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Characterization of Solids Deposited on the Modular Caustic-Side Solvent Extraction Unit (MCU) Coalescer Media Removed in October 2014

F. F. Fondeur

March 2016

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Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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

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EXECUTIVE SUMMARY

In February 2015, Savannah River National Laboratory (SRNL) received a Strip Effluent (SE) coalescer (FLT-304) from MCU. That coalescer was first installed at MCU in July 2014 and removed in October 2014. While processing approximately 31,400 gallons of strip solution, the pressure drop steadily increased from 1 psi to beyond the administrative limit of 20 psi. The physical and chemical analysis was conducted on this coalescer to determine the mechanism that led to the plugging of this coalescer.

Characterization of this coalescer revealed the adsorption of organic containing amines as well as MCU modifier. The amines are probably from the decomposition of the suppressor (TiDG) as well as from bacteria. This adsorption may have changed the surface energetics (characteristics) of the coalescer fibers and therefore, their wetting behavior.

A very small amount of inorganic solids were found to have deposited on this coalescer (possibly an artifact of cleaning the coalescer with Boric acid. However, we believe that inorganic precipitation, as has been seen in the past, did not play a role in the high pressure drop rise of this coalescer. With regards to the current practice of reducing the radioactive content of the SE coalescer, it is recommended that future SE coalescer should be flushed with 10 mM boric acid which is currently used at MCU.

Plugging of the SE coalescer was most likely due to the formation and accumulation of a water-in-oil emulsion that reduced the overall porosity of the coalescer. There is also evidence that a bimodal oil particle distribution may have entered and deposited in the coalescer and caused the initial increase in pressure drop.

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LIST OF ABBREVIATIONS

CSSX	Caustic-Side Solvent Extraction
DI-DD	De-ionized Doubled-distilled
DSS	Dissolved salt solution
EDS	Energy dispersive spectroscopy
FTIR	Fourier transform infrared
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
MCU	Modular caustic side solvent extraction unit
MST	Monosodium titanate
NAS	Sodium aluminosilicate
NGS	Next Generation Solvent
PPS	Polyphenylene sulfide
SB	Salt batch
SE	Strip effluent
SEM	Scanning electron microscopy
SRNL	Savannah River National Laboratory
XRD	X-ray diffraction

1.0 Introduction

During operations of the Modular Caustic-Side Solvent Extraction [CSSX] Unit (MCU), pressure drops across the MCU coalescers have been found to increase over time as the volume of solution processed through the coalescer increases. Such pressure drop increases have been attributed to pluggage and /or fouling of the coalescers associated with accumulation of inorganic /organic compounds and /or changes in the characteristics of the coalescer fibers. The net result is reduction in coalescer porosity.

When pressure drops reach a level impeding normal operations, the coalescers are replaced so that effective processing operations can resume. Alternatively, the coalescers are also replaced opportunistically as a routine maintenance practice when other facility outages occur. This applies to the decontaminated salt solution (DSS) coalescers, the SE coalescers, and the DSS coalescer prefilters. Another potential alternative to replacement of spent coalescers is a treatment that results in the dissolution of accumulated compounds and/or restoration of the original coalescer fiber characteristics by pulsing the appropriate dissolving solution through the coalescer. However, this method may require additional piping and tanks to effect continuous rinsing, recycling and pulsating flow at the coalescer. Furthermore, several dissolving solutions may be required when a wide chemical spectrum of solids are present in the coalescer. The potential to identify such a treatment requires a sound understanding of the compounds accumulated within the coalescers and the nature of any such coalescer fiber changes; however, the economics of in-situ coalescer cleaning preclude this idea from implementation (versus simply replacing with new coalescers).

In this document, characterization of spent SE coalescer samples is reported. The SE coalescer (FLT-304) examined in this report was removed in October 2014 (after it had processed 31,400 gal). As a back drop, a recent history of previous coalescer characterization analyses is shown in Table 1. Another objective is to determine any spatial variation in the solid deposition within a coalescer.

Table 1. A recent history of the coalescers sent to SRNL for characterization

Coalescer Type DSS (20 µ, 40” long) SE (10 µ, 24” long); (K= 1000 gallons processed)	Solution	Solids Found and Approximate Concentration on the Coalescer
DSS [1]	Simulated salt simulant (1.9 M [OH])	40 – 170 g of NAS
DSS[2]	Water with MST	15 -20 g of MST
DSS coalescer A[3]	Simulated salt simulant	Sodium Carbonate and Boehmite
DSS coalescer B (40K)[3]	Salt simulant	Sludge, Silica, Bayerite (1.4 g), and Titania
DSS coalescer C (80K)[3]	Salt simulant	Bayerite (7.8 g)
SE coalescer Alpha (9.5K)[4]	1 mM Nitric Acid	Bayerite $Al(OH)_3$ and NAS
SE coalescer Beta (40K)[4]	1 mM Nitric Acid	Bayerite and Boehmite $Al(OH)_3$
DSS5[5]	Macrobatch 3	$Al(OH)_3$, NAS, and Titania
DSS5[5]	Macrobatch 3	No solids found (Removed May 2010)
DSS6[6]	Salt Batch 6 and 7	Sludge, Titania, Oxalate, and $Al(OH)_3$
DSS (800K)[7]	3 mM boric acid (SB 5/SB 6)	Sludge, titania, NAS, Silica, and modifier
SE (65K)[7]	3 mM boric acid (SB 5/SB 6)	Sludge, titania, NAS, Silica, iron oxide, and modifier
DSS (700K) and SE (40K) [8]	Salt Batch 6 and 7	$Al(OH)_3$, Titania (48 mg /mL of coalescer)
SE[9]	3 mM boric acid (SB 6 / SB 7)	$Al(OH)_{3,}$ Silica (1.5 mg/ mL of coalescer)
SE (30K) [10]	3 mM boric acid (SB 7)	Stainless steel debris. Low solids concentration

2.0 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. [11] This report was developed in accordance with the protocols identified in Task Technical and Quality Assurance Plan SRNL-RP-2013-00536.[12]

3.0 Background Information

The coalescer samples addressed in this report are those associated with MCU operations during part of Salt Batch 7 (SB 7). Salt batches are blended in Tank 21, sampled, and analyzed for qualification. This designates the Salt Batch number. Once qualified the batch (or partial batch) is moved from Tank 21 to Tank 49. If partial batches are sent from Tank 21 to Tank 49, then an alphabetical designation is attached to the number. Salt batches may be adjusted with 50 wt% NaOH solution to reach a free hydroxide concentration of 2.0 ± 0.2 M.[9,13] A batch number is assigned to the content of Tank 49H when its compositional chemistry changes slightly due to the content transfer from Tank 21H. In the amount transferred along with cold chemical additions, the concentration of major chemical components of concern such as hydroxyl, sodium, carbonates, aluminates, phosphate, nitrate, nitrite, and sulfate are typically similar from batch to batch. Batches with slight change in chemical composition are identified with an alphabet letter (for example A, B, C, and D). Specifics of the coalescer media from which the samples were collected are summarized below.

