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Solvent Hold Tank Sample Results for MCU-19-569-571 (December 2019), MCU-20-1-28 (January 2020), and MCU-20-29-30-31 (June 2020): Quarterly Report

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October 2020

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EXECUTIVE SUMMARY

A trend summary of three Solvent Hold Tank (SHT) monthly samples MCU-19-569-570-571 (December 2019), MCU-20-1-28 (January 2020), and MCU-20-29-30-31 (June 2020) are reported. Most of the conclusions are based on the June 2020 SHT sample (MCU-20-29-30-31). Analyses of the June 2020 SHT sample indicated that the Modifier (Cs-7SB) and the Extractant (MaxCalix) concentrations were above their nominal recommended concentrations (169,000 mg/L and 46,900 mg/L respectively) by 6% and 7% respectively. The Suppressor (*N,N',N"*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has remained at 833 ± 16 mg/L, but it is above the minimum recommended concentration (479 mg/L).

The Semi-Volatile Organic Analysis (SVOA) and FT-HNMR did not detect any organic impurities. Another impurity observed in the samples was mercury. Based on the June 2020 SHT sample, up to 23 ± 5 micrograms of mercury per gram of solvent (or 19 ± 4 mg/L) was detected. The mercury concentration steadily decreased from 34.8 $ug/g_{solvent}$ (or 21.9 mg/L) in the December 2019 SHT sample to 34.8 $ug/g_{solvent}$ (or 19 mg/L) in the June 2020 SHT sample.

The gamma concentration (~3.33E4 dpm/mL) measured in the June 2020 SHT samples was consistent with previous values observed when MCU was idle (for example, between February 2017 and August 2017).

If additional SHT samples become available, the laboratory will continue to monitor the quality of the solvent for any new impurities or degradation of the solvent components.

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LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
CSSX	Caustic-Side Solvent Extraction
CVAA	Cold Vapor Atomic Absorption
DMA	Direct Mercury Analysis
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
HNMR	Hydrogen Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
MCU	Modular Caustic-Side Solvent Extraction Unit
MaxCalix	1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6
NGS	Next Generation Solvent
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
SWPF	Salt Waste Process Facility
TiDG	*N,N',N"*–tris(3,7-dimethyloctyl)guanidine
TOA	Trioctylamine
XRF	X-Ray Fluorescence

1.0 Introduction

In late FY13, MCU implemented the Next Generation Solvent (NGS) flow sheet. Facility personnel added a non-radioactive, NGS "cocktail" containing the new Extractant (MaxCalix) and a new Suppressor (TiDG) to the SHT heel to implement the NGS flow sheet. The resulting "blend" solvent ("NGS blend solvent") is essentially NGS with residual amounts of calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalixC6) and trioctylamine (TOA). For process monitoring, SHT samples are sent to Savannah River National Laboratory (SRNL) to examine solvent composition changes over time.[1] With the exception of Isopar™ L which is regularly added to the SHT due to its high vapor pressure, this report shows the cumulative chemical composition data, including impurities like mercury, of three SHT samples: MCU-19-569-570-571, MCU-20-1-28, and MCU-20-29-30-31. A summary report for each of the SHT monthly samples was issued earlier.[2,3,4] This report examines the cumulative results from these and several past monthly reports.

These samples are intended to verify that the solvent is within the specified composition range. A baseline "scratch" solvent – a scratch solvent is a preparation of all 6 solvent components of the composition that approximates the blend of cocktail[5] and heel solvent – was prepared in the lab (September 2018) and used for comparison and evaluation. The results from the analyses are presented in this document.

2.0 Experimental Procedure

2.1 Experimental Procedure

Table 2-1 lists a summary of relevant and recent trims to the MCU solvent as well as the arrival date of the samples currently being studied.

Table 2-1 Log of trims to MCU solvent for 2019 and SHT sampling dates

Event	Date
SHT special trim added	January 23, 2019
SHT sample MCU-19-2-3-4	January 26, 2019
9 gallons of Isopar™ L added to MCU	February 4, 2019
SHT sample MCU-19-83-84-85	February 17, 2019
11 gallons of Isopar™ L added to MCU	February 21, 2019
SHT sample MCU-19-138-139-140 special trim added	March 5, 2019
SHT sample MCU-19-208-209-210	March 19, 2019
9 gallons of Isopar™ L added to MCU	March 27, 2019
SHT sample MCU-19-366-367-368	April 13, 2019
SHT sample MCU-19-469-470-471	May 17, 2019
9 gallons Isopar™ L added to MCU	May 31, 2019
SHT sample MCU-19-524-525-526	June 23, 2019
SHT sample MCU-19-557-558-559	July 23, 2019
SHT sample MCU-19-560-561-562	August 13, 2019
SHT sample MCU-19-566-567-568	September 16, 2019
SHT sample MCU-19-569-570-571	Dec 16, 2019
SHT sample MCU-20-1-28	Jan 23, 2020
SHT sample MCU-20-29-31	June 8, 2020

Samples shown in Table 2-1 were received in P-nut vials containing ~10 mL each (see Figure 1). Once taken into a radioactive hood, the samples were visually inspected and analyzed for pH. Contents of the P-nut vials for each monthly SHT sample were composited before use. Aliquots of the composited sample were removed to perform the following analyses: density, SVOA, HPLC, titration for TiDG, gamma counting, DMA, and FT-HNMR. Results from analytical measurements were compared with the theoretical values shown in Table 2-2. Please note that the HPLC, DMA, density, titration for TiDG, and FT-HNMR results for each SHT sample are shown in the respective monthly reports. All reported values were checked against the values obtained from a scratch solvent made in September 2018. All error bars represent one-sigma (one standard deviation). In the case of the physical measurements (density, surface tension, and viscosity measurements), the one-sigma was obtained from three replicates (observations). Suppressor concentration derived from titration was performed in duplicate. The one-sigma from the DMA measurement was obtained from duplicate observations (replicates). Therefore, the error bars shown in this report are the variations within replicates (or fidelity of the analytical measurements).

Table 2-2 Nominal concentrations of the relevant components in NGS Blend at 25 °C (Ref. 5)

Component	mg/L	Molar
MaxCalix	~ 44,400♠ to 47,800♣	~ 0.0465 to 0.050
BOBCalixC6*	< 4,030	< 0.0035
TOA*	< 530	< 0.0015
Modifier	~ 169,000	~ 0.50
TiDG	~1,440♥	~ 0.003
Isopar™ L	~ 607,000♣ to 613,000♠	~ 73.05 to 73.69 wt. %

*Values represent starting values when NGS blend was implemented. These components are no longer added to or refurbished in MCU.

♣Solvent composition is closer to a pure NGS formulation.

♠ Solvent composition is closer to an NGS-CSSX blend formulation.

♥Assuming a molecular weight for caustic-washed TiDG of 479 g/mol (516 g/mol for TiDG*HCl).

