Modular Caustic-Side Solvent Extraction Unit (MCU) Improved Solvent Quality and Processing Results – 17496

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ABSTRACT

The Modular Caustic-Side Solvent Extraction (CSSX) Unit (MCU) is a process for Cs-137 removal from legacy nuclear waste. MCU began hot operations in 2008 with an initial planned operating life of three years and a design life of five years. After eight years of operation, MCU has processed more than 23.8 million liters (6.3 million gallons) of waste.

The MCU process uses a solvent developed by Oak Ridge National Laboratory (ORNL) to extract the fission product Cs-137 from liquid salt waste, or salt solution (SS), stored in the Tank Farms at Savannah River Site (SRS) after the material has been treated through the Actinide Removal Process (ARP). Batches of SS are prepared and first fed to the Actinide Removal Process (ARP), where it is treated to become clarified SS (CSS), then fed to MCU. Once the Cs-137 has been extracted by the solvent, the CSS becomes decontaminated SS (DSS), which is ultimately processed into a cementitious grout at the Saltstone Production Facility (SPF) and subsequently disposed of at the Saltstone Disposal Facility (SDF). The Cs-137 is then stripped from the solvent into an aqueous stream for incorporation into borosilicate glass at the Defense Waste Processing Facility (DWPF).

The solvent used in the MCU process is made of four components: the extractant (extracts Cs-137 from CSS), the modifier (increases solubility of extractant and suppressor in the diluent), the suppressor (suppresses the effects of anions and improves stripping), and the diluent (controls density and viscosity). There have been two solvents utilized during the lifetime of MCU. The first solvent was developed by ORNL and was used to design the plant based on its cesium removal capability. Due to the extended life of MCU, in order to continue to minimize the curies disposed at SDF, a new solvent capable of removing more cesium from the CSS was developed by ORNL and implemented at MCU. The second MCU solvent, Next-Generation Solvent (NGS), uses the same modifier and diluent as the original solvent, but a different extractant and suppressor. Subsequent changes to the overall MCU flowsheet were made for the use of NGS.

The success of cesium removal from the CSS is often presented as the cesium decontamination factor (DF) achieved for each batch processed. The DF is the ratio of the concentration of cesium in the CSS to the cesium concentration in the DSS. The BOBCalixC6 based solvent was capable of achieving DFs between 100 and 400 for each DSS batch. The NGS solvent is capable of achieving DFs greater than 40,000 for each DSS batch. The NGS blend solvent is currently meeting the goals of the pure NGS solvent.

INTRODUCTION

ARP/MCU is a part of the Liquid Waste Program at SRS, which is operated by Savannah River Remediation, LLC (SRR). The Liquid Waste Program consists of three main facilities: the Tank Farms, DWPF, and SPF/SDF. While there are two Tank Farms, they are operated as one facility. The Tank Farm Facility consists of fifty-one liquid waste storage tanks in total. Based on the type of tank, they range in capacity from 2.84 to 4.92 million liters (0.75 to 1.3 million gallons). The Tank Farm Facility receives and stores the liquid waste produced from processing nuclear material at SRS. DWPF processes high-level waste sent from the Tank Farm Facility, where it is vitrified and placed in stainless steel canisters. The stainless steel canisters are temporarily stored at DWPF as well, until they are relocated to a permanent storage location outside of South Carolina. SPF processes low-level waste sent from the Tank Farm Facility (and if necessary, DWPF), where it is used in grout production and ultimately disposed of at SDF where it will remain permanently in the state of South Carolina.

