Next Generation Solvent Performance in the Modular Caustic Side Solvent Extraction Process- 15495

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ABSTRACT

Changes to the Modular Caustic Side Solvent Extraction Unit (MCU) flow-sheet were implemented in the facility. Implementation included changing the scrub and strip chemicals and concentrations, modifying the O/A ratios for the strip, scrub, and extraction contactor banks, and blending the current BoBCalixC6 extractant based solvent in MCU with clean MaxCalix extractant based solvent.

During the successful demonstration period, the MCU process was subject to rigorous oversight to ensure hydraulic stability and chemical/radionuclide analysis of the key process tanks (caustic wash tank, solvent hold tank, strip effluent hold tank, and decontaminated salt solution hold tank) to evaluate solvent carryover to downstream facilities and the effectiveness of cesium removal from the liquid salt waste. Results indicated the extraction of cesium was significantly more effective with an average Decontamination Factor (DF) of 1,129 (range was 107 to 1,824) and that stripping was effective. The contactor hydraulic performance was stable and satisfactory, as indicated by contactor vibration, contactor rotational speed, and flow stability; all of which remained at or near target values. Furthermore, the Solvent Hold Tank (SHT) level and specific gravity was as expected, indicating that solvent integrity and organic hydraulic stability were maintained. The coalescer performances were in the range of processing results under the BOBCalixC6 flow sheet, indicating negligible adverse impact of NGS deployment.

After the Demonstration period, MCU began processing via routine operations. Results to date reiterate the enhanced cesium extraction and stripping capability of the Next Generation Solvent (NGS) flow sheet. This paper presents process performance results of the NGS Demonstration and continued operations of MCU utilizing the blended BobCalixC6-MaxCalix solvent under the NGS flowsheet.

INTRODUCTION

Savannah River Remediation (SRR) is working to remove, stabilize, and dispose of approximately ~38 million gallons of liquid radioactive waste in 45 underground waste tanks at the US DOE's Savannah River Site. As part of the liquid waste disposition project, SRR utilizes the Modular Caustic Side Solvent Extraction Unit (MCU) to extract Cs-137 from liquid salt waste via a solvent extraction process.

Historically, MCU has operated using a BobCalixC6 extractant based solvent that has provided Cs-137 DF of ~156. In December 2013, MCU began processing under the Next Generation flowsheet, which utilizes an MaxCalix extractant[a] with tris(3,7- dimethyloctyl)guanidine hydrochloride (TiDG) as the

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[a] The Next Generation Solvent (NGS) was developed by ORNL, with SRR, Parsons, Texas Tech University, INL, ANL, and SRNL.

suppressor to improve extraction, stripping, contactor hydraulics, and coalescer efficiency. Flowsheet changes included chemical changes to the associated scrub and strip feeds, the addition of the NGS, and changes in the organic to aqueous (O/A) ratios (see Figure 1) [1].
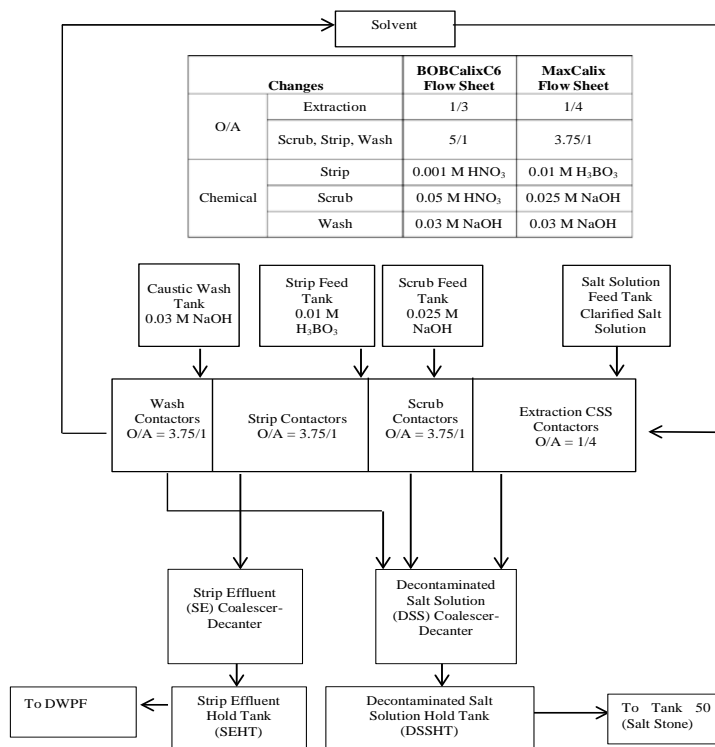
	Changes	BOBCalixC6 Flow Sheet	MaxCalix Flow Sheet
O/A	Extraction	1/3	1/4
	Scrub, Strip, Wash	5/1	3.75/1
Chemical	Strip	0.001 M HNO$_3$	0.01 M H$_3$BO$_3$
	Scrub	0.05 M HNO$_3$	0.025 M NaOH
	Wash	0.03 M NaOH	0.03 M NaOH

Fig. 1: NGS Flow Sheet

To minimize the waste and personnel exposure associated with disposal of the existing BobCalixC6 solvent in the MCU, NGS was equivalently blended into the solvent hold tank [1, 2]. The target components of each solvent can be seen in Table 1. All future solvent additions will consist of only NGS components causing the operating solvent to gradually approach the final, pure NGS concentrations.