2.2 Quality Assurance

This work was performed under the following production support request: Q. L. Nguyen, "Analyzing MCU Routine Samples" TTR-H-00026, Rev. 0 July 2013. The recorded data, analysis, and conclusions satisfied the requirements listed in T.B. Peters, A.L. Washington, II, and F. F. Fondeur, "Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU," SRNL-RP-2013-00536, Rev. 2, January 2019. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60 (design check requirements). SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

Each sample (and its corresponding P-nut vial) was visually examined. No floating debris or foam were observed (see Figure 1). However, several slightly caustic droplets (pH=8) and less than half of a millimeter in diameter were found on the inside walls of P-nut vial MCU-19-570. SRNL believes these caustic droplets are evidence that the solvent contacted a caustic solution which is consistent with the caustic wash step of the solvent at MCU. No droplets were found in the remaining samples. All solvent samples had a pH value of 5. No unusual reactions, solids, foaming, or immiscible layers were observed after combining the samples into one Teflon container for each set of monthly SHT samples.

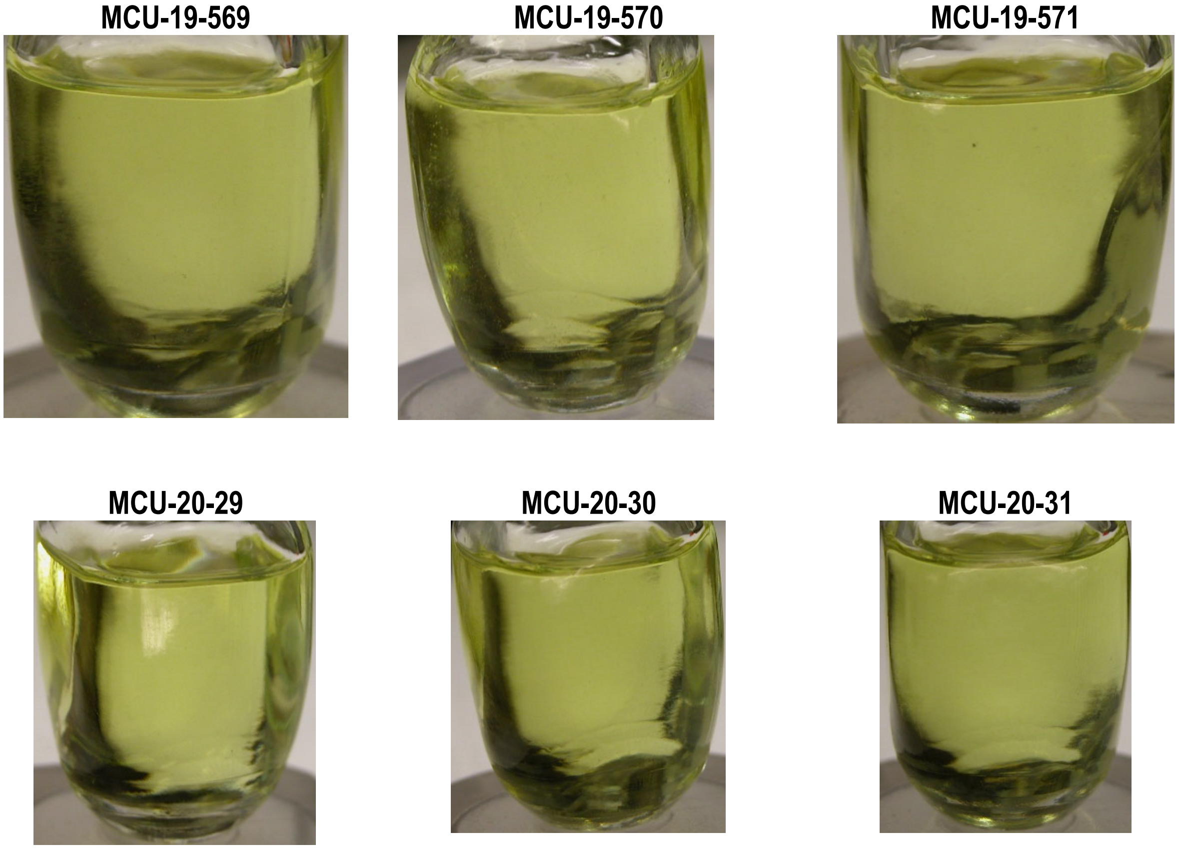


Figure 1. A picture of samples MCU-19-569-571 (top) and MCU-20-29-31 (bottom). Camera malfunctioned for samples MCU-20-1-28.

Modifier Concentrations and Density Measurements

MCU resumed operations in May 2018 (after suspending operations in January 2017) and since then, several Isopar™L additions and three trim additions were made to the solvent (MCU suspended operations on May 22, 2019 to support transfer line tie-in work for Salt Waste Process Facility or SWPF). Based on the December 2019, January 2020, and June 2020 results, both the density measurements and the Modifier concentration levels steadily increased possibly due to Isopar™L evaporation from the solvent but their corresponding error intervals included the nominal (0.830 mg/L at 25 °C in the case of the density measurement) and/or recommended value (in the case of the Modifier, the recommended level is 1.69E5 mg/L) [see Figure 2 and the tabulated data in Appendix A]. [2,4] A small positive bias was detected in the FT-HNMR measurements relative to the HPLC method for measuring the Modifier (HPLC is principal method for measuring the Modifier). Using the average of the two methods minimizes the bias effect. The reported density measurements were obtained from triplicate measurements of the sample (the density was measured by the vibrations of an especially calibrated tube filled with the organic liquid and corrected for temperature using the CSSX temperature correction formula).[7] The uncertainty (one sigma) by this method is 3%.

The upward trending values observed in the density (and in the Modifier concentration) for the December 2019, January 2020, and June 2020 samples are likely due to the evaporation of Isopar™L solvent. However, the observed density and Modifier values from the December 2019, January 2020, and June 2020 samples were consistent with previous measurements (for example in January 2018). Both the density data and the Modifier concentration correlated strongly with each other as expected (see Figure 2).[7] The Isopar™ L concentration (not shown) in the December 2019 and June 2020 samples were slightly below the Isopar™ L concentration of the baseline solvent (scratch made on September 2018). This finding is expected since the solvent density is a volume-weighed linear combination of the Modifier and Isopar™ L densities. Other physical measurements of the December 2019, January 2020, and June 2020 SHT samples such as viscosity and surface tension were trending upwards relative to the baseline solvent measurements (see Figure 3). No bias was detected in either the viscosity or surface tension measurements of the monthly solvent samples relative to the scratch baseline solvent.

All measurements indicate (based on the June sample) that the Isopar™ L concentration was slightly below (1%) its nominal value. The solvent might require an Isopar™ L trim to lower its Modifier concentration.