When the waste reaches the Tank Farm Facility, it is separated into two separate streams. The sludge waste stream consists mainly of actinides, other metal oxides, and insoluble particulates that settle out from the waste received. The salt waste stream is the remaining liquid which consists mainly of soluble cesium, other soluble salts, small concentrations of actinides, and other sludge particles that remain suspended in solution. The sludge waste stream is sent directly to DWPF. The salt waste is first processed through ARP where it is split into two streams with one being filtered solids and one being the CSS. The solids are transferred to DWPF to be incorporated into borosilicate glass. The CSS is then processed through MCU and further split into two streams, with one being highly concentrated in cesium and one with very low concentrations of cesium. The highly concentrated stream, or the Strip Effluent (SE) stream, is combined with sludge at DWPF, and the low concentration stream, or the DSS, is sent to SPF. In preparation for processing both sludge and salt waste, batches of waste with specific chemical make-up are prepared in designated waste tanks in the Tank Farm Facility to ensure a chemically balanced product in both glass and grout production. Once the waste batches are prepared, they are transferred into designated waste tanks that feed the respective processes (process feed tanks). Figure 1 provides a visual depiction of the salt waste flow path as it is processed.
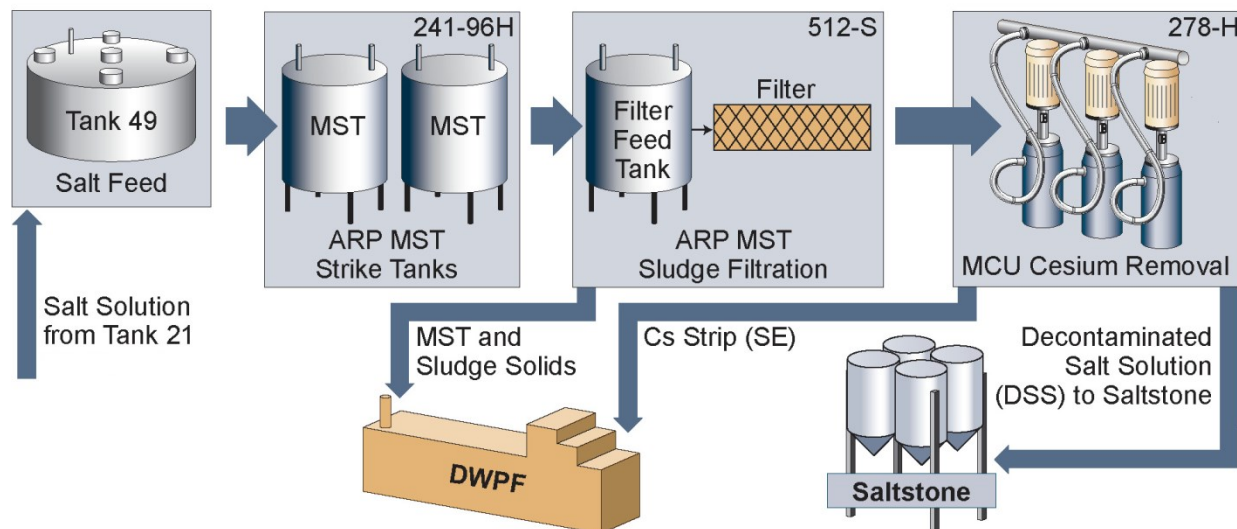
Fig. 1. Salt Waste Processing

ARP consists of the two MST Strike Tanks and the 512-S filter. MCU is a singular unit but is comprised mainly of several smaller tanks of various sizes and four contactor banks (extraction, scrub, strip, and wash). The respective contactor banks are where DSS and SE are produced by extracting Cs-137 from CSS into the solvent and then back extracting, or stripping, the Cs-137 out of the solvent.

MCU began hot operations in 2008 and was originally planned to process salt waste for three years with a design life of five years. MCU was developed as a pilot scale solvent extraction process to be used to meet DOE tank space objectives (as outlined in the *Basis for Section 3116 Determination for Salt Waste Disposal at the Savannah River Site,* or SWD 3116 Basis Document) in the interim while a larger scale plant was designed and constructed [1]. The MCU operating life was extended and it has now been processing salt waste for eight years. ARP/MCU is currently the only process used in the LWO for removing salt waste from the Tank Farms and has processed more than 23.8 million liters (6.3 million gallons) of salt waste so far in its lifecycle.

BACKGROUND

Salt batches are first prepared in the 4.9 million liter (1.3 million gallon) salt batch preparation tank (i.e. Tank 21) and then transferred to the process feed tank (i.e., Tank 49). Smaller batches (about 13.7K liters, or 3625 gallons) of salt waste are then fed from the process feed tank to ARP/MCU in a continuous batch process. The smaller batches are transferred from the process feed tank into one of the two MST strike tanks at ARP. Sr-90, Y-90, and actinides are removed from the salt waste by striking the smaller batch with an MST and water solution (about 757 liters, or 200 gallons) which is then agitated in the strike tank prior to being filtered through the 512-S cross-flow filter. Both strike tanks are utilized so that waste from one can be filtered while waste in the other is being struck. This method provides continuous feed material through ARP/MCU.

When the salt solution is struck, Sr-90, Y-90, and actinides adsorb onto the MST. As the salt solution passes through the cross-flow filter, the actinide laden MST particles, as well as any other entrained solids, are filtered out of the solution. The particles are collected and then sent to be combined with sludge and SE in the vitrification process, while the CSS is sent to MCU for cesium removal.

