Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Solvent Hold Tank Sample Results for MCU-16-596-597-598: April 2016 Monthly Sample

F. F. Fondeur

D. H. Jones

July 2016

SRNL-STI-2016-00297, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2016-00297
Revision 0

Keywords: *MCU, ARP, ISDP NGS*

Retention: *Permanent*

Solvent Hold Tank Sample Results for MCU-16-596-597-598: April 2016 Monthly Sample

F. F. Fondeur
D. H. Jones

July 2016

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

F. F. Fondeur, Advanced Characterization and Processing Date

D. H. Jones, Research Support Date

TECHNICAL REVIEW:

T. B. Peters, Advanced Characterization and Processing Date
Reviewed per Manual E7 Procedure 2.60

J. E. Laurinat, Environmental Modeling Date

APPROVAL:

B. J. Wiedenman, Manager Date
Advanced Characterization and Processing

D. E. Dooley, Director Date
E&CPT Research Programs

E. A. Brass, Manager Date
MCU & Salt/Sludge Processing

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) received one set of Solvent Hold Tank (SHT) samples (MCU-16-596-597-598), pulled on 04/30/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-596-597-598 indicated the Isopar™L concentration is above its nominal level (102%). The modifier (CS-7SB) is 14% below is nominal concentration while the TiDG and MaxCalix concentrations are at and above their nominal concentrations, respectively. This analysis confirms the solvent may require the addition of modifier. Based on the current monthly sample, the levels of TiDG, Isopar™L, MaxCalix, and modifier are sufficient for continuing operation but are expected to decrease with time. Periodic characterization and trimming additions to the solvent are recommended.

Two equations predicting TiDG degradation or loss are presented in an effort to predict or estimate dates for a TiDG trim addition. Dates and times are dependent upon many factors including actual gallons processed at MCU. The TiDG concentration is expected to drop and reach the minimum recommended level sometime in mid-September 2016. Predictive models can potentially be improved with the incorporation of additional processing history as it becomes available.

No impurities above the 1000 ppm level were found in this solvent by the SVOA. No impurities were observed in the (Hydrogen Nuclear Magnetic Resonance) HNMR. However, up to 15.8 ± 3.2 micrograms of mercury per gram of solvent (or 13 µg/mL) was detected in this sample (as determined by the CV-AA method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in salt batch 8 (Tank 49H).

The current gamma level (1.63E5 dpm/mL) confirmed that the gamma concentration has returned to the previous level where the process operated normally and as expected.

Evidence of bacteria deposition at Modular Caustic-Side Solvent Extraction Unit (MCU) may have been found in sample MCU-16-597. Pending future samples findings, filtration of the Strip feed aqueous solution and superwashing the solvent (pH > 12) may be required. A possible chemical cleaning of the centrifugal contactors 606 and 607 might be required.

The laboratory will continue to monitor the quality of the solvent in particular for any new impurities or degradation of the solvent components.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
CVAA	Cold Vapor Atomic Absorption Spectrometry
DSS	Decontaminated Salt Solution
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
FTIR	Fourier transform infra-red spectroscopy
HNMR	Hydrogen Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
ISDP	Integrated Salt Disposition Project
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
RSD	Relative Standard Deviation or the absolute value of the Coefficient of Variation
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TiDG	*N*,*N'*,*N"*–tris(3,7-dimethyloctyl)guanidine
TOA	Trioctylamine
XRF	X-Ray Fluorescence

1.0 Introduction

In late FY13, the MCU switched to the Next Generation Solvent (NGS) flow sheet. Facility personnel implemented the switch by adding a non-radioactive, NGS "cocktail" containing the new extractant (MaxCalix) and a new suppressor (TiDG) to the SHT heel. The resulting "blend" solvent ("NGS Blend solvent") is essentially NGS with residual amounts of BOBCalixC6 and trioctylamine (TOA). SHT samples are sent to SRNL to examine solvent composition changes over time.[1] On April 30, 2016, Operations personnel pulled and delivered three samples from the SHT (MCU-16-596, MCU-16-597, and MCU-16-598) for analysis. 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 at the same time to generate a solution of the appropriate composition that approximates the blend of cocktail[2] and heel solvent) was prepared in the lab (September 2015) and used for comparison and evaluation. The results from the analyses are presented in this document.

2.0 Experimental Procedure

2.1 Experimental Procedure

A summary of relevant and recent trims to the MCU solvent as well as the arrival date of the samples currently being studied are shown in Table 2-1. On April 29, 2016, a trim addition was made to MCU that was 3.6 kg of modifier, 4.5 kg of MaxCalix and 1 kg grams of TiDG in 65 kg of Isopar™L.

Table 2-1 Log of recent trims to the MCU solvent and sample pull-out dates

Event	Date
February solvent trim added to MCU	February 22, 2015
SHT sample MCU-15-389-390	February 25, 2015
SHT sample MCU-15-439-440-441	February 28, 2015
10 gallons of Isopar™L added to MCU	March 6, 2015
9 gallons of Isopar™L added to MCU	March 13, 2015
SHT sample MCU-15-556-557-558	March 16, 2015
SHT sample MCU-15-661-662-663	April 2, 2015
10 gallons of Isopar™L added to MCU	May 6, 2015
SHT sample MCU-15-710-711-712	June 15, 2015
SHT sample MCU-15-750-751-752	June 22, 2015
SHT sample MCU-15-802-803-804-805-806-807	August 31, 2015
November solvent trim added to MCU	November 28, 2015
SHT sample MCU-15-815-816-817-818-819-820	November 29, 2015
14 gallons of Isopar™L added to MCU	December 21, 2015
SHT sample MCU-15-914-915-916	December 22, 2015
SHT sample MCU-16-53-54-55	January 25, 2016
SHT sample MCU-16-270-271-272	February 21, 2016
12 gallons of Isopar™L added to MCU	March 6, 2016
SHT sample MCU-16-348-349-350	March 30, 2016
10 gallons of Isopar™L added to MCU	March 31, 2016
April Solvent Trim added to MCU*	April 29, 2016
SHT sample MCU-16-596-597-598	April 30, 2016

*Solvent trim: 143.4 lbs Isopar™L, 7.9 lbs modifier, 2.0 lbs TiDG, and 9.9 lbs of MaxCalix.