TABLE I. Solvent component specifications [2, 3]

	Chemical Component	Purpose	BOBCalixC6 Solvent (mol/m^3)	NGS-BOBCalixC6 Blended Solvent (mol/m^3)	NGS (mol/m^3)
Cs-7SB	1-(2,2,3,3-Tetrafluoropropoxy),-3-[4-(*sec*-butyl)phenoxy]-2-propanol	Modifier	750	500	500
TiDG	tris(3,7-dimethyloctyl)guanidine hydrochloride	Suppressor	-	3.0	3.0
TOA	tri-*n*-octylamine		3.0	1.5	-
MaxCalix	1,3-*alt*-25,27-Bis(3,7-dimethylocty-1-oxy)calix[4]arene-benzocrown-6	Extractant	-	50	46.5
BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzocrown-6)		7.0	3.5	-
Isopar-L		Diluent	*Balance*	*Balance*	*Balance*
Specific Gravity			0.852	0.8384	0.8386

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Upon initial startup under the NGS flowsheet, MCU operated in a batch-wise processing of salt at prescribed salt flowrates to evaluate NGS the performance before transitioning to routine, continuous operations. During batch-wise processing between ~4000 gallons and ~4800 gallons of salt solution feed (CSS feed) was processed per Micro-Batch [3]. This paper presents the facility startup and continuous processing data under the NGS flow sheet.

METHOD

During startup testing MCU processed six Micro-Batches at the prescribed salt solution feed rates that mimicked routine, continuous MCU processing flow rates i.e. between 1.52E+04 SCCM (4.0 GPM) and 3.22E+04 SCCM (8.5 GPM) to demonstrate process stability. Process performance was evaluated after each batch using online process indicators and sample result to ensure the hydraulic stability, coalescer performance, extraction and stripping performance was satisfactory. Once the process was determined to be stable and capable of meeting the minimum DF requirements (DF > 41), the MCU was released to continuous operations. Process efficiency is continuously measured via extraction and stripping performance. The following were evaluated to determine the NGS flowsheet performance:

TABLE II. **Process parameters and samples evaluated**

Parameter Evaluated	Justification	Hydraulic Stability	Extraction & Stripping Efficiency
Contactor Vibration	ensure surging, imbalances, or solids formation was not occurring	X	X
Contactor Rotor Speed	ensure sufficient mixing and to minimize solvent carryover	X	X
Flow rates Trends	ensure off-normal cascade flow condition did not occur	X	X
Solvent Specific Gravity	ensure sufficient separation within contactors is capable	X	X
Solvent Hold Tank Level	ensure an off-normal cascade did not occur that could result in carryover into or out of the solvent hold tank	X	
Caustic Wash Quality	hydroxide concentration and cesium was monitored to ensure sufficient removal of impurities, which could impact the solvent's ability to extract and release cesium occurred; visual analysis was performed to ensure emulsion or excess organic as a result of a hydraulic instability was not occurring		X
Solvent Quality	ensure the solvent's ability to extract/release cesium and maintain optimal hydraulics; monitored for impurities, degradation products, cesium-137 (Cs-137), and the concentration of the solvent components		X
DSSHT Chemistry	ensure density, free hydroxide, Cs-137 concentration, organic content, and uranium meet Saltstone's requirements		X
SEHT Chemistry	ensure density, pH, Cs-137 concentration, and organic content meet DWPF's requirements		X

RESULTS

Good contactor hydraulics is evident by stable flow rates throughout the contactor banks, contactor vibration within normal range, satisfactory contactor rotor speeds, and acceptable levels of organic carry-over into the product streams (SEHT and DSSHT). Process trends and sample results during operation indicated the NGS flowsheet process was hydraulically stable.

Sufficient, smooth inlet and outlet flows were maintained in the contactors. Small deviations between the

average CSS flow rate and target flow rate were likely due to the cycling of MCU as a result of mechanical and instrumentation issues associated with restarting after an extended outage. The deviations between the target and actual flow rates are minimal and were unlikely to impact NGS process performance (Table 5).

TABLE III: Average micro-batch flow ratios (O/A) at prescribed flow rates

Target CSS Flow Rate SCCM (GPM)		Extraction CSS		Scrub		Strip		Wash	
		O/A	Variance	O/A	Variance	O/A	Variance	O/A	Variance
	Target	0.250		3.750		3.750		3.750	
1.51E+04 (4.00 GPM)	**MB1**	0.250	0.000%	3.746	0.107%	3.754	0.107%	3.759	0.240%
2.27E+04 (5.99 GPM)	**MB2**	0.251	0.211%	3.753	0.090%	3.773	0.606%	3.754	0.110%
3.03E+04 (8.00 GPM)	**MB3**	0.250	0.066%	3.749	0.030%	3.759	0.241%	3.750	0.013%
2.87E+04 (7.57 GPM)	**MB4**	0.251	0.335%	3.740	0.271%	3.761	0.291%	3.745	0.142%
3.22E+04 (8.50 GPM)	**MB5**	0.250	0.077%	3.755	0.126%	3.726	0.639%	3.750	0.002%
3.22E+04 (8.21 GPM)	**MB6**	0.250	0.026%	3.751	0.038%	3.741	0.250%	3.920	4.521%
%Relative Standard Deviation (%RSD)		0.158%		0.146%		0.440%		1.820%	
Average		0.250		3.749		3.752		3.779	

Operation of the CWT recirculation system in manual mode during Micro-Batch #6 to support troubleshooting resulted in additional deviation (~4.5%) from the target O/A ratio. SHT results did not indicate the buildup of impurities signifying the minute deviation was acceptable. The deviation in the Micro-Batch #5 strip O/A ratio was likely an early indication of the strip feed flow meter failure that occurred during initial startup of Micro-Batch #6. Contactor vibration and rotor speed was acceptable.