Waste is processed in MCU through four banks of centrifugal contactors. Each bank serves a separate purpose. Contactors (see Figure 2) provide mixing between two fluids (one organic and one aqueous) and then use centrifugal force to separate them based on density differences.
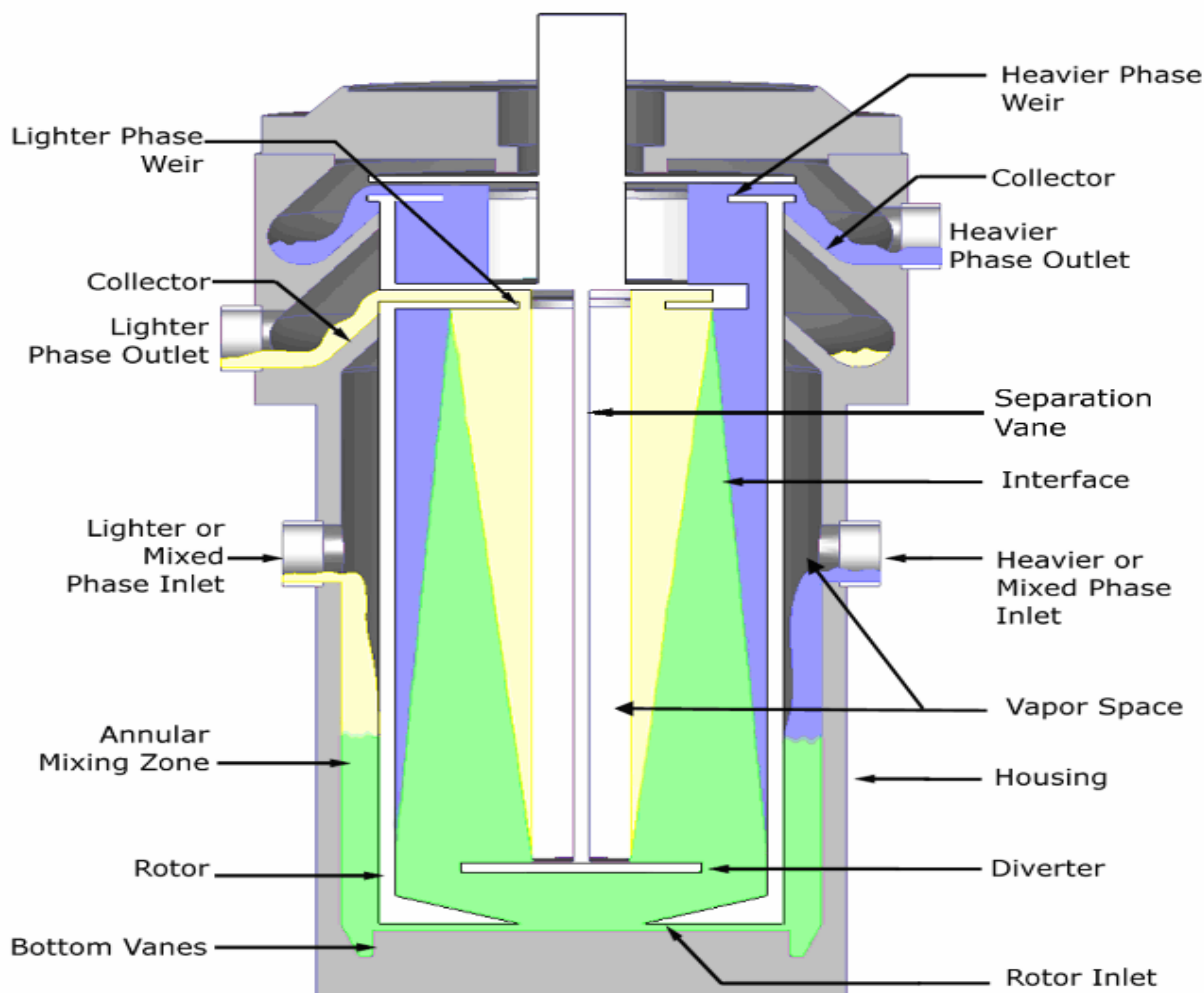

Figure 2. Centrifugal contactor diagram

The fluid mixing occurs in the annulus of the contactor. This mixing between the fluids is what allows the extraction, scrubbing, stripping, and washing to occur. The mixed fluid then enters into the rotor where the two liquids are separated again. Weirs divert the two liquids through the respective collector rings of the contactor. The lighter phase that passes through each contactor bank is the organic stream, which is the MCU solvent. The heavier phase that passes through each contactor

bank is the aqueous phase. The content of the aqueous stream depends on the contactor bank. In the extraction bank the aqueous stream is the CSS and scrub material that has contacted the solvent. In the scrub, strip, and wash contactor banks, the aqueous streams are "cold chemical" scrub, strip, and wash material, respectively.