Samples shown in Table 2-1 were received in p-nut vials containing ~10 mL each (see Fig 1). Once taken into a radioactive hood, the samples were visually inspected and analyzed for pH. MCU-16-596, MCU-16-597, and MCU-16-598 were composited before use. Aliquots of the composited sample were removed to perform the following analysis: Density, semi-volatile organic analysis (SVOA), high performance liquid chromatography (HPLC), titration, gamma counting, cold vapor atomic adsorption spectrometry (CVAA), X-ray fluorescence (XRF), and Fourier-Transformed Hydrogen Nuclear Magnetic Resonance (FT-HNMR). Results from analytical measurements were compared with the theoretical values shown in Table 2-2.

Table 2-2 Nominal concentrations of the relevant components in NGS Blend at 25 °C[2]

Component	mg/L	Molar
MaxCalix	~ 44,400	~ 0.0465
BOBCalixC6*	< 4,030	< 0.0035
TOA*	< 530	< 0.0015
Modifier	~ 169,000	~ 0.50
TiDG	~1440	~ 0.003
Isopar™L	~ 623,000	~ 74 wt%

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

2.2 Quality Assurance

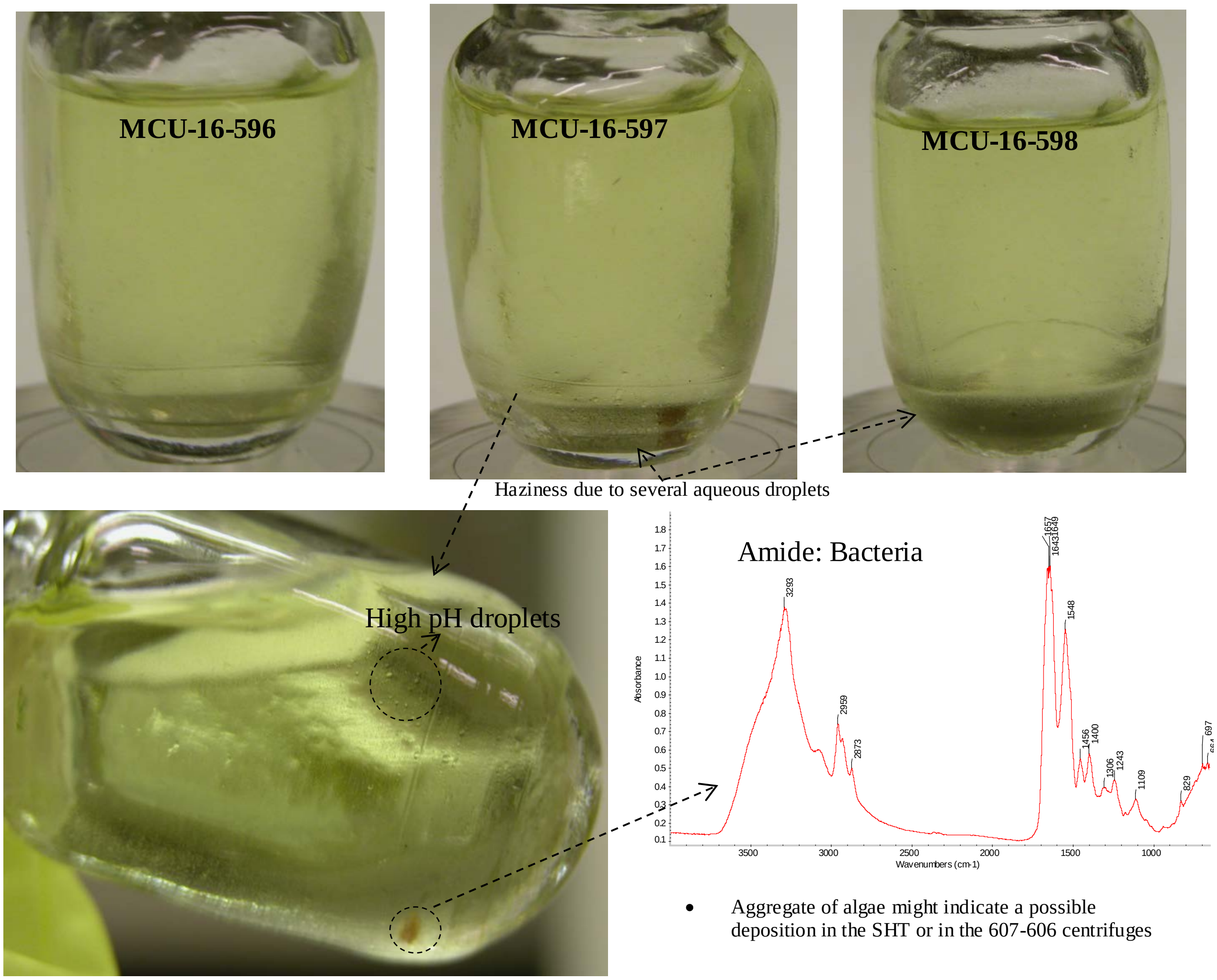
Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

Each sample (MCU-16-596, MCU-16-597, and MCU-16-598) was visually examined. A visible haziness was observed in all three samples. The haziness was determined to be associated with a significant concentration of micron-sized aqueous droplets based on the pH of the droplets (pH > 12) versus the bulk sample. The bulk sample had a pH value of 5.5. The pH of the droplets is more consistent with the pH of salt solution. Most droplets were attached to the p-nut vials interior surfaces. A 1 mm x 2 mm orange-colored particle was observed in MCU-16-597. The particle was removed from the sample, analyzed, and turned out to be an aggregate of bacteria (or algae). The particle may be an indication of bacteria deposition along the coalescers (FLT-304 and ACC-309) and the centrifuges (701, 702 and 601-607). The bacteria may have originated at the strip feed tank (TK-202) or past the strip aqueous heater (HTR-608). It is believed that most algae (bacteria) proliferate during the Spring and Fall season of the year. Especially, proliferation may be optimal while MCU was down and under stagnant conditions. It is unlikely the bacteria may have come from the salt solution receipt tanks (TK-101 or TK-102). All samples had a pH value of 5.5. No unusual reactions, solids, foaming, or immiscible layers were observed after combining the samples into one (MCU-16-596-597-598). Table 3-1 contains the results for the MCU-16-596-597-598 composite sample.

Isopar™ L and Modifier Levels

A density measurement of the sample gave a result of 0.8283 g/mL (0.09% RSD) (or 0.8241 g/mL at 25 °C when corrected for temperature using the Caustic-Side Solvent Extraction (CSSX) temperature correction formula)[3] for MCU-16-596-597-598 at 20 °C. The calculated density (0.828 g/mL) for MCU-16-596-597-598 is about 1% below the calculated density for the standard sample (0.835 g/mL at 25 °C for the scratch blend made in the laboratory).[2] Using the density as a starting point, we know that the concentration level of the Isopar™L component in the sample should be slightly above its nominal value (within analytical uncertainties) and the modifier concentration should be below its nominal value.