The Wash Contactor #2 online vibration instrumentation was known to be biased high (average over the Micro-Batches was ~0.833 cm/sec (0.328 in/sec); therefore skewing the average wash contactor bank vibration. Direct, redundant vibration measurements taken in the field and known to be more accurate, at a CSS flow rate of 3.03E+04 SCCM (Micro-Batch #3), indicated that Wash Contactor #2 vibration was actually ~0.075 in/sec. Therefore, the elevated vibration readings of Wash Contactor # 2 were not considered to be a concern. Wash Contactor #2 vibration remained stable, indicating it was free of solids accumulation and flows were stable. The percent relative standard deviation (%RSD) of the average Wash Contactor # 2 vibration during the prescribed CSS flow rates was 3.24%.

TABLE IV: Average contactor bank vibration and speed

Contactor Bank	Target RPMs	Extraction		Target RPMs	Scrub		Strip		Wash	
		Vibration (cm/sec)	Rotational Speed (RPM)		Vibration (cm/sec)	Rotational Speed (RPM)	Vibration (cm/sec)	Rotational Speed (RPM)	Vibration (cm/sec)	Rotational Speed (RPM)
MB1	**1200**	0.109	1195.70	**1800**	0.201	1802.75	0.284	1804.61	0.437	1801.30
MB2		0.391	1696.59		0.368	2102.70	0.348	2104.53	0.165	2100.15
MB3		0.462	1688.37		0.353	2101.60	0.368	2102.91	0.168	2099.05
MB4	**1700**	0.229	1690.67	**2100**	0.257	2102.15	0.300	2103.47	0.142	2100.15
MB5		0.201	1689.07		0.251	2101.70	0.305	2102.30	0.142	2097.30
MB6		0.206	1689.71		0.284	2102.75	0.297	2102.21	0.137	2097.75
Target Vibration		**< 0.762**			**< 0.762**		**< 0.762**		**< 0.762**	

At periods in the NGS Demonstration, Extraction Contactor #1 vibration readings were higher than expected, reaching a maximum during Micro-Batch #3. CSS enters into Extraction Contactor #1 first. Solids or salt accumulation occurring because of the cycling of MCU as a result of batch processing has historically been the probable cause of increased vibration. Salt deposits could have dissolved or otherwise sloughed away after Micro-Batch #3. Also during Micro-Batch #3, Extraction #1 was rotating ~1.035% lower than its target speed likely due to potential salt/solids accumulation. Elevated vibration and decreased rotor speed was not seen after Micro-Batch #3. All other contactor rotor speed variance was less than 0.8% for all Micro-Batches.

The average SHT level and specific gravity over the course of the Micro-Batches, seen in Figure 2, indicated negligible solvent carryover or process stream carryover into the SHT occurred. MCU Engineering evaluates the solvent monthly to correct for any Isopar-L evaporation and maintain the target specific gravity (see Table 1) [5]. The total volume of the monthly Isopar-L addition that was required to bring the SHT to the target specific gravity (0.8384) was added in small volume subsets to maintain the SHT tank level below the Operator Roundsheet upper limit i.e. 0.836 m^3 (220.9 gallons) [6, 7].
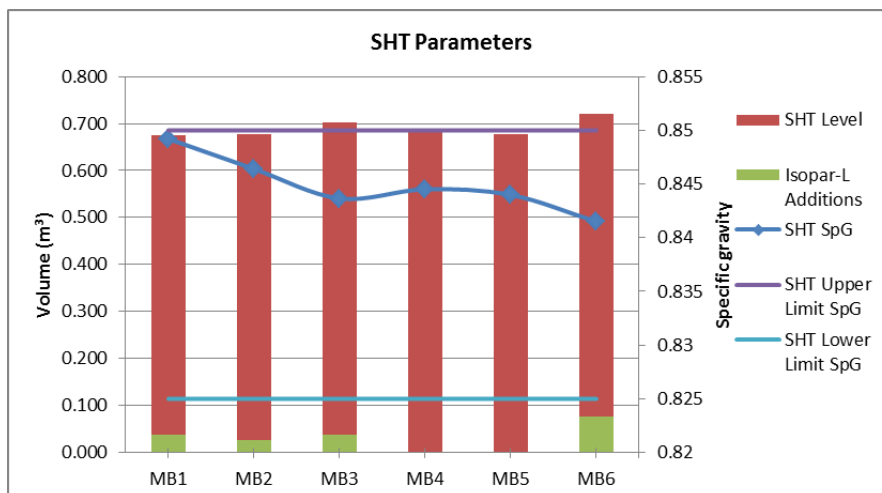

Fig. 2: SHT Parameters

SRNL predicted that ~90% of the solvent that is carried over is recovered in the coalescers-decanters [8]. DSSHT and SEHT Isopar-L results[b] seen in Table 5 indicate that the coalescer-decanters are effectively recovering the NGS and are statistically similar to the BOBCalixC6 results. In December 2012, MCU Engineering implemented a new sampling protocol to minimize organic cross contamination in the SEHT.