Figure 3 is a simplified process flow diagram of MCU. This illustrates the flow path of each individual stream.
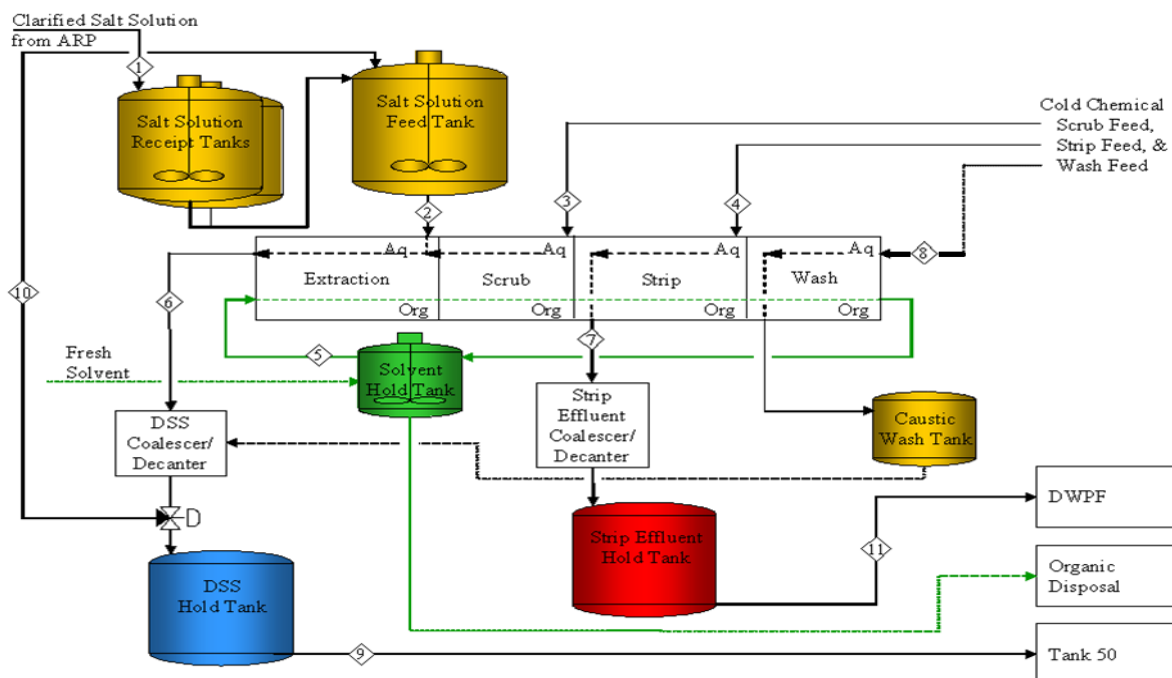

Figure 3. MCU Process Flow Diagram

CSS is received from the 512-S cross-flow filter into MCU in one of the two salt solution receipt tanks (SSRTs) and then moved forward into the salt solution feed tank (SSFT). Note that there are two SSRTs for the same reason as there are two MST strike tanks at ARP; while one SSRT feeds the SSFT, the other SSRT can receive more material so that MCU can continuously operate. The SSFT feeds CSS to the extraction contactor bank where it is mixed with solvent. The chemical properties of the solvent drive the cesium extraction. The salt solution that has undergone cesium extraction is DSS material. The DSS stream exits the extraction contactor bank and follows a flow path where it is ultimately collected in the DSS Hold Tank (DSSHT) and sampled prior to being transferred to SPF. The cesium laden solvent then passes to the scrub contactor bank. Scrub material is fed to this contactor bank from a "cold chemical" scrub feed tank and conditions the solvent and removes cationic impurities. Scrub solution then joins the salt solution and passes through the extraction contactor bank and follows the DSS flow path. The still cesium laden solvent passes from the scrub bank to the strip contactor bank. Strip material is fed to this contactor bank from a "cold chemical" strip feed tank. A pH swing drives the cesium and its associated ion pair to partition out of the

organic phase and into the aqueous stream. Cesium laden strip material, or SE material, leaves the strip contactor bank and follows its own flow path. This material is ultimately collected in the SE Hold Tank (SEHT) and sampled prior to being transferred to DWPF. The stripped solvent passes from the strip contactor bank to the wash contactor bank. Wash material is fed from a "cold chemical" wash feed tank and reconditions the solvent by removing any rogue anions and degradation products. Wash material exits the contactor bank and joins the DSS downstream of all the contactor banks. Solvent is recycled back from the wash contactor bank to the Solvent Hold Tank (SHT) before it is sent back through the contactors.