- Aggregate of algae might indicate a possible deposition in the SHT or in the 607-606 centrifuges

Figure 1. Typical appearance of the three MCU-16-596, MCU-16-597, and MCU-16-598

An examination of Table 3-1 shows that the Isopar™ L concentration is above its nominal value (~ 2%) while the modifier concentration is correspondingly lower (14% lower) than its nominal value. Of all the methods listed, density has the lowest uncertainty. Thus, the final reported values are closer to the density measurement. The data confirms the trim addition to MCU on April 29, 2016. Every component, except for the modifier possibly due to its high viscosity is above its nominal value.

All measurements indicate the Isopar™ L level is slightly above its nominal value while the modifier concentration level is below its nominal value (see Fig. 2 for recent modifier concentrations from HPLC measurements). We believe the current FTIR reported value is slightly biased high. Looking at Fig.2, the modifier level precipitously dropped from the March sample possibly due to the dilution effect of the trim addition done in March 2016. The relatively lower modifier concentration explains why the measured density is slightly below the standard sample density. The accuracies of the different measurements were within expectation as reflected in the total mass sum of the “average” results listed in Table 3-1. They added up to 0.828 ± 0.019 g/mL. Their sum is consistent with the measured and temperature corrected (to 25 °C) value of 0.824 g/mL, and also with the measured and corrected to 25 °C mass concentration (density) of the standard (0.835 g/mL). With a lower modifier concentration, the solvent chemical properties are closer to that of Isopar™L; thus, expect normal emulsification/de-emulsification at the centrifuges (as seen in the past), phase separation, rheology, and phase carry-over (but increased evaporation). The current modifier concentration is well above the minimum modifier concentration below which the extractant concentration may drop due to solubility limits.

Table 3-1 Sample Results for MCU-16-596-597-598

Analysis	**Method**	**LW-AD-Proj-160505-3**	**Result (mg/L)[#]**	**Nominal[*] Result (mg/L)**	**% of (Result ÷ Nominal Result)**
Isopar® L	FT-HNMR	NA	6.40E+05	6.23E+05	103
Isopar® L	FT-IR	NA	6.27E+05		101
Isopar® L	Density	NA	6.33E+05		102
Average[$]	All	NA	6.33E+05	6.23E+05	102
Modifier	HPLC	1142	1.40E+05	1.69E+05	83
Modifier	FT-HNMR	NA	1.39E+05		82
Modifier	FT-IR	NA	1.58E+05		93
Modifier	Density	NA	1.45E+05		86
Average[$]	All	NA	1.45E+05	1.69E+05	86
TiDG[♠]	Titration	NA	1.41E+03	1.44E+03	98
Average[$]	All	NA	1.41E+03	1.44E+03	98
trioctylamine	Titration	NA	2.02E+02	5.30E+02	38
Average[$]	All	NA	2.02E+02	5.30E+02	38
MaxCalix	HPLC	1142	4.56E+04	4.44E+04	103
MaxCalix	FT-HNMR	NA	4.73E+04		107
Average[$]	All	NA	4.62E+04	4.44E+04	104
BOBCalixC6	HPLC	1142	2.33E+03	4.03E+03	58
Average[$]	All	NA	2.33E+03	4.03E+03	58
Density (g/mL)	Direct Measurement	NA	0.8241	0.835	99

[#] Analytical uncertainty is 10% for HPLC. Titration method uncertainty is 10% for TiDG and 16% for TOA. Density results from the average of replicate volumetric trials typically have a percentage standard deviation of <3% between each value and the average. NMR analytical uncertainties are 10% for the modifier and 13% for MaxCalix, and 14% for Isopar™ L. FTIR analytical uncertainties are 15% for Isopar® L and 10% for Modifier. N/A = Not Applicable. Density estimations assume the combined weight percent of TiDG, MaxCalix, BOBCalixC6, and TOA to be approximately 6%. All uncertainties are 1 sigma.

[*] Nominal value is the expected value for freshly prepared blended solvent with a target density of 0.8352 g/mL at 25 °C.

[$] Reported value for a MCU component is the weighted average of the values reported by the techniques that measured that component.

[$] $x = \frac{\Sigma_1^i \left(x_i / \delta_i^2 \right)}{\Sigma_1^i \left(1 / \delta_i^2 \right)}$; x_i stands for the concentration obtained at a given method and δ_i is the corresponding uncertainty.

[♠] No TiDG value was estimated by FT-HNMR due to an aged (questionable) standard.