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[b] Solvent components are assumed to be carried over homogeneously. Only Isopar-L is analyzed by gas chromatography because it is the primary component in the solvent. All other solvent components carried over can be calculated using the target solvent component levels specified in TABLE.
[c] Sample results were omitted during the removal of solids accumulation (April 2014 – June 2013) because MCU was not processing routinely.

TABLE V: Comparison of organic carryover into the process hold tanks[b]

		DSSHT			SEHT	
	NGS	BOBCalixC6 (after new sampling protocol 12/2012 to 08/2013)	BOBCalixC6 (8/2011 – 08/2013)	NGS	BOBCalixC6 (after new sampling protocol 12/2012 to 08/2013)	BOBCalixC6 (8/2011 – 08/2013)
Average (mg/m^3)	6,900	9160	9,120	12,280	10,580	14,210
%RSD	56.6%	57.1%	60.6%	56.4%	25.31%	99.3%
N, Sample Population	27	241	505	21	187	394

The DSSHT and SEHT Isopar-L results (see Figure 3) have further stabilized during continuous operations[c].
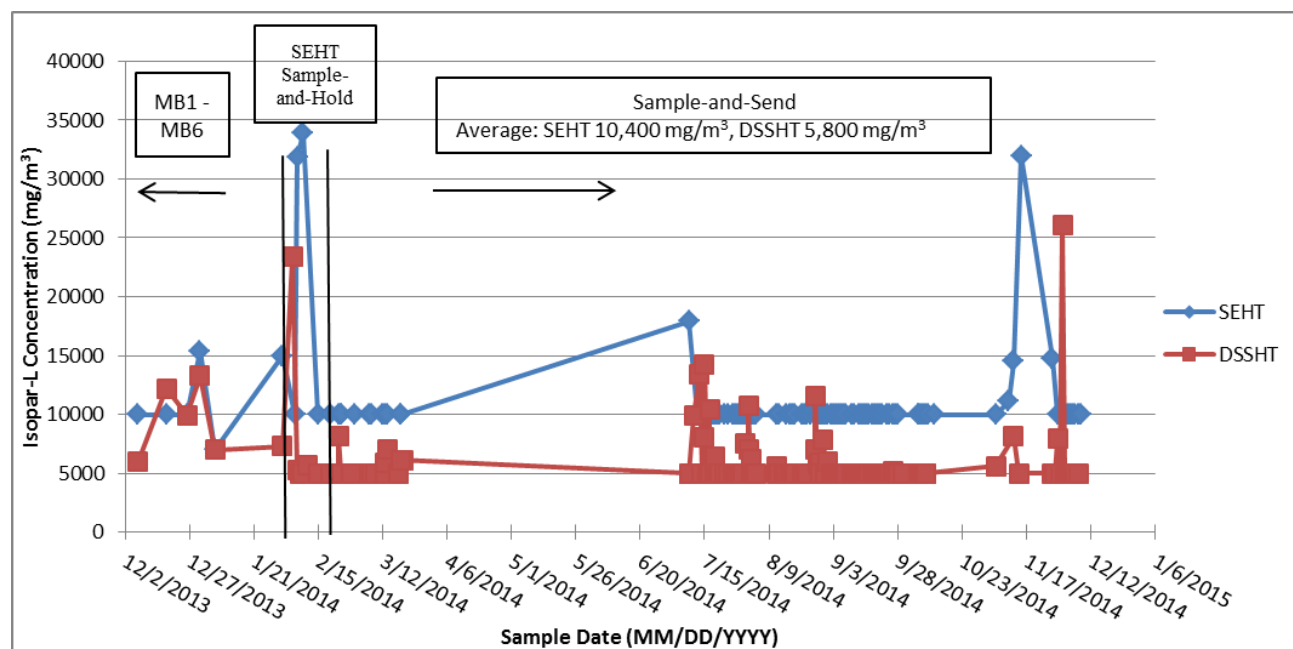

Fig. 3: Isopar-L Carryover into DSSHT and SEHT under NGS Flow Sheet

Because the coalescer-decanters are functioning effectively increased solvent carryover would result in increased organic pump overs from the decanter organic boots to the SHT. For a single 12 hour run at 3.22E+04 SCCM (8.5 GPM), PI data was used to evaluate the frequency of the DSS and SE organic pump overs. Results are seen in Table 6. The DSS and SE organic pumps are controlled automatically based on the specific gravity of the organic boots. The DSS organic boot pump turns on at a specific gravity of 0.92 and off at 0.98 [9]. The SE organic boot pump turns on at a specific gravity of 0.90 and off at 0.98 [9].