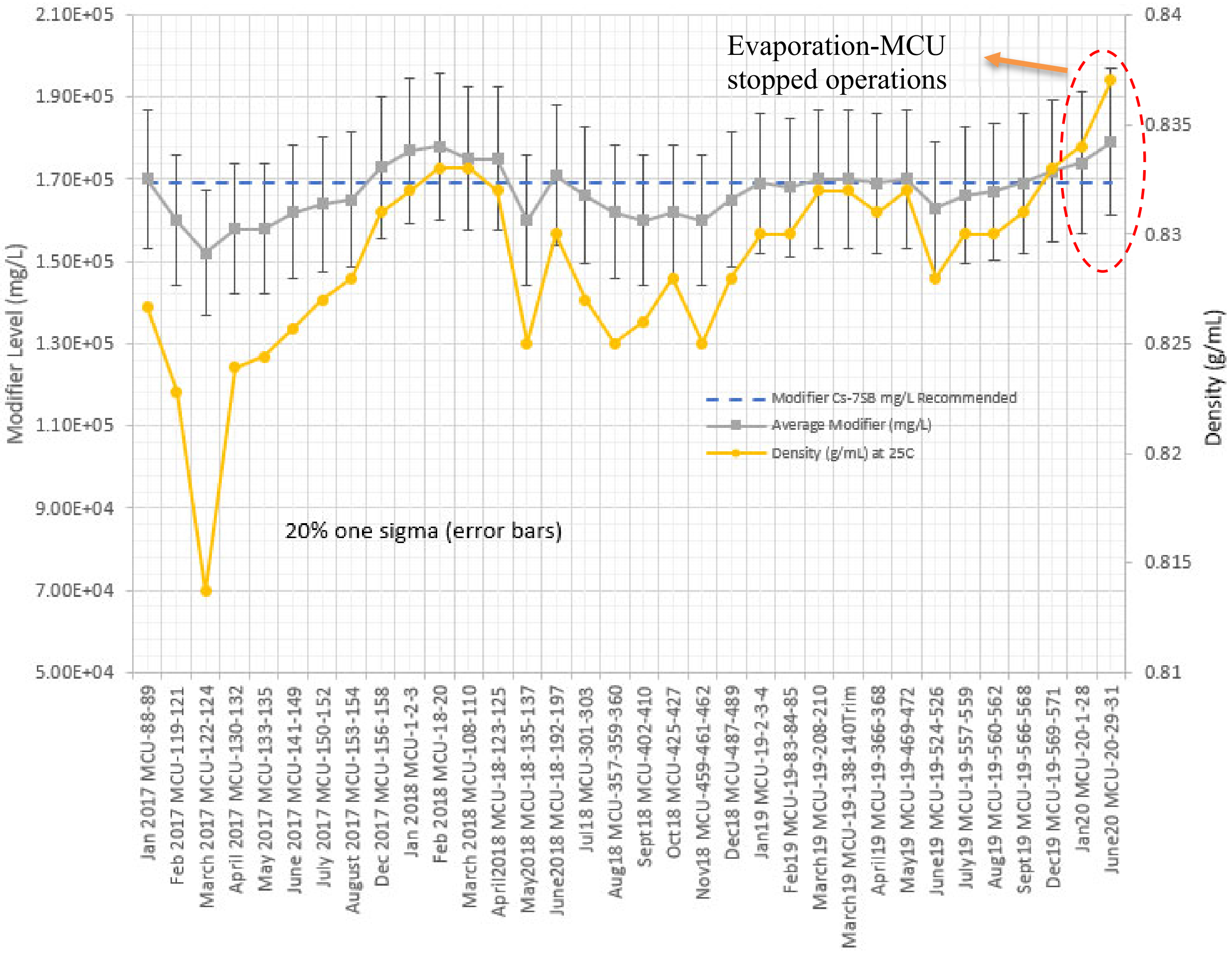


Figure 2. Modifier concentration in the solvent as measured by HPLC (one sigma is 10%).

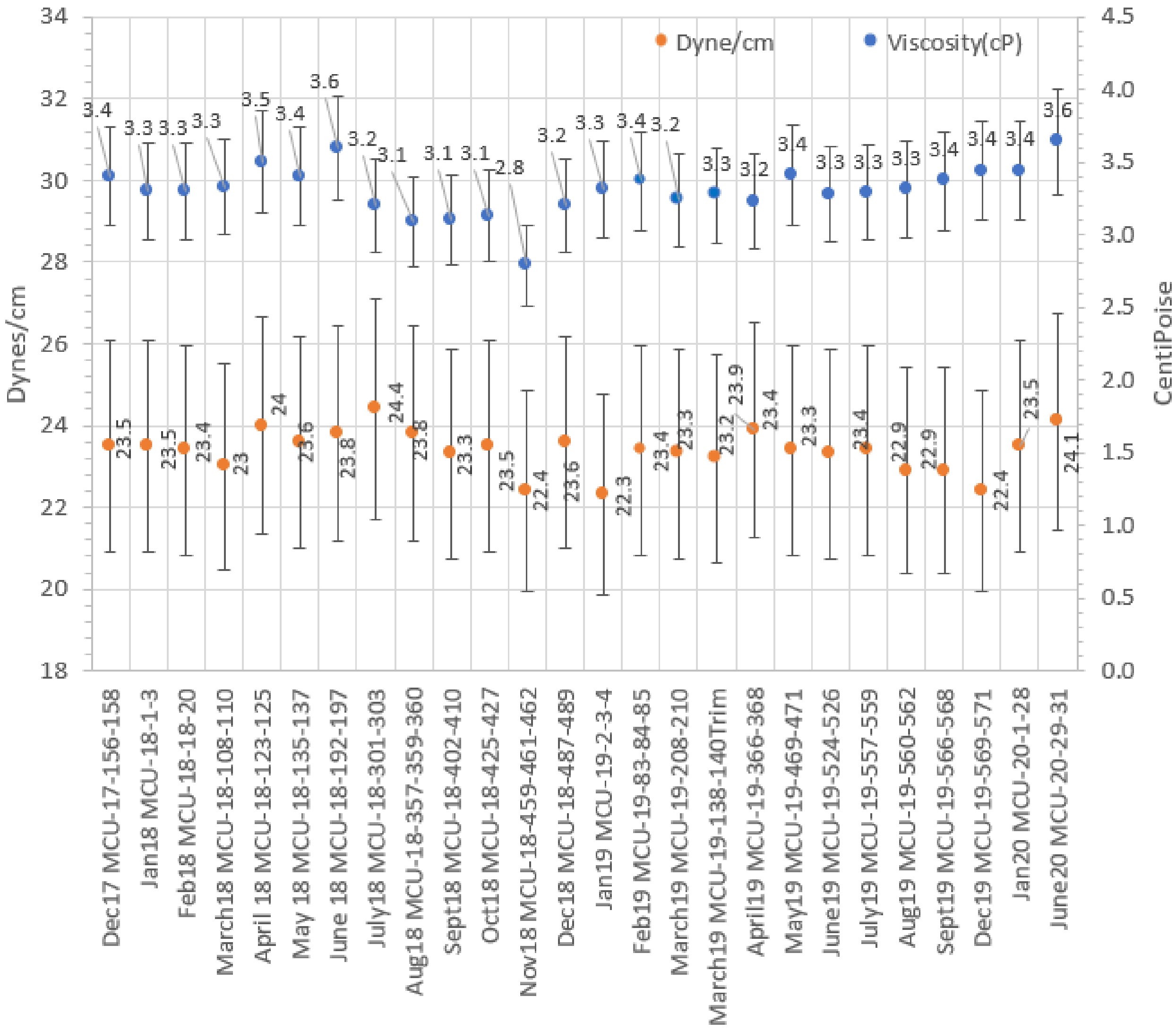


Figure 3. Viscosity and surface tension measurements of the last 26 SHT samples. The scratch blend measured a viscosity of 3 ± 0.3 cP and a surface tension of 23 ± 0.6 dynes/cm (at 25˚C).