DISCUSSION

The MCU solvent is an organic solution developed by ORNL for Cs-137 extraction. The MCU solvent is comprised of four components: the extractant, the modifier, the suppressor, and the diluent. The extractant extracts the cesium from the CSS. The modifier increases the solubility of the extractant and the suppressor in the diluent. The suppressor suppresses the effects of anions and improves stripping. The diluent promotes hydraulic stability by controlling density and viscosity. During processing, components of the solvent will either evaporate or degrade, and periodic additions of solvent components need to be made to the process. In the eight years of MCU operations, two solvents have been utilized. Both solvents are comprised of the same type of components; however they differ in the molecules used for the extractant and suppressor roles. The first solvent was comprised of the following [2]:

- Extractant: BOBCalixC6, 0.007 M
- Modifier: Cs-7SB, 0.75 M
- Suppressor: TOA, 0.003 M
- Diluent: Isopar™ L, Balance
- Density 0.85 g/mL

The cold chemicals used with the BOBCalixC6 based solvent are as follows [2]:

- Scrub Feed: 0.05 M Nitric Acid
- Strip Feed: 0.001 M Nitric Acid
- Wash Feed: 0.025 M Sodium Hydroxide

As salt waste processing continued, salt batches with higher Cs-137 concentrations were mixed. Since the operating life of MCU was extended, a solvent capable of removing the higher concentrations of Cs-137 was developed to ensure the commitment to the state of South Carolina was met. In October 2013, the Next Generation Solvent (NGS) was implemented at MCU. The pure NGS is comprised of the following [3]:

- Extractant: MaxCalix, 0.05 M
- Modifier: Cs-7SB, 0.5 M
- Suppressor: TiDG, 0.003 M
- Diluent: Isopar™ L, Balance
- Density: 0.8386 g/mL

The cold chemicals used with NGS are as follows [3]:

- Scrub Feed: 0.025 M Sodium Hydroxide

- Strip Feed: 0.01 M Boric Acid
- Wash Feed: 0.025 M Sodium Hydroxide

The chemical properties of MaxCalix make the molecule more soluble in the diluent than the BOBCalixC6, which allows for a decreased concentration of the modifier. Since the modifier is the heaviest component of the solvent, the decreased concentration also decreased the density of the overall solvent. Figure 4 shows the BOBCalixC6 molecule, and Figure 5 shows the MaxCalix molecule.
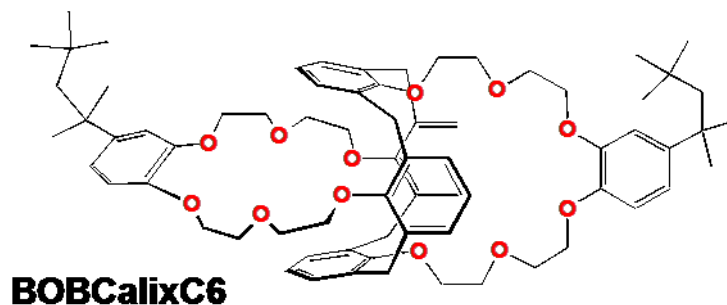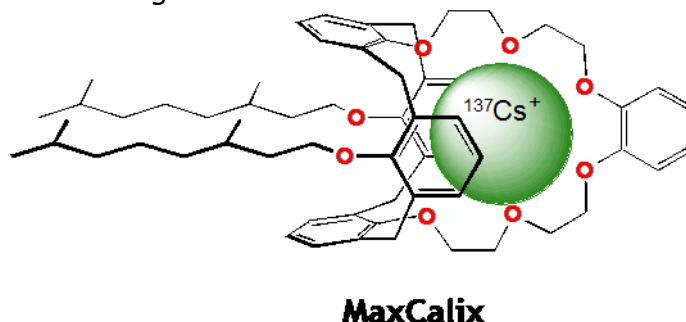