TABLE VI: DSS/SE organic pump overs

Process Conditions	DSS Decanter		SE Decanter
	Frequency in a 12 hr. Period	Rate (Frequency/min)	Frequency in a 12 hr. Period
NGS Sample-and-Send, 3.22E+04 SCCM (8.5 GPM)	5	7.87E-03	0
BOBCalixC6 Sample-and-Send, 3.22E+04 SCCM (8.5 GPM)	3	5.63E-03	0
	Difference	2.24E-03	0
	Variance	39.8%	0%

The SE organic pump over frequency was consistent with the BOBCalixC6 solvent. The SE organic boot routinely does not collect a sufficient volume of organic that would allow the organic boot pump to operate long enough to overcome the static head pressure. The increased frequency of DSS organic pump overs is a result of the change in solvent density. The DSS and SE organic boot specific gravity setpoints were not changed to reflect the NGS flow sheet because calculations concluded that the slight decrease in NGS density from BOBCalixC6 would not result in a significant or unsafe change in the quantity of organic that accumulate in the organic boots [9]. As seen in Table 7, the decrease in the solvent density without changing the organic boot setpoints would be expected to increase the frequency of organic pump overs assuming equivalent, uniform organic carryover into the decanter. The DSS decanter aqueous specific gravity is ~1.25 [8].

TABLE VII: Volume and time required to reach organic setpoint [9]

	Aqueous Specific Gravity	BOBCalixC6 Solvent	NGS Blended Solvent		NGS	
		Vol. Required to Reach Org. Setpoint (cm^3)	Vol. Required to Reach Org. Setpoint (cm^3)	Changes in Time to reach Org. Setpoint* (min)	Vol. Required to Reach Org. Setpoint	Change in Time to reach Setpoint* (min)
DSS Decanter Boot	1.35	2399.95	2343.17	1.76E-03	0.619	1.76E-03
	1.25	2820.13	2740.64	2.47E-03	0.724	2.47E-03
	1	6382.20	5893.89	1.52E-02	1.559	1.49E-02

* Assumed 8.5 GPM CSS Flow Rate

The calculated decrease in the amount of time until the NGS blended solvent would reach the volume of organic that would result in a pump over of the organic boot (2.47E-03 min) correlates well to the increased change in the rate of pump overs from BOBCalixC6 to the current NGS blended solvent, 2.24E-03 Frequency/min (Table 6), implying that the hydraulic stability and organic carryover is approximately equivalent to the BOBCalixC6 flow sheet.

CWT samples were taken during (blue) and after (white) each batch. All CWT samples were free of organic or gel layers indicative of emulsion and/or organic carryover. CWT results indicate that the caustic wash is somewhat depleted in free hydroxide [8]. Depletion of free hydroxide may indicate the wash is effectively removing degradation products from the solvent or indicate the deprotonation of a constituent in or being carried over with the organic stream is occurring. Analysis for boron indicated strip carryover was non-detectable (LOQ is 0.01 M). During operations after the six Micro-Batches, Engineering recommended sampling the CWT every four SEHT batches and partially refilling (~50% replenishment) the CWT once per shift during continuous operation or completely (100% replenishment) if MCU is shut down [13, 14]. There is no discernable trend between the CSS flow rate and the free hydroxide concentration. The CWT free hydroxide concentration trended back towards the target concentration after entering sample-and-hold on the SEHT likely due to the partial replenishment of the CWT during operations. There does not appear to be a trend between the free hydroxide levels and a time dependent correlation or volume dependent degradation of solvent components [8].

TABLE VIII: CWT sampling results

Micro-Batch#	Average Free Hydroxide M	Average Density g/cc	Average Boron mol/m^3		SEHT Batch#	Average Free Hydroxide mol/m^3	Average Density g/cc	Average Boron mol/m^3
1	0.024	1.009	1.0		567	22.0	1.000	1.0
1	0.024	1.007	1.0		568	23.0	1.002	1.0
1	0.024	1.007	1.0		569	23.0	1.009	1.0
2	0.026	0.993	1.0		570	12.0	1.002	1.0
2	0.025	0.993	1.0		571	25.0	1.006	1.0
3	0.025	1.002	1.0		574	25.0	1.000	1.0
3	0.025	1.004	1.0		578	27.0	1.014	1.0
4	0.024	1.004	1.0					
5	0.022	0.985	1.0					
5	0.023	0.980	1.0					
6	0.018	0.999	1.0					
6	0.018	1.004	1.0					

The caustic wash appears to be effectively cleaning the solvent. Solvent quality results are near expected concentrations. SRNL did not report any major impurities found in the solvent during Micro-Batch processing [8]. Therefore, as seen in Figure 4 and Table 9 the NGS blended solvent is more effectively extracting and stripping cesium from the CSS than the BOBCalixC6 solvent had been.