The SE coalescer was installed on July 2014 and remained in operations until October 2014. A total of 31.4K gallons of strip solution (mostly SB 7) were processed through the SE coalescer and the corresponding maximum pressure drop across the coalescer was approximately 17 psi (see Fig. 1). The recommended maximum pressure drop limit 17 psi (two sigma below that listed in Ref. 14). Before it was removed, the SE coalescer (FLT-304) was back flushed with 1 mM nitric acid to reduce its radioactive load with the risk of removing acid-soluble solids (for example aluminum hydroxide or carbonate compounds). A quick glance at Fig. 1 reveals the pressure drop data consists of two distinct lines (the second straight line is noticeable after 11,000 gallons of filtrate). The two lines in Fig.1 may indicate that the oil in boric acid emulsion is bimodal with the largest oil particles first settling at the coalescer (yielding the first rise in the pressure drop) and the remaining smaller oil particles depositing in the coalescer later (for about 7000 gallons of filtrate). Two lines can also be obtained in the pressure drop versus filtrate volume plot by a sudden increase in particle concentration of the solution that is filtered. The data does not appear to support other plugging mechanisms such as pore blocking or deep bed filtering.[15] The data can be fit with the mathematics of “cake filtration” or that of Kozeny-Carman equation for a porous media.[16] Prior to sampling (but following completion of the normal SE operations), the SE was rinsed with approximately 500 gallons of a solution containing 10 mM boric acid solution to reduce the gamma emitting radionuclide concentration in the media. That rinsing can remove any cake film from the inner surface of the SE coalescer.

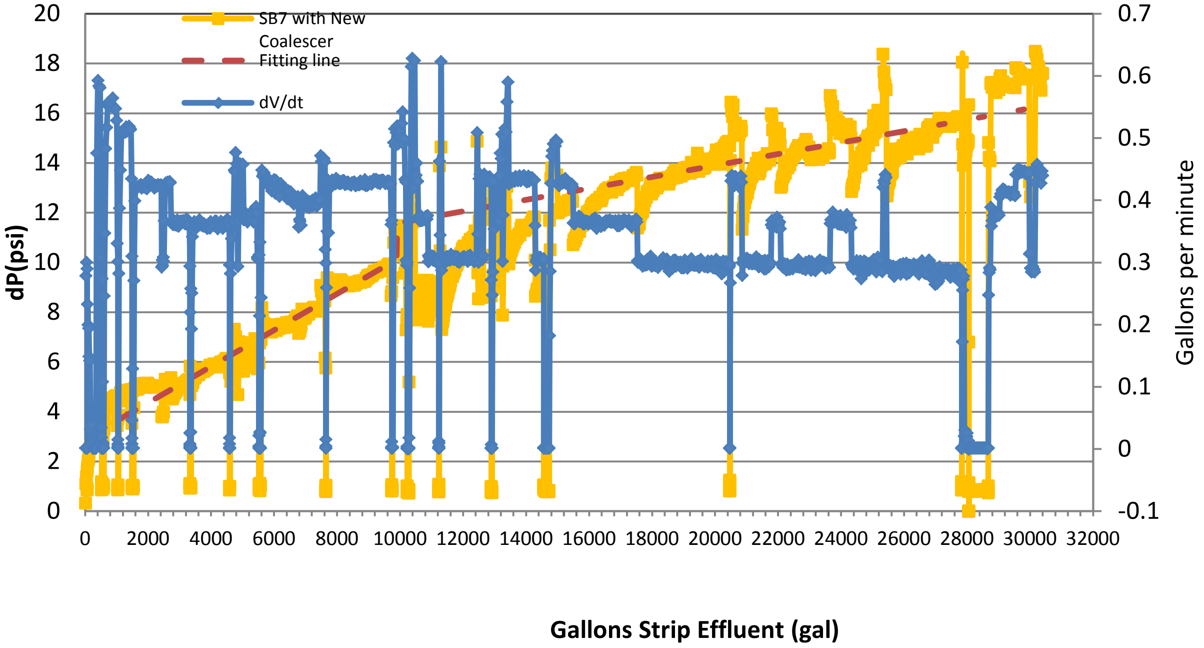


Figure 1. Pressure Drop Across the Oct. 2014 SE Coalescer

As indicated by the gold line in Figure1, there was an unexpected high rate of increase in differential pressure across this coalescer media over the short duration of its processing life. Although the data in Fig. 1 can be explained by assuming a cake formation at the entrance of the coalescer, the coalescer needs further microscopic and chemical leaching evaluation to verify the plugging mechanism.

The coalescer characterization activities at SRNL began in late May 2015. Given this time frame, it is clear that the lag times between the sample collection dates and sample analysis dates were on the order of 9 months for the SE coalescer sample. The lag times provide an indication of the extent that aging could possibly have caused potential crystallization and /or decomposition of compounds. The SE coalescer arrived at SRNL in February 2015.

4.0 Experimental Procedure

4.1 Sample Preparation and Laboratory Analyses

Upon arrival at SRNL (February 2015), the coalescer was placed in the Shielded Cells, where it was visually inspected for “gross” flaws and /or defects. No such abnormalities were found (See Fig. 2). The coalescer was then prepared for leaching and chemical analysis. Six one-inch wide “ring” segments of the coalescer were removed (cut). Three rings were cut from the closed-end of the coalescer and the other three from the middle. A picture of a cut ring from the SE Oct 2014 coalescer is shown in Figure 2. A closer look at one of the coalescer pieces is shown in Fig 3. The rings inner surfaces appeared clean. A set of two “ring” segments (one from the closed-end and one from the middle) were submitted to the laboratory “as is,” for solids characterization by XRD, Fourier Transform Infrared (FTIR) spectroscopy, SEM, and EDS. A second set of two “rings” were placed in its own “leaching bottle” and immersed in 400 mL of 3 M nitric acid at ambient temperature and under quiescent conditions. The remaining set of two “ring” segments was placed in 400 mL of deionized and double-distilled (DI-DD) water. The weights of each coalescer piece leached in water and nitric acid are listed in Table 2. Leachate aliquots (about 6 mL each) were removed from each bottle (both the nitric acid and DI-DD water) after periods of 1, 7, 14, and 28 days. The respective leachate aliquots from the nitric acid and DI water were submitted to the laboratory for elemental analysis byICP-AES and for anions by IC.

Table 2. Gravimetric weights of the cut samples used in the nitric acid and water leaching tests

Coalescer and cut piece location	Donut weight (g) Nitric acid leaching	Donut weight (g) Water leaching
SE middle piece	12.901	12.118
SE closed-end piece	10.560	9.280