Suppressor Concentrations

The average TiDG concentrations for MCU-19-569-570-571, MCU-20-1-28, and MCU-20-29-31 are shown in Figure 4. As can be seen in Figure 4, the TiDG concentration has remained steady at approximately 800 ± 30 mg/L since June 2019. Considering the December 2019, January 2020, and June 2020 samples, the steady-state TiDG concentrations have previously been observed before (for example from February to August 2017 in Figure 4) when MCU was not operational. Recall MCU stopped operations in December 2019. Based on the June SHT sample, the Suppressor concentration (8.33 ± 0.8E2 mg/L) is above its minimum recommended operating concentration (479 mg/L for caustic washed TiDG: See the communication that set the minimum level in Appendix A). The TOA concentration appears to have remained steady at 188 ± 30 mg/L. Since May 2016, the TOA level range can be estimated by 188 ± 30 mg/L. Since MCU no longer adds TOA, the persistent detection of TOA at this concentration level is not expected (it was expected to have declined with processing time). We believe the TOA concentration persists because of possible and expected degradation rate of TiDG into primary amines, which have previously been identified as degradation products of the Suppressor when heated (3 ºC, 25 ºC and 36 ºC).[8]

The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine) making the equivalent points coincide, and therefore difficult to distinguish.[9]

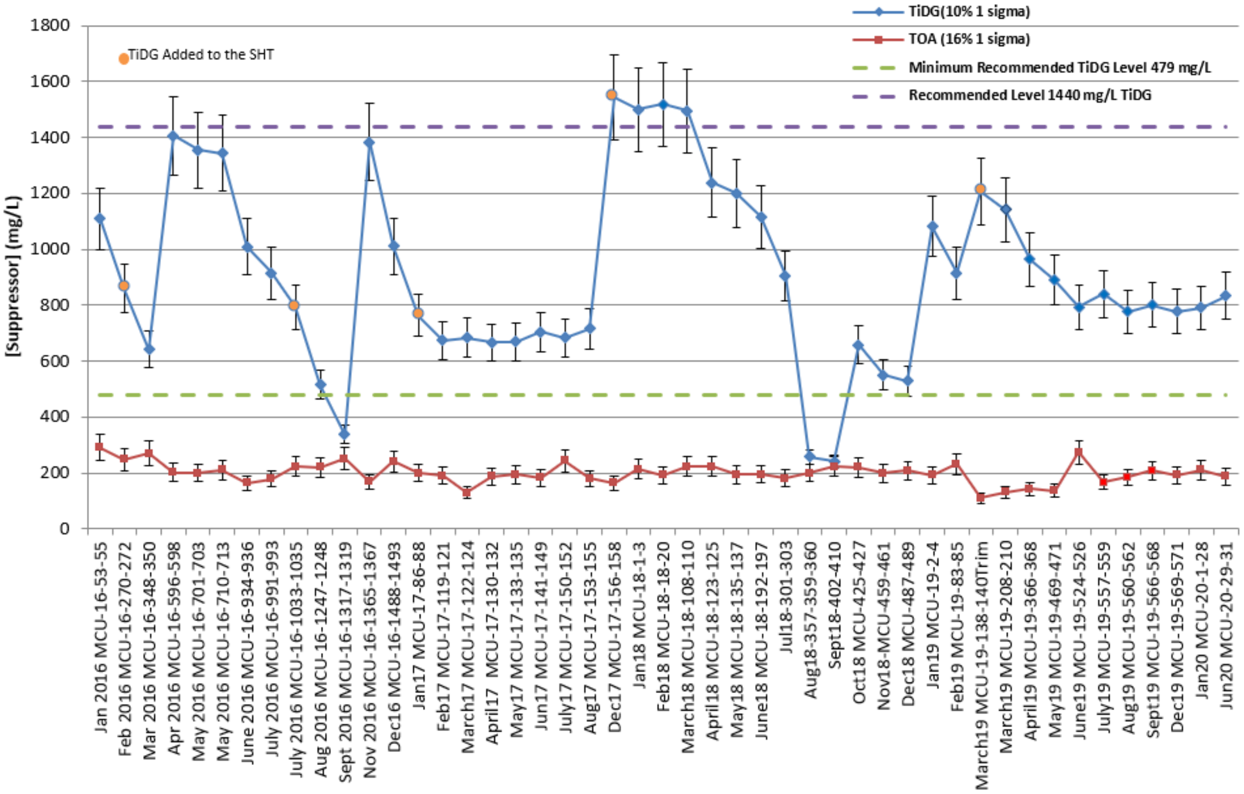


Figure 4. Suppressor concentration as measured by titration in the SHT samples since NGS implementation. The minimum recommended concentration is 479 mg/L for TiDG.

Extractant Concentrations

The calculated MaxCalix concentration steadily increased from 4.60E4 to 4.92E4 mg/L in the last 3 SHT samples (see Figure 5). Furthermore, the range and scatter of the data have been previously observed (for example, from January to March 2018) when MCU operated as expected. Note the current recommended value of 46,027 mg/L is the difference between 47,800 mg/L (50 mM MaxCalix as referred to in Table 2.2) and the BOBCalixC6 concentration in the SHT (972 mg/L in the June sample). Also note that a positive bias was detected in the FT-HNMR relative to the HPLC method that is minimized by using the average of the two methods. The recent upward trend in the MaxCalix concentration seen in Figure 5 is within the analytical uncertainty range for this measurement despite the addition of MaxCalix to the solvent on March 2019. The residuals between the measured Modifier values and its recommended value correlates (correlation coefficient of 0.77) with the residuals from the MaxCalix measurements with its recommended value (see Figure 6). This indicates that both the Modifier and the MaxCalix are miscible and have similar physical-chemical behaviors.