Figure 4. BOBCalixC6 Molecule

Figure 5. MaxCalix Molecule

Note that the BOBCalixC6 molecule has a double helix (crown), while MaxCalix has a single helix (crown). This structure means that BOBCalixC6 has the potential to extract two Cs-137 ions per extractant molecule from the CSS while MaxCalix is capable of extracting only one Cs-137 ion per extractant molecule. Based solely on the molecular shape, BOBCalixC6 has the potential to be the better extractant. However, the BOBCalixC6 molecule does not readily extract two Cs-137 ions per every molecule unless the cesium concentration is high, much higher than what can be processed through MCU; therefore, it does not occur often in the process. BOBCalixC6 is also not as soluble as MaxCalix and is limited to a lower extractant concentration in the solvent. Since NGS utilizes a higher concentration of MaxCalix, this allows for better overall extraction.

When NGS was implemented, a blend strategy was used [4]. 378.54 liters (100 gallons) of the BOBCalixC6 based solvent and 378.54 liters (100 gallons) of NGS were combined in the SHT to make the solvent blend. The concentrations of each component for the 50/50 blend were as follows [4, 5]:
- Extractant: BOBCalixC6, 0.0035 M

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- Extractant: MaxCalix, 0.0465 M
- Modifier: Cs-7SB, 0.5 M
- Suppressor: TOA, 0.0015 M
- Suppressor: TiDG 0.003 M
- Diluent: Isopar^{TM} L, Balance
- Density: 0.8384 g/mL

The cold chemicals used with the blend solvent are the same as for pure NGS. The MCU solvent is periodically adjusted as solvent components shift out of concentration due to carry-over, evaporation, or degradation; however, the only additions ever made to the solvent are NGS components. This allows for the BOBCalixC6 and TOA to bleed out of the solvent and for the solvent to shift towards pure NGS concentrations [4, 6]. As the BOBCalixC6 concentration continues to decrease, the blend target concentration for MaxCalix increases in order to maintain a 0.05 M extractant component concentration in the blended solvent.

The decontamination factor (DF) is the ratio of the concentration of Cs-137 in the CSS feed to the concentration of Cs-137 in the DSS:

$$DF = \frac{[^{137}_{55}Cs]_{CSS}}{[^{137}_{55}Cs]_{DSS}} \qquad\qquad \text{(Eq. 1)}$$

MCU was designed to achieve a DF of 12 with the BOBCalixC6 solvent. Historically the DF achieved with BOBCalixC6 was typically between 100 and 400 for each DSS batch [7, 8]. Figure 6 shows typical DF values for the first 30 DSS batches of a salt batch while utilizing the BOBCalixC6 based solvent.
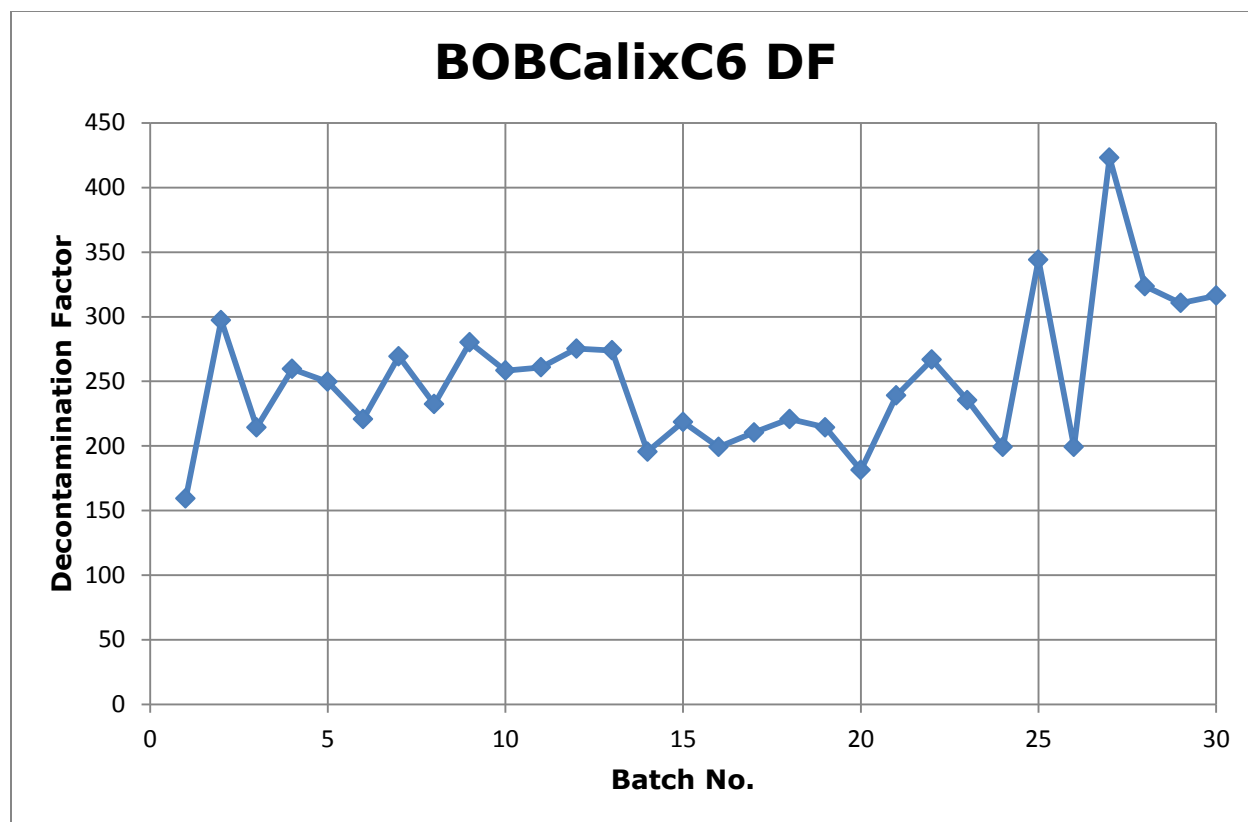
Figure 6. BOBCalixC6 DF