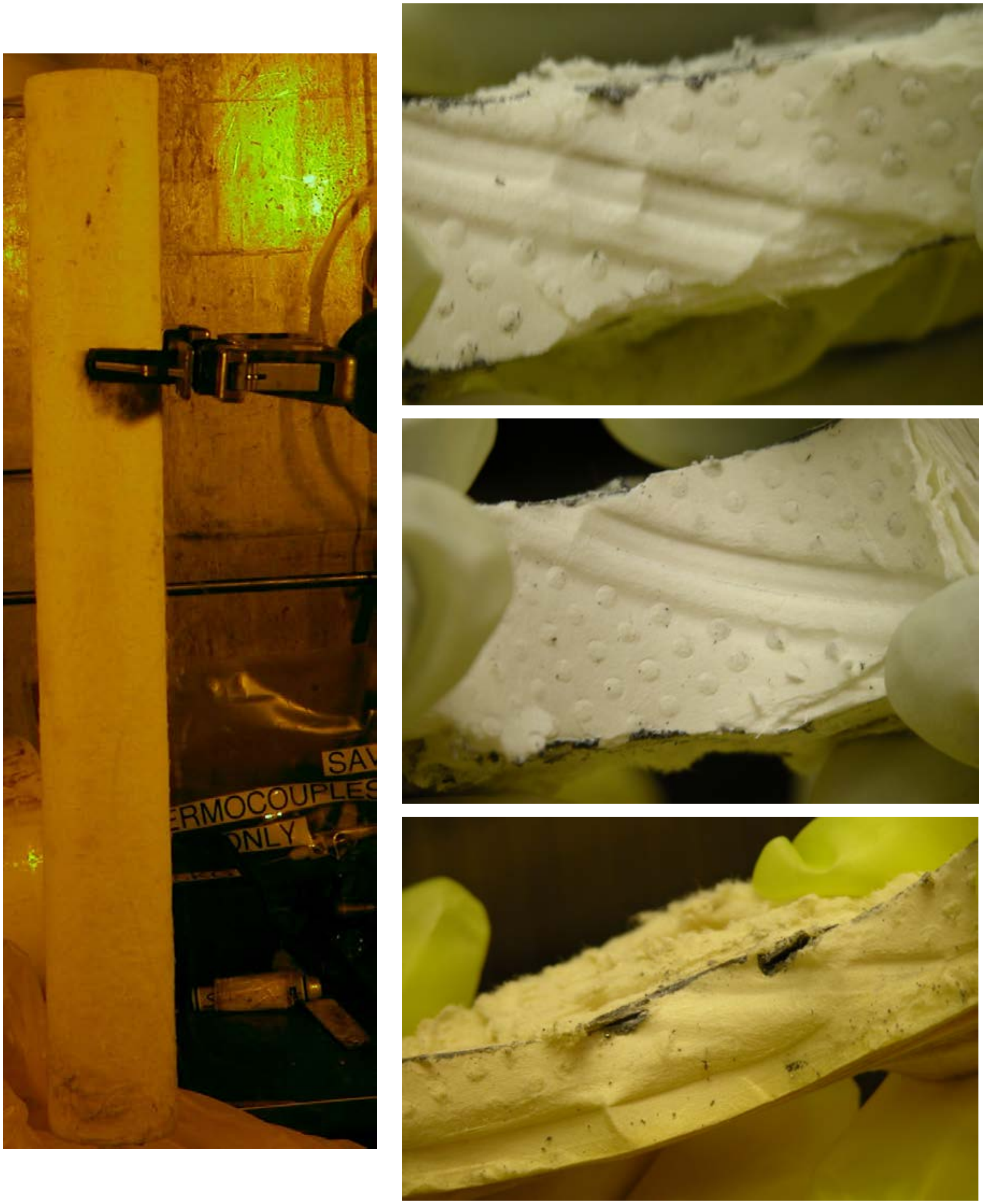


Figure 2. **A picture of the October 2014 SE coalescer sent to SRNL. The coalescer is relatively clean**

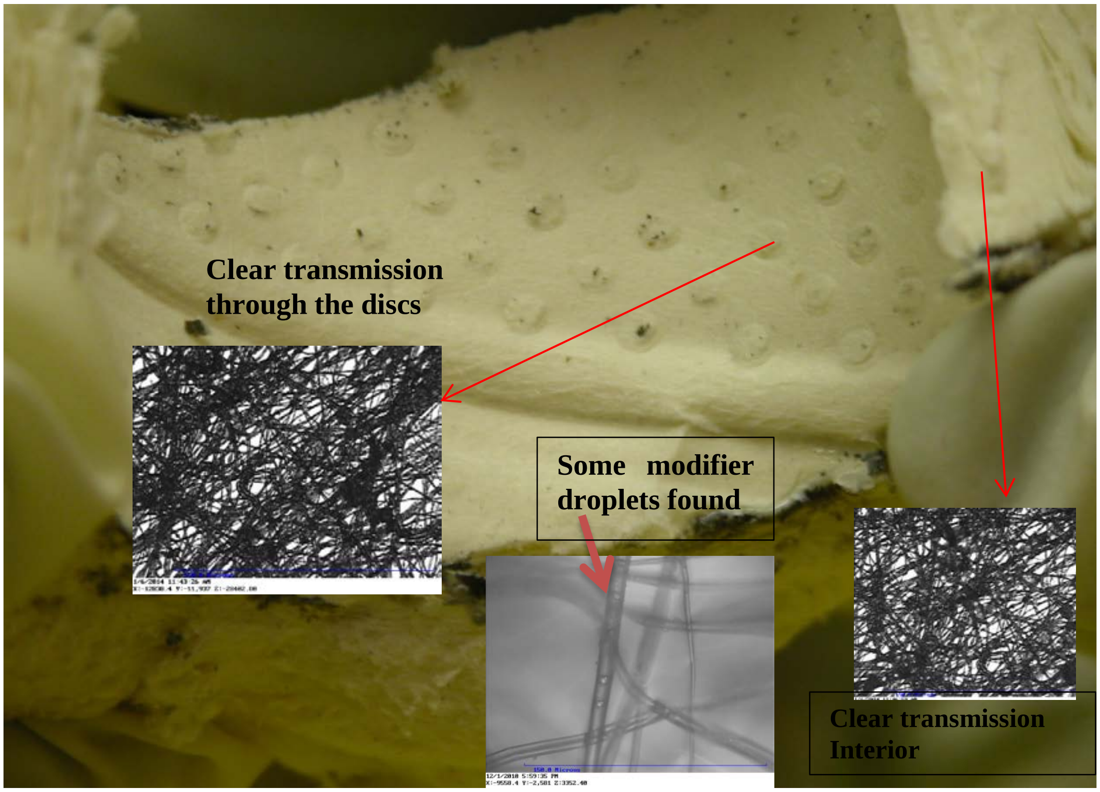


Figure 3. A picture of a cut ring from the SE Oct 2014 coalescer (coalescer appears relatively clean)

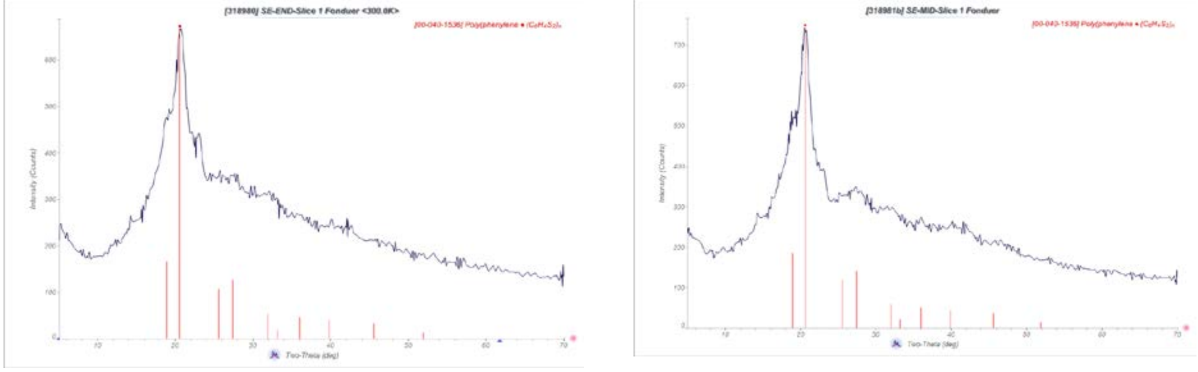
5.0 Results and Discussion

5.1 X-ray Diffraction (XRD)

No crystalline compounds were detected by XRD in this coalescer. Non-detection of solid-phase constituents does not necessarily mean that these constituents were absent from the samples, but it indicates that such constituents did not dominate the solids and/or were not present in crystalline form. Also, given the likely spatial variations associated with solids precipitating in the coalescer media, there is the understanding that concentrations of deposited solids in one segment of a given sample can be markedly different from those in another segment.