The residual concentration of BOBCalixC6 concentration is (based on the June sample) at 27% of the concentration measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). The upward trend of the BOBCalixC6 concentrations in the last three SHT samples is possibly due to Isopar^{TM} L evaporation from the solvent. The BOBCalixC6 concentration range in the last three SHT samples has been previously observed (for example, before November 2018). Since no BOBCalixC6 is added to the SHT, the variability in the BOBCalixC6 concentration data with time is more reflective of the analytical uncertainty (the standard deviation of the BOBCalixC6 concentration since January 2018 is 9.3% which is similar to the 10% method of uncertainty reported by HPLC). Since January 2018, the BOBCalixC6 concentration range can be estimated as 1.00 ± 0.05E3 mg/L. Given that no BOBCalixC6 is added to the solvent, the concentration is expected to decrease with time.

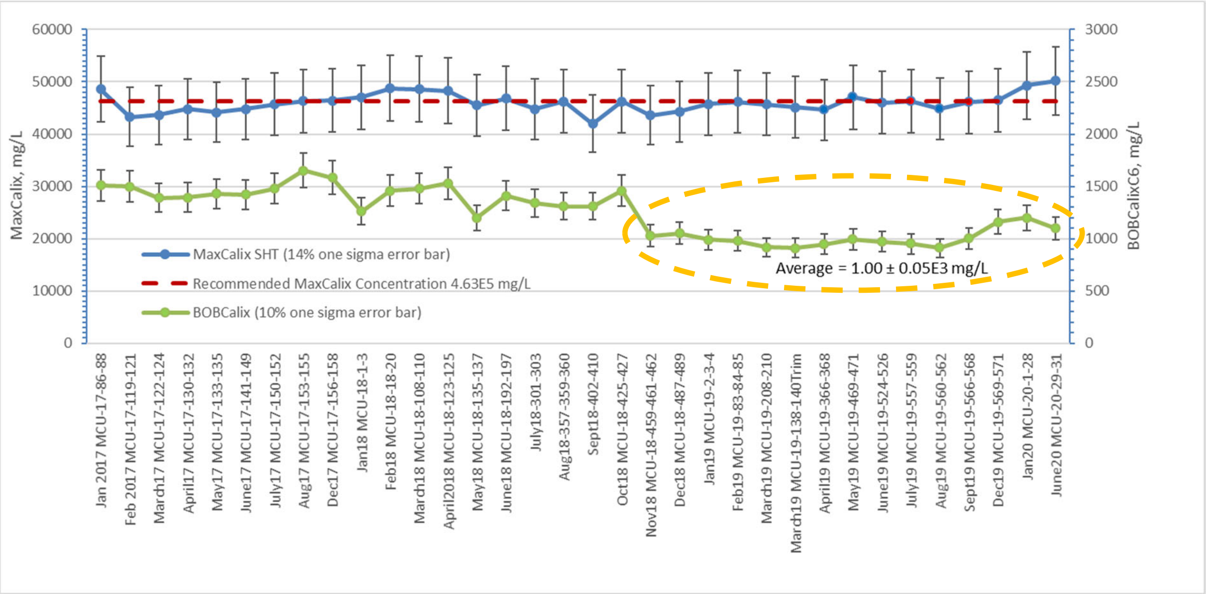


Figure 5. Average MaxCalix concentration from the average of the HPLC and FT-HNMR of recent samples since NGS implementation (46,000 mg/L is the nominal concentration).

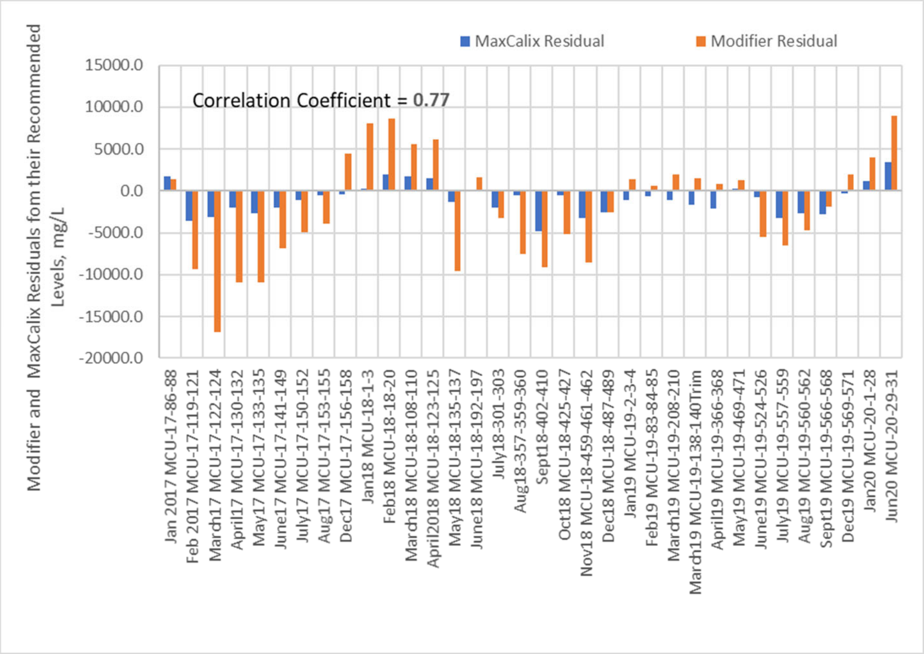


Figure 6. MaxCalix and Modifier residuals from their recommended levels

Gamma Measurements

The gamma measurements for the December 2019, January 2020, and June 2020 samples are shown in Figure 7 in relation to past measurements. The values in the December 2019, January 2020, and June 2020 samples are consistent with previous levels observed when MCU was not operating (for example from February to August 2017). The slight gradual rise in the gamma counts in the last three SHT samples is probably due to Isopar™L evaporation. The low variability in the gamma measurements from June 2019 to June 2020 is consistent with MCU being idle.