TABLE IV: Comparison of average gross DF, gross CF and SHT [3, 8, 16]

	BOBCalixC6 Salt Batch 6-D (SB 6-D) Average	BOBCalixC6 Historical Average	NGS MB1 – MB6 Average (SB 6-D)	NGS Average (SB 6-D and SB 7A/B)
DF	124	157	1,129	12,727
CF	12.34	11.9	8.0	11.36
SHT (Bq/m^3)	2.41E+10 (2.47E-03 Ci/gal)	N/A	5.11E+08 (5.23E-05 Ci/gal)	

The gross DF is defined as the concentration of Cs-137 in Tank 49 salt solution (2.16E+12 Bq/m^3 or 0.221 Ci/gal) divided by Cs-137 (Ci/gal) concentration in the full (completion of a Micro-Batch) or near full (during sample-and-send operations) DSSHT [15]. The gross CF is defined as the SEHT Cs-137 concentration at the completion of the Micro-Batch, after the SEHT is full (completion of a SEHT sample-and-hold batch) or near full (during sample-and-send operations) divided by the concentration of Cs-137 (2.16E+12 Bq/m^3) in Tank 49 salt solution [15]. All hold tank density results (see Table 10) were within the expected ranges, thus confirming the integrity of the samples.
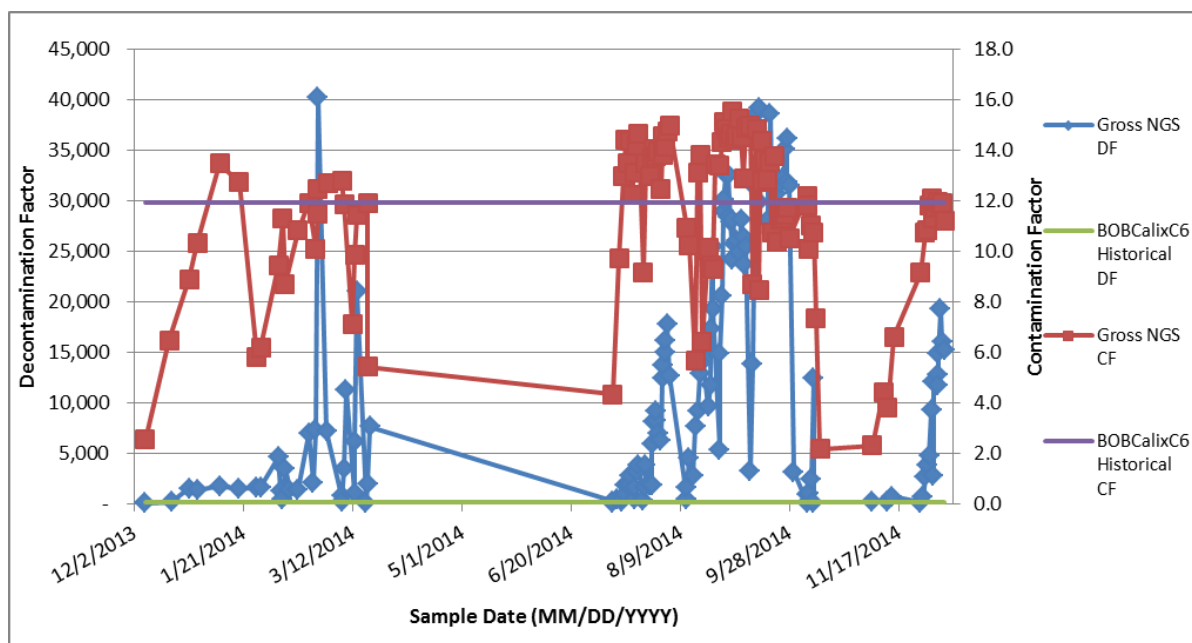
Fig. 4: Gross DF and CF

The curie concentration of the SEHT, and thus the CF, trended low during the Micro-Batch Demonstration due to several factors: (1) residual flush material in the SE decanter and SEHT heel prior to the NGS Demonstration, (2) the introduction of excess strip acid due to the batch cycling of MCU, (3) the size of the SEHT batches during Micro-Batch processing being unable to overcome the dilution effects, and (4) the failure of the strip flow meter as a result of cold weather damage at the beginning of Micro-Batch #6 [3, 17]. Although both the DSSHT and SEHT were subject to dilution, the DSS decanter has a significantly higher turnover, and thus is better able to overcome dilution effects. The average solvent Cs-137 concentration across the Micro-Batches (5.11E+08 Bq/m^3 or 5.23E-05 Ci/gal) was quite low [8]. Therefore, Cs-137 is being effectively stripped from the solvent.

The significant increase in DF is the result of continuous sample-and-send operations. The significant drops in the DF and CF are a result of the shutdown and restart of MCU reaffirming the adverse effects of stop/go operational modes on the DF and CF. Similar trends were seen for processing during the BOBCalixC6 flow sheet. The correlation between the decreased DF and cycling are a result of how long the DSSHT is recirculated, the time to reach the process flow rate upon startup of the CSS, if MCU is started on hot feed, the number of flowrate changes, and/or the length of time the CSS is run prior to the introduction of the solvent.

The DF and CF show clear impacts of dilution due to the residual flush material and non-contiuous processing. Additional run time is needed for each flow rate under sample-and-send operations to effectively reach a concentration equilibrium between the decanter and hold tank to generate a more representative operating curve. The DF especially continuous to improve with extended, continuous operations. During periods of continuous processing, the DF has reached ~40,000 and the CF has reached ~15.