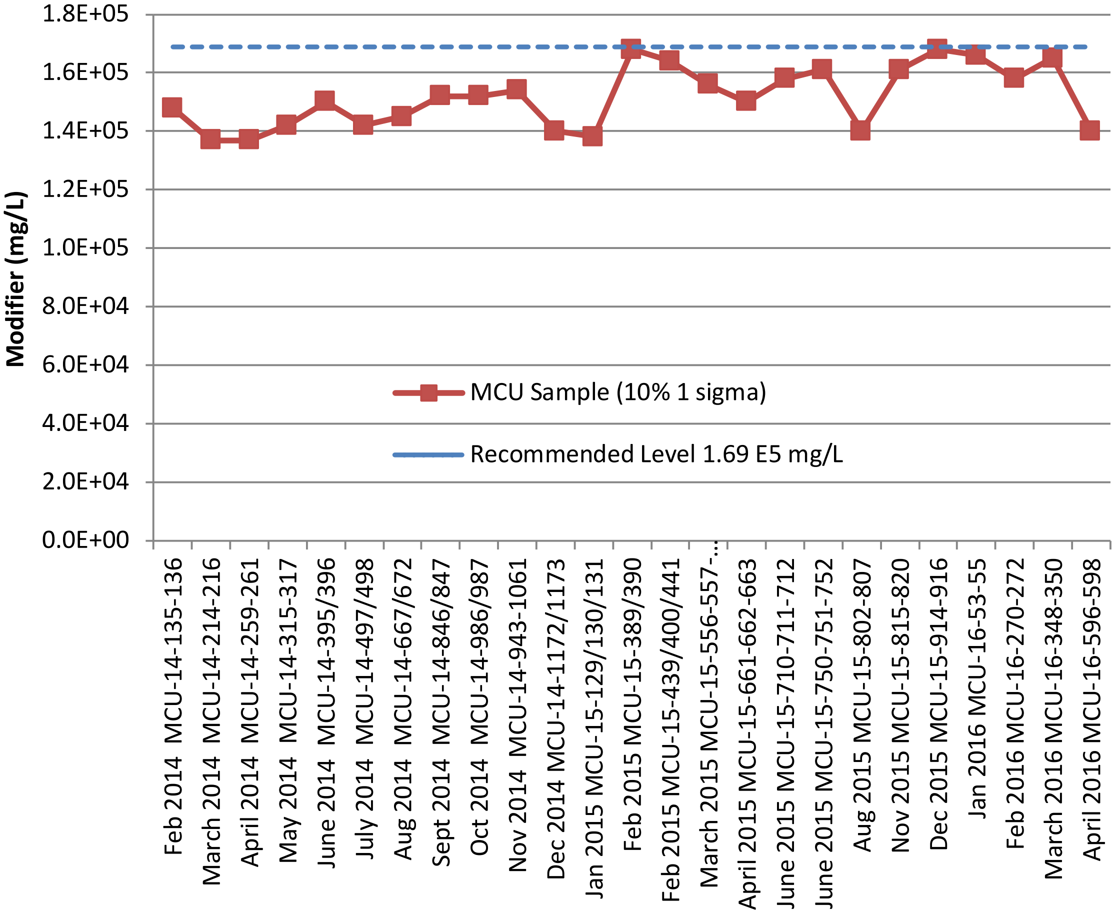


Figure 2. Modifier level in the solvent as measured by HPLC (one sigma is 10%).

Suppressors Levels

The average TiDG concentration level (1.41 ± 0.14 E3 mg/L) is 98 % of its nominal value of 1440 mg/L, confirming the trim addition to the solvent done in March 2016 (a noticeable spike in the TiDG concentration level was observed in Fig. 3). The suppressor concentration is above the minimum recommended operating level (479 mg/L); thus, the solvent does not require a TiDG addition at the time sample MCU-16-596-597-598 was collected.

Inferring from past TiDG concentration level trends (see Fig. 3), in the absence of new additions or new removal mechanisms (and assuming continuous steady operation), the TiDG concentration is expected to drop and reach the minimum recommended level sometime in mid-September 2016.

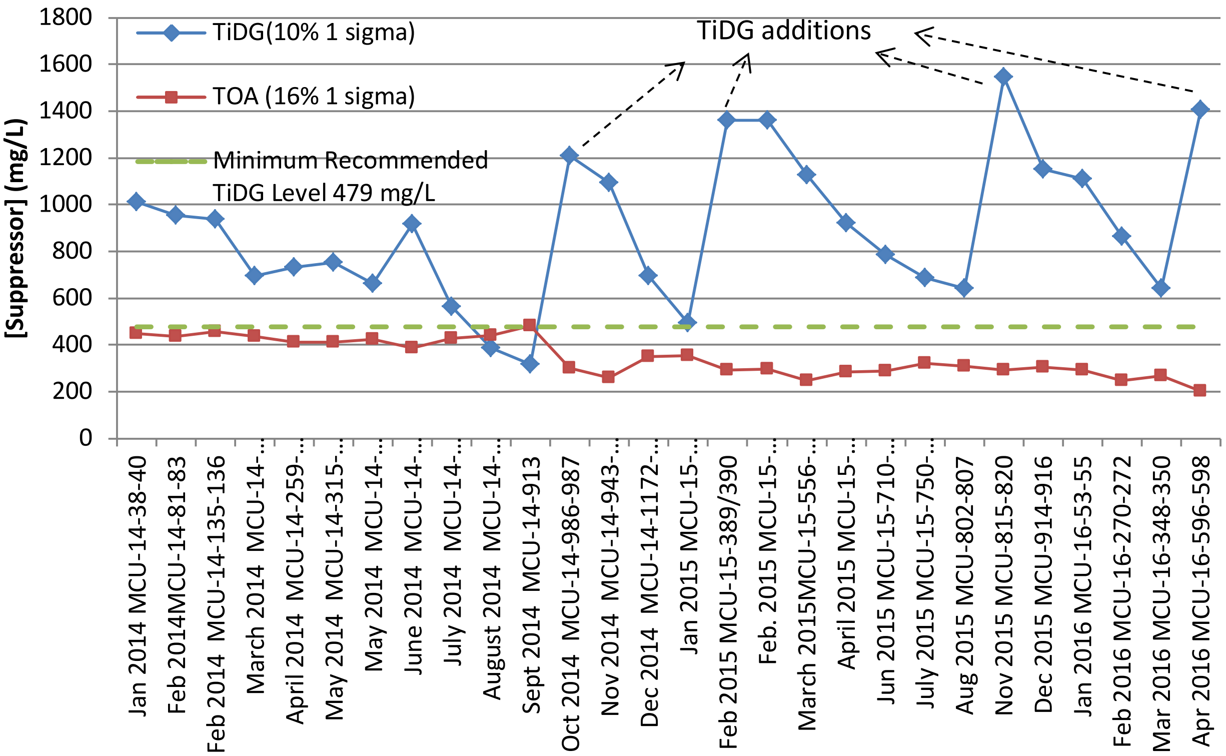


Figure 3. Suppressor concentration as measured by titration in SHT samples since NGS implementation. The minimum recommended level is 479 mg/L for TiDG.

The shape of the TiDG concentration profile is due to a decomposition reaction (assumed to be first order) and phase transfer to aqueous solutions (salt and stripping feed solution). Without loss of generality (a true analysis is more complicated than that shown below), one approximates the organic phase concentration to be governed by diffusion, reaction, and phase transfer as described by Eq. 1.[4]

$$\frac{dC}{dt} + kC + \frac{1}{Volume_{organic}} \times R \times a \times \left(C - C_{equilibrium}\right) - D\frac{\partial^2 C}{\partial x^2} + velocity_{organic}^{superficial} \times \frac{\partial C}{\partial x} = 0 \qquad (1)$$

In Eq. 1, "*k*" stands for the rate constant (days^{-1}), "*R*" stands for interfacial transfer speed (m/day), "*a*" stands for the surface area of the droplets (during emulsion) per volume of emulsion (m^{-1}) which depends on rotor speed[5], "*D*" stand for diffusion (m^2/day), "*t*" is time in days, and "*C*" stand for the concentration of TiDG in the organic droplets (mM). The $C_{equilibrium}$ is assumed to be small due to the relatively large DSS volume. But recent TiDG data examination (Ref. 6) revealed that the amount of TiDG transferred to the DSS stream per unit volume of DSS solution is constant. That is the depletion rate of TiDG due to interfacial transfer can be approximated with the concentration and flow of droplets in the emulsion as shown in Eq. 2.