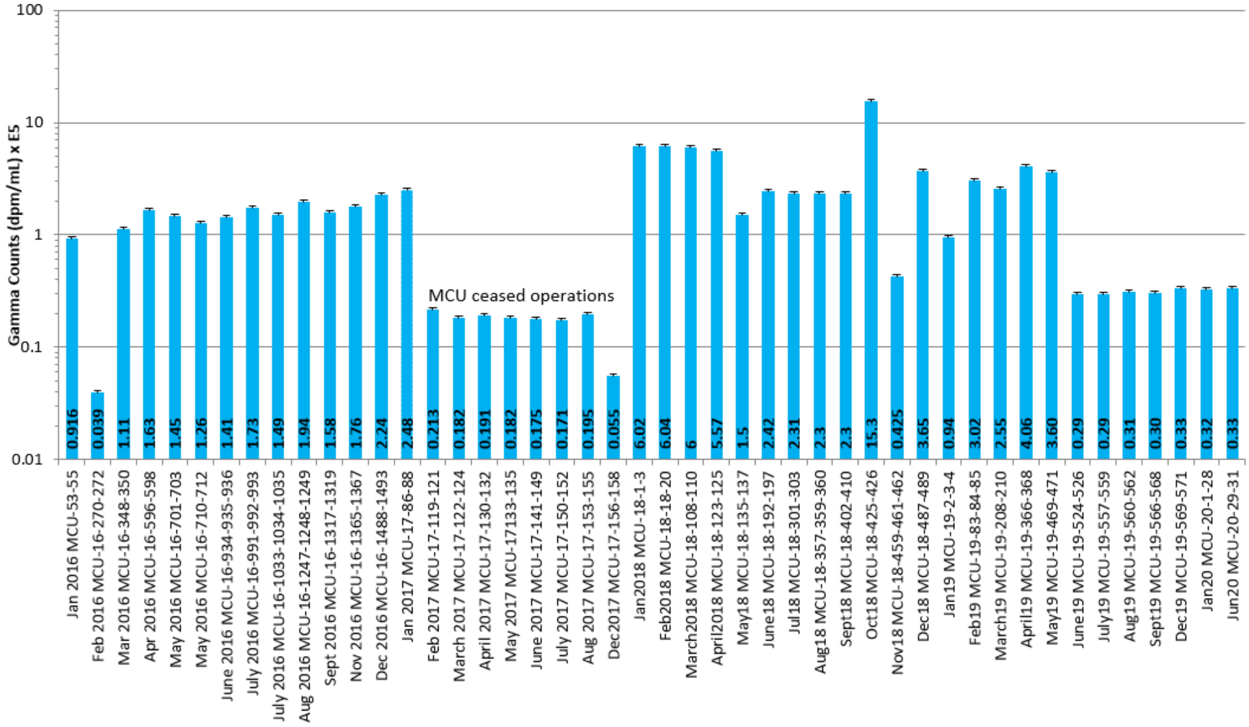


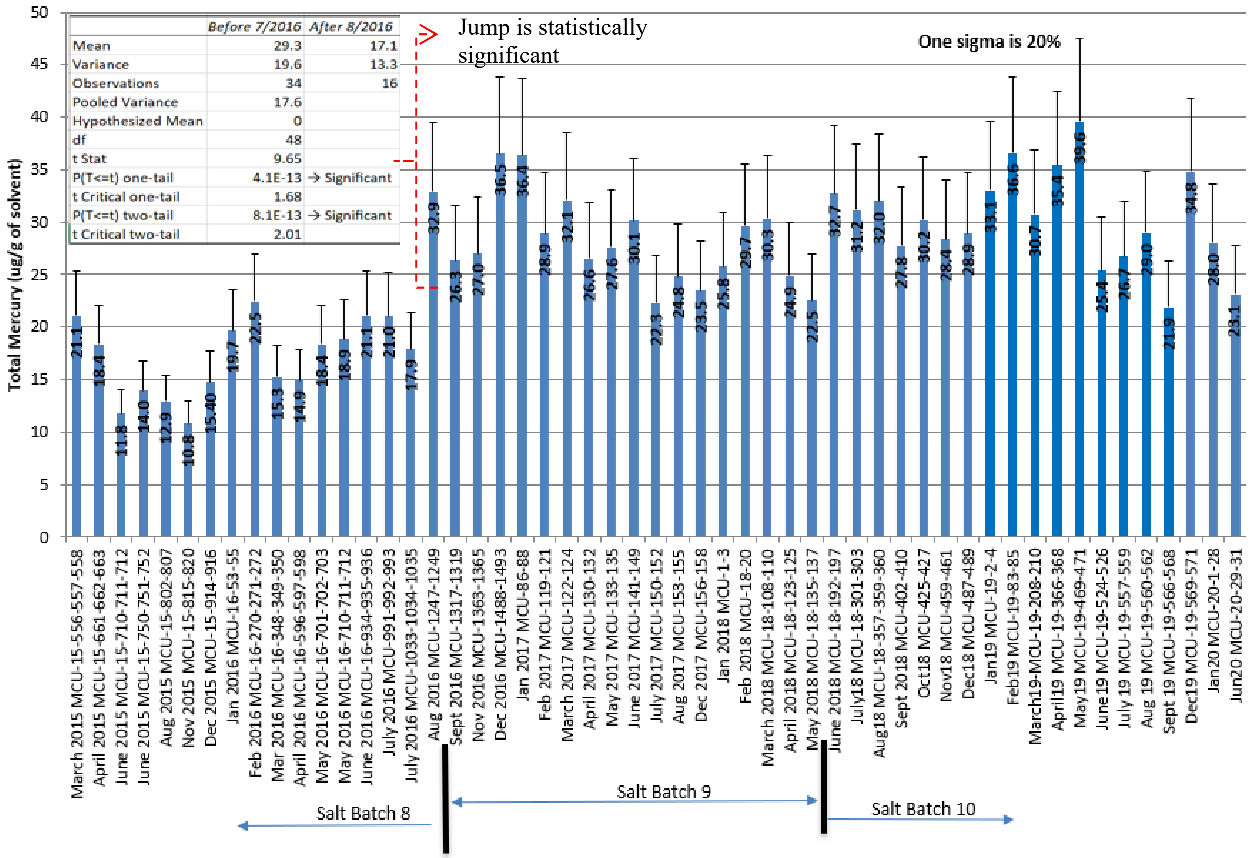
Figure 7. The gamma count of selected SHT samples.

Impurities

No organic impurities were observed in the December 2019, January 2020, and June 2020 SHT samples from the SVOA and the FT-HNMR analysis.

However, another impurity being tracked in the SHT solvent is the concentration of mercury. A few mL of each sample was digested and analyzed for total mercury by the DMA method. The average mercury concentrations in the December 2019, January 2020, and June 2020 SHT samples were 35 ± 7 ug/g, 28 ± 6 ug/g, and 23 ± 5 ug/g, respectively (see Figure 8). The downward trend (opposite to the upward trend observed with the SHT component mentioned earlier) in the last three mercury measurements, if it is real, is possibly due to MCU being idle (the solvent does not contact a source of mercury like supernate) and that the remaining mercury species in the solvent is either volatizing or sorbing on surfaces or precipitating. However, the measurements from the December 2019, January 2020, and June 2020 SHT samples are similar with the measurements obtained in early 2016 and it may indicate a possible solubility limit. Future additional sampling and analysis may reveal if the mercury concentration will level off or continue below detection limits.

The concentration of mercury observed in the December 2019, January 2020, and June 2020 samples is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm),[10] implying that other solubility-enhancing mechanisms are at play (for example extraction by an extractant or sorption on trapped solids: Solids were not observed in these samples) or a more soluble form of mercury is present (organo-mercury like ethyl or dimethyl mercury). Organo-mercury compounds were recently detected in Tank 22H.[11] Based on the June 2020 SHT sample DMA mercury measurements, for 200 gallons of solvent (757.1 L), the solvent could contain up to 15 ± 3 g of mercury.



	Before 7/2016	*After 8/2016*
Mean	29.3	17.1
Variance	19.6	13.3
Observations	34	16
Pooled Variance	17.6	
Hypothesized Mean	0	
df	48	
t Stat	9.65	
P(T<=t) one-tail	4.1E-13	→ Significant
t Critical one-tail	1.68	
P(T<=t) two-tail	8.1E-13	→ Significant
t Critical two-tail	2.01	

Jump is statistically significant

One sigma is 20%

Figure 8. Total mercury in recent SHT samples (one sigma is 20%).