All DSSHT and SEHT sample results were satisfactory or as expected during the NGS demonstration; however, the pH of the SEHT began trending upward above the original limit (pH = 8.0). SRNL compared the analytes in the STFT samples and SEHT samples (results seen in Table 10) to evaluate the

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cause of the elevated pH [8]. The STFT analytes were as expected; therefore, the gap between the theoretical SE pH (~5.6) and the pH measurement must be due to the consumption of the boric acid in the SE system downstream of the STFT and/or the presence of even a small amount of material with a base association constant, pKb, sufficient enough to raise the pH above 7 [13]. Potentially, the consumption of boric acid could be due to the partitioning of elevated residual anions as a result of increased cesium uptake, caustic carryover from the scrub, CSS carryover, deprotonation of the boric acid due to the free base form of guanidine, or partition of amines that could form after the degradation of the guanidine [21].

Therefore, a minimum of five additional sample-and-hold batches on the SEHT for pH and sodium was performed to gain continued confidence that the pH and sodium would remain within the revised receipt limits. Sample-and-hold data is seen in Table 10. The sample-and-hold batches are identified by the SEHT batch number and sample date. Upon review of the five sample-and-hold SEHT batches, Engineering found all process trends and sample results to be satisfactory or expected. MCU transitioned into continued sample-and-send processing. During continuous processing, all sample results have remained within limits.

TABLE X: Sample-and-hold DSSHT and SEHT sample results

	Micro-Batch # or Sample Date	CSS Flow Rate SCCM	SEHT				DSSHT			
			SEHT Density g/m^3	SEHT Bq/m^3	SEHT pH	SEHT Na g/m^3	DSSHT Density g/cc	DSSHT Bq/m^3	DSSHT $^-$OH mol/m^3	DSSHT Uranium g/m^3
Sample-and-Hold for DSSHT and SEHT	MB1	1.51E+04 (4.00 GPM)	1.012	5.49E+12	6.83	N/A	1.214	2.01E+10	1,874	8.70E+00
	MB2	2.27E+04 (5.99 GPM)	1.015	1.40E+13	7.65	N/A	1.231	9.55E+09	1,977	1.21E+01
	MB3	3.03E+04 (8.00 GPM)	1.027	1.92E+13	6.35	N/A	1.246	1.38E+09	2,139	1.21E+01
	MB4	2.87E+04 (7.57 GPM)	1.037	2.23E+13	8.32	N/A	1.248	1.57E+09	2,242	1.20E+01
	MB5	3.22E+04 (8.50 GPM)	1.000	2.90E+13	8.7	49.6	1.252	1.18E+09	2,070	1.26E+01
	MB6	3.22E+04 (8.21 GPM)	1.027	1.34E+13	8.17	32.2	1.252	1.28E+09	2,182	1.17E+01
Sample-and-Hold for SEHT on pH and sodium only	2/5/2014	3.22E+04 (8.50 GPM)					1.252	4.67E+08	2,264	1.10E+01
	567 (2/6/2014)	3.22E+04 (8.50 GPM)	1.037	2.03E+13	8.45	43.5				
	2/7/2014	3.03E+04 (8.00 GPM)					1.253	1.69E+09	2,193	1.23E+01
	568 (2/7/2014)	3.03E+04 (8.00 GPM)	1.023	2.43E+13	8.41	41.6				
	2/8/2014	3.22E+04 (8.50 GPM)					1.248	4.55E+09	2,289	1.19E+01
	2/9/2014	2.27E+04 (6.00 GPM)					1.231	6.11E+08	2,244	1.14E+01
	569 (2/9/2014)	2.27E+04 (6.00 GPM)	1.029	1.88E+13	8.43	38.3				
	2/11/2014	3.22E+04 (8.50 GPM)					1.235	1.49E+09	2,199	1.19E+01
	570 2/15/2014	3.03E+04 (8.00 GPM)	1.016	2.34E+13	8.35	40.9				
	2/15/2014	3.22E+04 (8.50 GPM)					1.235	1.49E+09	2,262	1.16E+01
	2/20/2014	2.84E+04 (7.50 GPM)					1.246	3.10E+08	2,284	1.43E+01
	571 2/20/2014	2.84E+04 (7.50 GPM)	1.010	2.57E+13	8.28	44.1				

CONCLUSION

The NGS Demonstration has shown that the NGS flow sheet resulted in satisfactory contactor hydraulics, improved stripping performance denoted by the low cesium concentration in the solvent, a significant increase in the extraction efficiency, and compliance with downstream facility limits.

Plant Information (PI) data was used to monitor the contactor vibration, rotor speed, and flow stability, none of which indicated any off-normal conditions or significant trends [3]. The SHT level and specific gravity did not indicate any off-normal flow conditions or increased solvent carryover into or out of the SHT [3, 17]. DSSHT and SEHT sample results did not indicate increased organic carryover was occurring. Hold tank organic sample results were similar to BOBCalixC6 flow sheet. The organic carryover results indicated contactor carryover, coalescer, and decanter performance is similar for both flow sheets. Therefore, contactor hydraulics are considered stable under the NGS flow sheet.

There were minor losses of the Isopar-L and TOA, and moderate loss of TiDG in the MCU NGS blended solvent composition; however, the losses were expected. ORNL results suggest that at current levels, ~65%, the TiDG should effectively overcome organophillic impurities, thus indicating that stripping performance was not impacted [10]. This is substantiated by the low concentrations of Cs-137 in the solvent. The CWT samples indicated that the solvent was effectively washed to remove impurities and degradation products since no solvent impurities were reported during processing of CSS under the NGS flow sheet [8].

