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Solids Precipitation Event in MCU
Causal Analysis and Recommendations from Solids Recovery Team

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Executive Summary

A process upset occurred in the Modular Caustic-Side Solvent Extraction Unit (MCU) facility on April 6th, 2014. During recovery efforts, a significant amount of solids were found in the Salt Solution Feed Tank (SSFT), Salt Solution Receipt Tanks (SSRTs), two extraction contactors, and scrub contactors. The solids were identified by Savannah River National Laboratory (SRNL) as primarily sodium oxalate and sodium alumina silicate (NAS) with the presence of some aluminum hydroxide. NAS solids have been present in the SSFT since simulant runs during cold chemical startup of MCU in 2007, and have not hindered operations since that time. During the process upset in April 2014, the oxalate solids partially blocked the aqueous outlet of the extraction contactors, causing salt solution to exit through the contactor organic outlet to the scrub contactors with the organic phase. This salt solution overwhelmed the scrub contactors and passed with the organic phase to the strip section of MCU. The partially reversed flow of salt solution resulted in a Strip Effluent (SE) stream that was high in Isopar™ L, pH and sodium.

The primary cause of the excessive solids accumulation in the SSRTs and SSFT at MCU is attributed to an increase in the frequency of oxalic acid cleaning of the 512-S primary filter. Agitation in the SSRTs at MCU in response to cold weather likely provided the primary mechanism to transfer the solids to the contactors. Sources of the sodium oxalate solids are attributed to the oxalic acid cleaning solution used to clean the primary filter at the Actinide Removal Process (ARP) filtration at 512-S, as well as precipitation from the salt batch feed, which is at or near oxalate saturation.

The Solids Recovery Team was formed to determine the cause of the solids formation and develop recommendations to prevent or mitigate this event in the future. A total of 53 recommendations were generated. These recommendations were organized into 4 focus areas:

- Improve understanding of oxalate equilibrium and kinetics in salt solutions
- Reduction/elimination of oxalic acid cleaning in 512-S
- Flowsheet optimization
- Improving diagnostic capability

The recommendations implemented prior to resumption of MCU operations provide a risk mitigation or detection function through additional sampling and observation. The longer term recommendations provide a framework to increase the basic process knowledge of both oxalate chemistry and filtration behavior and then facilitate decisions that improve the salt flowsheet as a system.

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Acronyms

ANL	Argonne National Laboratory
ARP	Actinide Removal Process
CDT	Contactor Drain Tank
CSS	Clarified Salt Solution
dP	Differential Pressure
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
LPPP-PPT	Low Point Pump Pit Precipitate Pump Tank
LWHT	Late Wash Hold Tank
LWPT	Late Wash Precipitate Tank
MCU	Modular Caustic-Side Solvent Extraction Unit
NAS	Sodium Aluminum Silicate
NGS	Next Generation Solvent
ORNL	Oak Ridge National Laboratory
SCAMPER	Substitute, Combine, Adapt, Modify, Put to another use, Eliminate, Reverse
SE	Strip Effluent
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SSFT	Salt Solution Feed Tank
SSRT	Salt Solution Receipt Tank
TiDG	Tris-dimethyloctyl guanidine hydrochloride
TOA	Trioctylamine

1.0 Introduction

On April 6, 2014, MCU experienced a process event caused by oxalate solids present in extraction and scrub contactors. The solids partially blocked the aqueous outlet of the extraction contactors, causing salt solution to exit through the contactor organic outlet to the scrub contactors with the organic phase. This salt solution overwhelmed the scrub contactors and passed with the organic phase to the strip section of MCU. This resulted in a Strip Effluent stream that was high in Isopar™ L, pH and sodium. Analysis of the solids found in the contactor rotor indicated that the solids were primarily sodium oxalate. Subsequent inspection of the SSFT led to the discovery of precipitated solids (primarily sodium oxalate) in the SSFT and SSRTs. The Solids Recovery Team was formed to determine the cause of the solids formation and develop solutions to prevent or mitigate this event in the future. The purpose of this report is to document the results and recommendations of the Solids Recovery Team.

2.0 Background

2.1 Salt Process Description

The existing process has been operating at Savannah River Site (SRS) since April 2008 as an interim salt treatment system to remove actinides and cesium from high level waste salt solutions. MCU is the first production-scale solvent extraction process for cesium separation. While the application of this solvent extraction process is unique, the process uses commercially available centrifugal contactors for the primary unit operation as well as other common methods of physical separation of immiscible liquids (i.e. coalescers and decanters). This process enables permanent disposal of the raffinate, Decontaminated Salt Solution (DSS), as cementitious grout, and the SE containing cesium in a vitrified waste form. MCU is operated in series with ARP where ARP first removes sludge solids, soluble strontium and actinides from the salt waste solution by sorbing them onto Monosodium Titanate (MST). This MST slurry is then filtered through 512-S and the resulting filtrate is the Clarified Salt Solution (CSS) fed to MCU for cesium extraction. Figure 1 provides an overview of the SRS Salt Processing Facilities.

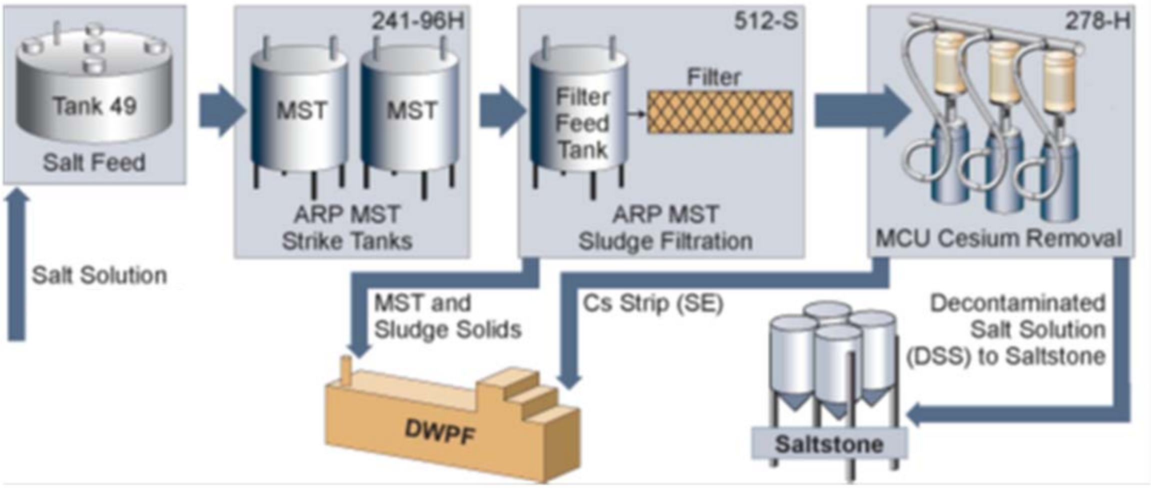


Figure 1: Salt Processing Overview

2.2 MCU Process Description

Batches of filtered salt solution are introduced into one of the SSRTs via a single transfer line from the 512-S (ARP) Facility and later transferred to the SSFT. Salt solution is transferred to the extraction contactors. The solvent is used to extract cesium from the aqueous feed solution in the extraction contactor bank consisting of seven centrifugal contactors. The DSS raffinate is sent to a coalescer and decanter to remove any entrained solvent before transfer to Tank 50. The cesium laden solvent from the extraction bank is scrubbed in the scrub contactor bank consisting of two centrifugal contactors. The scrub solution removes ionic impurities in the solvent, and optimizes stripping. Cesium is then stripped from the solvent to an aqueous strip solution in the strip contactor bank consisting of seven centrifugal contactors. This concentrated cesium SE is then sent to a coalescer and decanter to remove any remaining solvent. The cesium laden SE is sent to Defense Waste Processing Facility (DWPF) to be vitrified. The solvent stream exits the strip contactor bank and is sent to the wash contactor bank consisting of two centrifugal contactors to clean the solvent of any impurities and is recycled back into the solvent hold tank for reuse in the solvent extraction system. [1]

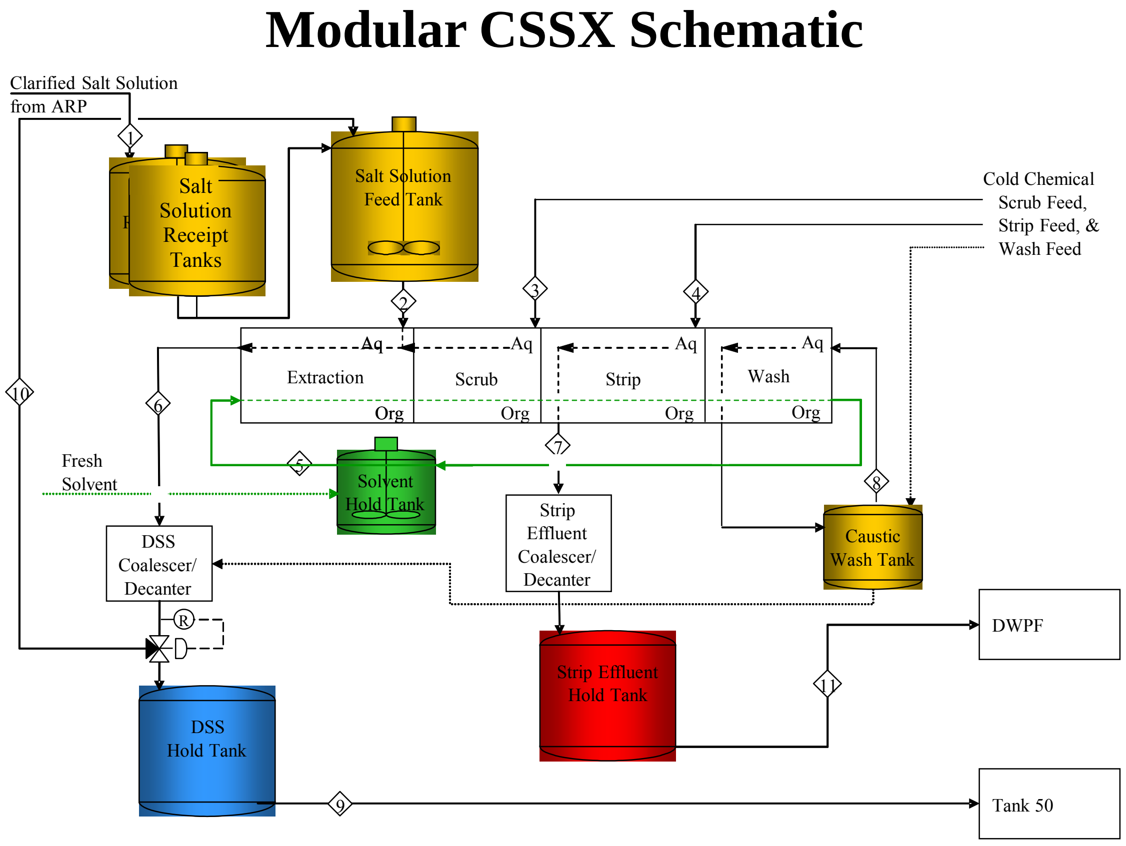


Figure 2: MCU Process Description

2.3 Event

On April 6, 2014, MCU startup was initiated at 4 gpm with CSS from Salt Batch 6D after a two week outage to replace the Salt Solution flow control valve from the SSFT to the MCU process (FCV-1026). Salt solution feed was stepped up to 5 gpm after about 3 hours of operation. The strip solvent feed temperature low alarm and the strip solvent heater high temperature alarm were received. The strip effluent accumulator high level alarm sounded. The salt solution feed was reduced to 4 gpm and the strip effluent accumulator high level alarm cleared. The strip effluent coalescer differential pressure was trending up abnormally and the solvent hold tank level fluctuation was abnormal. MCU was shut down due to concerns of solvent carryover into the strip effluent.

Subsequent troubleshooting identified high contactor vibration readings in Extraction Contactor 401 and high sodium and Isopar™ L in the strip effluent. Isopar™ L detection is used to indicate the presence of solvent. Flushing with 13% nitric acid did not improve the contactor vibration readings.

More extensive trouble shooting led to identification of oxalate solids in Extraction Contactors 401 and 402 and Scrub Contactors 501 and 502. The drain line to Extraction Contactor 401 was also found to be plugged with NAS solids. [2] [3] Solids were not found in Extraction Contactor

403 or Strip Contactor 607. Solids were also not found in the SPA-100 or the extraction aqueous heat exchanger, although flushing completed prior to the observation could have removed oxalate solids. Solids were found in the SSRTs and the SSFT. Approximately 300 kgs of sodium oxalate solids were found in the system.

The solids in Extraction Contactor 401 blocked the normal aqueous outlet and forced a portion of the salt solution backwards to the scrub contactors. Solids in the two scrub contactors also forced salt solution and scrub solution through the organic outlet to the Strip Contactor 607. The aqueous solution exited through the normal aqueous outlet of Strip Contactor 607 to the strip effluent system contaminating the strip effluent system with salt solution. [4]

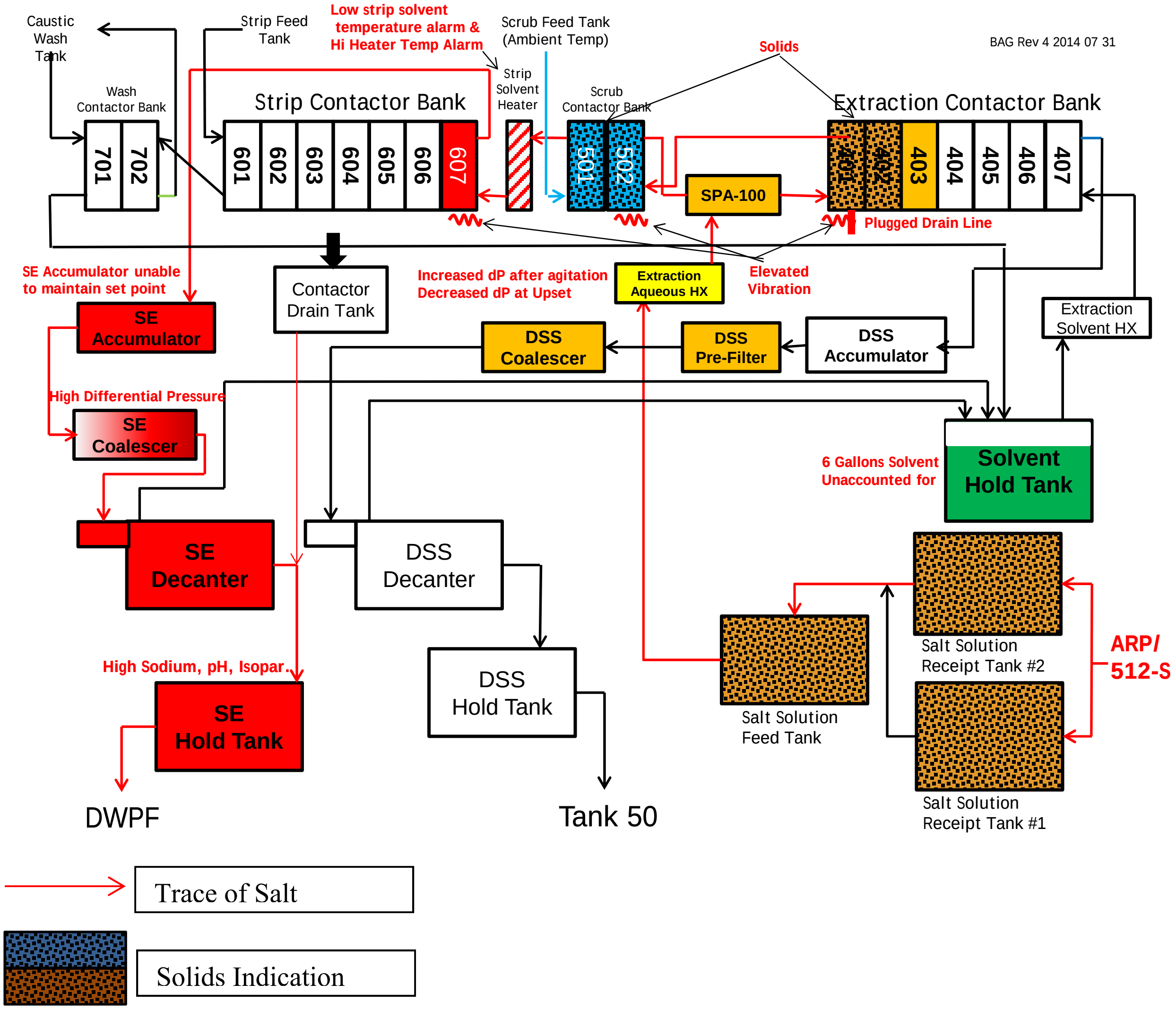


Figure 3: MCU Process Indicators

3.0 Problem Solving Process

A standard problem solving process was employed to determine the cause of the solids precipitation in MCU and develop recommendations to prevent reoccurrence: [5]

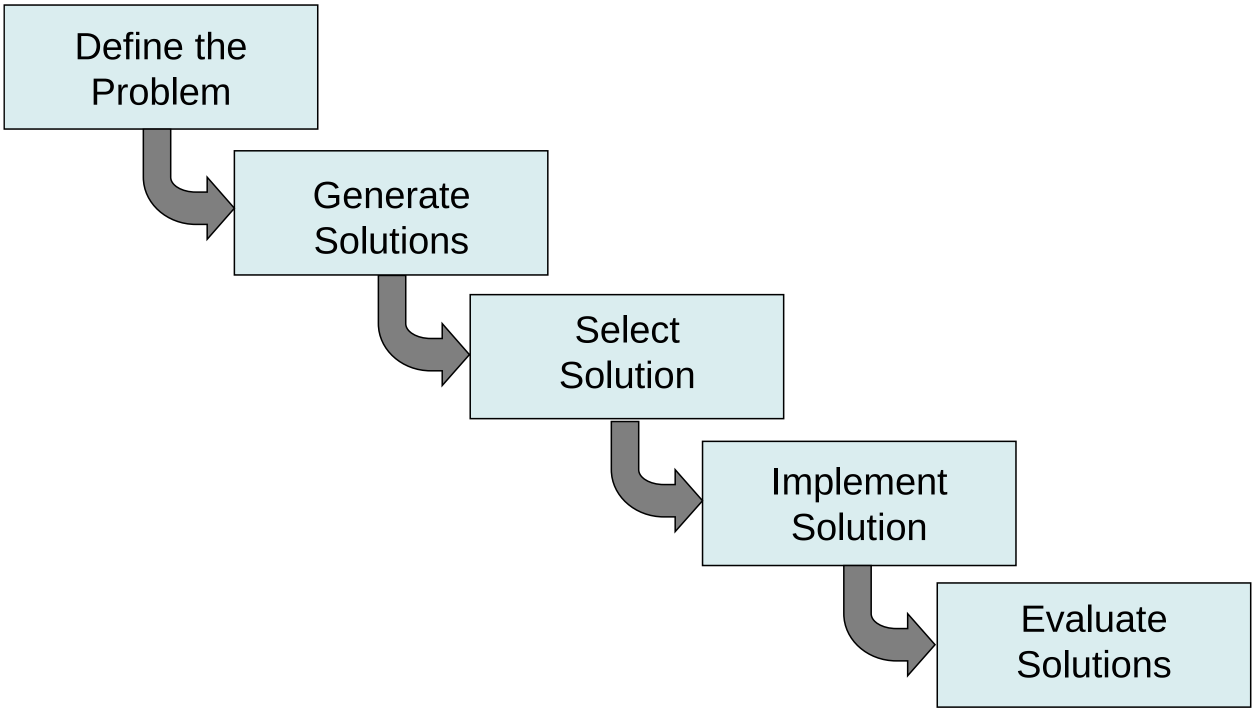


Figure 4: Problem Solving Plan

3.1 Define the Problem

The steps in defining the problem include gathering information, developing a problem statement, defining probable causes and collecting data to evaluate the causes. Process history related to solids formation for ARP and MCU was collected. The Kepner-Tregoe problem analysis technique was used to bound the problem. [5]

A problem statement was developed and then the probable causes were identified and organized into a fishbone diagram. Data was collected and each cause was evaluated against the data. A hypothesis was formed to describe what happened. As data was collected, the hypothesis was tested and revised.