$$\frac{dC_{Phase\ transfer}^{TiDG}}{dt} = \frac{dC}{dVolume} \times Flow\ Rate\ \ or = \beta \times F \qquad (2)$$

In Eq. 2, "*F*" stands for flow rate (gal/day) and β is a constant. That is the loss of TiDG per volume of DSS that it contacts is constant (this changes with rotor speed). Substituting Eq. 2 for the interfacial mass transfer in Eq. 1, ignoring diffusion effects and solving the equation, the solution is shown in Eq. 3.

$$\frac{dC}{dt} + kC + \beta \times F = 0 => C = C_{initial} \times e^{-kt} + \frac{\beta \times F}{k} \times (\,e^{-kt} - 1) \qquad (3)$$

$$Eq.3\ is\ not\ valid\ for\ times\ greater\ than\ \left(1/_k\right) \times \ln\left(\frac{kC_{initial}}{\beta F} + 1\right)$$

The curves in Fig. 3 resulted from intermittent aqueous flow and no flow conditions. We are still trying to obtain data (aqueous flow rate, and SHT volumes) to perform a two-constants fit; one constant captures the characteristics of the emulsion and interfacial speed and the other constant is the decomposition reaction rate. Between February and August 2015, there was virtually no salt solution flow at MCU for 83% of the time (or F =0). In that case only the caustic decomposition reaction is expected, and fitting that data gave a rate constant (k) of 0.004 per day (after normalizing the TiDG concentration to a constant volume). This rate may differ from a rate obtained in the lab where a constant volume of aqueous solution contacts a fixed volume of organic. In that case, the solution is given in Eq. 4.

$$\frac{C(mM)}{C_{initial}} = e^{-\frac{kt(days)}{\left(1+\frac{Volume_{aqueous}}{Volume_{organic}\times D}\right)}} \qquad (4)$$

As can be seen in Eq. 4, the apparent rate constant from the lab contains the volume ratio of the aqueous to organic phase as well as the distribution coefficient (D) of TiDG between the two phases. To obtain both variables “k” and “D” several kinetic experiments with different organic to aqueous ratios must be performed.

An earlier publication[6] determined the lifetime of TiDG in the spent solvent (after contacting caustic solution) by subtracting from it the degradation rate of TiDG in caustic NGS obtained from laboratory experiments and then fitting the residues to the accumulated processed DSS volume (assuming no flow rate effects). That effort yielded Eq. 5.

$$C\ (mM) = C_{initial} \times e^{-\,(9E-4)t} - (5.39E-6) \times DSS\ volume_{processed}(gallons) \qquad (5)$$

Since Eq. 5 was generated using the actual TiDG data from 2014 and 2015, it explains that data well. For example, if the time and the volume of salt solution to be processed are fixed, Eq. 5 predicts the TiDG concentration at the end of that campaign as shown in Figure 4. For example, at 2000 gpm, Eq. 5 predicts 176 days for a 37% reduction in the TiDG concentration. A comparison of Eq 3 and Eq. 5 is shown in Fig. 4. The line for Equation 3 was constructed using the same time constant that was used in Equation 5.

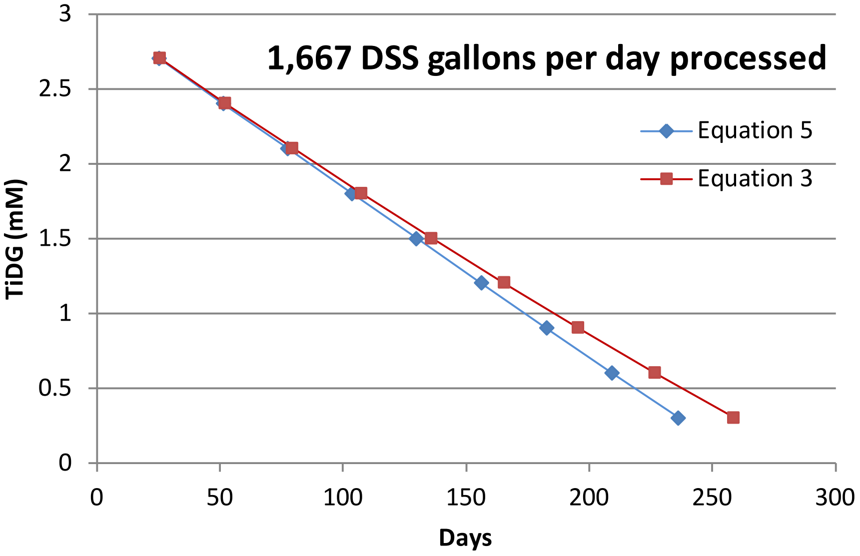


Figure 4. Predicted TiDG decrease with time using Eq. 3 and Eq. 5.

As can be seen from Fig. 4, both equations predict the same TiDG depletion with time. Further future data may improve the prediction capability of Eq. 3 and Eq. 5(perhaps better coefficients). Equation 3 is similar to Eq. 5 except the constant is related to physical parameters associated with the emulsion.

In Eq. 3, if $(kt)^2 \approx 10^{-3}$ or much less than one (for example short times after the NGS contacted the caustic solution (or time is less than $0.04/k$), then $e^{-kt}-1 \approx -kt$ and $F \times t = Volume_{DSS}$, and Eq. 3 becomes Eq. 5 as shown in Eq. 6.

$$C = C_{initial} \times (1 - kt) - \beta \times Volume_{DSS} \qquad (6)$$

The exponential constant in Eq. 5 (9E-4 day^{-1}) was obtained from a laboratory test. This implies a TiDG half-life of 2 years and one month. A comparison with the TiDG data from February to August 2015 where the solvent sat idle for more than 88% of the time, it appears that the TiDG degraded faster than implied in Eq. 8. When fitting the TiDG data from February to August 2015 with an exponential decay, the constant value appears to be 4E-3 day^{-1}. The breadth (the time period for the TiDG concentration to reach pre-addition levels) of the last three TiDG additions to MCU appears to be 4 to 5 months (and that includes intermittent process stoppage). Plugging 4 to 5 months (120 to 150 days) into Eq. 8 and assuming 250k gallons to be processed without interruptions, it predicts the TiDG concentration to decrease by 55%, which is consistent with the data in Fig.