Typically aluminosilicates or pure aluminum hydroxide compounds have been observed in previous SE coalescers.[14,3-10] Silica has been observed in the pre-filter element (coalescer), used for filtering the macrobatches of salt solution from Tank 49H, and in the extraction contactors (SEP-401)[13]. Carry-over salt solution from centrifugal contactor 501 (heated to 33ºC) may be the source of silicon to the SE coalescer. In a low dielectric media, such as the MCU solvent, silica (as well as other elements capable of forming oxygen polyhedral) readily precipitates as a crystalline oxide. As discussed above, the few peaks in the XRD spectrum do not assure the absence of solids – it merely indicates that solid-phase constituents were not present in high concentrations and /or that existing solids were non-crystalline. Moreover, the pore network in the coalescer is radially directional and the deposited solids in this network may appear unidirectional to the X-ray beam from the XRD. Thereby, XRD peaks may not be proportional to the solid concentration (bias low relative to solid concentration) on the coalescer. As can be seen in Figures 4 and 5, except for one plot, the amorphous polyphenylene sulfide (PPS) peak is as large as the other peaks assigned to salts and glass giving the impression of a coalescer packed or saturated with lots of crystalline solids.

Despite the relatively long storage period of the SE coalescer (~ 9 month), it is unusual that no bicarbonate was observed by XRD given the continuous absorption of carbon dioxide from the air into the residual solution (neutral pH) of the coalescer during storage. However, no Trona ($Na_3(CO_3)(HCO_3)•2H_2O$) compound was detected in any section of the SE coalescer; they may have been flushed out (dissolved) during the boric acid rinsing of this coalescer. This is consistent with the clean optical pictures shown in Fig. 2 and they may have flushed out (dissolved) during the boric acid rinsing of this coalescer.


October 2014 Closed-end SE

October 2014 Mid-point SE

Figure 4. XRD spectra of the mid and end-section of the SE (Oct 2014) coalescer

5.2 Fourier Transform Infrared (FTIR) Spectroscopy

Small concentration of silicate particles, some with modifier and amines-containing material on it, was observed by the FTIR (see Fig. 5). The silicate is consistent with previous observations of sodium aluminum silicate (NAS) and compounds of aluminum in past SE coalescers characterizations.[9,10] The amines are possibly from two sources: the decomposition of the TiDG suppressor and/or bacteria.

The FTIR also detected a high concentration of the MCU modifier. The presence of MCU modifier in the coalescer is reasonably consistent with past observations of the modifier sorbing on different surfaces (as the Isopar™L evaporates during storage), as seen in previous cold simulant testing.

The inner most surface of the media that touches the perforated tube had minimal solid loading. The lateral porosity (the available empty space between the fibers when viewing the inner surface in a normal direction) at the hole entries was found to be closer to 68% (which is the same lateral porosity of an “As Received” or un-used coalescer). The fiber thickness in these media ranged from 18 to 23 microns. Thus, these media were less efficient when coalescing oil droplets less than 18 microns.

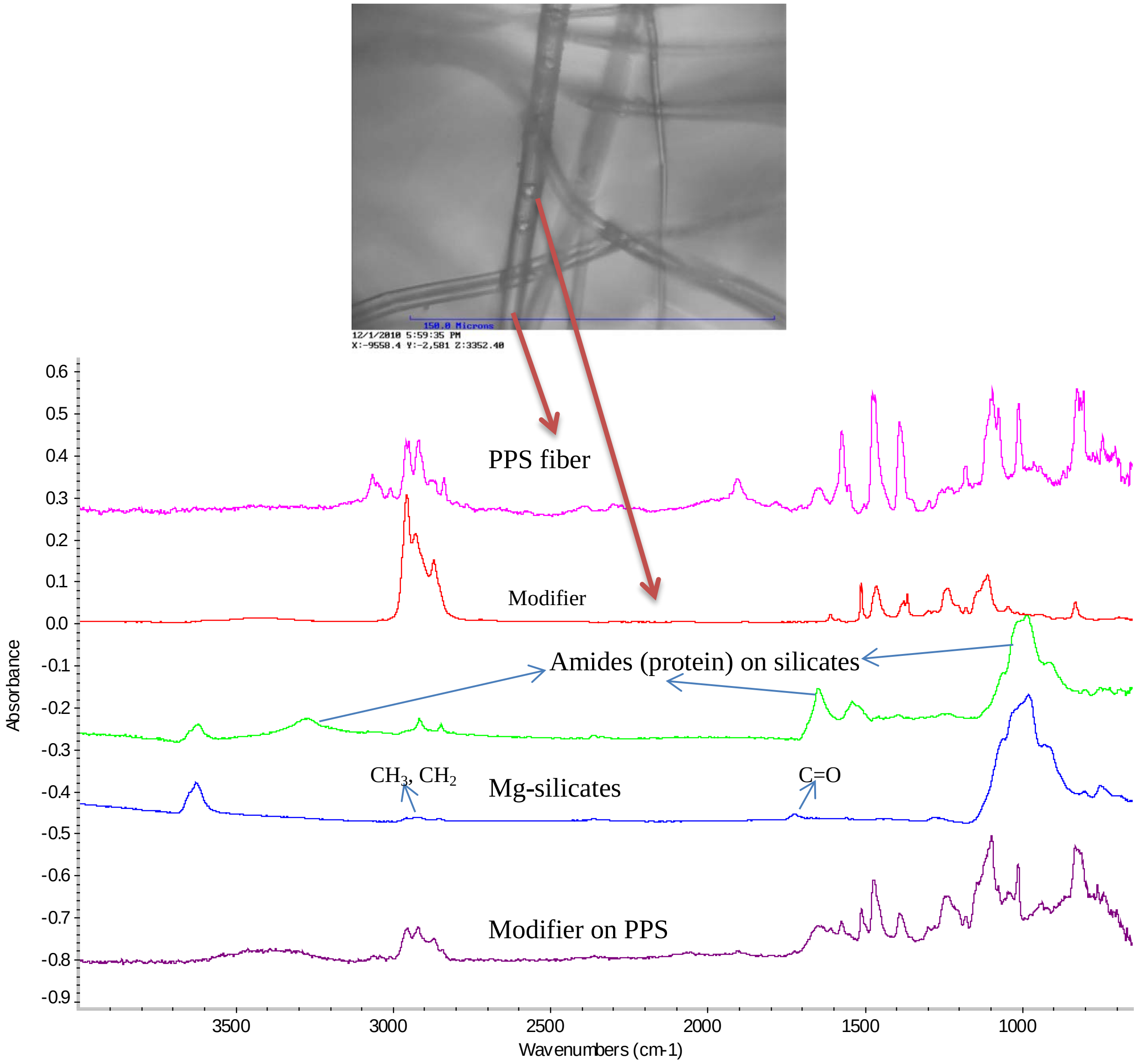


Figure 5. **FTIR Results of the middle portion of the SE coalescer Oct 2014**

5.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Based on the results of the EDS analyses (shown in Fig. 6 and 7), a relatively low concentration of aluminum silicate was identified on both the middle and closed end of the SE Oct. 2014 coalescer. A few particles of stainless steel were also observed. Aluminosilicates have a strong IR adsorption band at 1000 cm^{-1}

Elements such as potassium, a potential competitor to cesium for MaxCalix in the next generation Solvent (NGS), are possibly an impurity from the cold chemical additions to the tanks for corrosion control or from radioactive decay processes in the Tank Farm. No titanium was detected as it was in the past [Ref. 5].