3.2 Generate Solutions

Once the causes of the solids formation had been identified, then solutions were generated through a series of exercises. General brainstorming resulted in a number of potential solutions. Another technique called SCAMPER was also used. With SCAMPER, key words (Substitute, Combine, Adapt, Modify, Put to another use, Eliminate, Reverse) are used as triggers to improve the list of ideas.

3.3 Select Solution

Each recommendation was categorized by benefit and time to implement. High Benefit was defined as any recommendation that solved the problem or added monitoring for early detection. Short Term (quick) was identified as any action that could be implemented before MCU startup. Each quadrant was assigned a priority number. Then each recommendation was placed in a quadrant based on benefit and time to implement. High benefit, quick recommendations were categorized as priority 1. High benefit, slow recommendations were categorized as priority 2. Low benefit, quick recommendations were categorized as priority 3. And low benefit, slow recommendations were categorized as priority 4.

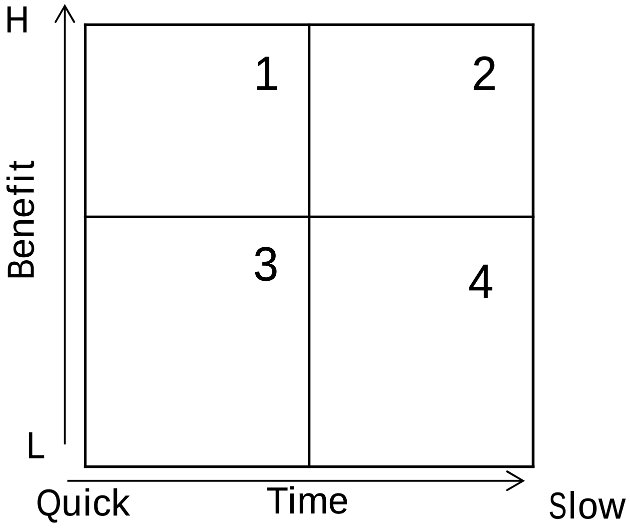


Figure 5: Time/Benefit Matrix

3.4 Implement Solution

The priority 1 recommendations were documented in an engineering pathforward. [6] Actions were entered into STAR and will be tracked to closure through that system. Implementation of the priority 2 and 3 recommendations is currently being planned. Priority 4 recommendations are not scheduled for implementation.

3.5 Evaluate Solutions

Performance data will be collected and analyzed by Engineering as these solutions are implemented. This is currently being done on a monthly basis.

4.0 Results

4.1 Primary Cause

The primary cause of the excessive solids accumulation in the SSRTs and SSFT at MCU is attributed to an increase in the frequency of oxalic acid cleaning of the 512-S primary filter. Agitation in the SSRTs at MCU in response to cold weather likely provided the primary mechanism to transfer the solids to the contactors. Sources of the sodium oxalate solids are attributed to the oxalic acid cleaning solution used to clean the primary filter at 512-S, as well as precipitation from the salt batch feed, which is at or near oxalate saturation.

Under normal conditions, the oxalate concentration in batches from 512-S after primary filter cleanings is high. During normal processing there are approximately 40 batches between cleanings. The number of batches between filter cleanings is limited by filter performance and a 5 wt. % solids limitations in the Late Wash Precipitate Tank (LWPT). This provides a dilution function that dissolves/re-suspends the oxalates so that there is no buildup.

In August 2013 through February 2014, the number of batches between cleaning cycles was less than 20 batches between cleanings, with two cleaning cycles back to back. This prevented the normal oxalate purging process from occurring likely resulting in precipitation of oxalates in the SSRTs. This is a chronic precipitation buildup exacerbated by the increased cleaning frequency. In late January to early February, 2014, the SSRTs were agitated in an attempt to maintain process temperatures within limits, suspending small NAS particles and oxalates. The solids were moved to the SSFT and the contactors. Some of the solids were carried with the DSS as indicated by an increase to the differential pressure in the DSS coalescers. A 512-S primary filter cleaning followed this batch, likely precipitating more oxalates. In mid-February, the SSRTs were agitated again, possibly suspending more NAS particles and oxalates and moving more solids to the SSFT and the contactors. In March, 512-S filter flushes completed prior to the cross-flow filter replacement solubilized oxalates that then precipitated in the SSRTs and SSFT when combined with salt feed.

A timeline showing the sequence of events is shown in Figure 6**.**

In addition to the more frequent filter cleanings and filter flushes prior to the cross flow filter replacement, there were several other events that were investigated as part of the causal analysis. These items included unusually low temperatures during the winter months. MCU implemented a new solvent flowsheet called Next Generation Solvent (NGS) and changed flow ratios of the aqueous and organic streams. The crossflow filter was replaced, which was accompanied by a number of flushes that were not part of the normal flowsheet. All of these changes were considered as potential causes.

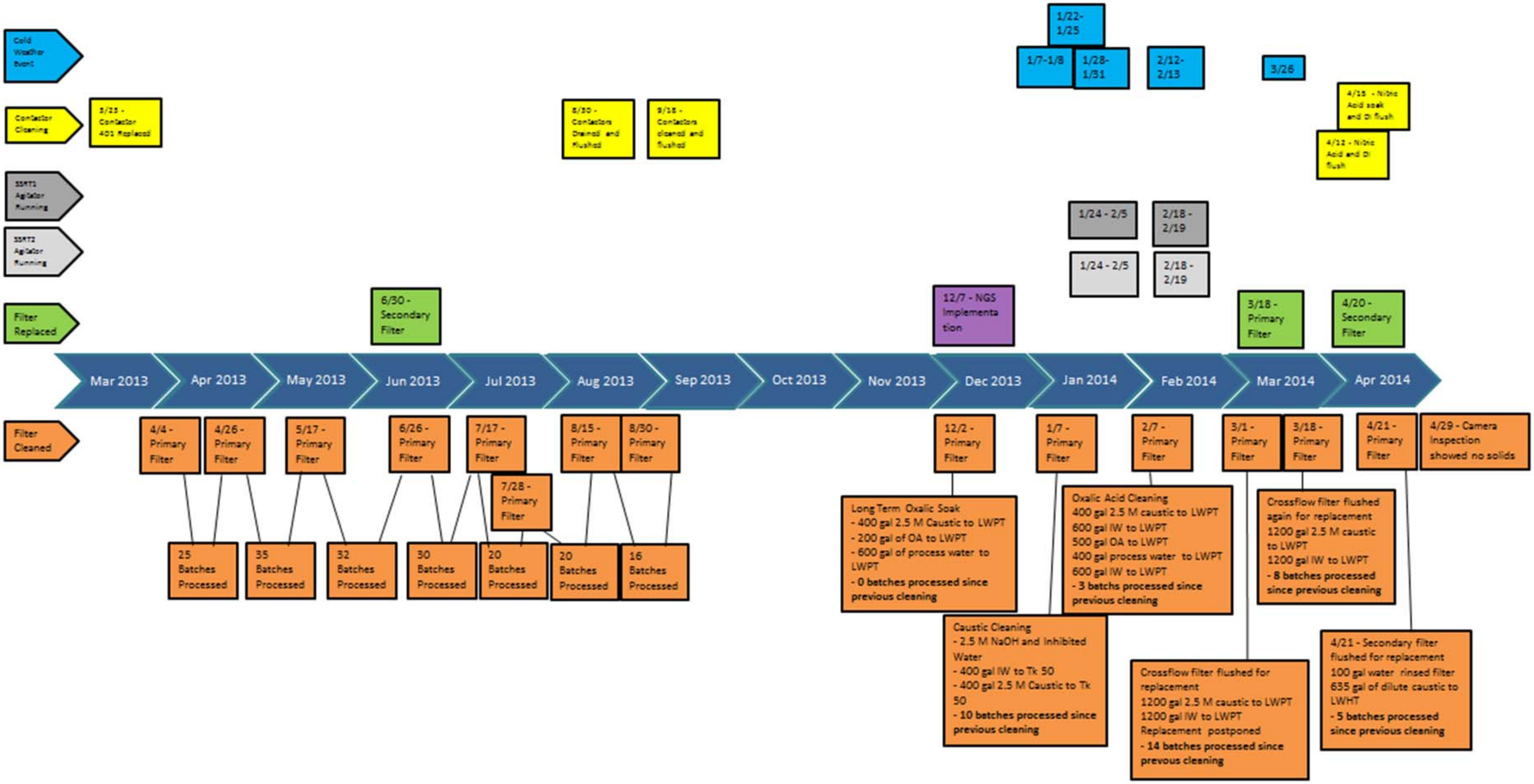


Figure 6: Timeline of Events Leading to Process Upset

4.2 Causal Analysis

The Kepner-Tregoe problem analysis technique was used to bound the problem and explore other possibilities for the event in addition to solids pluggage as shown in Attachment A. Emulsions in the solvent extraction process and misoperation in the plant were evaluated and determined not to be contributors to the problem.

The following problem statement was developed by the team:

> Solids are plugging extraction and scrub contactors and preventing MCU from operating properly.

The probable causes were identified and organized into a fishbone diagram:

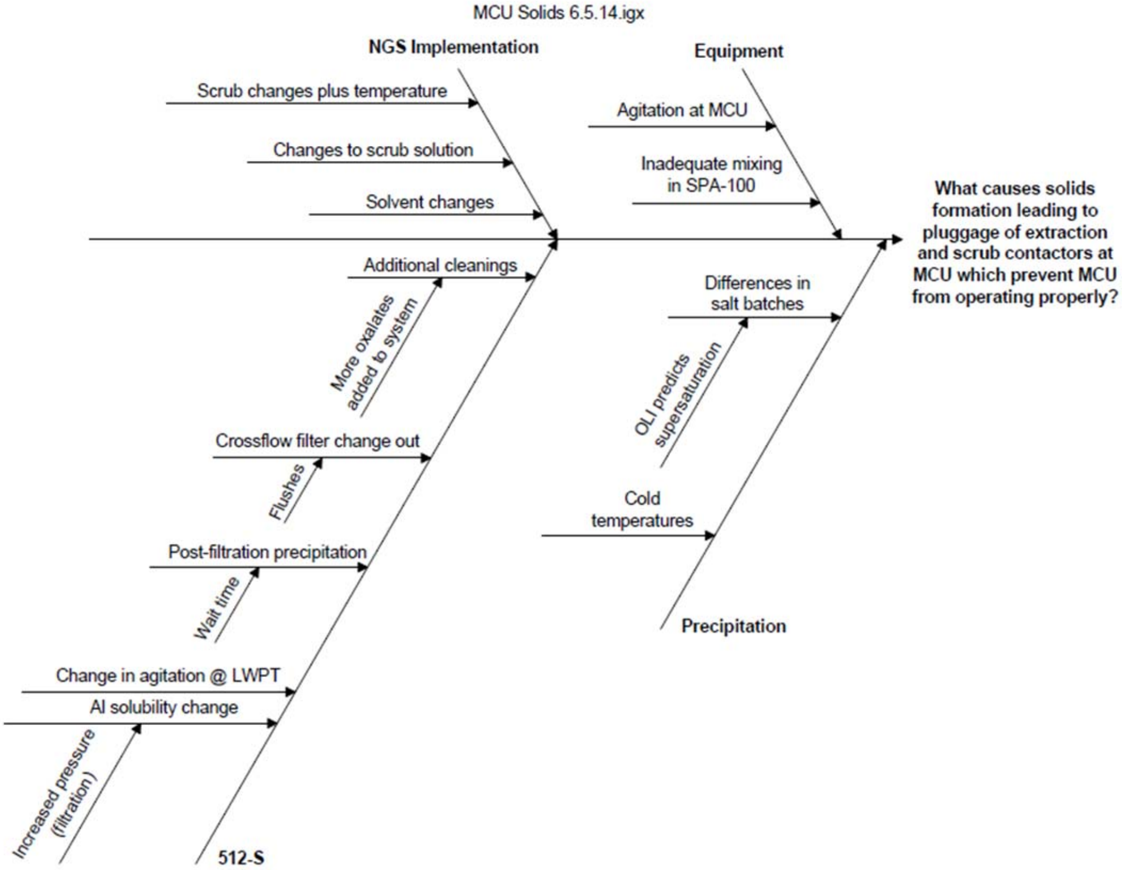


Figure 7: Fishbone Diagram of Potential Causes

From the fishbone diagram, eight potential causes were identified as follows:

- Salt Batch chemistry
- Cold temperatures
- 512-S additional cleaning

- Chronic Buildup
- Post filtration precipitation
- NGS
- Equipment Operation
- 512-S filter changes

4.2.1 Salt Batch Chemistry

Salt batches consistently show a propensity to precipitate solids. The solids that have been of concern include various aluminum hydroxide compounds, sodium oxalate solids and NAS. Solids found in MCU have caused processing problems in the past. A historical perspective of solids found in MCU is shown in Attachment B. Cold feed solutions processed to test the plant before commencement of radioactive operations precipitated NAS solids in both SSRTs and the SSFT. These solids have been in the receipt and feed tanks since that time, but had not hindered operation. The NAS solids were physically moved away from the pump suction and the plant has operated with these solids in place. Agitation in the SSRTs and the SSFT was prohibited to limit the transfer of solids to the contactors. In early 2009, aluminum hydroxide compounds were causing fouling problems in the Strip Effluent Coalescers. Sodium hydroxide was added to keep the aluminum hydroxide in solution. The additional sodium, however, decreased the solubility of sodium oxalates.

The salt waste blended into batches has a tendency to precipitate solids because of the inherent chemistry of the salt waste in the Tank Farms. Chemical adjustments are made to the salt batches to optimize the performance of the salt batch processing through ARP and MCU. The original baseline for salt processing at 512-S and MCU was 5.6 M sodium salt solution, and testing for ARP and MCU was based on salt solution simulants at 5.6 M sodium. However, salt batches have been processed through ARP/MCU with higher sodium concentrations. Significant solids precipitation was observed in downstream facilities for Salt Batches 1, 2, and 6D, with deterioration of performance at 512-S attributed to solids for Salt Batches 1, 2, 5, 6A, 6B, 6C, and 6D (based on the reduction in batches between filter cleanings). OLI Analyzer ™ has been utilized to plan salt batches and determine chemical adjustments required to minimize or prevent solids formation. For this evaluation, OLI Analyzer ™ Version 9.1.2 was used to predict the precipitation of solids in the ARP/MCU Feed Tank (Tank 49H) based on the chemistry of the salt batch. A simple reconciliation was performed, utilizing the Public Mixed Solvent Electrolyte (MSE) database with MSE (Redox) turned on. Table 1 provides the specific salt batch chemistry input into the model. [7]

Table 1: Salt Batch Chemistry in Tank 49H

Salt Batch	**Salt Batch Analyte Concentration [M]**								
	Silicon [Si] [OLI Input SiO_2]	Sodium [Na^+]	Free Hydroxide [OH^-]	Nitrite [NO_2^-]	Nitrate [NO_3^-]	Carbonate [CO_3^{-2}]	Aluminum [Al] [OLI Input $Al(OH)_4^-$]	Oxalate [$C_2O_4^{-2}$]	Sulfate [SO_4^{-2}]
1	6.57E-03†	5.05E+00	7.59E-01	2.76E-01	2.82E+00	3.15E-01	3.85E-01	6.65E-03†	1.28E-01
2	1.72E-03	5.55E+00	2.14E+00	2.22E-01	2.13E+00	1.98E-01[a]	2.62E-01	2.84E-03†	9.29E-02
3	6.00E-03[b]	6.83E+00[b]	2.68E+00[b]	9.76E-01	2.50E+00	9.08E-02	1.96E-01[b]	1.33E-03[b]	6.03E-02
4A‡	5.61E-03	7.34E+00	2.88E+00	9.65E-01	2.68E+00	1.57E-01	2.00E-01	1.65E-03	6.17E-02
4B	2.19E-03	6.57E+00	2.81E+00	8.48E-01	2.52E+00	5.20E-02	1.52E-01	1.38E-03	5.09E-02
5	1.64E-03	6.56E+00	2.36E+00	5.51E-01	2.78E+00	2.34E-01	2.59E-01	2.70E-03	7.48E-02
6A	1.55E-03	6.57E+00	2.28E+00	5.27E-01	2.61E+00	2.26E-01	2.41E-01	3.16E-03	7.24E-02
6B	1.52E-03	6.58E+00	2.25E+00	5.20E-01	2.56E+00	2.24E-01	2.36E-01	3.29E-03	7.18E-02
6C	1.50E-03	6.58E+00	2.23E+00	5.15E-01	2.53E+00	2.22E-01	2.32E-01	3.38E-03	7.12E-02
6D	1.48E-03	6.58E+00	2.22E+00	5.11E-01	2.50E+00	2.21E-01	2.29E-01	3.45E-03	7.09E-02

To investigate precipitation of solids from the salt batch as a potential cause, models of previous salt batches were reviewed and compared. As shown in Figure 8 and Figure 9 below, aluminum hydroxide precipitation was minimized with the addition of sodium hydroxide after Salt Batch 1.