The TOA concentration appears to fluctuate and it is currently 202 ± 32 mg/L (in the previous sample the TOA level was at 269 mg/L). The difference between this and last months measurement is within the analytical error. Since MCU no longer adds TOA, a drop in TOA concentration is expected with time as observed in Fig. 3. However, the rate of TOA concentration decrease appears slower than expected perhaps due to TiDG degradation into primary amines, which have previously been identified as degradation products of the suppressor when heated.[7] The primary amine degradation products would likely have a similar pKa to the TOA (tertiary amine), making the equivalent points coincide.[8]

Extractant Levels

The average calculated MaxCalix level is 4.56E4 mg/L (±10%) and it is slightly above its nominal value. The sudden drop in the MaxCalix concentration in the month of February 2016 is probably due to analytical variance (see Figure 5). However, the current MaxCalix concentration level is consistent with its historical trend (Fig. 5). The residual concentration of BOBCalixC6 level is currently at 58% of the level measured when the NGS was implemented in late FY13 (the concentration variability is due to analytical fluctuations). Since no BOBCalixC6 is added to the SHT, it can not be explained at this time the constancy of the BOBCalixC6 concentration in the solvent.

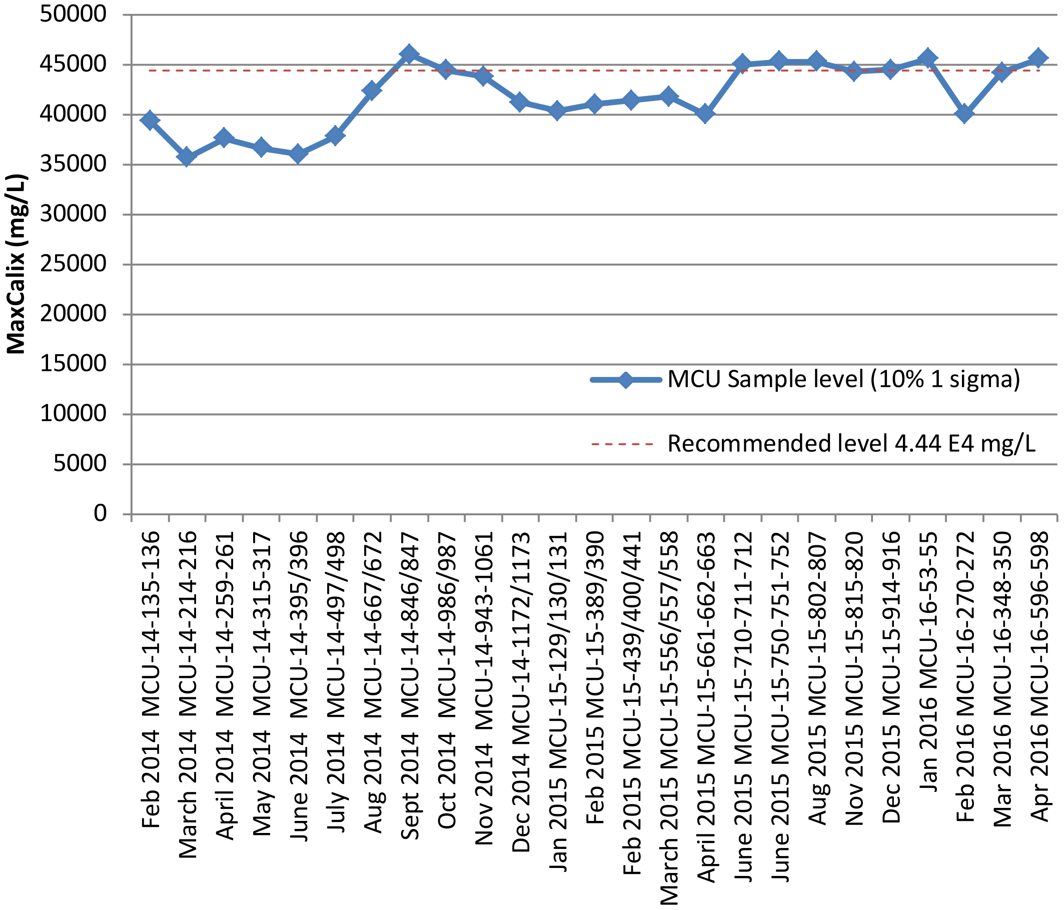


Figure 5. MaxCalix concentration as measured by HPLC and FT-HNMR of recent samples since NGS implementation (44,400 mg/L is the nominal concentration).

Gamma Level

The gamma measurement of MCU-16-596-597-598 is 1.63E5 dpm/mL (±5%). This level of activity is consistent with the previous gamma levels when the process was operating normally in late 2015. It confirms the steady state trend level observed since June 2015 (see Fig. 6).