4.0 Conclusions

A trend summary of three Solvent Hold Tank (SHT) monthly samples MCU-19-569-570-571 (December 2019), MCU-20-1-28 (January 2020), and MCU-20-29-30-31 (June 2020) are reported. Most of the conclusions are based on the June 2020 SHT sample (MCU-20-29-30-31). Analyses of the June 2020 SHT sample indicated that the Modifier (Cs-7SB) and the Extractant (MaxCalix) concentrations were above their nominal recommended concentrations (169,000 mg/L and 46,900 mg/L respectively) by 6% and 7% respectively. The Suppressor (*N,N',N"*–tris(3,7-dimethyloctyl)guanidine or TiDG) concentration has remained at 833 ± 16 mg/L, but it is above the minimum recommended concentration (479 mg/L).

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The gamma concentration (~3.33E4 dpm/mL) measured in the June 2020 SHT samples was consistent with previous values observed when MCU was idle (for example, between February 2017 and August 2017).

If additional SHT samples become available, the laboratory will continue to monitor the quality of the solvent for any new impurities or degradation of the solvent components.

5.0 References

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Appendix A: Average Modifier concentration in the SHT samples

Sample	Average (mg/L)	HPLC (mg/L)	FT-HNMR (mg/L)	Density (mg/L)
Jan 2017 MCU-88-89	1.68E+05	1.65E+05	1.70E+05	1.70E+05
Feb 2017 MCU-119-121	1.53E+05	1.55E+05	1.51E+05	1.60E+05
March 2017 MCU-122-124	1.51E+05	1.50E+05	1.51E+05	1.52E+05
April 2017 MCU-130-132	1.59E+05	1.58E+05	1.59E+05	1.58E+05
May 2017 MCU-133-135	1.57E+05	1.56E+05	1.57E+05	1.58E+05
June 2017 MCU-141-149	1.58E+05	1.57E+05	1.59E+05	1.62E+05
July 2017 MCU-150-152	1.57E+05	1.56E+05	1.57E+05	1.64E+05
August 2017 MCU-153-154	1.59E+05	1.58E+05	1.59E+05	1.65E+05
Dec 2017 MCU-156-158	1.66E+05	1.63E+05	1.69E+05	1.73E+05
Jan 2018 MCU-1-2-3	1.73E+05	1.72E+05	1.73E+05	1.77E+05
Feb 2018 MCU-18-20	1.75E+05	1.77E+05	1.72E+05	1.78E+05
March 2018 MCU-108-110	1.75E+05	1.78E+05	1.72E+05	1.75E+05
April 2018 MCU-18-123-125	1.75E+05	1.66E+05	1.68E+05	1.75E+05
May 2018 MCU-18-135-137	1.60E+05	1.59E+05	1.53E+05	1.60E+05
June 2018 MCU-18-192-197	1.71E+05	1.68E+05	1.64E+05	1.71E+05
Jul 2018 MCU-301-303	1.63E+05	1.64E+05	1.61E+05	1.66E+05
Aug 2018 MCU-357-359-360	1.52E+05	1.54E+05	1.49E+05	1.62E+05
Sept 2018 MCU-402-410	1.50E+05	1.50E+05	1.49E+05	1.60E+05
Oct 2018 MCU-425-427	1.51E+05	1.40E+05	1.61E+05	1.62E+05
Nov 2018 MCU-459-461-462	1.55E+05	1.52E+05	1.58E+05	1.60E+05
Dec 2018 MCU-487-489	1.56E+05	1.47E+05	1.64E+05	1.65E+05
Jan 2019 MCU-19-2-3-4	1.59E+05	1.51E+05	1.67E+05	1.69E+05
Feb 2019 MCU-19-83-84-85	1.60E+05	1.50E+05	1.69E+05	1.68E+05
March 2019 MCU-19-208-210	1.54E+05	1.48E+05	1.59E+05	1.70E+05
March 2019 MCU-19-138-140Trim	1.52E+05	1.48E+05	1.55E+05	1.70E+05
April 2019 MCU-19-366-368	1.66E+05	1.47E+05	1.57E+05	1.69E+05
May 2019 MCU-19-469-472	1.68E+05	1.55E+05	1.59E+05	1.70E+05
June 2019 MCU-19-524-526	1.62E+05	1.55E+05	1.61E+05	1.63E+05
July 2019 MCU-19-557-559	1.63E+05	1.47E+05	1.57E+05	1.66E+05
Aug 2019 MCU-19-560-562	1.65E+05	1.52E+05	1.63E+05	1.67E+05
Sept 2019 MCU-19-566-568	1.67E+05	1.57E+05	1.61E+05	1.69E+05
Dec 2019 MCU-19-569-571	1.71E+05	1.65E+05	1.69E+05	1.72E+05
Jan 2020 MCU-20-1-28	1.73E+05	1.67E+05	1.71E+05	1.74E+05
Jun 2020 MCU-20-29-31	1.78E+05	1.76E+05	1.71E+05	1.79E+05

Viscosity and surface tension of the SHT samples

SHT sample (Rheology)	Viscosity (cP)	Surface Tension (Dyne/cm)	Control Viscosity (cP)	Control Surface Tension (dyne/cm)
Dec 2017 MCU-17-156-158	3.4	23.5	3.1	22.4
Jan 2018 MCU-18-1-3	3.3	23.5	3.08	22.9
Feb 2018 MCU-18-18-20	3.3	23.4	3.08	23.44
March 2018 MCU-18-108-110	3.3	23	3.28	22.6
April 2018 MCU-18-123-125	3.5	24	3.47	22.9
May 2018 MCU-18-135-137	3.4	23.6	3.6	23.7
June 2018 MCU-18-192-197	3.6	23.8	3.6	23.6
July 2018 MCU-18-301-303	3.2	24.4	4	24
Aug 2018 MCU-18-357-359-360	3.1	23.8	3.16	24
Sept 2018 MCU-18-402-410	3.1	23.3	3.11	23.2
Oct 2018 MCU-18-425-427	3.1	23.5	3.15	23
Nov 2018 MCU-18-459-461-462	2.8	22.4	3.12	22.5
Dec 2018 MCU-18-487-489	3.2	23.6	3.17	23.8
Jan 2019 MCU-19-2-3-4	3.3	22.3	3.17	23.7
Feb 2019 MCU-19-83-84-85	3.4	23.4	3.2	23.2
March 2019 MCU-19-208-210	3.2	23.3	3.18	22.9
March 2019 MCU-19-138-140Trim	3.3	23.2	3.21	23.4
April 2019 MCU-19-366-368	3.2	23.9	3.17	23.3
May 2019 MCU-19-469-471	3.4	23.4	3.19	22.9
June 2019 MCU-19-524-526	3.3	23.3	3.21	23.4
July 2019 MCU-19-557-559	3.3	23.4	3.19	23.4
Aug 2019 MCU-19-560-562	3.3	22.9	3.19	23.4
Sept 2019 MCU-19-566-568	3.4	22.9	3.2	22.9
Dec 2019 MCU-19-569-571	3.4	22.4	3.18	22.4
Jan 2020 MCU-20-1-28	3.4	23.5	3.16	23.4
Jun 2020 MCU-20-29-31	3.6	24.1	3.18	22.4