Pure NGS was anticipated to achieve DFs above 40,000; however, on average the blended solvent exceeds this expectation [8, 9]. Figure 7 shows typical DF values for the first 30 DSS batches of a salt batch while utilizing the NGS blend solvent [10].
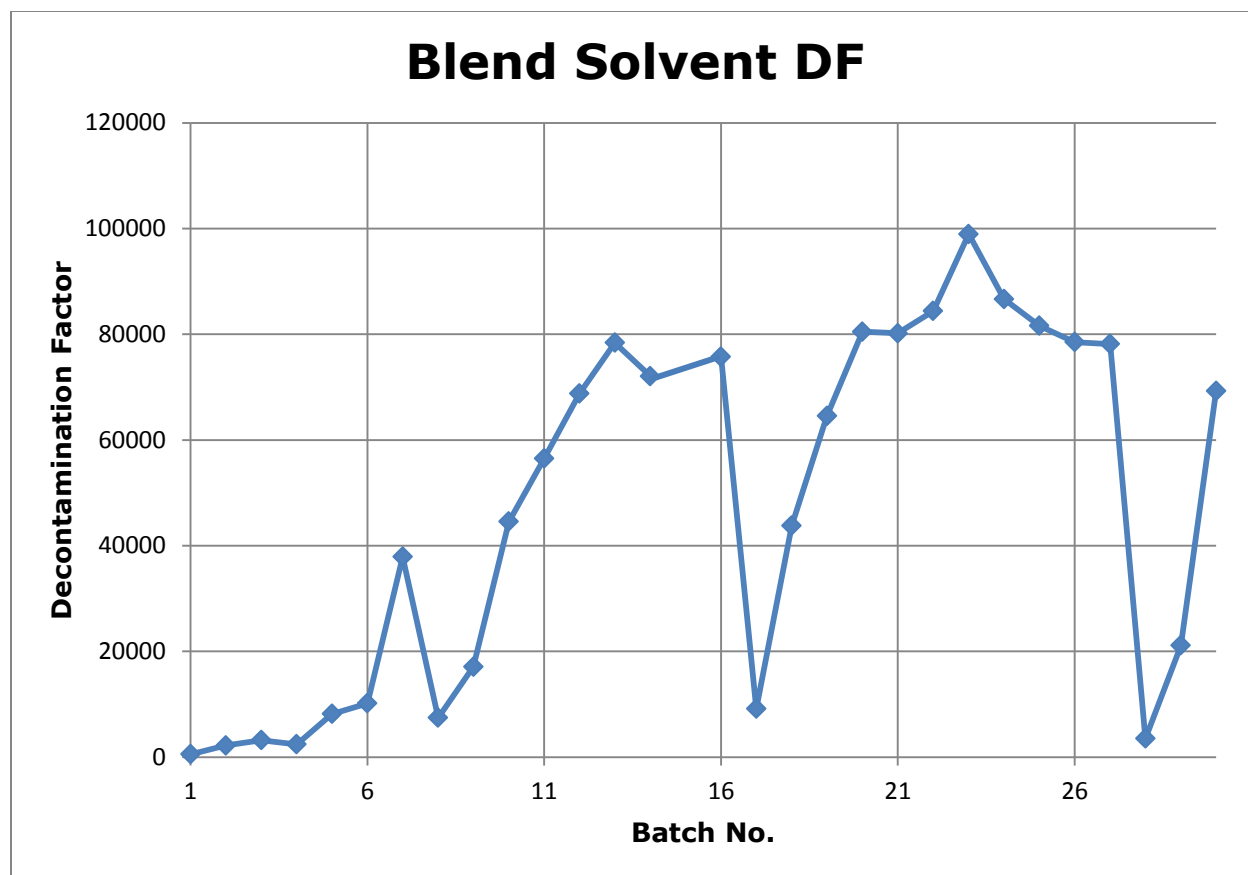
Figure 7. Blend Solvent DF