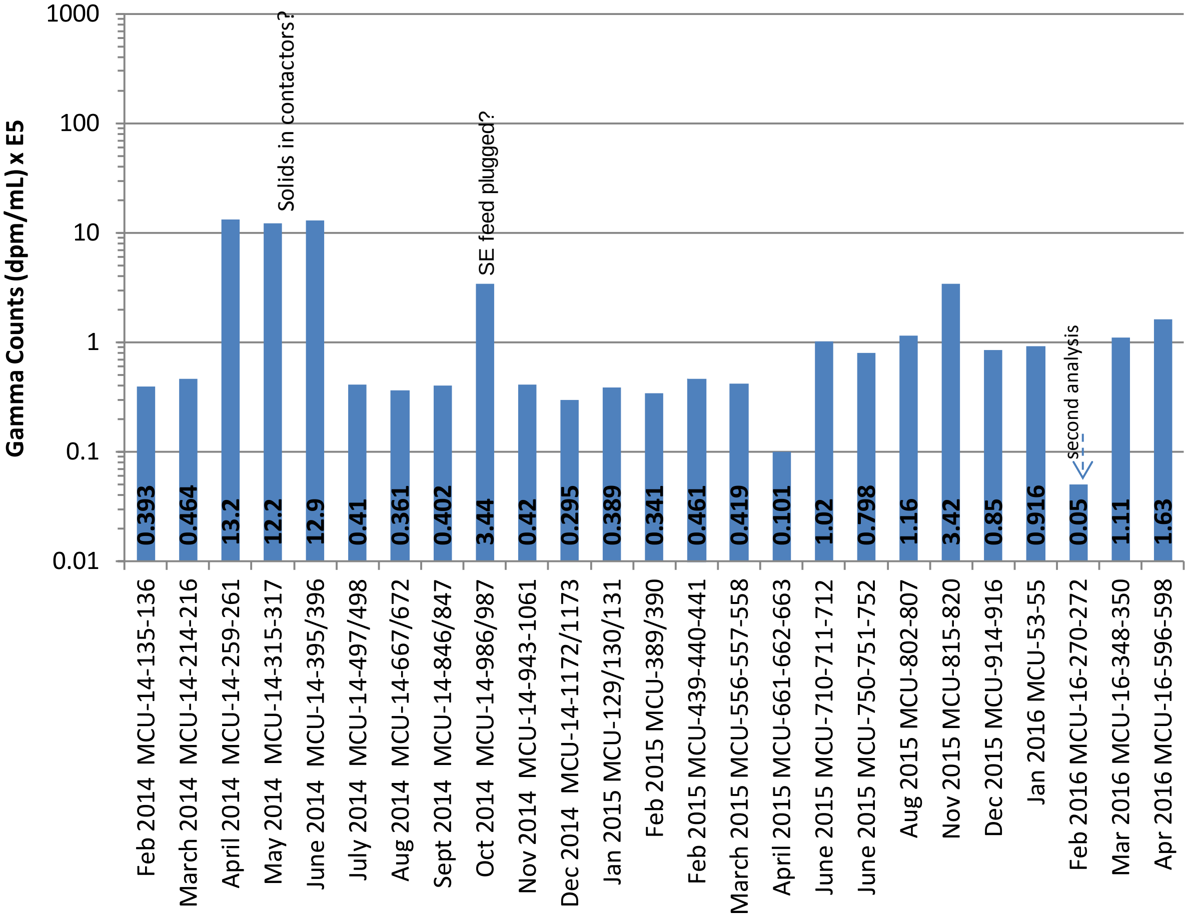


Figure 6. The gamma count of selected SHT samples. One sigma is 5%.

Impurities

No impurities were seen at the 1000 ppm level or higher as indicated by the SVOA method (± 20% uncertainty or 1 sigma). No impurities were observed in the HNMR spectrum.

A few mL of MCU-16-596-597-598 was digested and analyzed for total mercury by the CV-AA method. The concentration of measured mercury by the CV-AA method was 15.8 ± 3.2 ug/g$_{solvent}$ (or 13 ug/mL$_{solvent}$). The XRF method detected 14± 2.8 ug/g$_{solvent}$ mercury (or 11.5 ug/mL$_{solvent}$ at 25°C) of the undigested MCU-16-596-597-598 sample. Both results are similar.

This level of mercury is significantly higher than the solubility of metallic Hg in dodecane (~3 ppm)[9] implying that other solubility-enhancing mechanisms are at play (for example extraction by an extractant or sorption on trapped solids) 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.[10] For 200 gallons of solvent (757.1 L) and assuming a density of 0.8241 g/mL, the solvent could contain a total of 9 ± 2 g of mercury. A comparison of this measurement with previous month confirms a positive trend in the mercury concentration in the solvent (data is shown in Fig. 7). The positive trend in Fig. 7 might be due to a higher mercury concentration in salt batch 8 (Tank 49H).

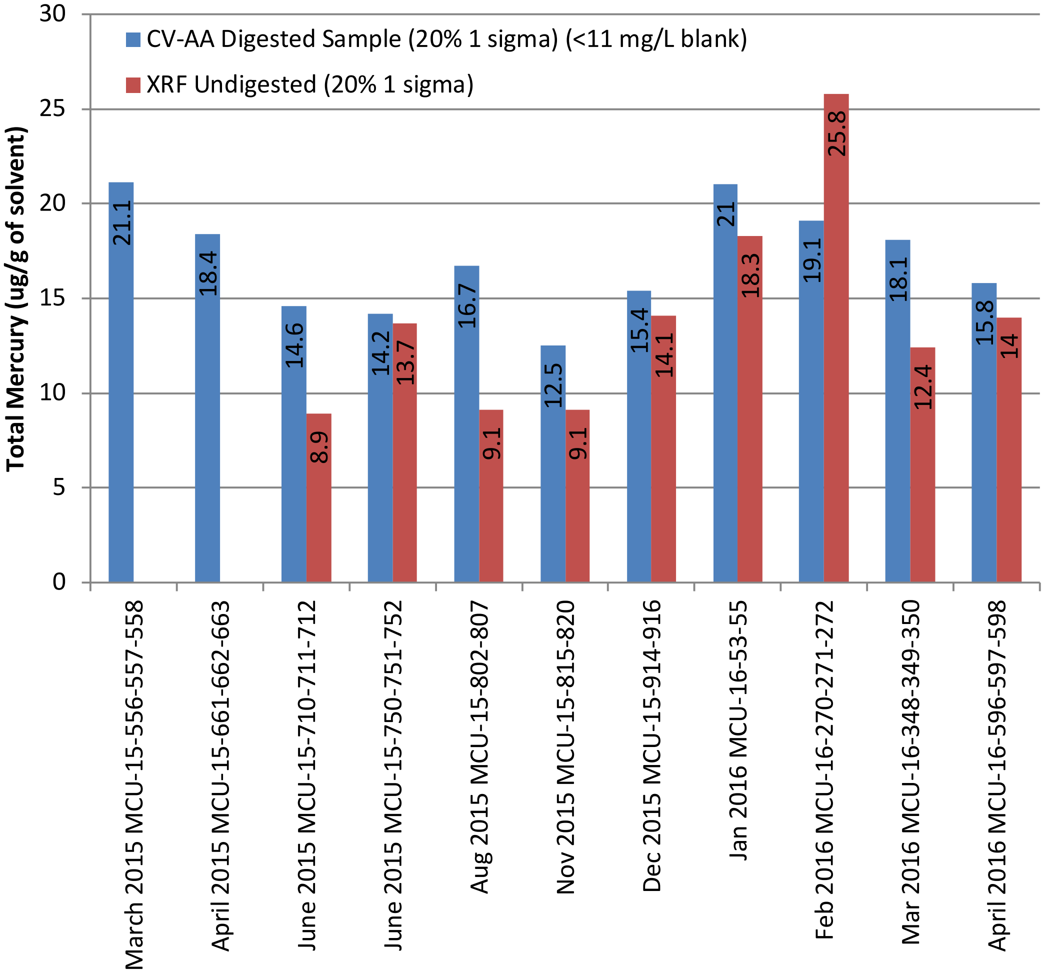


Figure 7. Total mercury in recent SHT samples. One standard deviation is 20%. CVAA = Cold Vapor Atomic Absorption Spectrometry. XRF =X-ray Fluorescence (20% one sigma).