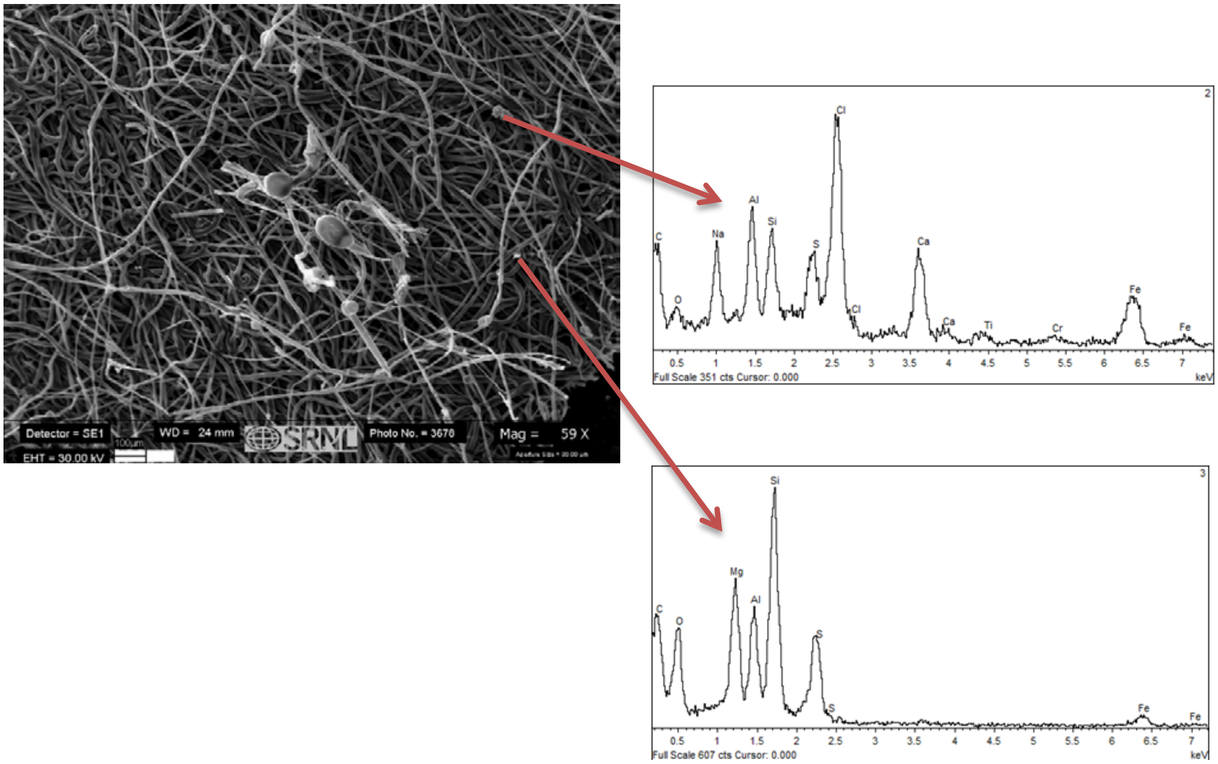


Figure 6. SEM and EDS spectra of the closed-end portion from the SE coalescer (Oct 2014)

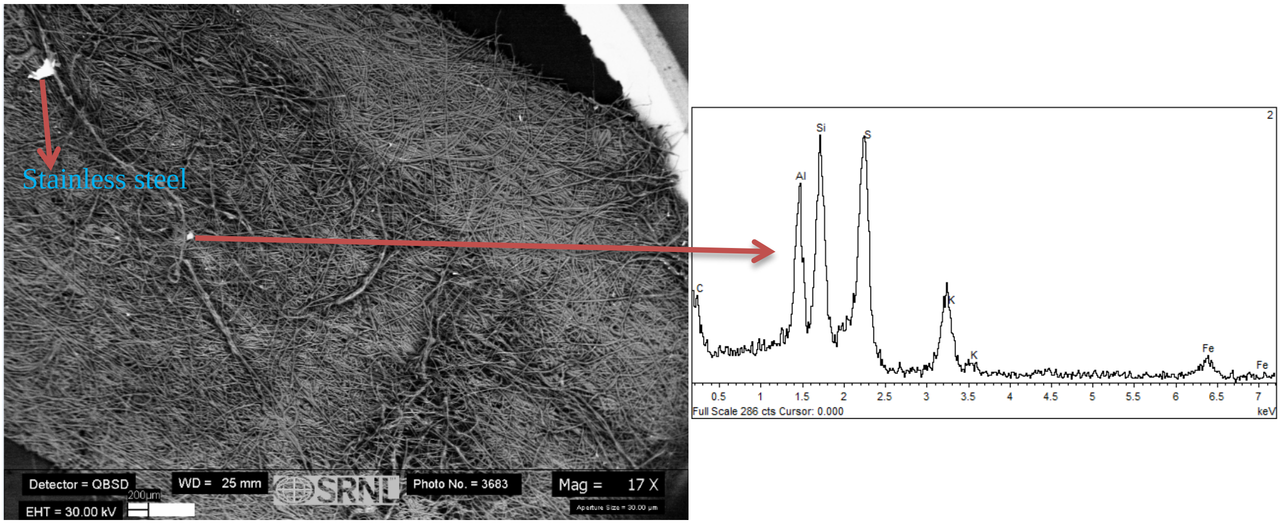


Figure 7. SEM and selective EDS spectra of the mid-section portion of the SE coalescer (Oct 2014)

5.4 Inductively Coupled Atomic Emission Spectroscopy (ICP-AES) of Coalescer Leachates

A summary of the most dominant metals found in the coalescer leachate solutions at the end of the leaching period (t = 28 days) is given in Table 3. Twenty eight days were sufficient for the dominant metals in the leachates to reach steady state (see Fig. 8). As clearly seen in Table 3, the elemental concentrations of the leachates are very low compare to a similar characterization done in Ref. 7. The elements found were Sodium, Iron, Aluminum, Silicon, Titanium, and Phosphorous. Given the low metal concentration in the leachates, no discernable difference was detected in the extent of solid deposition on the mid-section versus that of the closed-end of the coalescer.

A complete listing of the ICP-AES results, for all of the elemental constituents measured, is given as a function of the leaching time in Table 4.

Table 3. Dominant Elements in Leachates from the closed-end of each coalescer

Sample Descriptor	Metal Concentration, mg/L (t = 28 days)						
	Na	Ti	Al	Fe	Si	P	K
SE Coalescer: Middle End	2.18	0.03	1.0	5.2	0.9	0.3	< 6
SE Coalescer: Closed End	1.8	0.03	0.7	4.3	0.8	0.3	< 6