Note that the DF trends low for the first several batches and occasionally dips. The low values are attributed to a start-up of the MCU process. While processing batches 1 through 5, MCU started up and processed enough CSS to produce one DSS batch and then shut-down until sample results for that batch were received. This was done to ensure there were no operational issues while processing a new salt batch. Batches 8, 17, and 28 were due to start-ups after MCU shutdown for normal operational reasons.

When MCU starts up after a shutdown, the CSS runs for a period of time before the solvent stream runs. Although some solvent remains in the contactors and the piping while MCU is shut down, this adds Cs-137 to the DSSHT that has not been contacted by fresh solvent and therefore, increases the Cs-137 concentration in the DSS batch. After running the process for several batches, the DF recovers. Continuous operation promotes higher DF values, due to fewer start-ups and shutdowns, as indicated by batches 17 through 27 in Figure 7.

As solvent components degrade, some degradation products are washed out of the solvent (e.g., carboxylic acid based degradation products), but some build up and cannot be removed by the regular wash feed material (e.g., phenol based degradation products). The build-up of these degradation products can be monitored both by sample results and performance. When enough build-up has occurred to affect the solvent quality and degrade performance, a "super-wash" is

performed. The normal wash material is aimed to remove the carboxylic acid based degradation products from the solvent while the "super-wash" is aimed to remove the phenol based degradation products. Since phenols are much weaker organic compounds than carboxylic acids, the phenols require a stronger base to remove them from the solvent; hence, the "super-wash" is a much more concentrated sodium hydroxide solution than the normal operations wash material (0.3 M NaOH as compared to 0.025M NaOH respectively) [11]. Since the solvent components that degrade to the phenols (modifier) do not degrade quickly, these degradation products build up slowly in the solvent over time [6]. Therefore, "super-washes" are not needed during normal operations like the normal wash material, and thus are only performed for a designated period of time while the MCU is shut down so that only the solvent contacts the higher molarity solution. The "super-wash" historically has a noticeable, positive impact on the solvent quality and performance, noted by both an increase in the DF itself as well as the DF recovery time.

CONCLUSION

In the eight years of operation, MCU has utilized two solvents. The original solvent was the BOBCalixC6 based solvent, and the second was the MaxCalix based solvent, or NGS. NGS was implemented using a blend strategy, so the solvent is currently a blend of the two, with concentrations biased towards pure NGS. The change in MCU solvent has proven to be effective. The blend solvent and pure NGS utilize component concentrations that promote hydraulic stability, better separation in all contactor banks, and improved performance. Both the blend solvent and pure NGS consist of higher concentrations of extractant and lower concentrations of modifier, which helps to lower the density and viscosity of the solvent as well as provide greater opportunity for Cs-137 extraction. Based on the increased DF, the blend solvent is currently meeting the expectations of the pure solvent by achieving the desired levels of Cs-137 extraction from the salt waste.

To ensure performance is maintained, the solvent quality is monitored by solvent sample results, field equipment, and DF trending. With the initial BOBCalixC6 based solvent, samples of the solvent were pulled quarterly. As part of the initial implementation for NGS, solvent sampling frequency was increased to monthly. This allows for stricter monitoring of overall solvent health. Solvent component adjustments (NGS only) and "super-wash" frequency are determined based on these sample results. "Super-washes" of the solvent are performed as required to remove degradation products of the solvent components that cannot be removed by the normal wash cycle in the process. The removal of these products improves solvent quality and processing performance, as evidenced by DF trending.

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