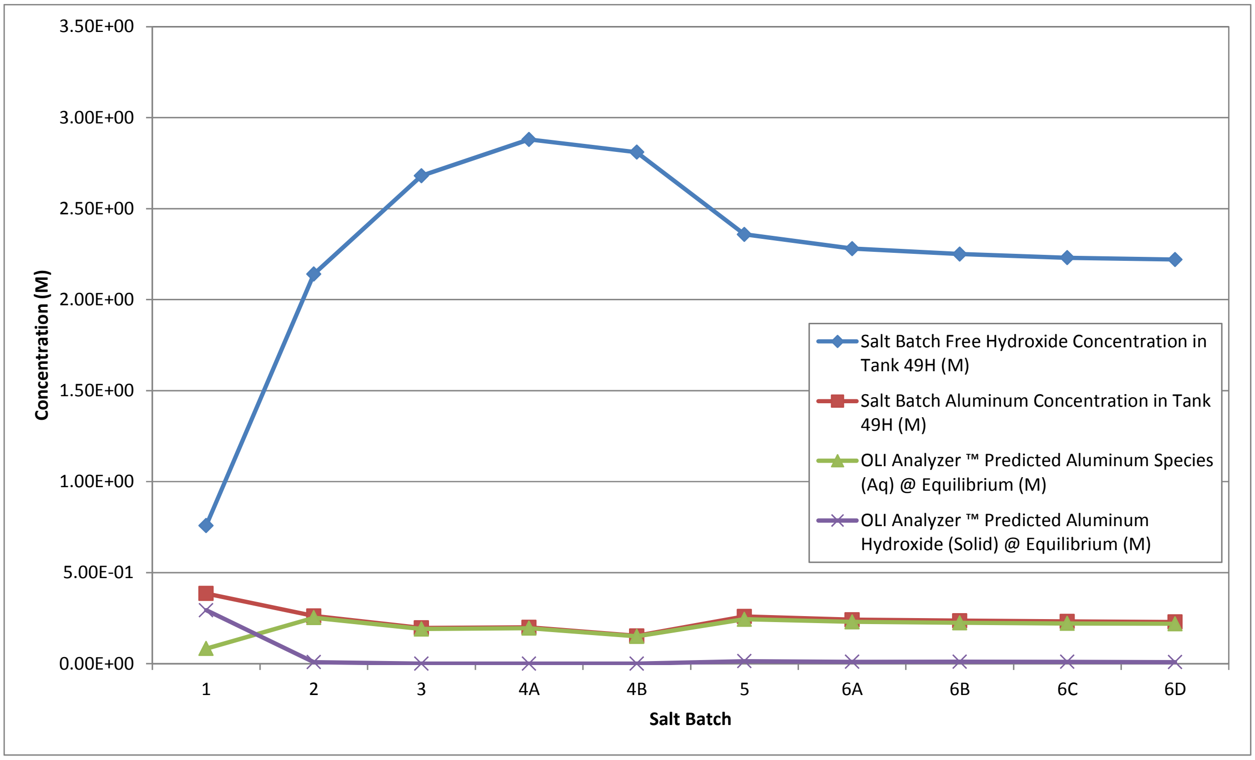


Figure 8: Predicted Aluminum Hydroxide

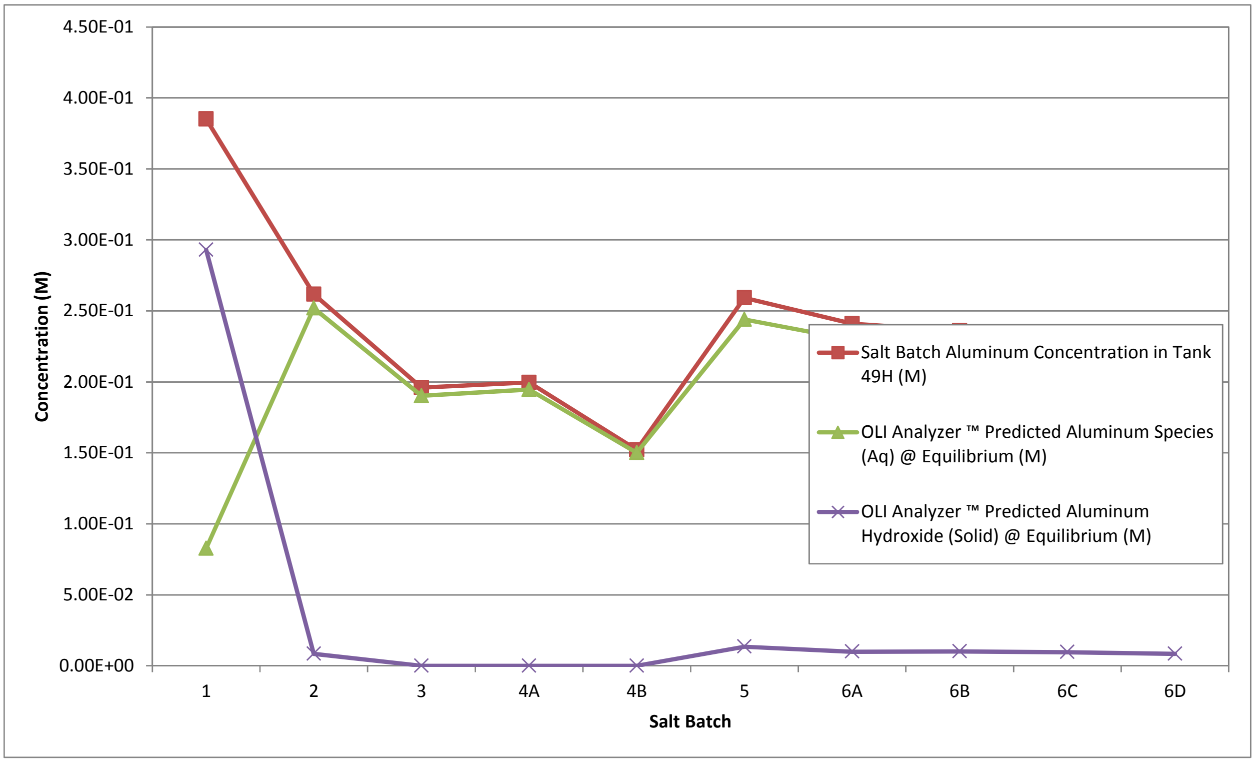


Figure 9: Predicted Aluminum Hydroxide (without sodium hydroxide shown)

NAS is predicted to form in two of the salt batches. This is not a significant concern because the kinetics to form cancrinite are very slow. High temperatures are needed to accelerate the formation.

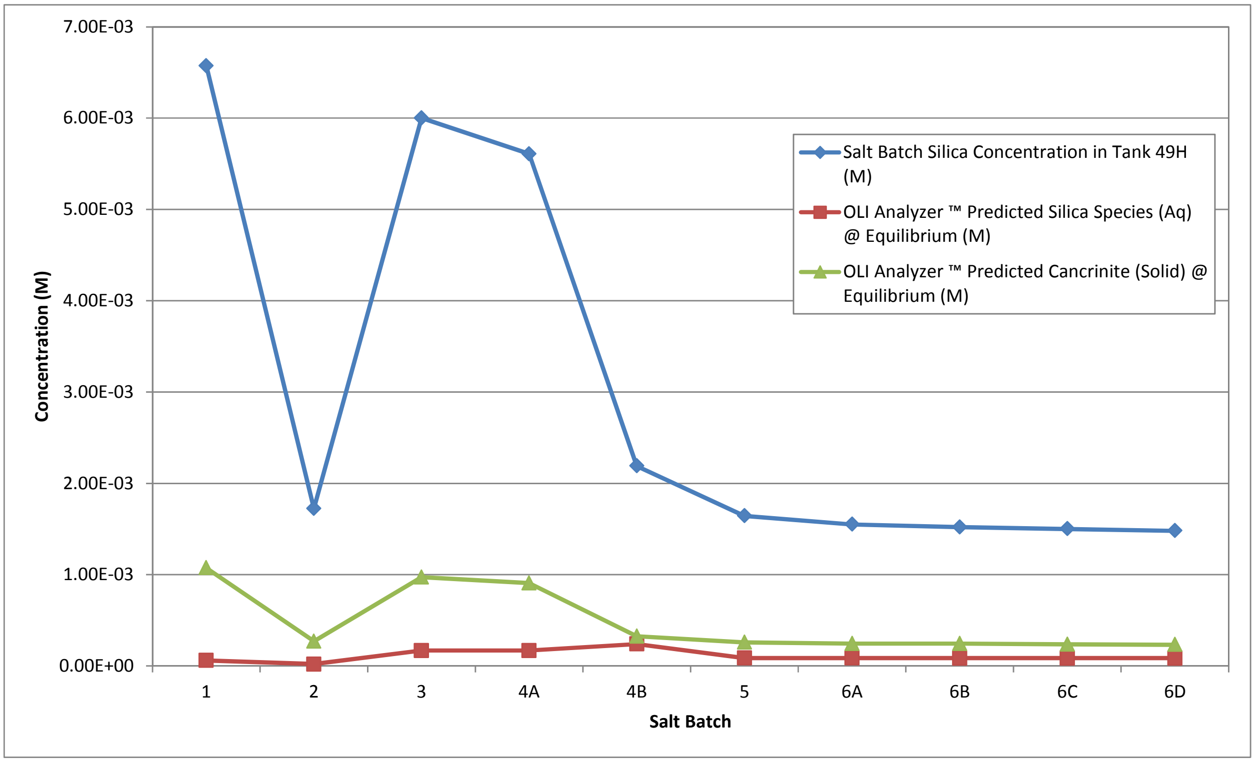


Figure 10: Predicted NAS Formation (in the form of cancrinite)

In every salt batch processed thus far, OLI software predicts that the batch is supersaturated in oxalates and that solids will form. However, salt samples taken in Tank 49 do not normally show solids. Either OLI software overestimates solids precipitation or the solutions are not at equilibrium.

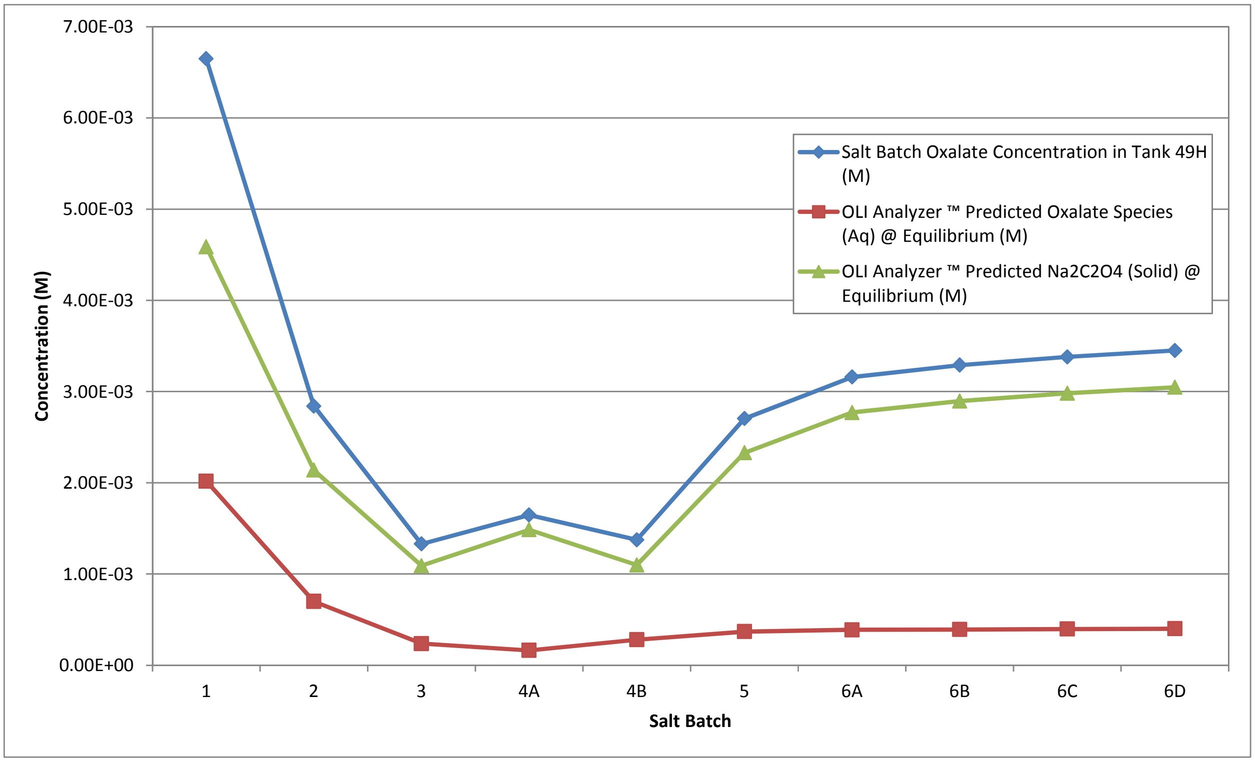


Figure 11: Predicted Oxalate Formation

Therefore, the OLI software predictions were used with a measure of caution. Large changes in OLI software predicted precipitation between model cases were reviewed as discriminators, rather than an absolute value of precipitation or no precipitation. All of the salt batches processed so far have had the propensity to precipitate. However, there have been not any previous issues with oxalate precipitation that caused processing problems in MCU prior to this recent event. The conclusion from this review is that salt batch saturation is likely a contributing cause. Process changes could impact the stability of the salt batch chemistry.

4.2.2 Cold Temperatures

Temperature timeline for the last several years show that this was a very cold year with prolonged periods below freezing.

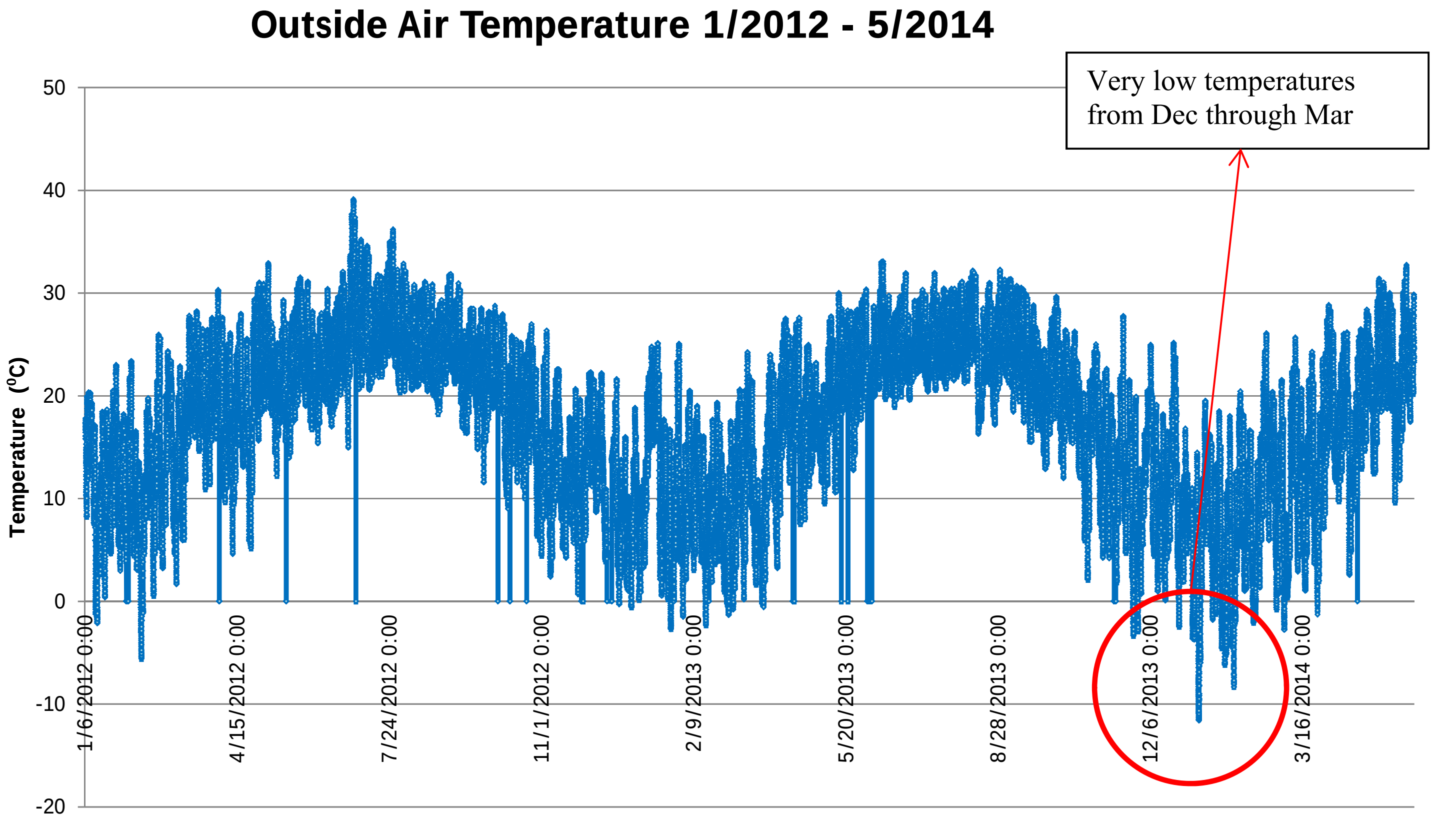


Figure 12: Outside Air Temperature

Generally speaking the ARP strike tanks and the LWPT were between 25-30°C during the cold snaps. The LWPT dipped below 18°C once and one of the ARP strike tanks dipped below 18°C once. The Late Wash Hold Tank (LWHT) and the MCU receipt tanks and feed tanks were between 18-23°C during the cold snaps. The March cold snap did not influence the event because none of the material in the feed system was moved forward for processing in MCU. Also the tanks were at heel volume in March, so that the temperatures measures were vapor space, not solution temperatures. Temperatures in MCU reached 18°C. 18°C is the lower processing limit in MCU and was used as the determining factor. Temperature traces for the time periods in question are shown on the next several pages.