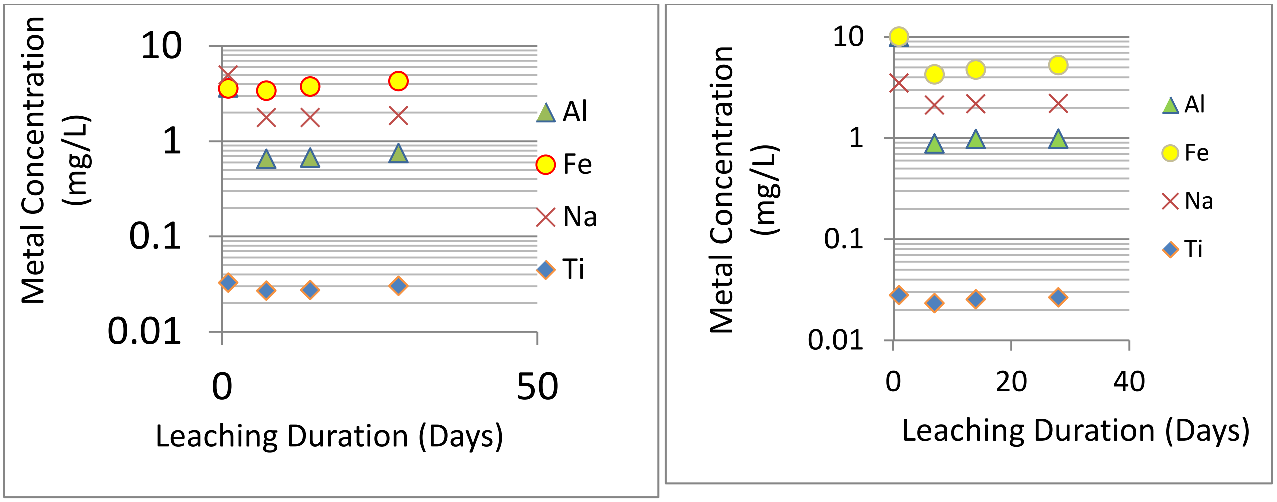

Closed End SE Coalescer **Mid Area of SE Coalescer**

Figure 8. Dominant metal concentration from the closed-end and middle portion of the SE coalescer leachates

Table 4. Elemental Constituent Concentrations in SE Coalescer

Element	SE February 2015 Concentration, mg/L							
	Closed End				Middle Portion			
	t = 1 day	t = 7 days	t = 14 days	t = 28 days	t = 1 day	t = 7 days	t = 14 days	t = 28 days
Ag	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029
Al	3.65*	0.65	0.669	0.745	9.91	0.881	0.972	0.985
B	1.94	2.35	2.5	2.58	1.11	2.04	2.34	2.48
Ba	0.0732	0.0672	0.0538	0.0578	0.0674	0.0496	0.0514	0.0518
Be	<0.0008	<0.0008	<0.0008	<0.0008	0.001	<0.0008	<0.0008	<0.0008
Ca	1.08	0.613	0.636	0.677	1.38	0.567	0.594	0.596
Cd	0.0234	<0.021	<0.021	<0.021	0.028	<0.021	0.0282	0.0212
Ce	<0.084	<0.084	<0.084	<0.084	<0.084	<0.084	<0.084	<0.084
Co	0.02920	0.0276	0.0314	0.0346	0.0708	0.0602	0.0674	0.0698
Cr	0.19600	0.153	0.173	0.212	1.67	0.245	0.285	0.334
Cu	0.35400	0.277	0.282	0.298	0.225	0.158	0.159	0.159
Fe	3.56	3.38	3.75	4.26	10	4.23	4.73	5.23
Gd	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014
Hg[$]	NM	NM	NM	0.271	NM	NM	NM	0.0682
K	<0.631	<0.631	<0.631	<0.631	<0.631	<0.631	<0.631	<0.631
La	<0.008	<0.008	<0.008	<0.008	0.0078	<0.008	<0.008	<0.008
Li	0.15	<0.034	<0.034	<0.034	0.842	0.039	<0.034	<0.034
Mg	0.457	0.172	0.181	0.193	0.791	0.17	0.176	0.18
Mn	0.519*	0.073	0.0754	0.0822	3.29	0.102	0.106	0.111
Mo	<0.056	<0.056	<0.056	<0.056	0.072	0.0844	0.106	0.111
Na	4.95	1.77	1.77	1.85	3.49	2.11	2.17	2.18
Ni	0.464	0.257	0.258	0.279	1.44	0.33	0.388	0.426
P	0.513	0.256	0.267	0.346	2.74	0.372	0.269	0.318
Pb	<0.118	<0.118	<0.118	<0.118	<0.118	<0.118	<0.118	<0.118
S	<18	<18	<18	<18	<18	<18	<18	<18
Sb	<0.571	<0.571	<0.571	<0.571	<0.571	<0.571	<0.571	<0.571
Si	1.44*	0.643	0.676	0.773	2.87	0.772	0.821	0.864
Sn	<0.182	<0.182	<0.182	<0.182	<0.182	<0.182	<0.182	<0.182
Sr	0.0136	<0.002	<0.002	<0.002	0.0172	<0.002	<0.002	<0.002
Th	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073
Ti	0.0324	0.0268	0.0272	0.0302	0.0278	0.0232	0.0254	0.0266
U	<0.72	<0.72	<0.72	<0.72	<0.72	<0.72	<0.72	<0.72
V	<0.006	<0.006	<0.006	<0.006	<0.006	0.0108	0.0128	0.0152
Zn	0.645	0.309	0.317	0.327	0.975	0.286	0.286	0.292
Zr	0.0098	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[$] Mercury was measured by Cold Vapor Atomic Adsorption (CVAA). NM means “Not Measured”.

*Initial high concentration is believed to be due to contamination from handling that sample in the Shielded Cells.

An inspection of Table 4 shows that the concentration levels of the elements in these tables are less than those reported in Ref. 7. The differences are attributed to the lower volume of boric acid processed by the SE coalescer. Despite using a lower density and lower viscosity solvent (NGS vs. CSSX), the coalescer reached noticeable pressure drops (closer to the administrative limit of 25 psi) at much lower stripping solution volumes. It is not a surprise to see a low deposition of inorganics on the stripping coalescer. Therefore, we believe that the plugging of this coalescer may be caused by the formation of water-in-oil emulsion inside the coalescer. Oil-in-water emulsion droplets on PPS fiber are possibly repelling each other and that reduces their removal from the coalescer. The accumulation of oil-in-water emulsion on the coalescer reduces the available porosity.

The sources of many of the metals listed in Table 4 were recently explained in Ref. 7. All detectable metals listed in Table 4 have origins from site processes. The Ca, Zn, and P might originate from the additives in degraded oil (oil used at the centrifuges). Phosphate may also originate from the phosphate-based extractant used at the solvent extraction process at the HB-line. Boron is believed to come from the strip solution (boric acid) used at MCU.

The aluminum, iron, manganese, nickel, chromium, uranium, and silicon are prevalent in the SRS supernatant from different processes (spent fuel dissolution H-Canyons) at the site. The titanium is from the known solubility of titanium (in Monosodium Titanate (MST)) in caustic solution).[17] Potassium, calcium and barium may originate from both nuclear decay processes of the nuclear waste as well as trapped chemicals in the cold additions to the Tanks for corrosion control and batch qualification. Boron is believed to come from the strip solution (boric acid) used at MCU.

Using the data in Table 4, an estimate of the amount of solids deposited on the coalescer was found to be 0.002 g of solids per gram of coalescer (or 235 micrograms of solids per mL of coalescer). This calculation assumed, excluding P, Ba, Ca, and Na, all detectable metals listed in Tables 4 are non-hydrated oxides. Examples include AlOOH for aluminum, Fe_2O_3 for iron (instead of ferric hydride), SiO_2 for silicon, TiO_2 for titanium, ZnO_2 for zinc, and UO_2 for uranium.

The estimated solid loadings on the SE coalescer is approximately one order of magnitude lower than the concentration observed in the pluggage of other packed bed systems[15,16] where a 50% increase in the pressure drop was observed with just 5 mg of carbon particles per mL of packed bed. Excluding the dissolution effect of flushing with nitric acid, this further supports the view that the small concentration of inorganic solids in the SE coalescer was not responsible for the high pressure drop in this coalescer. It is likely that an interplay between hydrodynamics and chemistry of the NGS-CSSX solvent and the coalescer fiber played a role in the plugging of this coalescer.