The extraction and stripping performance of the NGS flow sheet was evaluated during the NGS Demonstration, under the SEHT sample-and-hold operations, and sample-and-send operations. The average DF (~12,727) indicates NGS blended solvent is more effectively extracting cesium from the CSS than the BOBCalixC6 solvent. The average CF (~9.92) did not accurately representative of NGS performance due to residual flush material in the SE decanter and SEHT heel, the introduction of excess strip acid due to the batch cycling of MCU, and the failure of strip flow meter at the beginning of Micro-Batch #6. Cs-137 was not building up in the solvent and the DSSHT Cs-137 concentration was low; therefore, stripping was effective. The average CF (~11.4) better indicates that Cs-137 is being stripped from the solvent.

The hold tanks sample results indicated that the NGS flow sheet did not cause changes in the DSSHT and SEHT material that challenged the downstream facility limits. The SEHT pH limit was revised because the SEHT pH began trending upward starting in Micro-Batch #4. The gap between the theoretical SE pH (~5.6) and the pH measurement is likely due to the consumption of the boric acid in the SE and/or the presence of material with a pKb sufficient to raise the pH above 7 [21].

REFERENCES

1. SRR-SPT-2013-00033, Rev. 1, "Salt Disposition Project (SDP) Next Generation Solvent (NGS) Demonstration Plan," A. Garrison, December 2013.
2. ORNL-LTR-NGCSSX-010, "Solvent Blending Strategy to Upgrade MCU CSSX Solvent," L. H. Delmau and B. A. Moyer, July 2011.
3. X-ESR-H-00570, Rev. 8, "Technical Evaluation of Micro-Batchwise Next Generation Solvent Demonstration and Engineering Recommendations," T. E. Smith, May 2014.
4. WSRC-IM-95-98, 15242-G, Rev. 2. "Engineering Guide: Equipment Vibration." June 2010.
5. WSRC-SA-2002-00007, Rev. 15, "Concentration, Storage, and Transfer Facilities Documented Safety Analysis." September 2013.
6. SW9.6-RS(2H)E-7-2, Rev. 40. "MCU Control Room Operator Rounds." April 2014.
7. X-ESR-H-00657, Rev. 0. "MCU Evaluation of MCU Solvent and Recommended Isopar-L Addition to Maintain Specifications: March 2014." T. E. Smith, March 2014.
8. SRNL-STI-2014-00101, Rev. 0, "Results from the Salt Disposition Project (SDP) Next Generation Solvent (NGS) Demonstration Plan." T. B. Peters et al., April 2014.
9. X-ESR-H-00555, Rev. 0, "Modular Caustic-Side Solvent Extraction Unit (MCU) Decanter Organic Collection Boot Setpoint Evaluation for Next Generation Solvent (NGS)." A. Garrison, August 2013.
10. ORNL/TM-2013/224, Rev. 1, "Next Generation Solvent Development for Caustic-Side Solvent Extraction of Cesium." B. A. Moyer et al., June 2013.
11. ORNL-LTR-NGSCSSX-020, Rev. 1. "Thermal Degradation of Next Generation Solvent using Triisodecylguanidine Suppressor: Impacts on Solvent Performance and Organic Content of Aqueous Effluents." B. A. Moyer et al., July 2013.
12. ASTM E 178 - 08, "Standard Practice for Dealing with Outlying Observations," ASTM International, West Conshohocken, PA, 2013, DOI: 10.1520/E0178-08.
13. SRNL-L3100-2014-00028, Rev. 0. "Consideration of the Strip Effluent (SE) pH and Sodium Content." T. B. Peters and S. D. Fink, February 2014.
14. X-ESR-H-00605, Rev.0. "MCU Operations Plan: Continued NGS Demonstration Operations." T. E. Smith, February 2014.
15. X-ESR-H-00501, Rev. 0. "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 6-D." S. E. Campbell, April 2013.
16. SRNL-STI-2014-00661, Rev. 0. "Solvent Hold Tank Sample Results for MCU-13-1403/1405/1406/1407/1408: Quarterly Sample from September 2013." F. F. Fondeur and K. M. L. Taylor-Pashow, November 2013.
17. SRR-SPT-2013-00055, Rev. 1. "Interim Path Forward for Data Collection and Troubleshooting of the Recent Event of an Unexpected Solvent Carryover into the Decontaminated Salt Solution Decanter." T. E. Smith et al., May 2014.
18. SRNS-L4700-2013-00014, "Evaluation of Method Uncertainties and Performance Characteristics of MCU Analytical Methods." C. B. Stoyle, January 2014.
19. X-SD-G-00008, Rev. 13, "Waste Acceptance Criteria for Sludge, ARP, and MCU Process Transfers to 512-S and DWPF (U)." December 2013.
20. SRNL-L3100-2017-00012, Rev. 0. "Initial analysis of Strip Effluent and Strip Feed Samples." T. B. Peters and M. S. Hays, January 2014.
21. SRNL-l3100-2014-0013, Rev. 0. "Recommended Strip Effluent pH Limits for New Generation Solvent." D. P. Lambert, January 2014.