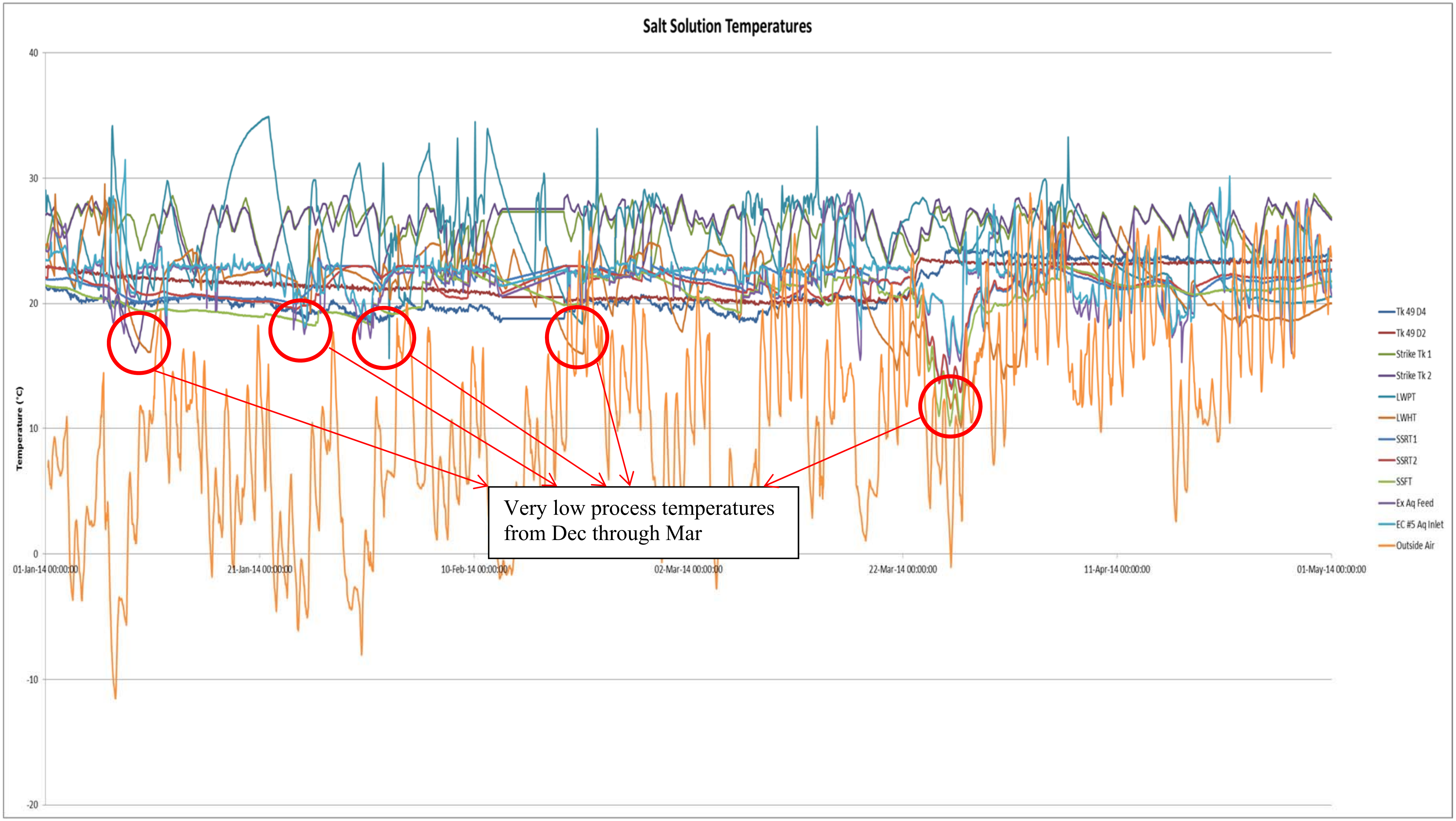


Figure 13: Process Temperatures from January through March

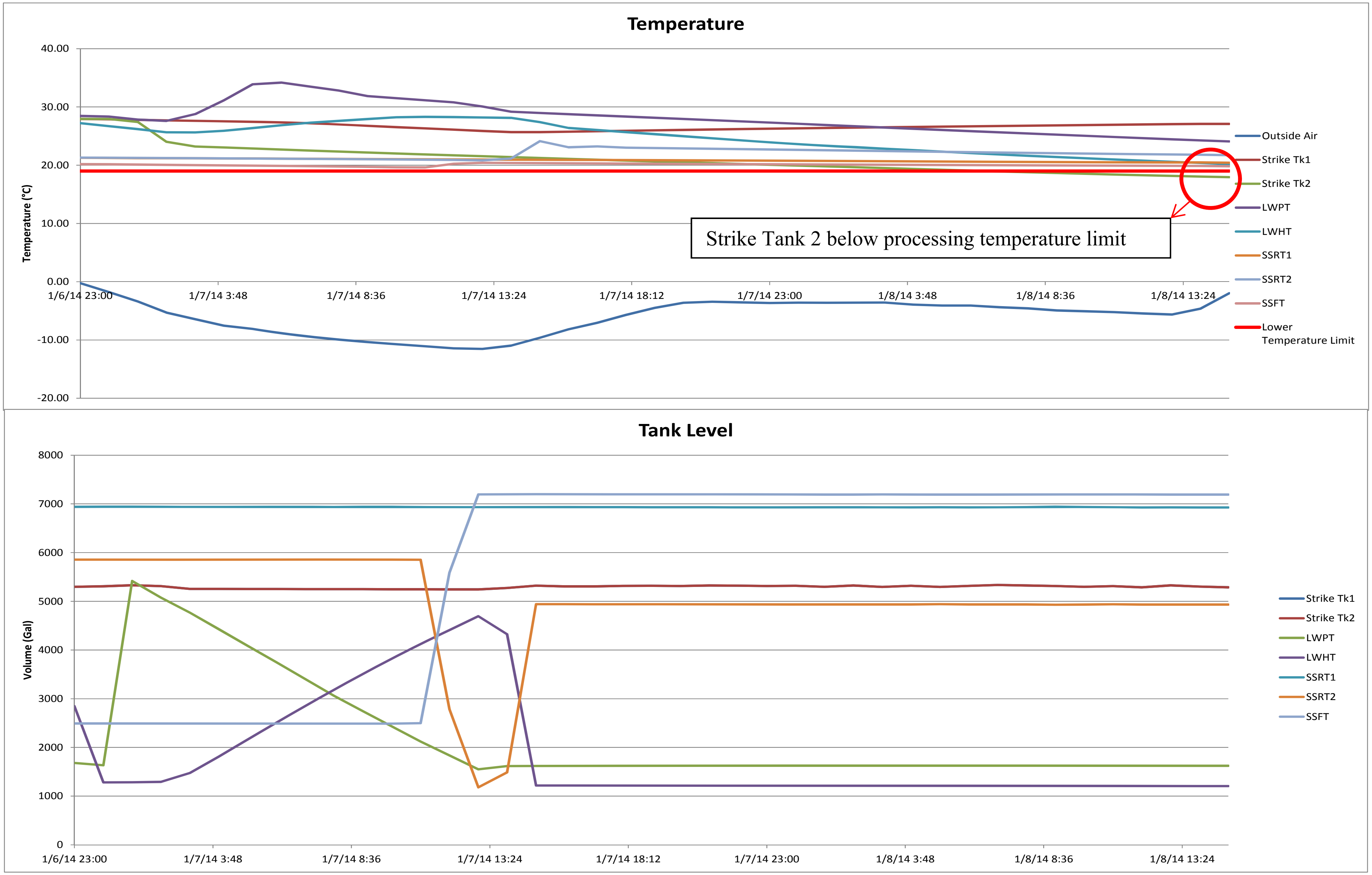
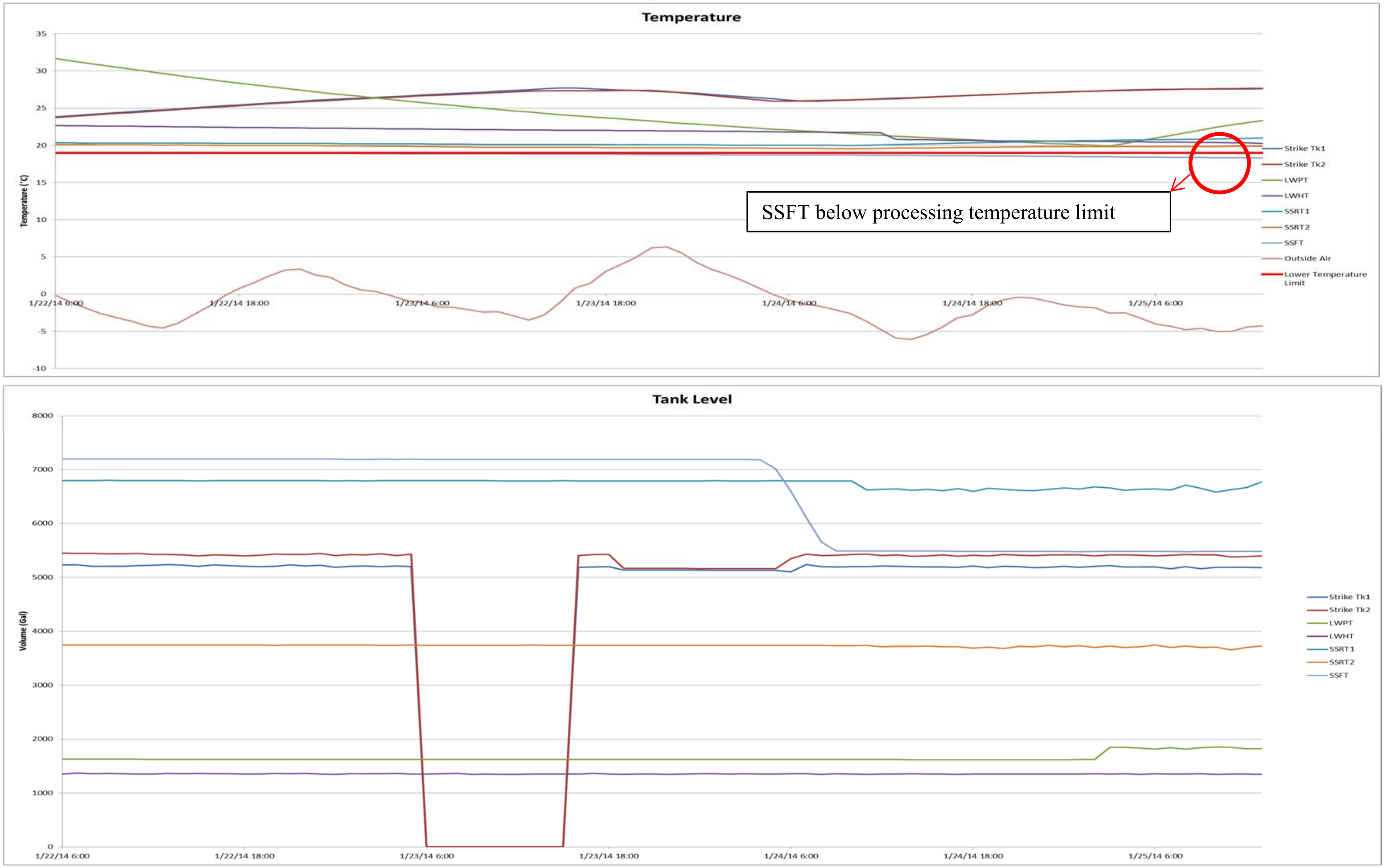

Strike Tank 2 below processing temperature limit

Figure 14: Temperature Trace from 1/6-1/8



SSFT below processing temperature limit

Figure 15: Temperature Trace from 1/22-1/25

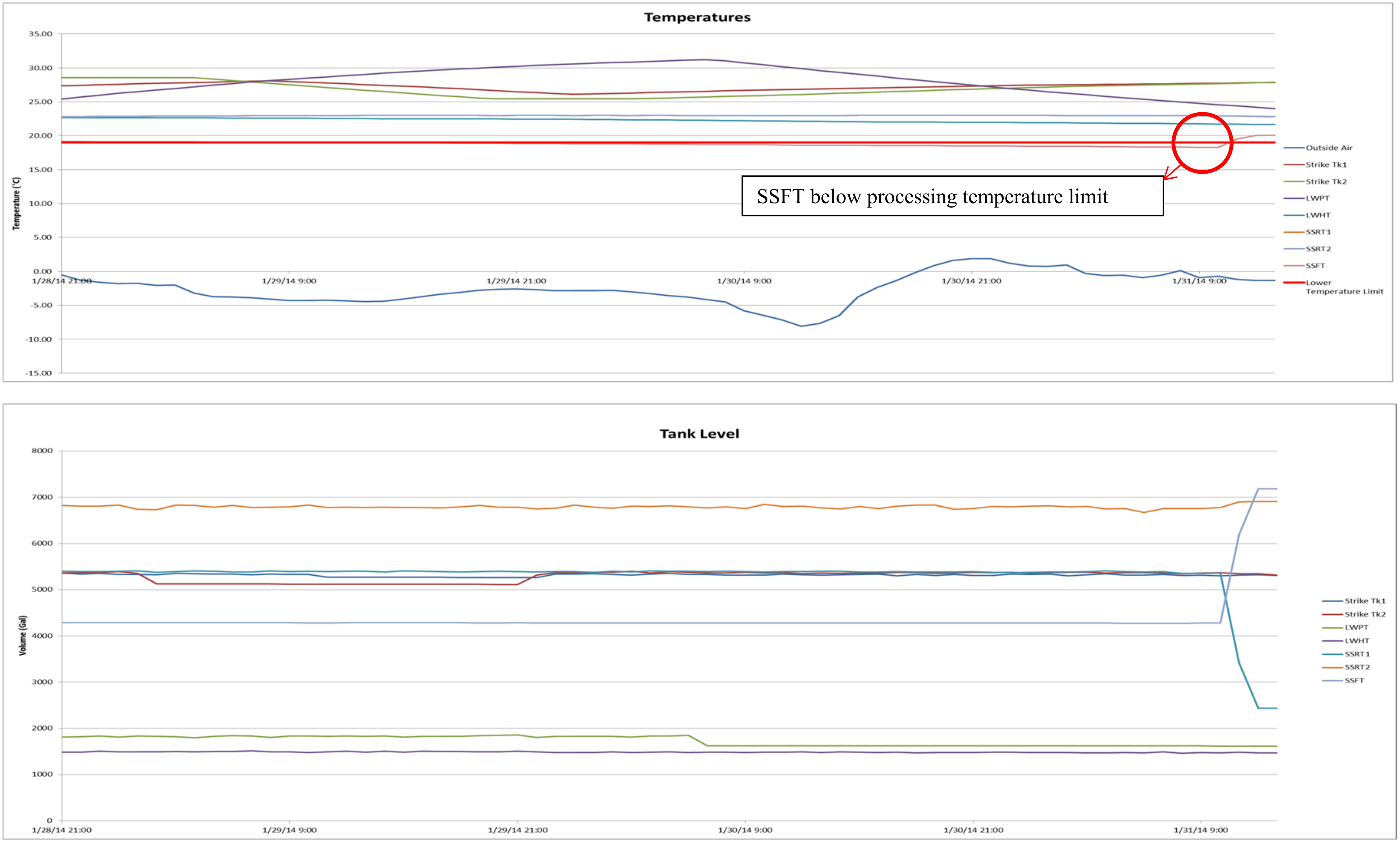
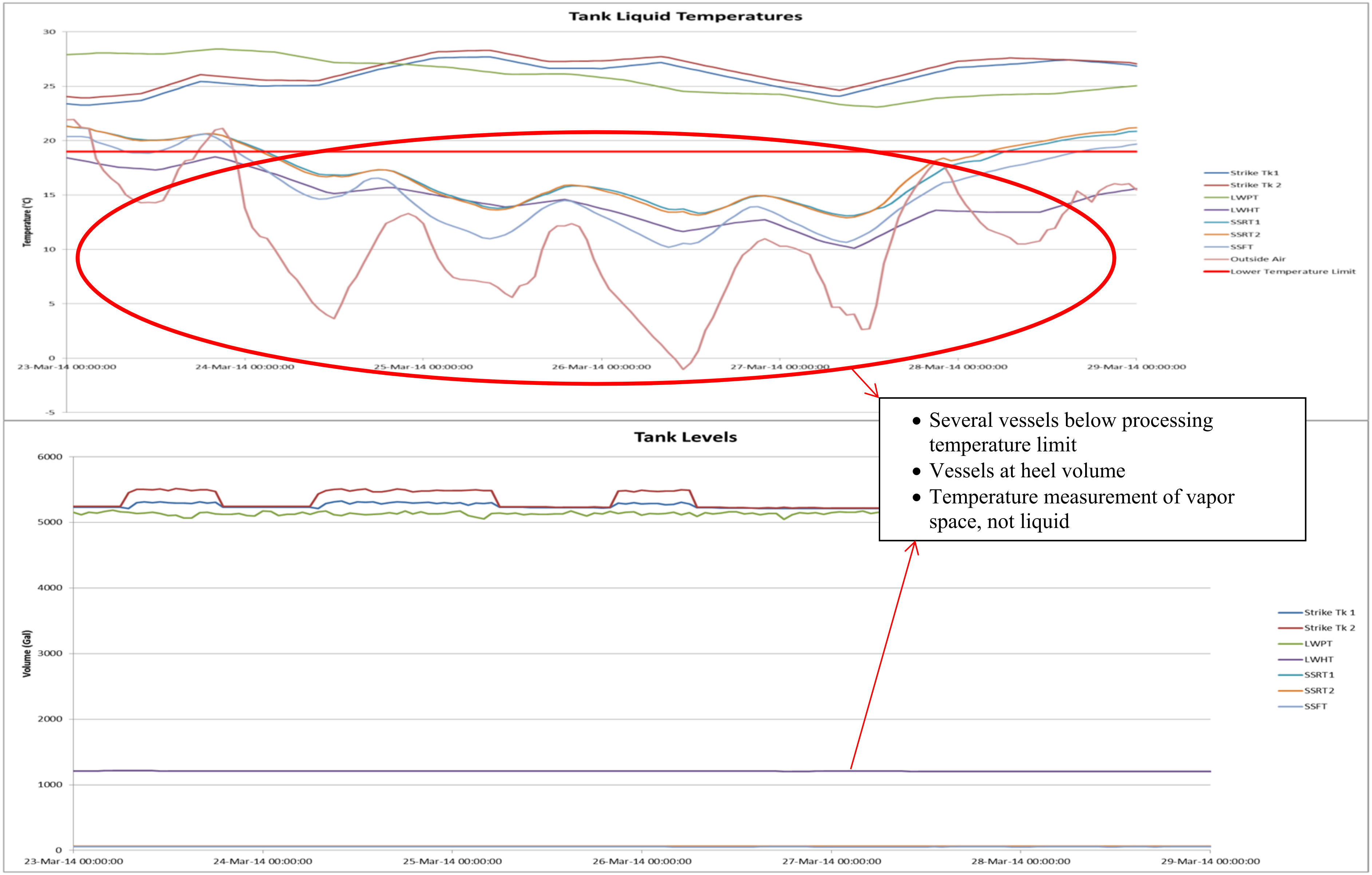

SSFT below processing temperature limit

Figure 16: Temperature Trace from 1/28-1/31



- Several vessels below processing temperature limit
- Vessels at heel volume
- Temperature measurement of vapor space, not liquid

Figure 17: Temperature Trace from 3/26

OLI Analyzer ™ modeling was then completed to identify the impact of the temperature swings during the cold weather periods on precipitation. Modeling shows that decreasing temperature can contribute to aluminum hydroxide precipitation and to a lesser degree oxalate precipitation. A change in temperature from 25°C to 18°C could cause up to 40% of the available Al to precipitate and about 6% of the oxalate to precipitate. NAS seems fairly impervious to the change in temperature. Since the problem encountered in MCU was precipitated oxalate solids, the temperature changes do not appear to be a primary contributor.

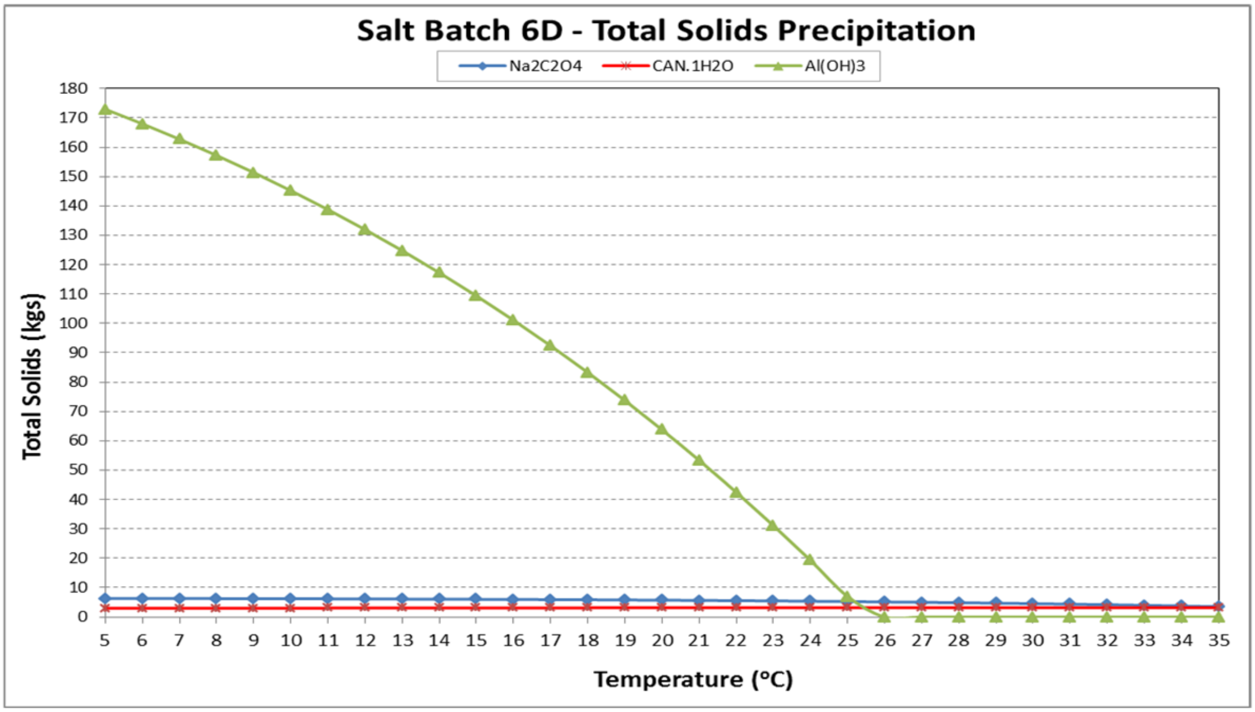


Figure 18: Predicted Solids Precipitation

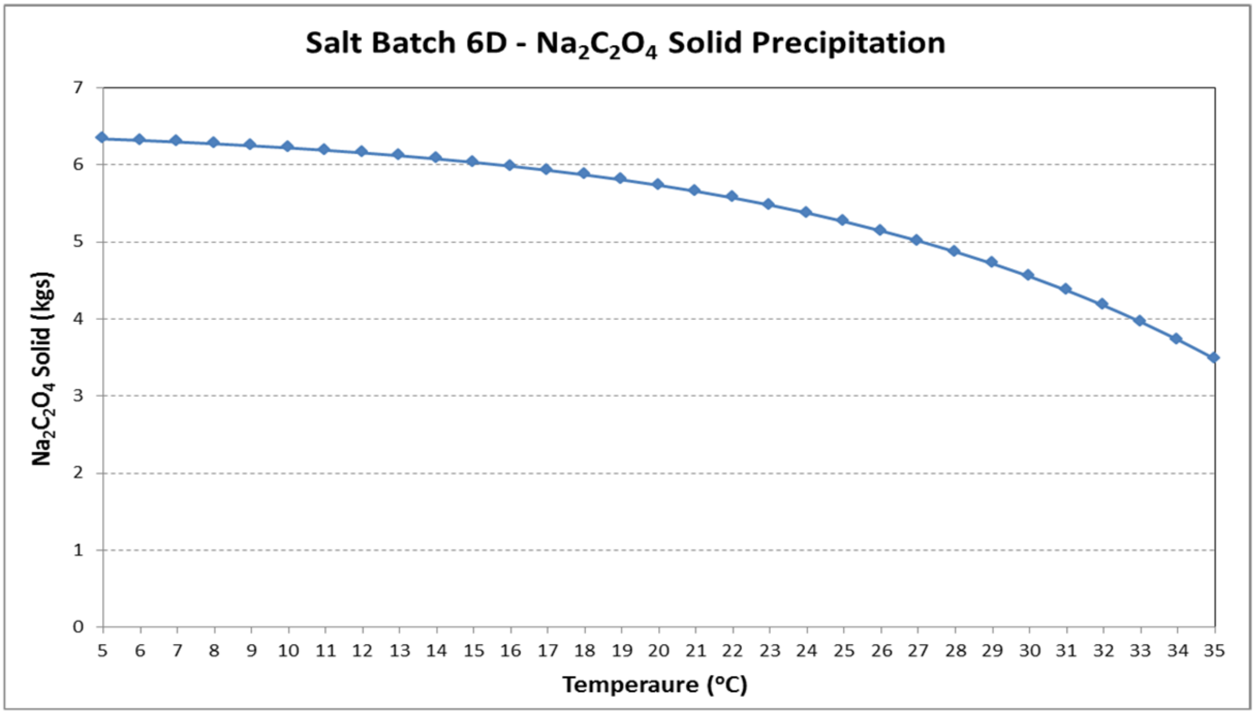


Figure 19: Predicted Oxalate Precipitation

In an attempt to add heat to the system and keep the temperatures within limits to allow operation, the agitation prohibition was lifted. The agitators are not normally operated because the SSRTs and SSFT contain a quantity of NAS solids remaining from cold chemical operation. These solids have been in these tanks since the beginning of radioactive operation without causing any process upsets. The SSRT agitators were operated from 1/24-2/7 and again from 2/18-2/19. A four hour settling period was established before the transfer from the SSRT to the SSFT. The SSFT agitator was not operated. However, it appears that NAS solids were transferred from the SSRT through the SSFT and into the contactor. The evidence supporting this conclusion is that during the first agitation, the DSS coalescers showed a slight increase in differential pressure (dP) and NAS solids were also found in the Extraction Contactor 401 drain line. Analysis showed the NAS solids are cancrinite. Cancrinite requires high temperature, high pressure or extended time to form. Therefore, the material found in the drain line of the contactor was not freshly precipitated and was concluded to be the existing NAS known to be in the tanks. Particle transfer theory would contend that the SSFT pump does not create enough velocity to move particles greater than approximately 10 microns. However, the actual data supports that several kilograms of NAS were transferred. The time line and data traces are shown on the next two pages.