The ratios of the elemental analysis of the leachate from the closed-end to the middle portion of the coalescer was calculated and no conclusion could be reached on the spatial distribution of solid deposition on the SE coalescer which could confirm the hydrodynamics of a closed-end perforated tube.[14] Since the coalescers are approximately one meter long, the pressure drop along the perforated tube (mandrel) is insufficient to slow the axial flow down the coalescer and the highest discharge flow out of the coalescer (or out of the perforated tube) then occurs at the closed-end of the tube. Thus, if a suspension of solids enters the coalescer, it will flow down the coalescer and exit at the closed-end first. Once the discharge friction at the closed-end of the coalescer increases, the discharge flow out of the coalescer shifts toward the inlet of the coalescer. In the case of a supersaturated solution, a high liquid flow over the polyphenylene sulfide fibers may cause heterogeneous precipitation over these fibers. Longer coalescers or increased axial flow friction (possibly from solid deposition along the wall of the coalescer) may cause significant discharge flow at the middle and inlet region of a coalescer.

In a previous report (Ref. 9), it was recommended to look for oxalates in the leachate of the coalescers. Along this line, Ion Chromatography analysis of the water leachate from the coalescer showed no anions (those that can be observed by IC-Anion) were detected (see Table 5).

Table 5. IC-Anion analysis of the water leachates from the closed-end and mid-point of the SE coalescer

IC-Anions	Coalescer Closed End, µg L				SE Coalescer, µg L			
Component	1 day	7 days	14 days	28 days	1 day	7 days	14 days	28 days
Fluoride	<10	<10	<10	<10	<10	<10	<10	<10
Formate	<10	<10	<10	<10	<10	<10	<10	<10
Chloride	<10	<10	<10	<10	<10	<10	<10	<10
Nitrite	<10	<10	<10	<10	<10	<10	<10	<10
Bromide	<10	<10	<10	<10	<10	<10	<10	<10
Nitrate	17	<10	<10	<10	<10	<10	<10	<10
Phosphate	<10	<10	<10	<10	<10	<10	<10	<10
Sulfate	<10	<10	<10	<10	<10	<10	<10	<10
Oxalate	<10	<10	<10	<10	<10	<10	<10	<10

Given that both coalescers have aluminum and titanium compounds, these compounds are soluble in low ionic strength caustic media but their rate of dissolution may be different (particle size and shape) and a once-pass through rinsing of the coalescer may not remove sufficient amount of solids to restore the permeation through a bed of nonwoven fibers. Given that it is far easier to trim the salt solution to prevent NAS precipitation and replace the coalescers with new elements rather than clean a plugged coalescer, it is recommended that this practice should be continued.

Mercury analysis (CV-AA) of the 3 M nitric acid leaching of the coalescer measured 0.271 mg/L for the closed-end and 0.0682 mg/L for the mid-point of the coalescer.

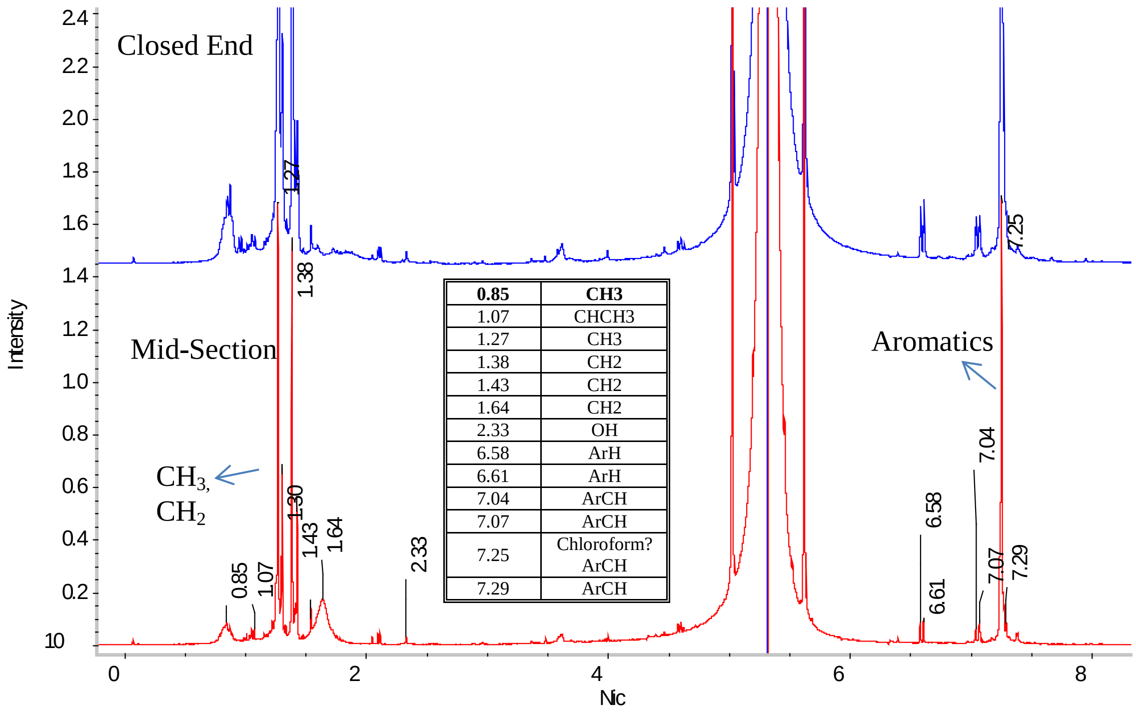
Leaching with dichloromethane

A portion of the coalescer was leached with dichloromethane (5 to 1 liquid to solid volume ratio) for 4 hours. The SVOA analysis of the leachate is shown in Table 6. Several alkylated ring compounds were detected. The presence of these compounds was also observed in the Hydrogen Nuclear Magnetic Resonance of the organic leachate (see Fig. 9). These compounds are added to the polymer to suppress oxidation and deterioration under UVA-UVB rays. It is believed that these chemicals are not released when the coalescer contacts caustic and/or boric acid solution. These chemicals are released only when they are in contact with a favorable organic solvent. However, it is likely that these chemicals may leach when the coalescers contact the NGS-CSSX solvent.

Table 6. SVOA analysis of the dichloromethane leachate of the October 2014 SE coalescer. All units are given in mg/kg of coalescer.

Component Result	Mid-point 300317364	Closed-End 300317363	Control*
2 6 di-t-butylphenol	390	250	180
2 4 di-t-butyl-6-nitrophenol	<5	38	5.9
4-t-butyl phenol	9.1	7.3	5.7
All Other SVOA Organics	<5	<5	<1

*“As received” coalescer (unused).



0.85	CH3
1.07	CHCH3
1.27	CH3
1.38	CH2
1.43	CH2
1.64	CH2
2.33	OH
6.58	ArH
6.61	ArH
7.04	ArCH
7.07	ArCH
7.25	Chloroform? ArCH
7.29	ArCH

Figure 9. H-NMR spectra of the dichloromenthane leachate of the closed-end and mid-section of the SE October 2014 coalescer.

It is believed that the plugging of this coalescer is due to the formation of water-in-oil emulsions on the coalescer fibers as argued below.