Average MaxCalix concentration in the SHT samples

SHT Sample (MaxCalix)	HPLC (mg/L)	HNMR (mg/L)	Average (mg/L)
Jan 2017 MCU-17-86-88	4.82E+04	49300	48597
Feb 2017 MCU-17-119-121	4.30E+04	43700	43255
March 2017 MCU-17-122-124	4.33E+04	44300	43661
April 2017 MCU-17-130-132	4.41E+04	46000	44769
May 2017 MCU-17-133-135	4.39E+04	44700	44191
June 2017 MCU-17-141-149	4.42E+04	45800	44768
July 2017 MCU-17-150-152	4.58E+04	45600	45725
Aug 2017 MCU-17-153-155	4.65E+04	46000	46312
Dec 2017 MCU-17-156-158	4.61E+04	46900	46391
Jan 2018 MCU-18-1-3	4.64E+04	48300	47071
Feb 2018 MCU-18-18-20	4.83E+04	49600	48767
March 2018 MCU-18-108-110	4.89E+04	48100	48596
April 2018 MCU-18-123-125	4.84E+04	48100	48288
May 2018 MCU-18-135-137	4.63E+04	44200	45473
June 2018 MCU-18-192-197	4.67E+04	47100	46847
July 2018 MCU-301-303	4.50E+04	44400	44773
Aug 2018 MCU-357-359-360	45200	48400	46289
Sept 2018 MCU-402-410	4.28E+04	40700	41969
Oct 2018 MCU-18-425-427	4.52E+04	48400	46289
Nov 2018 MCU-18-459-461-462	4.18E+04	47600	43617
Dec 2018 MCU-18-487-489	4.24E+04	48500	44300
Jan 2019 MCU-19-2-3-4	44800	47600	45763
Feb 2019 MCU-19-83-84-85	44900	48800	46202
March 2019 MCU-19-208-210	4.42E+04	48800	45703
March 2019 MCU-19-138-140Trim	4.34E+04	48800	45122
April 2019 MCU-19-366-368	4.22E+04	50700	44671
May 2019 MCU-19-469-471	4.45E+04	53300	47070
June 2019 MCU-19-524-526	4.32E+04	53300	46027
July 2019 MCU-19-557-559	4.36E+04	53300	46351
Aug 2019 MCU-19-560-562	4.41E+04	46200	44836
Sept 2019 MCU-19-566-568	4.40E+04	50700	46065
Dec 2019 MCU-19-569-571	4.53E+04	48800	46482
Jan 2020 MCU-20-1-28	4.61E+04	57700	49280
Jun 2020 MCU-20-29-31	4.84E+04	53900	50177

Mercury concentration measured by the DMA and XRF Methods

SHT Sample (mercury)	DMA (ug/g)	XRF (ug/g)
April 2018 MCU-18-123-125	24.40	25.44
May 2018 MCU-18-135-137	19.90	25.11
June 2018 MCU-18-192-197	33.20	32.15
July 2018 MCU-18-301-303	28.60	33.75
Aug 2018 MCU-18-357-359-360	26.20	37.79
Sept 2018 MCU-402-410	26.70	28.82
Oct 2018 MCU-425-427	28.00	32.4
Nov 2018 MCU-459-461	25.90	30.8
Dec 2018 MCU-487-489	25.80	32.0
Jan 2019 MCU-19-2-4	25.10	41.0
Feb 2019 MCU-19-83-85	38.50	34.61
March 2019-MCU-19-208-210	29.00	32.43
April 2019 MCU-19-366-368	33.70	37.16
May 2019 MCU-19-469-471	37.40	41.8
June 2019 MCU-19-524-526	25.40	NM
July 2019 MCU-19-557-559	26.70	NM
Aug 2019 MCU-19-560-562	29.00	NM
Sept 2019 MCU-19-566-568	21.90	NM
Dec 2019 MCU-19-569-571	34.80	NM
Jan 2020 MCU-20-1-28	28.00	NM
Jun 2020 MCU-20-29-31	23.10	NM

NM = Not Measured

Appendix B: Minimum recommended level for TiDG in NGS-CSSX solvent

Re: Dr. Moyer, if you have the time , we have a question for you .
Moyer, Bruce A. to: fernando.fondeur@srnl.doe.gov 06/24/2014 12:36 AM

Hi Fernando,
Our laboratory tests with simulants indicate that the solvent strips adequately even if the TiDG concentration falls to 10% of its nominal value of 3 mM. My recommendation is to trim when the TiDG gets to 1 mM. That should give some margin.
That said, our study of TiDG decomposition rate is making me rethink the nominal value of 3 mM TiDG. The rate data show that the decomposition slows down as the TiDG concentration decreases. The decomposition is rather fast at 3 mM. Since you want to minimize organics going to salt stone and DWPF, it might be advisable to trim only up to 2 mM and operate in the range 1-2 mM TiDG. With more experience in operating NGS in the MCU, that range might eventually be reduced even further.
Thanks for sharing your analytical data. It would be good to see the X-axis as time, though, but I suspect you are showing data back to December. That means the TiDG has not decomposed as fast as I would have thought based on our recent study. Perhaps the cold weather has been helpful in that regard. The TiDG concentration will bear careful watching in the warm summer months, as decomposition definitely speeds up with increasing temperature.
Bruce
From: "fernando.fondeur@srnl.doe.gov<mailto:fernando.fondeur@srnl.doe.gov>" <fernando.fondeur@srnl.doe.gov<mailto:fernando.fondeur@srnl.doe.gov>>
Date: Monday, June 23, 2014 3:49 PM
To: Bruce Moyer <moyerba@ornl.gov<mailto:moyerba@ornl.gov>>
Subject: Dr. Moyer, if you have the time, we have a question for you.
Dr. Moyer:
Please pardon my numerous e-mails on this topic. Thank you for your last reply on the effect of high [K] and low temperature on third phase formation. But we need your advice. The TiDG concentration, since the implementation of NGS-CSSX blend, is around 750 mg/L (as you may see below) which is well below the nominal concentration of 1,550 mg/L. If this condition continues (that is without trimming more TiDG), is the solvent susceptible to soaps affecting the stripping? From your extensive experience on this, do you happen to know what is the lowest level of TiDG the solvent can have without any deleterious effect on mass transfer and/or hydrodynamics in the stripping stages? Thanks.

Sincerely,
Fernando Fondeur
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