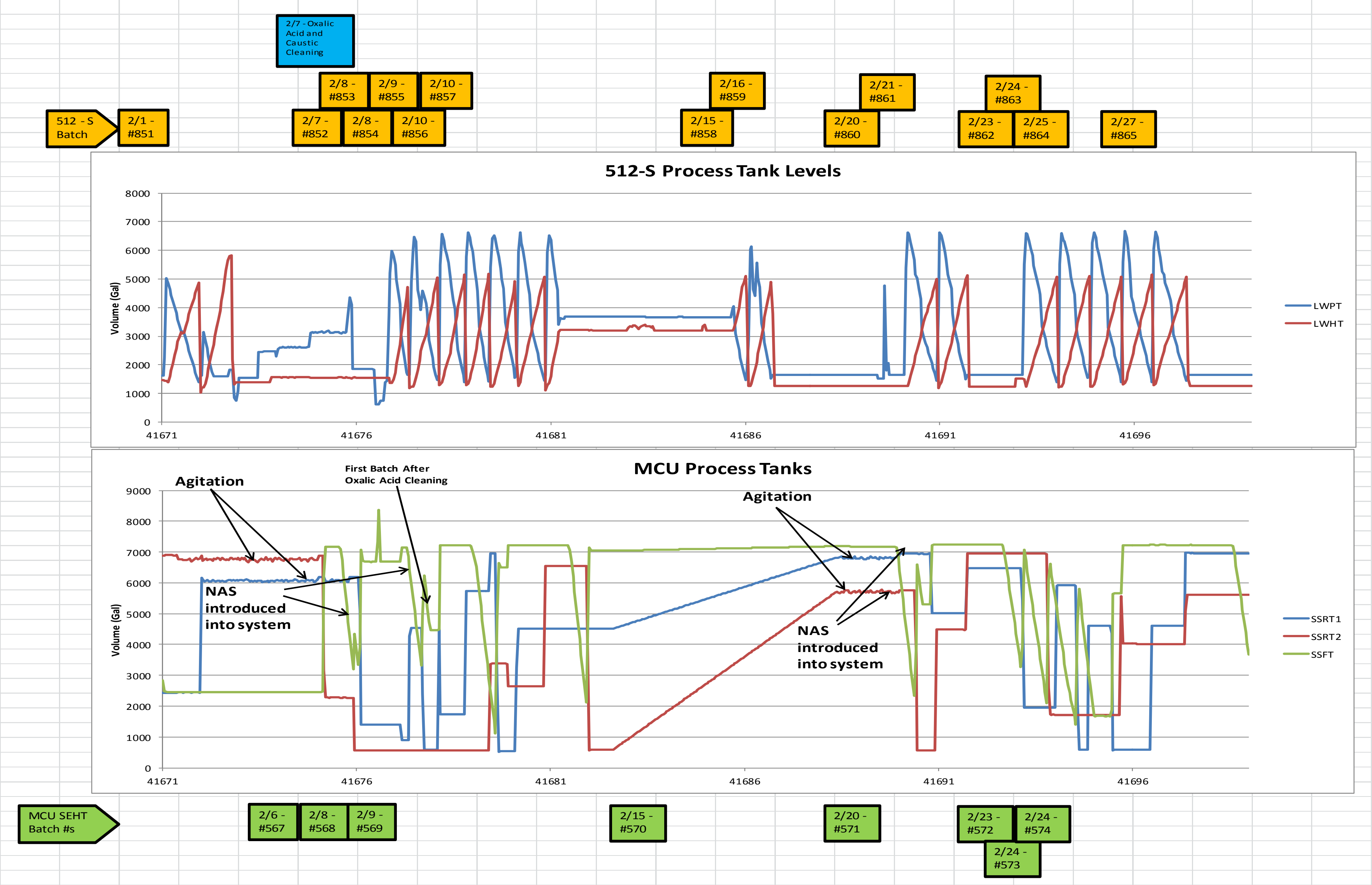


Figure 20: February Process History

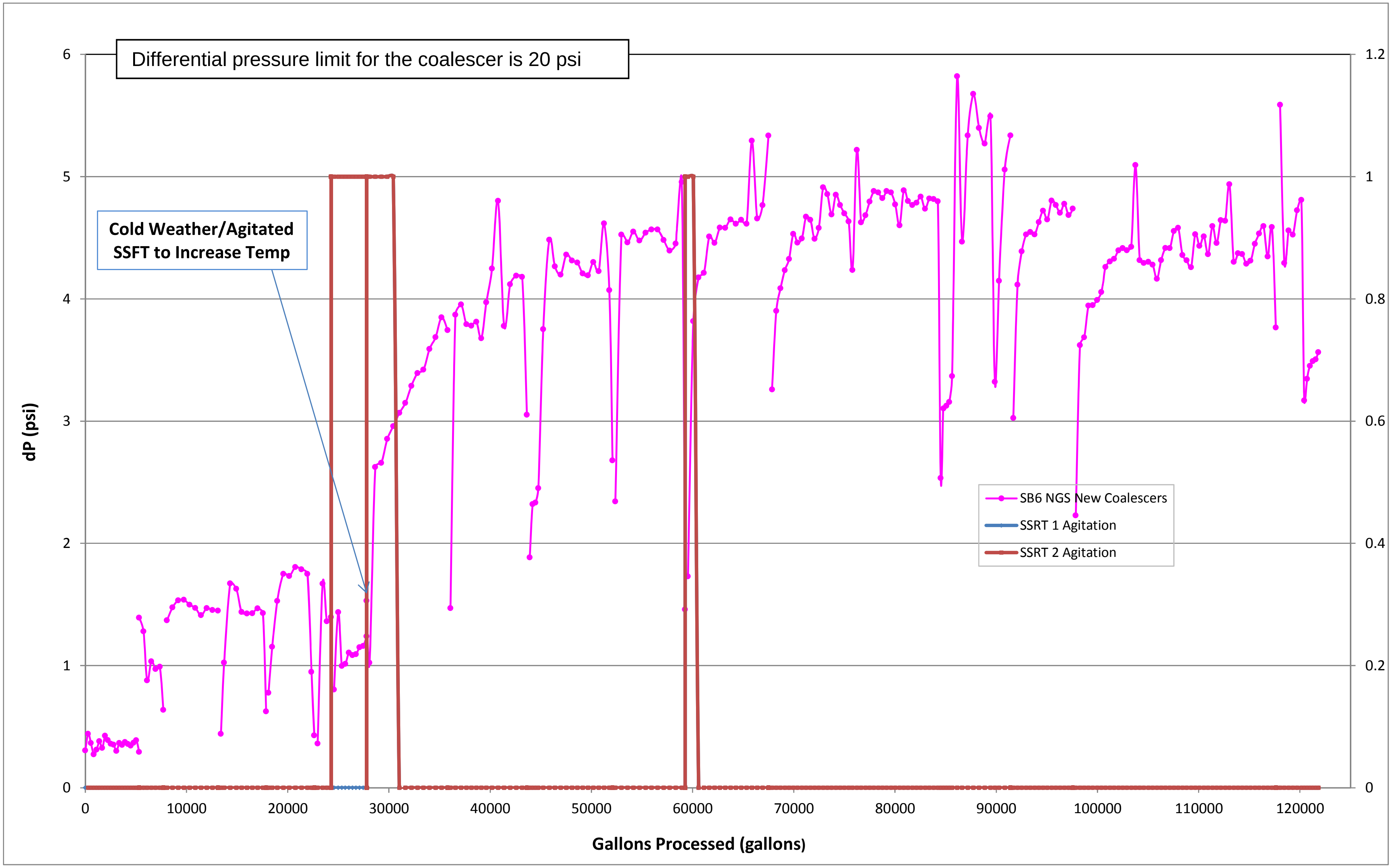
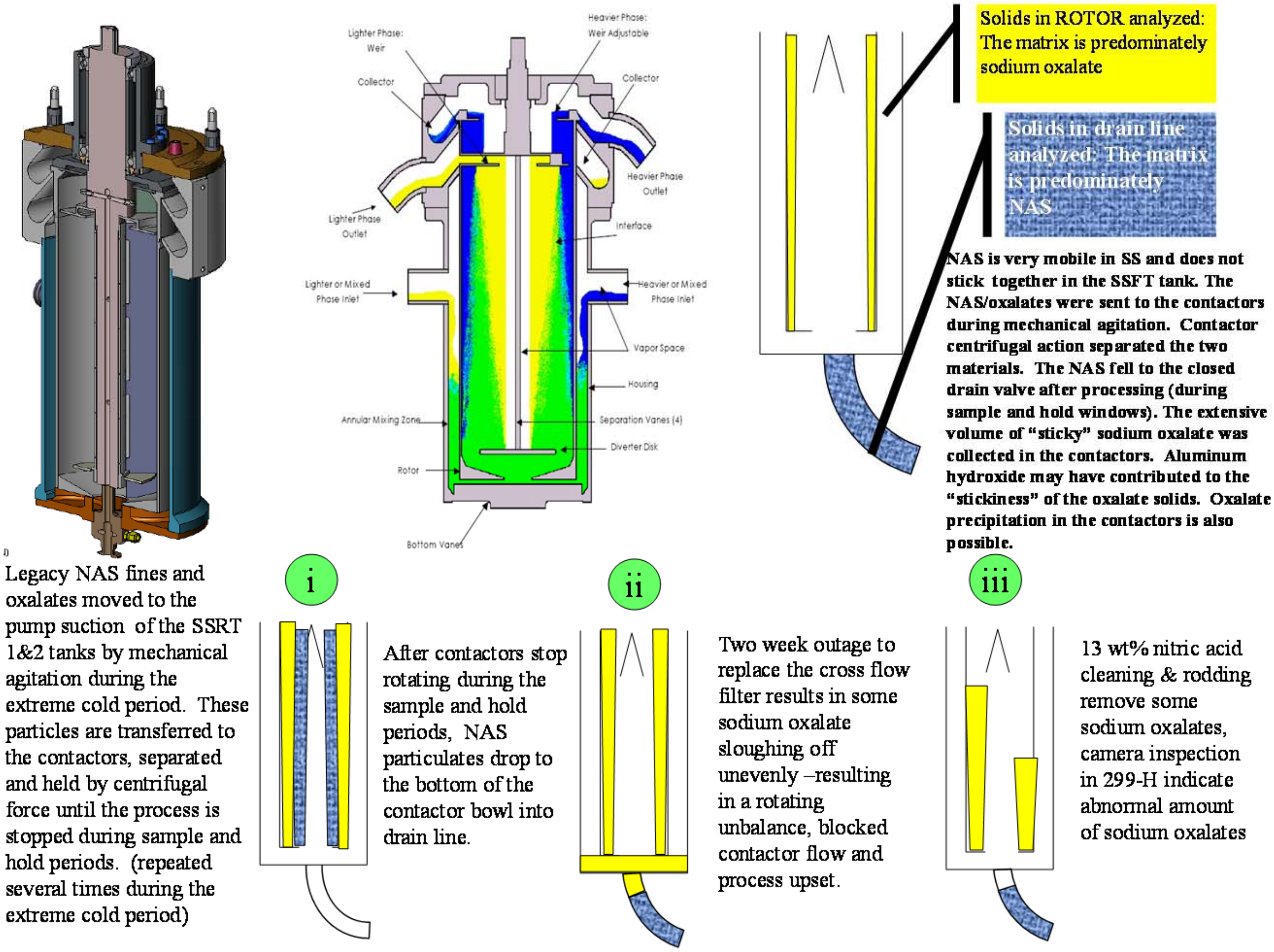


Figure 21: DSS Coalescer Increased dP

Oxalate solids were also likely moved during this agitation. Oxalate solids were found in Extraction Contactor 401. There is a clear demarcation of the NAS solids in the bottom of the drain line and the oxalate solids in the contactor bowl. One possible explanation of this behavior is shown below.



Solids in ROTOR analyzed: The matrix is predominately sodium oxalate

Solids in drain line analyzed: The matrix is predominately NAS

NAS is very mobile in SS and does not stick together in the SSFT tank. The NAS/oxalates were sent to the contactors during mechanical agitation. Contactor centrifugal action separated the two materials. The NAS fell to the closed drain valve after processing (during sample and hold windows). The extensive volume of "sticky" sodium oxalate was collected in the contactors. Aluminum hydroxide may have contributed to the "stickiness" of the oxalate solids. Oxalate precipitation in the contactors is also possible.

Legacy NAS fines and oxalates moved to the pump suction of the SSRT 1&2 tanks by mechanical agitation during the extreme cold period. These particles are transferred to the contactors, separated and held by centrifugal force until the process is stopped during sample and hold periods. (repeated several times during the extreme cold period)

After contactors stop rotating during the sample and hold periods, NAS particulates drop to the bottom of the contactor bowl into drain line.

Two week outage to replace the cross flow filter results in some sodium oxalate sloughing off unevenly –resulting in a rotating unbalance, blocked contactor flow and process upset.

13 wt% nitric acid cleaning & rodding remove some sodium oxalates, camera inspection in 299-H indicate abnormal amount of sodium oxalates

Figure 22: Explanation of Solids found in Extraction Contactor 401 and Drain Line

Although the temperature changes did not directly cause the oxalate precipitation, the agitation done in response to the cold temperatures likely caused the oxalates to be moved from the SSRTs and SSFT to the contactors.

4.2.3 Increased Frequency of 512-S Filter Cleaning

The ARP is housed within two separate facilities, with the MST addition performed in 241-96H and the filtration of MST solids in 512-S. Batches of salt waste are contacted with MST at a dose of 0.2 grams of MST per liter of waste. For each cycle, the solids from a series of batches are combined in the LWPT. The filtrate from the process is sent to the MCU for cesium removal.

The solids are washed to a sodium molarity of nearly 0.5 M, after which they are concentrated and sent to DWPF via the Low Point Pump Pit-Precipitate Pump Tank (LPPP-PPT).

During crossflow filtration, slurry is recirculated through the tube side of the filter from the LWPT. Filtrate emerges on the shell side of the crossflow filter, is forced through a secondary filter, and enters the LWHT. Cold chemicals are added to the surge tank for filter cleaning.

During crossflow filtration, slurry is recirculated through the tube side of the filter from the LWPT. Filtrate emerges on the shell side of the crossflow filter, is forced through a secondary filter, and enters the Late Wash Hold Tank (LWHT). Cold chemicals are added to the surge tank for filter cleaning.

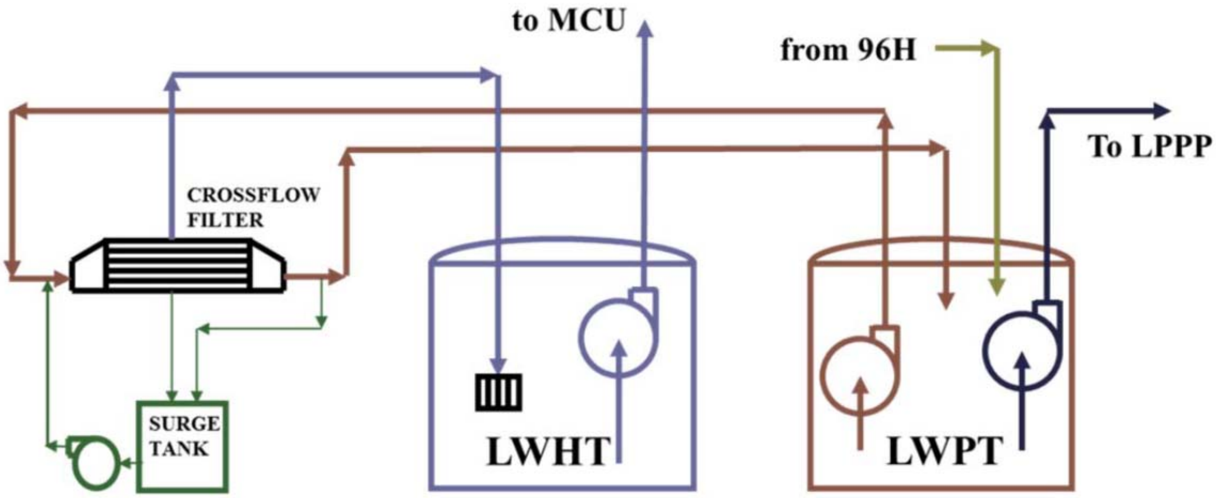


Figure 23: Simplified 512-S Process Flow

A filtration batch is a single 241-96H strike tank batch that has been filtered through the crossflow filter. The processing of multiple batches with accumulation of solids, is referred to as a cycle. Once a cycle is complete, the slurry from the multiple batches in the cycle in the LWPT is washed to lower the sodium concentration. Cleaning of the crossflow filter with oxalic acid takes place at the end of each cycle.

Modeling shows that the washing steps associated with the crossflow filter cleaning solubilize oxalates because of a decreased sodium molarity. This solution is transferred to Tank 50 from the LWHT. The LWHT heel after a transfer is large (~1300 gallons) which leaves a significant amount of oxalates to be combined with high sodium salt feed. The mixing of the high sodium salt feed and the oxalate washing heel can precipitate oxalates. After about four batches are transferred through the LWHT to MCU, the oxalate concentration returns to feed levels.