In order to have a 16x increase in the pressure drop, the coalescer porosity must be reduced from 0.9 (for an unused coalescer) to 0.6 and based on the optical pictures where the PPS fibers are nearly pristine (with an occasional coverage of solids in some places), the concentration of solids found could not have reduced the porosity of the SE coalescer (assuming the solids were not affected by the coalescer flushing). It is more likely that if the deposited solids had any effect, it would be at the closed-end of the SE coalescer. There is no evidence that precipitated solids caused the pressure drop increase. Instead, this data seems to indicate that possibly another plugging mechanism may have reduced the SE coalescer permeability. Although no direct evidences have been obtained, it is believed that secondary emulsion formation or sorption may be occurring at the coalescer fibers (illustrated in Fig. 10). Droplets of secondary emulsions (aqueous droplets inside NGS droplets) have less buoyancy than pure NGS droplets and it is expected that these types of droplets will grow to bigger sizes before they detach from the coalescer fibers. Therefore, a significant reduction in porosity may occur (these structures are reversible and can be removed in higher flow regimes).

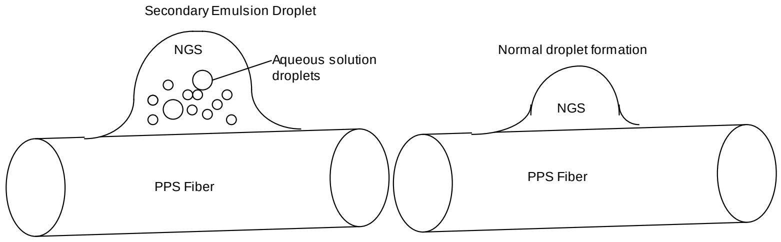


Figure 10. A pictorial description of a secondary emulsion droplet on a PPS fiber

One possible mechanism for the formation of secondary emulsion is the relative speed of large NG-CSSX droplets as they pass narrow openings. At high flow rates, the rear of an NG-CSSX droplet may accelerate relative to its front-end as the droplet passes a narrow passage (for example two PPS fibers) and deform to the point of capturing water as the droplet passes the fibers and recovers its shape. Although the Weber number (inertia/surface tension) for an NG-CSSXemulsion in the strip side is small (~8 E-3), the speed of the droplets inside the PPS media may be a lot higher with a Weber number in the range for secondary emulsion formation. Coalescers with high tortuosity have a greater potential for secondary emulsion formation.

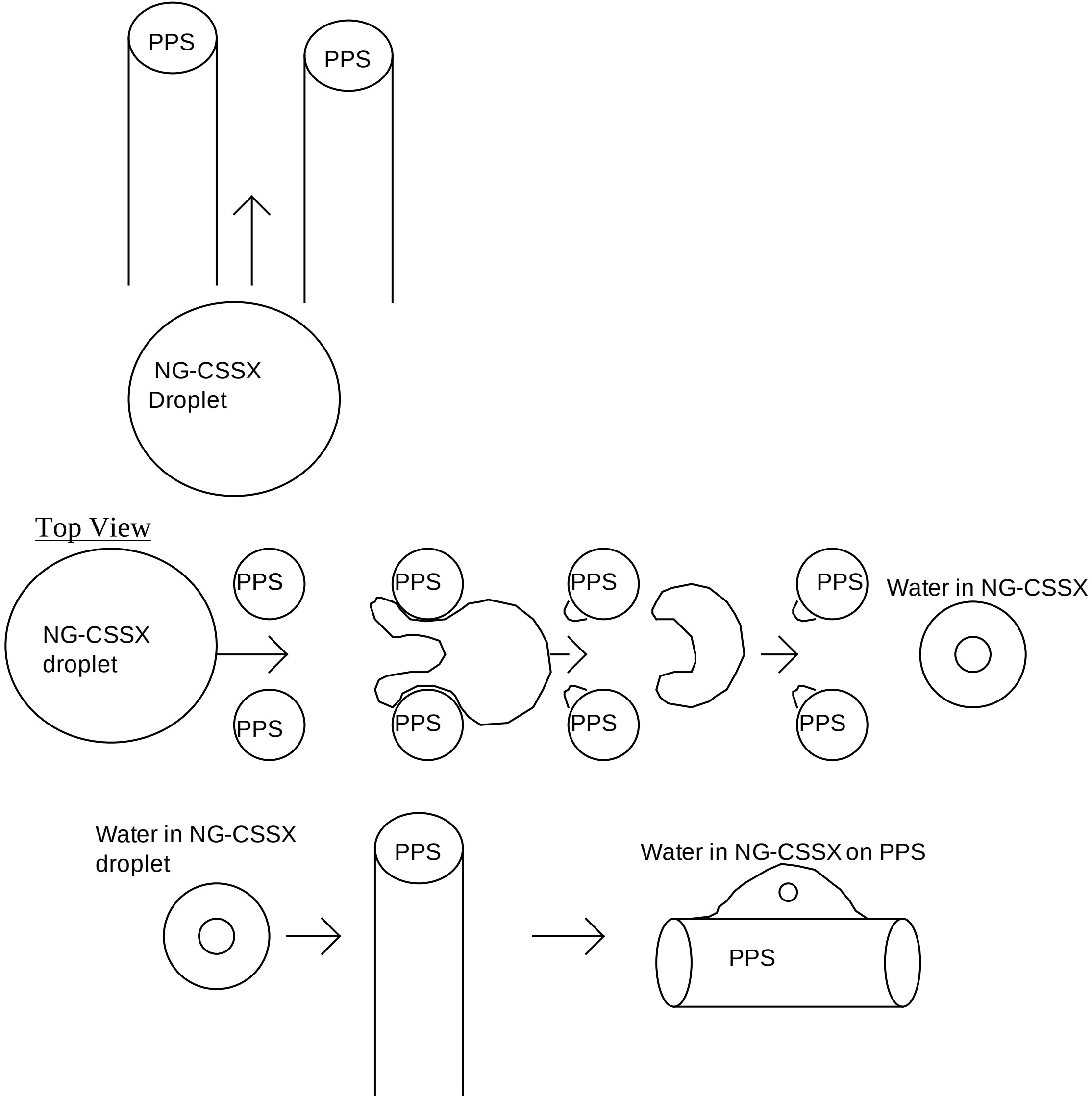


Figure 11. A possible mechanism for generating water in NG-CSSX emulsion in the coalescer at high flow rates (high Weber numbers)

6.0 Conclusions

On February 2015, SRNL received a SE coalescer (FLT-304) from MCU. That coalescer was first installed at MCU in July 2014 and removed in October 2014. While processing approximately 31,400 gallons of strip solution, the pressure drop steadily increase from 1 psi to beyond the administrative limit of 17 psi. The physical and chemical analysis was conducted on this coalescer to determine the mechanism that led to the plugging of this coalescer.

Characterization of this coalescer revealed the adsorption of organic containing amines as well as MCU modifier. The amines are probably from the decomposition of the suppressor (TiDG) as well as from bacteria. This adsorption may have changed the surface energetics (characteristics) of the coalescer fibers and therefore, their wetting behavior.

Plugging of the SE coalescer was most likely due to the formation and accumulation of a water-in-oil emulsion that reduced the overall porosity of the coalescer. There is also evidence that a bimodal oil particle distribution may have entered and deposited in the coalescer and initiated the increase in pressure drop.

A very small amount of inorganic solids was found to have deposited on this coalescer. Therefore, inorganic precipitation or deposition, as has been seen in the past, did not play a role in the plugging of this coalescer.

7.0 Recommendation

The recommendations listed in Ref. 7 will benefit and improve lengthening the services of the SE and DSS coalescers.

Future testing may include tests to determine the conditions under which secondary emulsion may form in the coalescer and whether aged modifier and aged suppressor can change the coalescing behavior of the coalescer.

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