Recommendations

The current analysis indicates the solvent has a lower modifier (86% of its nominal concentration) relative to the standard. The lower MaxCalix concentration observed in the February 2016 sample was due to analytical measurement fluctuations. The TiDG, MaxCalix and Isopar™L levels are expected to trend downward with time. In order to remain two-sigma above the minimum recommended level, it is recommended the addition of modifier in the next solvent trim assuming that complete mixing of the existing modifier inventory in the solvent has occurred. It is also recommended that filtration of the SE aqueous solution and superwashing of the solvent should be conducted to minimize the concentration of algae (or bacteria) in the MCU system. It is recommended the continuing periodic surveillance of the solvent to verify concentration and cleanliness.

The temperature dependence of the current gravimetric density equation for solvent composition (originally obtained from CSSX solvent) needs reverification with the current NGS-CSSX solvent to improve the formula accuracy in extracting the components concentration in the solvent.

4.0 Conclusions

SRNL received one set of SHT samples (MCU-16-596-597-598), pulled on 04/30/2016 for analysis. The samples were combined and analyzed for composition. Analysis of the composite sample MCU-16-596-597-598 indicated the Isopar™L concentration is above its nominal level (102%). The modifier (CS-7SB) is 14% below is nominal concentration while the TiDG and MaxCalix concentrations at and above their nominal concentrations respectively. This analysis confirms the solvent may require the addition of modifier. Based on the current monthly sample, the levels of TiDG, Isopar™L, MaxCalix, and modifier are sufficient for continuing operation but are expected to decrease with time. Periodic characterization and trimming additions to the solvent are recommended.

Two equations predicting TiDG degradation or loss are presented in an effort to predict or estimate dates for a TiDG trim addition. Dates and times are dependent upon many factors including actual gallons processed at MCU. The TiDG concentration is expected to drop and reach the minimum recommended level sometime in mid-September 2016. Predictive models can potentially be improved with the incorporation of additional processing history as it becomes available.

No impurities above the 1000 ppm level were found in this solvent by the SVOA. No impurities were observed in the HNMR. A 3 mm x 1 mm particle consisting of bacteria was found in MCU-16-597. It may indicate the presence of bacteria in the SHT that may have originated from Strip Feed solution. The bacteria is an amine source and it could interfere with some of the analytical methods used here (for example titration). The bacteria can also interfere with basic operations at MCU that include mass transfer, hydrology, and interfacial phenomena. Other than plugging the Strip Feed solution piping, no evidence of process interference due to bacteria has been observed. Also, up to 15.8 ± 3.2 micrograms of mercury per gram of solvent (or 13 µg/mL) was detected in this sample (as determined by the CV-AA method). The higher mercury concentration in the solvent (as determined in the last four monthly samples) is possibly due to the higher mercury concentration in salt batch 8 (Tank 49H).

The current gamma level (1.63E5 dpm/mL) confirmed that the gamma concentration has returned to previous level where the process operated normally and as expected.

Evidence of bacteria deposition at MCU may have been found in sample MCU-16-596-598. Pending on future samples findings, filtration of the Strip Effluent (SE) aqueous solution and superwashing the solvent (pH > 12) may be required. A possible chemical cleaning of the centrifugal contactors 606 and 607 might be required pending on observations of future samples or process upsets. Cleaning may require the use of a strong caustic solution (3 M) since caustic is known to peptize proteins into more basic byproducts.

The laboratory will continue to monitor the quality of the solvent in particular for any new impurities or degradation of the solvent components.

5.0 References

---

[1] W. M. Matthews, HLW-CRF-10006, Rev. 0, May 18, 2010.

[2] T. B. Peters and M. R. Williams, “Results of Analysis of NGS Concentrate Drum Samples” SRNL-STI-2013-00521, September 2013.

[3] L. H. Delmau, J. F. Birdwell, Jr., P. V. Bonnesen, L. J. Foote, T. J. Haverlock, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloop, Jr., B. A. Tomkins, “Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent”, ORNL/TM-2002/190, October 2002.

[4] S. Wronski, V. Vladimirov, and A. Adach, “Modelling of Mass Transfer from Multiple Emulsions”, International Journal of Heat and Mass Transfer 55 (2012), 4241-4245.

[5] S. Vedantam and J. B. Joshi, “Annular Centrifugal Contactors-A Review”, Chemical Engineering Research and Design, 84(A7), 2006, 522-542.

[6] T. B. Peters, “Tris(isodecyl) guanidine Degradation in the MCU System”, SRNL-STI-2015-00372, June 2016

[7] B. A Moyer, L. H. Delmau, B. D. Roach, and N. J. Williams, “Thermal Degradation of Next Generation Solvent using Triisodecylguanidine Suppressor: Impacts on Solvent Performance and Organic Content of Aqueous Effluents” ORNL-LTR-NGCSSX-020, Rev. 1, July 2013.

[8] K. M. L. Taylor-Pashow, F. F. Fondeur, T. L. White, D. P. Diprete, and C. E. Milliken, “Development of Analytical Methods for Determining Suppressor Concentration in the MCU Next Generation Solvent (NGS)” SRNL-STI-2013-00435, Rev. 0, July 2013.

[9] H. L. Clever and M. Iwamoto, “Solubility of Mercury in Normal Alkanes”, *Ind. Eng. Chem. Res.* (1987), 26, 336-337.

[10] C. J. Bannochie, “Result of Preliminary Hg Speciation Testing on Tank 22 and Waste Concentrate Hold Tank (WCHT) Material”, SRNL-L3100-2015-00079, Rev. 1, May 4, 2015.

Distribution:

A. P. Fellinger, 773-43A
T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 773-A
S. D. Fink, 773-A
C. C. Herman, 773-A
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
K. M. Kostelnik, 773-42A
B. B. Looney, 773-42A
D. A. McGuire, 773-42A
T. O. Oliver, 773-42A
F. M. Pennebaker, 773-42A
G. N. Smoland, 773-42A
M. E. Stone, 999-W
B. J. Wiedennan, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

E. A. Brass, 241-121H
C. K. Chiu, 704-27S
J. S. Contardi, 704-56H
A. G. Garrison, 241-121H
V. X. Jain, 241-121H
C. M. Santos, 241-152H
P. E. Fogelman, 241-121H
C. J. Scherman, 241-152H
K. M. Marra, 241-120H
B. A. Gifford, 704-56H
R. T. McNew, 766-H
V. Jain, 766-H

P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, 703-46A

T. B. Peters, 773-42A
C. A. Nash, 773-42A
F. F. Fondeur, 773-A
K. M. L. Taylor-Pashow, 773-A
D. H. Jones, 999-W