Over a period of time, the number of filtration batches processed between cleanings has been decreasing therefore increasing the amount of oxalates that enter the ARP/MCU system through this washing step. [8]

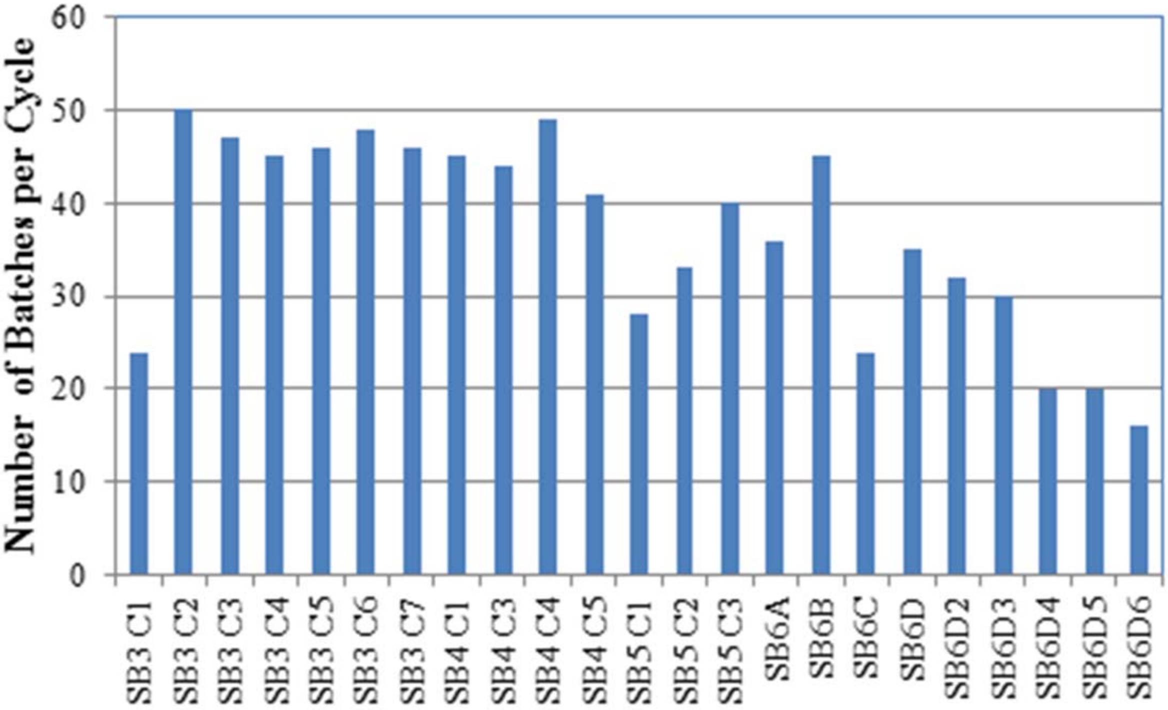


Figure 24: Batches per Cycle

During the period from August, 2013 through April, 2014, there were two oxalic acid cleanings completed back to back and only 13 batches processed before the next oxalic acid cleaning in February of 2014. Contactor vibration readings did increase at about the same time that the cleaning solutions were processed in MCU providing evidence of the presence of solids. [9] There were also two filter flushes with 2.7M sodium hydroxide that were sent to MCU for processing.

A material balance over this time period in question shows about 297 kg were transferred to MCU. Details can be found in Attachment I.

Table 2: Estimate of Oxalates from 512-S added to System

Filter Cleaning Dates/Types	**Sodium Oxalate Accumulation from Salt Batch Prior to Filter Cleaning [kg]**	**Sodium Oxalate Generated from Oxalic Acid Cleaning [kg]**
8/15/2013 Oxalic Acid Primary Filter Cleaning	0.0	36.3
8/30/2013 Oxalic Acid Primary Filter Cleaning	67.5	Included in 12/2/2013 cleaning
12/2/2013 Oxalic Acid Primary Filter Cleaning	0.0	26.0
1/7/2014 Caustic Primary Filter Cleaning	42.2	not applicable
2/7/2014 Oxalic Acid Primary Filter Cleaning	12.7	20.3
3/1/2014 Caustic Primary Filter Cleaning	59.1	not applicable
3/18/2014 Primary Filter Flush	33.7	not applicable
Sodium Oxalate Mass Subtotal [kg]	*215*	*83*
Sodium Oxalate Mass Total [kg]	***297***	

This is an estimate of oxalates that precipitated from solution in the LWPT and were subsequently solubilized and sent to the LWHT. The volume of salt solution processed is based on the number of batches and average batch volume (3700 gal). Heels remaining from oxalic acid cleanings contribute to the precipitated oxalates in the LWPT. Oxalates in the LWPT are predicted to be solubilized with the LWPT solids wash. These oxalates are transferred to the LWHT, where they are anticipated to precipitate upon contact with the salt solution heel.

This correlates very well with the amount of sodium oxalate estimated in the SSRTs, SSFT and contactors. The contactors are estimated to contain about 58 kg of sodium oxalate. The SSRTs and SSFT contained an estimated 239 kg of sodium oxalate by sample analysis for a total of 297 kg. Details can be found in Attachment J.

Table 3: Oxalate Estimate from SSRTs and SSFT

Tank Cleaned	DSSHT Maximum Clean Out Volume (gal)	DSSHT Volume Post Transfer to Tank 50 (gal) Heel Volume	Volume Added to DSSHT (gal)	Volume Added to DSSHT (L)	Oxalate Conc. [mg/L]	Oxalate Conc. [mol/L]	Oxalate Content of DSSHT Maximum Clean Out Volume [mol]	Oxalate Content of DSSHT Heel Volume [mol]	Oxalate Added From Cleaned Tank [mol]	Mass of Sodium Oxalate added from the Cleaned Tank [kg]
DSSHT Heel	-	288	-	-	≤100	1.14E-03	-	1.24E+00	-	
SSFT	6340	278	6062	22946	2806	3.19E-02	7.65E+02	3.36E+01	7.64E+02	102.32
SSFT	2995	256	2739	10367	436	4.95E-03	5.61E+01	4.80E+00	2.26E+01	3.02
SSRT #2	3173	245	2928	11082	2989	3.39E-02	4.08E+02	3.15E+01	4.03E+02	53.99
SSRT #2	3229	451	2778	10517	1049	1.19E-02	1.46E+02	2.03E+01	1.14E+02	15.30
SSRT #2	3850	502	3348	12672	413	4.68E-03	6.83E+01	8.91E+00	4.80E+01	6.43
SSRT #1	6584	484	6100	23089	1498	1.70E-02	4.24E+02	3.12E+01	4.15E+02	55.61
SSRT #1	3497	466	3031	11475	292	3.32E-03	4.40E+01	5.85E+00	1.28E+01	1.71
SSRT #1	3524	484	3039	11505	≤100	1.14E-03	1.51E+01	2.08E+00	9.30E+00	1.25
Total										**239**

The data supports that the additional oxalic acid cleanings at 512-S and the flushes processed in MCU were a primary contributor to the oxalate precipitation.

4.2.4 Chronic Buildup

Modeling and sample results show that the washing step in 512-S solubilizes oxalates that precipitate when salt solution is added. Recent events show that the oxalates precipitated in the SSRTs and the SSFT. No sample or visual data exists to show precipitation in the LWHT, however, the modeling does support this. Modeling also showed it takes about 4 batches through the system before the oxalate concentrations return to feed levels. Sample data from the DSSHT from January 2014 indicated a higher concentration of oxalate in solution than anticipated. The high concentration of oxalate in solution in the DSSHT samples may indicate that oxalate solids are transferred or precipitated in the SSRTs at MCU in large quantities and are subsequently reincorporated into subsequent low oxalate concentration CSS batches transferred to MCU as supported by the samples shown below. [7]

Table 4: DSSHT Oxalate Sample Analysis

MCU DSSHT ~10 512-S batches after oxalic acid cleaning		
DSSHT - Microbatch 5	DSSHT sample associated with NGS Demonstration microbatch 5 on 1/6/2014	304
DSSHT - Microbatch 6a	DSSHT sample associated with NGS Demonstration microbatch 6a on 1/16/2014	340
Anticipated DSSHT (LWHT-1)	This is what would be expected in the DSSHT, with the concentration observed in the LWHT-1 sample with typical 15% dilution at MCU.	87.55

Current data does support that there is a chronic buildup of oxalates in the system. However, successful operations over 4 years show that the system is capable of purging the oxalates. No oxalates were observed during visual inspections of the SSFT in 2010 and 2012. No solids were observed by maintenance personnel when Extraction Contactor 401 was replaced in March of 2013. Extraction Contactor 401 was also successfully drained in September, 2013. The increased cleaning frequency of the 512-S filter in late 2013 did not allow the system to purge the precipitated oxalates.

4.2.5 Post Filtration Precipitation

Clearly, there is precipitation occurring after filtration has been completed as described earlier. The kinetics of post filtration precipitation were investigated. Post-filtration kinetic data collected for Hanford shows that solutions have a tendency to precipitate. The test data shows that oxalate precipitation is not heavily influenced by the components tested by Hanford (phosphates and fluorides which are not key components at SRS). The test data also shows that the oxalate precipitation is not heavily influenced by temperature, which is consistent with the OLI modeling. The test data also shows that the oxalates come to equilibrium within a day or two. [10]

Batches sat in MCU for 10-20 days in January, 2014 before processing at the beginning of February, 2014. This is not very unusual since the plant has been down in the past without being de inventoried for more than 10 days. While post filtration precipitation is occurring, there is no supporting evidence that time between filtration and MCU processing was a primary cause.

4.2.6 NGS

One of the significant changes made before the process upset was the change in flowsheet to NGS. MCU uses a four-part organic solvent developed by Argonne National Laboratory (ANL), SRNL and Oak Ridge National Laboratory (ORNL): 1) diluent/fluidic carrier; 2) calixarene extractant; 3) solubility modifier, and 4) suppressor. An improved flowsheet based on a new solvent (NGS) originated by ORNL has been developed to improve the extraction and stripping of cesium from clarified salt solution. This new flowsheet employs a new extractant and suppressor in the solvent as well as new scrub and strip cold chemical feeds. NGS utilizes the new extractant MaxCalix, more formally known as 1,3-alt-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6. Like BOBCalixC6, MaxCalix is a highly selective calixarene extractant which has a high affinity for cesium ions and a low affinity for sodium ions. The cesium affinity for both extractants is roughly the same; however, MaxCalix has a significantly increased solubility over BOBCalixC6 in the diluent Isopar™ L, thus enabling the extractant concentration to be increased from 7 mM to 50 mM (i.e., a 7x increase).
The suppressor is present in the solvent to improve stripping performance by suppressing the effects of anion impurities and lipophilic surfactants. The BOBCalixC6 based solvent system utilizes trioctylamine (TOA) as the suppressor. However TOA does not successfully function in the NGS system with the new strip chemistry. An alternative suppressor, TiDG, also known as (tris(3,7-dimethyloctyl)guanidine hydrochloride), was chosen for the NGS system because of its effectiveness, stability, and lipophilic characteristics.

The BOBCalixC6 based solvent system operated under a nitrate swing principle, which drives the transfer of ions between the aqueous and solvent phases depending on the concentration of nitrate in the aqueous phase. The NGS system operates under a pH-swing principle, which drives the transfer of ions between the aqueous and solvent phases depending on the pH of the aqueous phase. In the BOBCalixC6 based solvent system the scrub solution is 0.05 M nitric acid. The NGS flowsheet changes the scrub solution to 0.025 M sodium hydroxide. In the

BOBCalixC6 based solvent system the strip solution is 0.001 M nitric acid. The NGS system utilizes a 0.01 M boric acid as the strip solution.

To avoid the costly removal of the original solvent, the NGS solvent was introduced as a blend with the BOBCalixC6 into the system resulting in the following composition. [1]

Table 5: MCU Solvent Composition

Solvent	Constituent Concentrations (Nominal)
BOBCalixC6 Based Solvent	BOBCalixC6 = 0.007 M Cs-7SB = 0.750 M TOA = 0.003 M Isopar-L balance (69 wt. %)
NGS Blend	MaxCalix = 0.0465 M Cs-7SB = 0.500 M BOBCalixC6 = 0.0035 M TiDG = 0.003 M TOA = 0.0015 M Isopar-L balance (74 wt. %)
Pure NGS	MaxCalix = 0.050 M Cs-7SB = 0.500 M TiDG = 0.003 M Isopar-L balance (74 wt. %)

The initial evaluation of the flowsheet focused on the mixing of the scrub and salt solution feed since all of the solids were found in the extraction and scrub contactors. OLI Analyzer ™ results indicated no impact to solids precipitation by changing the scrub solution from acidic (0.05M HNO_3) to basic solution (0.025M NaOH). The scrub actually performs a dilution function for the oxalates.

Table 6: Impact of Scrub Addition on Oxalate Precipitation

Case 1 - Maintain Constant Temperature Throughout Tk49, 96H, 512-S, &MCU (NGS Flowsheet - SB6D)										
Stream	SB #6D Sol		Water Addition	SB#6D After Water Addition @96H		Temperature Impact		Scrub Addition (0.025M NaOH)	After Mix with Scrub	
	Liquid	Solid	Liquid	Liquid	Solid	Liquid	Solid	Liquid	Liquid	Solids
Temp (oC)	25	25	25	25	25	25	25	25	25	25
Pressure (atm)	1	1	1	1	1	1	1	1	1	1
pH	14.46		6.998	14.42		14.42		12.32	14.35	
Unit		kg			kg		kg			kg
Al(OH)3		6.81			7.80		7.80			11.15
Na2C2O4		5.09			4.90		4.90			4.31
CAN. 1H2O		3.07			3.07		3.07			3.05
Total Mass of Solid (kgs)		14.96			15.76		15.76			18.51
Volume of Solids (gals)	3713.69	1.31	100	3810.72	1.40	3810.72	1.40	254	4057.36	1.69

The impact of the change in strip solution was also evaluated. Since oxalate, like borate, is among the least extractable anions, it will remain in the aqueous phase in competition with highly extractable nitrate. Thus, oxalate is not expected to be significantly extracted as the anion of any cationic species in the organic phase. Under the alkaline conditions of the extraction and scrubbing sections, the guanidine will be neutral and not an active participant in extraction. Therefore guanidine will not contribute to the precipitation of oxalates.

A survey of the entire scope of NGS testing was completed to determine if any testing anomalies could be attributed to oxalate precipitation. No anomalies were noted that could have been caused by oxalate precipitation. In fact, the Savannah River Remediation (SRR) simulant used in NGS and BOBCalixC6 testing was at the baseline 5.6M. No oxalate solids precipitation was noted during the testing; however, the oxalates were not at saturation. Parsons ran a high sodium molarity test (around 7.6M Na) with supersaturated oxalates. However, Parsons filters the simulants directly prior to testing and did not observe any indications of solids during their testing.

- Vibration was performed occasionally via a hand held unit.
- Solids were not noted in any other the samples, this includes inter-stage samples as well normal DSS & SE samples.
- Inter-stage samples did not indicate high O/A in Aqueous streams or high A/O in organic streams.
- Hydraulic performance was normal, no indications of solids (weir) pluggage.

Parsons did not visually inspect contactors upon completion of testing. Contactors were acid cleaned and the acid was disposed of without analysis.

The data does not support that NGS caused any of the oxalate precipitation, especially considering that the oxalates were found upstream of the solvent extraction system. However, some limited testing in SRNL is recommended to resolve concerns.

4.2.7 Equipment Operation

MCU equipment operation was evaluated as a cause of the solids precipitation. The scrub and salt solution feed come together in the SPA-100. Inadequate mixing of the differing pH streams might contribute to solids precipitation. The test configuration of the SPA-100 is shown below.

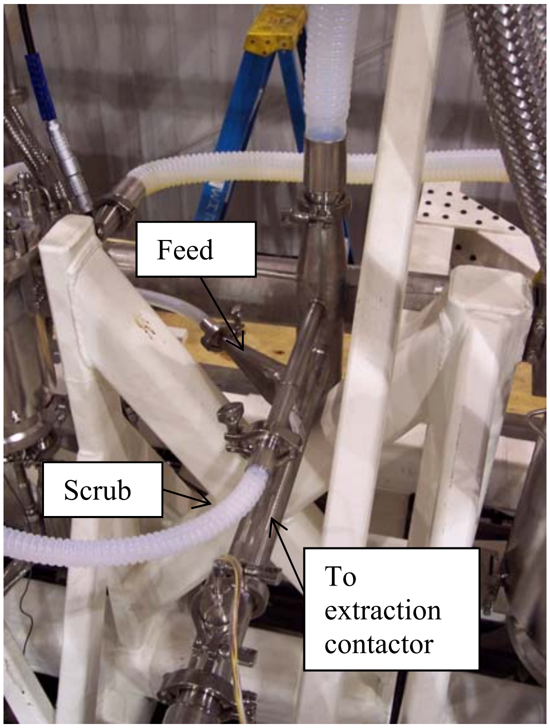


Figure 25: SPA 100

OLI Analyzer ™ results indicate that minimal impact to solids precipitation with respect to partial mixing in SPA-100. The SPA-100 was also inspected with no sign of solids, although flushing completed before inspection might have removed oxalates.

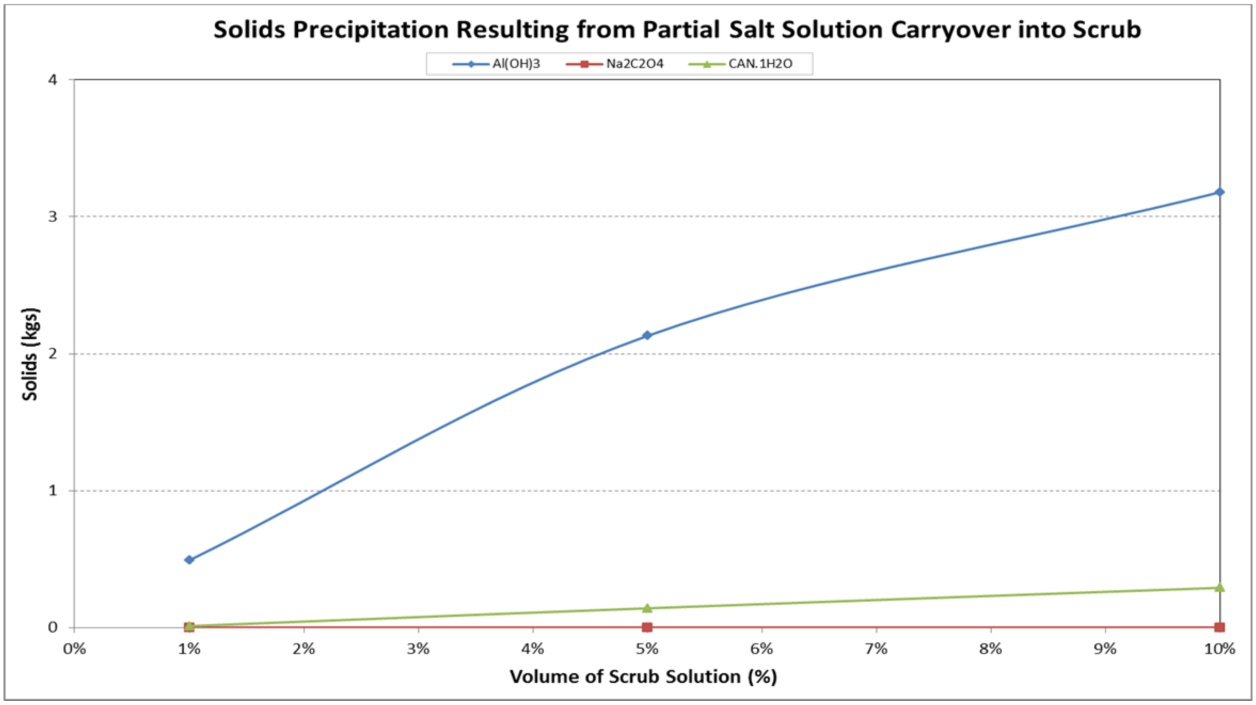


Figure 26: Solids Precipitation Resulting from Partial Salt Solution Carryover into Scrub

Malfunction of Extraction Contactor 401 drain line valve was also identified as a possible contributor. If the valve was not operating properly, then solids might build up in the drain line and into the contactor. During an entry into the contactor enclosure, the valve was verified to open and close properly through video inspection. Data does not support equipment malfunction as an apparent cause of the solids precipitation.

4.2.8 512-S Filter Change

The 512-S 0.1 micron crossflow filter had reached the end of its life and was replaced on 3/18/2014 with a 0.5 micron filter. The larger pore size of the replacement filter might allow solids to pass through and deposit in MCU. However, only 3 hours of feed solution was processed after the filter was replaced. Three hours of process feed is not enough to accumulate the mass of solids observed in the MCU system. The high vibrational data upon startup indicates that solids were likely present prior to processing the post-filter replacement feed material. Therefore, the replacement filter did not contribute to the oxalate precipitation.

