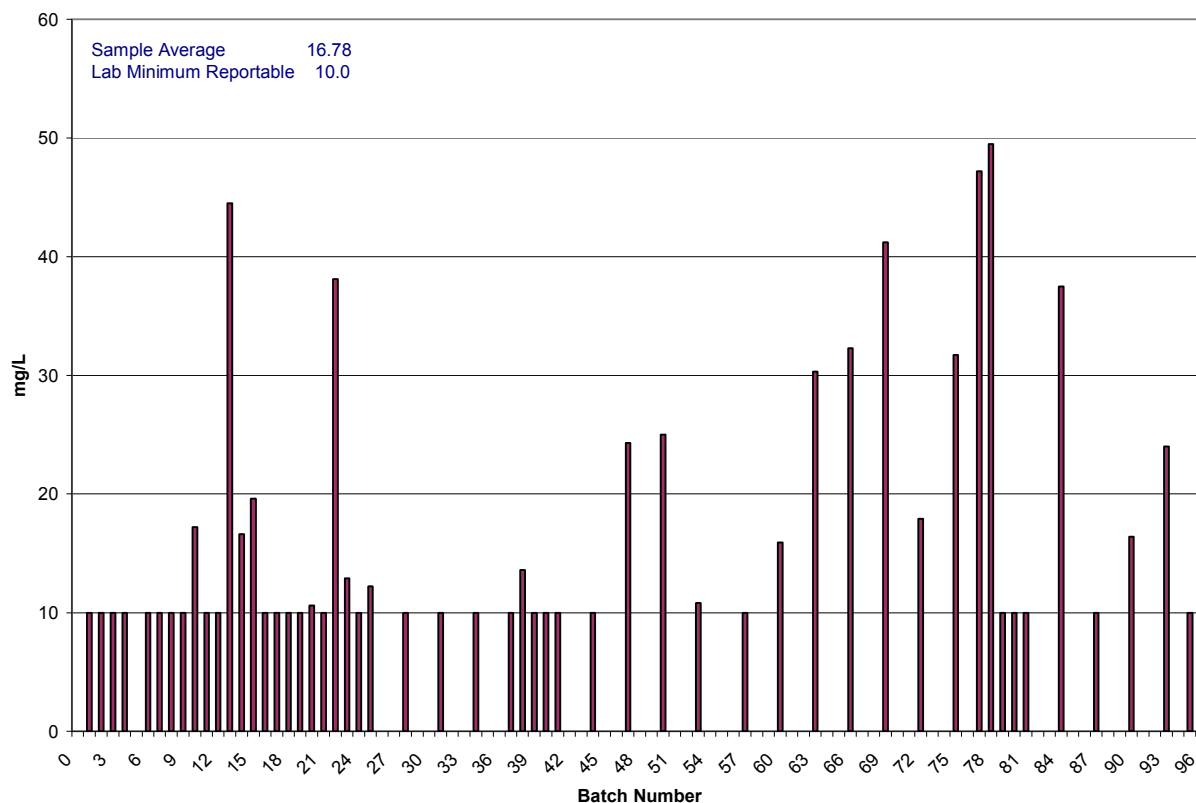


Figure 10 Salt Batch 2 SE Isopar L Carryover Results

CONCLUSION

To date, the process improvements implemented for Salt Batch 2 have increased the life of the DSS coalescer media with no impact on the decontamination factor, concentration factor, and Isopar carryover results which all continue to exceed requirements. Analysis of the coalescer and pre-filter media will be performed at the end of Salt Batch 2 to determine if any other process improvements can be recommended. All of the lessons learned in the MCU facility have been and will continue to be transmitted to the SWPF project to help ensure a successful start-up and operation of that facility.

REFERENCES

1. P. V. BONNESEN, L. H. DELMAU, B. A. MOYER, and R. A. LEONARD, "A Robust Alkaline Side CSEX Solvent Suitable for Removing Cesium from Savannah River High-Level Waste," *Sol. Extr. Ion Exch.* 19(6), 1079-1108 (2000)
2. R. A. LEONARD, "Caustic-Side Solvent Extraction Flowsheet for Optimized Solvent", ANL-02/19, (2002)