4.3 Summary of Causal Analysis

The primary cause of the event was an increase in the amount of oxalic acid cleaning at 512-S, leading to precipitation in the SSRTs and SSFT when combined with salt solutions at or near oxalate saturation. Agitation in response to the cold weather provided a mechanism to transfer the solids to the contactors. Flushing done to facilitate changing the cross flow filter likely solubilized oxalates in 512-S adding to the precipitation in the SSRTs and SSFT. The flowsheet change to NGS, direct temperature changes, equipment malfunction and the 512-S crossflow filter replacement did not contribute to the oxalate precipitation problem. Each potential cause, the data needed to evaluate, the expected result and the actual result is summarized in Attachment C.

5.0 Recommendations

A total of 53 recommendations were generated. Each recommendation was prioritized for benefit and time to implement. High Benefit was defined as any recommendation that solved the problem or added monitoring for early detection. Short Term was identified as any action that could be implemented before MCU startup. Each quadrant was assigned a number.

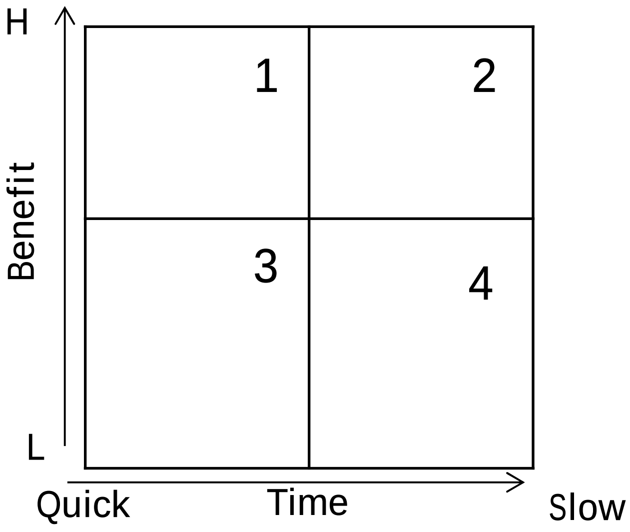


Figure 27: Time/Benefit Matrix

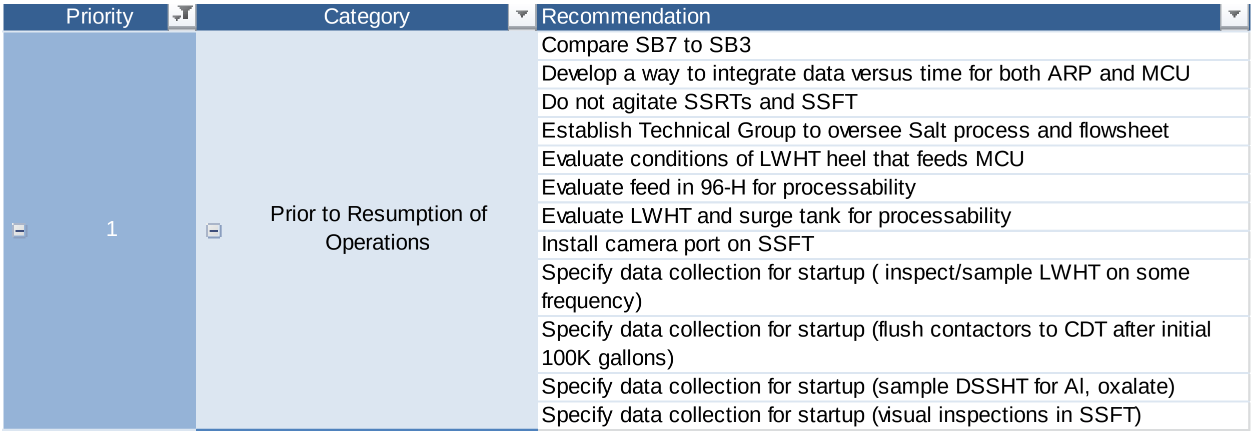
Then each recommendation was placed in a quadrant based on benefit and time to implement, resulting in the following matrix.

Table 7: Priority Matrix

	Priority	Number of Recommendations
High Benefit/Short Term	1	12
High Benefit/Long Term	2	32
Low Benefit/Short Term	3	1
Low Benefit/Long Term	4	8

The priority 1 recommendations were documented in an engineering pathforward and all actions were entered into STAR and will be tracked to closure through that system. [6] All of the priority 1 recommendations are risk mitigation and not preventative in nature.

Table 8: Priority 1 Recommendation Completed Prior to Resumption of MCU Operations



Priority	Category	Recommendation
1	Prior to Resumption of Operations	Compare SB7 to SB3
		Develop a way to integrate data versus time for both ARP and MCU
		Do not agitate SSRTs and SSFT
		Establish Technical Group to oversee Salt process and flowsheet
		Evaluate conditions of LWHT heel that feeds MCU
		Evaluate feed in 96-H for processability
		Evaluate LWHT and surge tank for processability
		Install camera port on SSFT
		Specify data collection for startup (inspect/sample LWHT on some frequency)
		Specify data collection for startup (flush contactors to CDT after initial 100K gallons)
		Specify data collection for startup (sample DSSHT for Al, oxalate)
		Specify data collection for startup (visual inspections in SSFT)

The priority 2 and 3 recommendations develop the additional knowledge and skills to prevent reoccurrence. These recommendations were organized into 4 focus areas:

- Improve understanding of oxalate equilibrium and kinetics in salt solutions
- Reduction/elimination of oxalic acid cleaning in 512-S
- Flowsheet optimization
- Improving diagnostic capability

A time-logic overview of the integration of the recommendations is shown below.

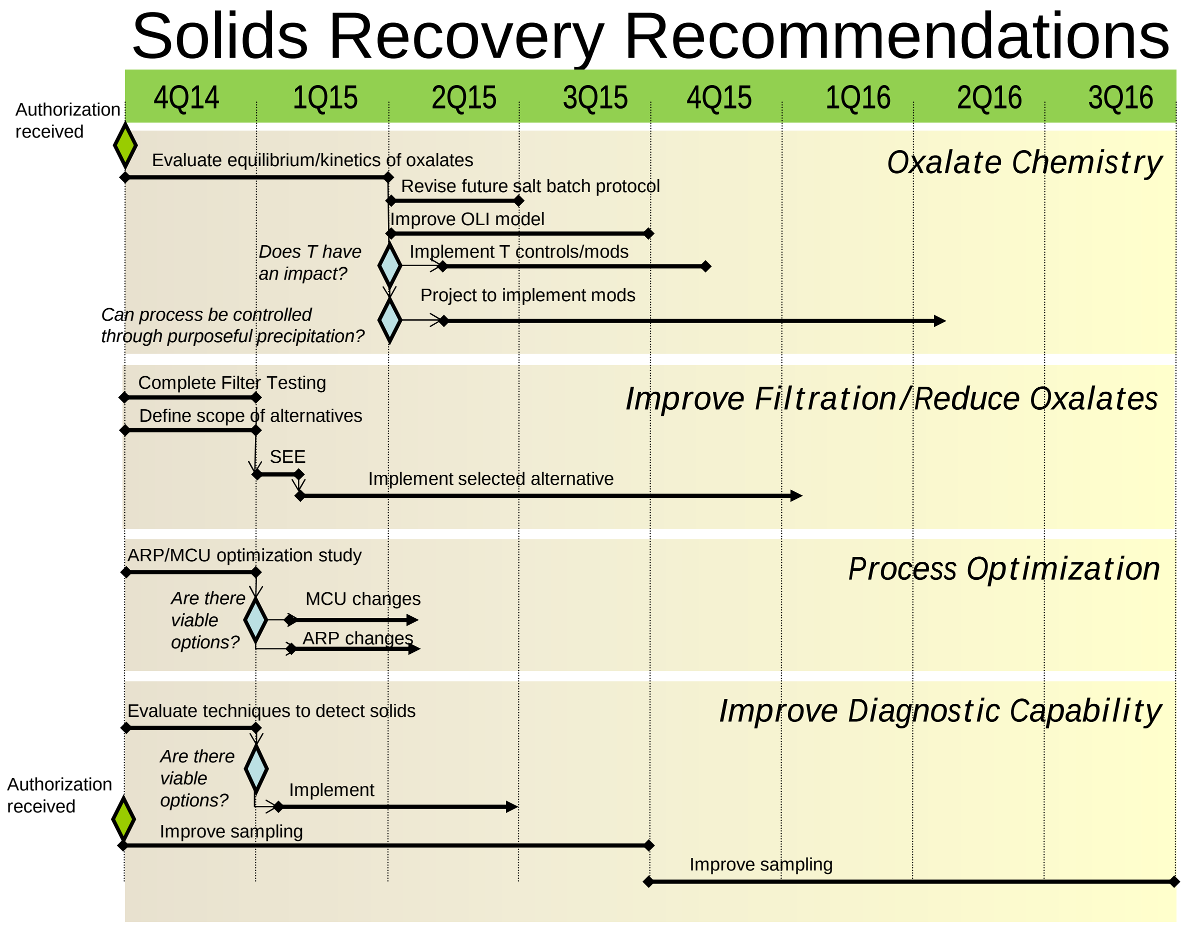
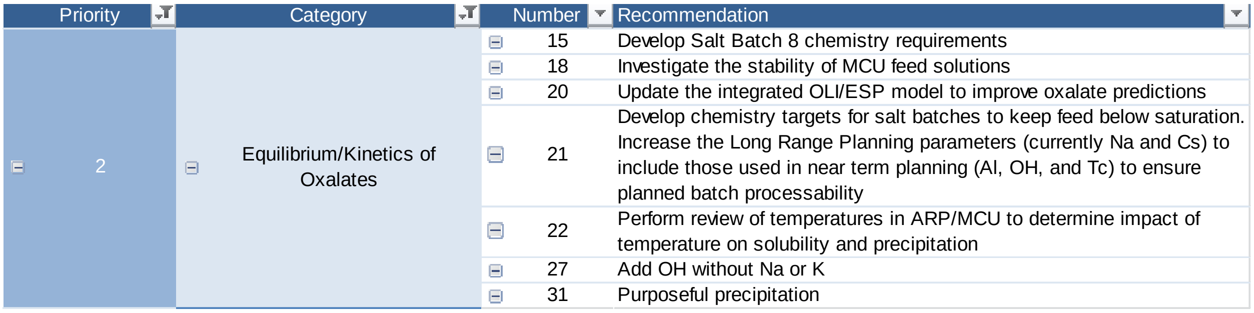


Figure 28: Time/Logic Overview showing the Integration of the Recommendations

The activities were logically tied as represented in Attachments D-G at a more detailed level. Schedules should be developed from the logic diagram and loaded into facility schedules. Only one priority 4 recommendation will be implemented at this time. This task was a risk mitigator for NGS implementation and recommended by the Oxalate Resumption Advisory Committee, an independent group charted to review the Solids Recovery Team causal analysis and the MCU pre-start recommendations related to solids precipitation. Priority 4 recommendations are shown in Attachment H.

5.1 Improve Understanding of Oxalate Equilibrium and Kinetics in Salt Solutions

Table 9: Oxalate Chemistry Recommendations

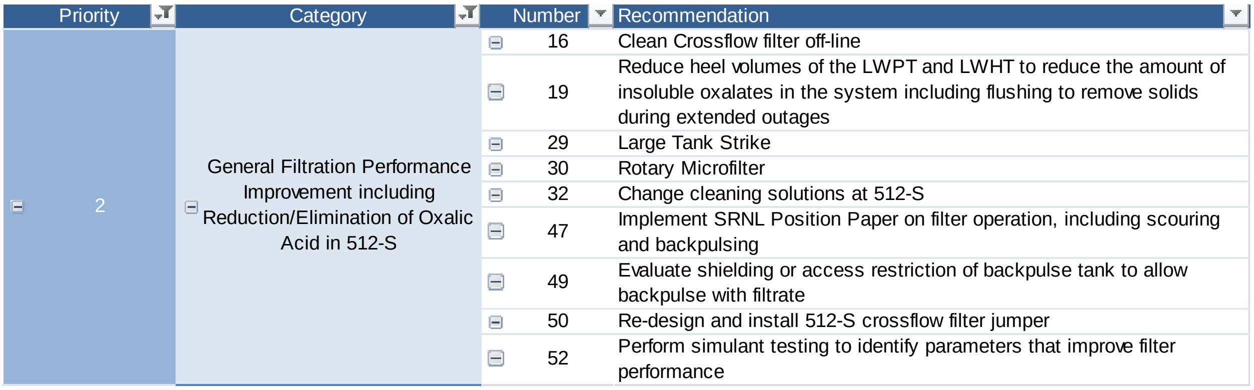


Priority	Category	Number	Recommendation
2	Equilibrium/Kinetics of Oxalates	15	Develop Salt Batch 8 chemistry requirements
		18	Investigate the stability of MCU feed solutions
		20	Update the integrated OLI/ESP model to improve oxalate predictions
		21	Develop chemistry targets for salt batches to keep feed below saturation. Increase the Long Range Planning parameters (currently Na and Cs) to include those used in near term planning (Al, OH, and Tc) to ensure planned batch processability
		22	Perform review of temperatures in ARP/MCU to determine impact of temperature on solubility and precipitation
		27	Add OH without Na or K
		31	Purposeful precipitation

These recommendations improve the basic understanding of the chemistry of oxalate precipitation in the complex salt matrix.

5.2 General Filtration Performance including Reduction/Elimination of Oxalic Acid in 512-S

Table 10: General Filtration Performance Recommendations



Priority	Category	Number	Recommendation
2	General Filtration Performance Improvement including Reduction/Elimination of Oxalic Acid in 512-S	16	Clean Crossflow filter off-line
		19	Reduce heel volumes of the LWPT and LWHT to reduce the amount of insoluble oxalates in the system including flushing to remove solids during extended outages
		29	Large Tank Strike
		30	Rotary Microfilter
		32	Change cleaning solutions at 512-S
		47	Implement SRNL Position Paper on filter operation, including scouring and backpulsing
		49	Evaluate shielding or access restriction of backpulse tank to allow backpulse with filtrate
		50	Re-design and install 512-S crossflow filter jumper
		52	Perform simulant testing to identify parameters that improve filter performance

One of the recommendations is to change the cleaning solution for the crossflow filter. All of the testing that was done to select oxalic acid as the cleaning solution was based on an assumption that the feed would have a quantity of sludge material in it that would collect on the filter. Actual processing experience shows that the feed does not contain very much sludge, but does contain insoluble salts. There is likely a better cleaning solution for the actual material captured by the filter. Elimination of the addition of oxalic acid to the system in 512-S is the single most important preventer of oxalic acid precipitation in the salt system.

There are a number of recommendations to improve filtration performance that are not currently integrated and some are mutually exclusive. For example, if large tank strike is implemented with the rotary microfilter, then a large effort should probably not be expended on redesign of the crossflow filter jumper. These ideas should be developed into specific process applications for the strike and for filtration with cost and schedule information. A systems engineering evaluation should be used to downselect the process and set the path.

5.3 Flowsheet Optimization

Table 11: Flowsheet Optimization Recommendations

Priority	Category	Number	Recommendation
2	Flowsheet Optimization	23	Remove NAS from SSRTs/SSFT and restore agitation to move solids through the system
		24	Evaluate coordination of filter cleanings with contactor flushes
		25	Reduce cleaning frequency on cross-flow by defining minimum number of batches or taking a graded approach to cleaning
		26	Eliminate feed and bleed and wash sludge batches more (higher sodium in DWPF). Conduct a study that optimizes the ARP throughput by balancing concentrating the MST solids, crossflow filter flux, and wash water (including elimination) without introducing an unacceptable evaporation load on DWPF or other downstream impacts. Evaluate eliminating the MST wash step and accept higher sodium levels at DWPF
		28	Clean tanks periodically to remove solids
		33	Direct all washes to somewhere besides MCU
		37	Flush after filter cleaning
		53	Perform statistical process control on selected parameters
3		35	Salt soundings in T49 and T50

This effort involves a review and analysis of the salt flowsheet so that decisions are made that optimize the whole, not the parts. Coresim, OLI modeling and engineering analysis can be used in this evaluation. There is one priority 3 activity that could give some information on whether solids are precipitating upstream or downstream of the salt unit operations.

5.4 Improving Diagnostic Capability

Table 12: Diagnostic Capability Recommendations

Priority	Category	Number	Recommendation
2	Improve Diagnostic Capability	12	Specify contactor inspection/maintenance requirements(rotor inspection)
		13	Specify contactor inspection/maintenance requirements (CDT material balance)
		14	Inspect contactors on a pre-determined frequency
		17	Evaluate flowrate when deinventorying
		34	Evaluate techniques to detect solids (establish online enhanced vibration monitoring)
		42	Install sampling capability on the LWPT and LWHT to provide diagnostic capability
		43	Install sampling capability on MCU to provide diagnostic capability
		51	Install sampling capability for the SSRT and SSFT to provide diagnostic capability for the long term operation of MCU

These activities improve diagnostic capability by improving instrumentation and sampling capability.

6.0 Conclusions

The process upset at MCU was caused by additional oxalates introduced through increased frequency of filter cleanings. The oxalates were then solubilized by flushes used to facilitate filter replacements in a system that is at the oxalate solubility limit. The event was exacerbated by agitation in the SSRTs in response to the cold weather event.

The recommendations implemented prior to resumption of MCU operations provide risk mitigation and detection through additional sampling and observation. The longer term recommendations provide a framework to increase the basic process knowledge of both oxalate chemistry and filtration behavior and then facilitate decisions that improve the salt flowsheet as a system.

7.0 References

[1] 14266, "Implementation of Next Generation Solvent in the Caustic-Side Solvent Extraction Process for Increased Removal of Cesium at Savannah River Site," 2014.

[2] SRNL-L3100-2014-00121, "Initial Analyses of Solids from the Extraction, Scrub Contactors," 2014.

[3] SRNL-L3100-2014-00128, "Results of Further Analyses of Solids Removed from MCU," 2014.

[4] SRR-LWE-2014-00094, "Path Forward for Addressing Solids Accumulation in the Extraction Contactor 401, 402 and Scrub Contactors 501 and 502 at Modular Caustic Side Solvent Extraction Unit (MCU)," 2014.

[5] L. Folger, Strategies for Creative Problem Solving, Upper Saddle River, NJ: Prentice Hall, 2008.

[6] SRR-LWE-2014-00096, "Path Forward for Startup of MCU after April 2014 Process Upset," 2014.

[7] X-ESR-G-00039, "Evaluation of the Impact of Increasing Sodium in the Salt Batch Feed to ARP, MCU, Tank Farm, and Downstream Facilities," 2014.

[8] SRNL-STI-2013-00700, "Actinide Removal Process Sample Analysis, Chemical Modeling, and Filtration Evaluation," 2014.

[9] X-ESR-H-00665, "Engineering Evaluation of the Next Generation Solvent Demonstration," 2014.

[10] WTP-RPT-205, "Laboratory Tests on Post-Filtration Precipitation in the WTP Pretreatment Process," 2009.

8.0 Attachments

Attachment A. Kepner-Tregoe Analysis
Attachment B. Historical Perspective on Solids found in MCU
Attachment C. Causal Analysis
Attachment D. Logic Diagram Equilibrium/Kinetics of Oxalates in Salt Solutions
Attachment E. General Filtration Performance
Attachment F. Flowsheet Optimization
Attachment G. Improve Diagnostic Capability
Attachment H. Priority 4 Recommendations

Attachment A. Kepner-Tregoe Analysis

MCU				
	IS	IS NOT	DISTINCTION	CAUSE
WHAT (Identify)	Salt Solution Feed found in Strip		NGS Flowsheet	NGS (Scrub Chemistry)
	Solids in Contactors		Plugged Extraction Contactor	solids
	Organic in SEHT	Solids in the SEHT (Caused by post-event activities)	Emulsion	Explained by the solids
WHERE (Location)	Coalescers	Misoperation	Solids (mostly oxalate)	
	Material in 1026			
	Extraction Contactor 401 and 402	Downstream Extraction Contactors		
	Scrub Contactors 501 and 502	DSS was clean (to the best of our knowledge)		
	Drain Line			
TIMING (When)	Startup	Startup of wash and strip flow	Vibration may not always tell when solids are present	Solids could have been there and solids added through feed
	Increase flow from 4-5 gpm		Different solids than before	Solids are mostly oxalate, not Al
MAGNITUDE (Extent)	MCU	ARP - LWHT samples were clear	May not have looked in all the right places yet	Cleaning of filter
				Sump Transfer

Attachment B. Historical Perspective on Solids found in MCU

Location	Date	Observation	Sample Results
Tank 49	9/2013	No solids in samples	One sample taken 8 inches from the bottom of the tank, VDS samples taken, no layering identified [B-1]
Tank 49	5/2014	Solids observed in 2 of 3 samples taken 9/2013	Not enough solids collected to be analyzed [B-2]
96H		Will not look in 96-H, MST solids are expected	
512-S LWPT	9/2013	Oxalate solids found in post clean and adjusted sample	Solids are expected from the cleaning/neutralization step [B-1]
512-S LWHT	9/2013	No solids observed in sample	
512-S LWHT	5/2014	No solids observed in samples taken 9/2013	
512-S LWHT	4/2014	Video inspection showed no solids	Tank probably contained caustic and water from secondary filter replacement
DWPF PRFT	6/2013	MST solids only	[B-3]
ARP Secondary Filter	4/2009	MST in a mixture of carbonate and oxalate salts	[B-4]
SSFT	2010	Solids	NAS and aluminum hydroxide (cold feed solutions) [B-5]
SSFT	6/2014	Solids	Sodium oxalate solids [B-6]
SSRT	2010	Solids	NAS and aluminum hydroxide (cold feed solutions) By camera inspection
SSRT	6/2014	Solids	Not sampled
Extraction Contactor 401	2012	Solids	Si, NAS, Ti [B-7]
Extraction Contactor 401	4/2014	Solids (estimated 42-52 kgs in contactor and drain line)	Sodium oxalate, sodium nitrate, bayerite Sodium nitrate precipitated from the recovery actions- addition of nitric acid to unplug [B-2]
Extraction Contactor 402	4/2014	Solids	Not sampled
Extraction Contactor 403	4/2014	No solids	
Scrub Contactor 501	4/2014	Solids	Sodium oxalate, sodium nitrate, bayerite, gibbsite [B-2]

Location	Date	Observation	Sample Results
Scrub Contactor 502	4/2014	Solids	Not collected
Strip Contactor 607	4/2014	No solids	
Extraction Contactor 401 drain line	4/2014	Solids	Solids in the drain line are predominately NAS [B-2]
Heat Exchanger	5/2014	No solids	
SPA-100	5/2014	No solids	Observed through X-Ray, camera inspection
DSSHT	6/2014	Solids showed up after a transfer from the SSFT	No solids found after transport to SRNL
SEHT	4/2014	Solids observed in F/H labs	No solids found after transport to SRNL Believe solids in the SEHT was an artifact of the process upset, not a causal factor
Contactor Drain Tank	6/2014	No solids observed, but solids are expected	
Lines between contactors	6/2014	No solids observed	Camera inspection
DSS Coalescers	5/2008	Aluminum hydroxide (Bayerite or Boehmite)	[B-8]
DSS Pre-Filters/Coalescer	2/2011	Aluminum Hydroxide and NAS	[B-9]
DSS Pre-Filter	9/2013	Aluminum Hydroxide, Sodium Oxalates, NAS, sludge particles, MST	[B-10]
DSS Coalescer	4/2013	Aluminum Hydroxide, Sodium Oxalates, NAS, MST, modifier	[B-10]
DSS Pre-Filter/Coalescer	6/2014	TBD	
SE Coalescer	10/2008	Aluminum Hydroxide and NAS	At the end of Salt Batch 1 [B-11]
SE Coalescer	3/2009	Aluminum Hydroxide	At the beginning of Salt Batch 2 [B-11]
SE Coalescer	5/2010	No evidence of solids fouling	Salt Batch 3 [B-12]
SE Coalescer	5/2013	NAS, silica, iron oxide, sludge particles, MCU modifier, MST	All of SB5 and part of SB6 [B-10]

References

[B-1] SRNL-STI-2013-00700, Revision 0,"Actinide Removal Process Sample Analysis, Chemical Modeling, and Filtration Evaluation," 2014.

[B-2] SRNL-L3100-2014-00121, Revision 0, "Initial Analyses of Solids from the Extraction, Scrub and Tank 49H Variable Depth Sample," 2014.

[B-3] SRNL-STI-2013-00735, Revision 0, "Characterization of a Precipitate Reactor Feed Tank (PRFT) Sample from the Defense Waste Processing Facility (DWPF), " 2014. http://www.osti.gov/scitech/biblio/1130781

[B-4] SRNL-STI-2009-00456, Revision 1, “Results From Analysis of Actinide Removal Process Guard Filter,” 2010.

[B-5] SRNL-STI-2011-00022, Revision 0, “Sample Results from Solids Isolated from the SSFT,” 2011.

[B-6] SRNL-L3100-2014-00133, Revision 0, “Analyses of Salt Solution Feed Tank Solids and Supernate,” 2014.

[B-7] SRNL-STI-2012-00505, Revision 0, “Identification and Characterization of the Solids Found in Extraction Contactor SEP-401 in June 2012,” 2012.

[B-8] SRNL-STI-2008-00369, Revision 0, “Diagnostic Analyses of the Decontaminated Salt Solution Coalescers from Initial Radiological Operations of the Modular Caustic-Side Solvent Extraction Unit,” 2008.

[B-9] SRNL-STI-2011-00513, Revision 0, “Results of Analyses of Macrobatch 3 Decontaminated Salt Solution (DSS) Coalescer and Pre-filters,” 2012.

[B-10] SRNL-STI-2014-00097, Revision 0, “Characterization of Solids in Fouled Modular Caustic Side Solvent Extraction Unit (MCU) Prefilter/Coalescer Media,” 2014.

[B-11] SRNL-STI-2010-00088, Revision 0, “ Results from Analysis of the First and Second Strip Effluent Coalescer Elements from Ratioactive Operations of the Modular Caustic-Side solvent Extraction Unit,” 2011.

[B-12] SRNL-STI-2012-00698, Revision 0, “Results of Analysis of Macrobatch 3 Decontaminated Salt Solution Coalescer from May 2010,” 2012.

Attachment C. Causal Analysis

#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
1. Salt Batch Chemistry					
1	Chemistry changes between Salt Batches (and sub batches) cause precipitation OLI modeling indicates that Salt Batches are supersaturated	Modeling of the salt batch mixtures Add chart of OLI concentrations and actual sample concentrations from Salt Batches (completed at 25C) OLI model case 6 (6D) Add charts of Al, Si concentration versus OLI predictions Determine the dilution needed to return system to subsaturation Search on precipitation of supersaturated sodium oxalate solutions	Scaling factors are above 1 per OLI modeling	• Scaling factor of all salt batches show some tendency to scale • Al precipitation somewhat controlled by addition of NaOH • Salt Batch 3 chemistry seems to be a sweet spot. Best operation of MCU. Sodium oxalate solids prediction by OLI was fairly low. No aluminum hydroxide was predicted to form. NAS was predicted to form. Coalescer operation was the best. • 20 vol% addition gets oxalates back in solution (5M), 30% volume reduction gets all components back into solution (4.7M) • Calcium oxalate solubility is fairly well understood in the aluminum industry. The calcium values are very low numbers compared to the oxalate in solution. There are three points to make. 1) Calcium was below detection limits in the solution phase of 512-S samples. However, we did get one measurement above detection limit after oxalic acid cleaning. 2) We measured calcium in both the 512-S solids and the contactor solids, so calcium is present to some extent. 3) Calcium is shown to precipitate during the washing in 512-S (also in our 512-S report). • MCU only uses reagent grade >99.5% pure boric acid. Also solids were only formed in the extraction and scrub contactors, not the strip contactors.	6/9/2014
2. Temperature					
2a	Cold Temperatures from this winter causes precipitation in MCU	Identify location of solids within MCU (solids chart) Develop temperature timeline Model or calculate impact to in MCU solubility based on temperature(Cases 1-3)	The solids predicted by the model increase	Temperature timeline for last several years show that this was a very cold year with prolonged periods below freezing. Temperatures in MCU got to 18C. Modeling shows that decreasing temperature can contribute to aluminum hydroxide precipitation and to a lesser degree oxalate precipitation. A change in temp from 25 to 18 could cause up to 40% of the available Al to precipitate and about 6% of the oxalate to precipitate. NAS seems fairly impervious to the change in T.	5/29/2014

#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
2b	Cold Temperatures from this winter causes precipitation in the feed system that was moved forward to MCU	Identify location of solids within the feed system (solids chart) Develop temperature timeline On coldest days, develop temperature by process vessel Model or calculate impact to solubility in feed system based on temperature (Cases 1-3)	Observe solids in the feed system and the solids predicted by the model increase	Temperature timeline for last several years show that this was a very cold year with prolonged periods below freezing. Generally speaking the ARP strike tanks and the LWPT were between 25-30C during the cold snaps. The LWPT dipped below 18C once and one of the ARP strike tanks dipped below 18C once. The LWHT and the MCU receipt tanks and feed tanks were between 18-23C during the cold snaps. The LWHT dipped to 10C in March when it was at heel. The March cold snap did not influence the event because none of the material in the feed system was moved forward to MCU.	5/29/2014
2c	Agitation in the SSRTs to control the temperature lead to precipitation or carryover of solids	Review agitation and coalescer dP	Agitator operation and coalescer dP show a positive correlation Agitator operation and contactor vibration show a positive correlation	Agitator operation and coalescer dP show a correlation. Could not see a correlation between the agitator operation and contactor vibration. The last oxalic acid filter cleaning also took place at this time.	6/9/2014
3. Increased Frequency of 512-S Filter Cleaning					
3a	Additional cleanings on 512-S primary filter increased oxalates in system above solubility	Model or calculate impact to solubility of salt solution based on frequency of cleanings Sample secondary filter(s)	Solids predicted by model increases for the increased cleaning frequency Solids found in secondary filter	Oxalate solids predicted by model increased based on the increased cleaning frequency Modeling also shows that the wash step likely dissolves oxalates, sending the oxalates directly to the LWHT	6/9/2014
3b	Chemistry was not normal from 9/2013 because of the number of filter cleanings, changes, and flushes from the various outages causing precipitation	Model actual chemistry from 3/2013 (last time contactor 401 was replaced)	Modeling will show precipitation was greater than the “normal” flowsheet	Evaluation showed that approximately 297 kgs of sodium oxalate were added to the system between August and April when the process upset occurred. This correlates very well to the amount of sodium oxalate recovered from the flushes of the SSRTs, SSFTs and the oxalates in the contactors.	6/27/2014

#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
3c	Increased pressure at filtration causes a change in Al solubility	Review literature for impact	Literature will show a positive correlation	Not at this pressure levels. You need huge pressures (geological or oceanic) to constraint the Al(OH)4- , OH-, and water random movements (Brownian motion) for Al and OH to run into each other. The variable pressure at this range may affect gas solubility and perhaps the CO2 => CO3-- may vary and lead to CaCO3 (or SrCO3 precipitation or dissolution depending if the pressure goes up or down). I believe the effect you mentioned has little impact on Al(OH)-- to Gibbsite/Norstradine formation or dissolution.	5/29/2014
3d	Change in agitation in the LWPT caused precipitation or carryover of solids	Review LWPT agitator operation and coalescer dP Review LWPT agitator operation and contactor vibration	Agitator operation and coalescer dP show a positive correlation Agitator operation and contactor vibration show a positive correlation	Agitation in LWPT was changed on 2/6. No impact was identified as a result of the agitator change.	5/29/2014

#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
4. Chronic Buildup					
4a	Chronic buildup	Data on contactor cleaning and flushing Vibration data Modeling data Calculate/estimate volume of solids collected Calculate/estimate volume of feed needed to precipitate solids (need to assume some rate of precipitation) Oxalate Balance Calculate volume added to Contactor Drain Tank (CDT) last time contactors were drained	Engineering judgment on data evaluation that the solids can be building up over time	• Extraction contactor 401 was replaced in March 2013. It was flushed twice with nitric acid in April. It was drained during the NGS outage in November. The volume received in the CDT shows that the contactor drained in November. • Contactor vibration is not a fool-proof indicator of solids. • Estimated 42-52 kgs in the contactor 401and drain line. Only takes about 25K gallons of feed to produce this amount of material, assuming 100% oxalate precipitation. • Before the secondary filter oxalic acid cleaning was eliminated, it was cleaned about every 100 batches. The heel left in the LWHT was about 1300 gallons of neutralized, oxalic acid sent directly to MCU. Direct correlations can be made from secondary filter cleanings to MCU contactor vibrations. • Modeling and Sampling data show that the filter flushes and cleanings contribute oxalates to the system. • Oxalate concentration in DSSHT on par with Salt Batch 6D concentrations for micro-batches 5 and 6a when lower concentrations are anticipated. This supports the idea that oxalates are being transferred to MCU in large “slugs”, precipitating in the Receipt/Feed and being reincorporated into salt solution that is processed through MCU as more lower oxalate concentration material is received.	6/27/2014

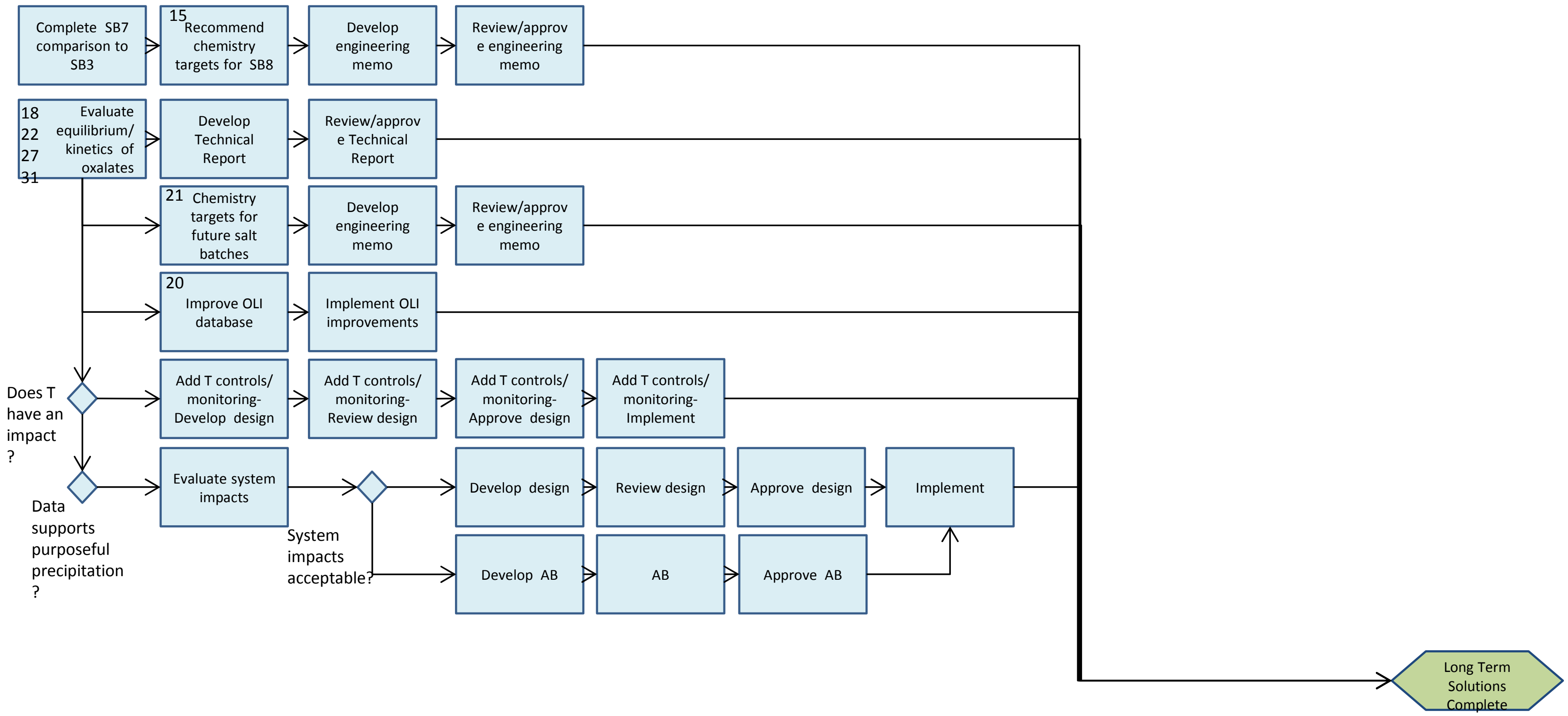
#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
5. Post Filtration Precipitation					
5	Post filtration precipitation	Batch timeline- Time at rest in a vessel Kinetic data on oxalate precipitation	Kinetic data shows that material spent enough time between 512-S and processing at MCU to precipitate	Post-filtration kinetic data collected for Hanford shows solutions have a tendency to precipitate. The test data shows that oxalate precipitation is not heavily influenced by the components tested by Hanford (phosphates and fluorides which are not present in our waste). The test data also shows that the oxalate precipitation is not heavily influenced by temperature, which is consistent with the modeling we have done. The test data also shows that the oxalate come to equiplibrium within a day or two, which is not consistent with our experience. Batches sat in MCU for 10-20 days in January before processing at the beginning of February. This is not very unusual since the plant has been down in the past without being de inventoried for more than 10 days. While post filtration precipitation is occurring, there is no supporting evidence that batches at rest in MCU feed tanks was a primary cause.	6/9/2014
6. NGS					
6a	NGS Change to a basic scrub stream causes precipitation	Model or Calculate impact to solubility when the scrub stream and salt stream are mixed (Cases 1-3)	The solids predicted by the model will increase	The modeling results indicated no impact to solids precipitation by changing the scrub solution from acidic (0.05M HNO3) to basic solution (0.025M NaOH).	6/2/2014
6b	NGS Change to a basic scrub stream plus low temperature from this winter caused precipitation	Model or Calculate impact to solubility with temperature impacts when the scrub stream and salt stream are mixed (Cases 1-3)	The solids predicted by the model will increase	Initial results show that low temperature of the scrub did not contribute to oxalate precipitation, does contribute to a reduction in Al solubility	6/2/2014

#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
6c	NGS changes to solvent cause precipitation through guanidine affinity to oxalates	Review of test data with guanidine Consultation with solvent extraction expert	Test data would show this tendency	Since oxalate, like borate, is among the least extractable anions, it will remain behind in the aqueous phase in competition with highly extractable nitrate. Thus, oxalate is not expected to be significantly extracted as the anion of any cationic species in the organic phase. Under the alkaline conditions of the extraction and scrubbing sections, the guanidine will be neutral and not an active participant in extraction. The calix-potassium cationic complex formed upon potassium extraction is expected to be the cationic complex of highest concentration (several mM) in the organic phase in the extraction section, but again, nitrate would be major anion.	5/22/2014

6d	NGS causes impact from solubility from unknown cause	Comparison of Bob flowsheet to Max flowsheet-OLI (case 4)
		Comparison of Bob test data to Max test data
		SRNL testing based on flowsheet/test data comparison
			Recognize a difference in the way the flowsheets behave	The simulant used in NGS and Bob testing was at the baseline 5.6M. The oxalates were not at saturation during the testing. Modeling does not show any difference in the flowsheets versus precipitation.
				• Had a discussion on comparison of the SRR Salt Batch 6D constituents and the SWPF Testing Salt Simulant constituents @5.6M Na. Parsons ran a high molarity test (around 7.6M Na). In making this simulant they butted up all constituents, so the oxalates should be supersaturated. Parsons did not see any indications of solids during their testing.
				  ◦ Vibration was performed occasionally via a hand held unit.
				  ◦ Solids were not noted in any other the samples, this includes inter-stage samples as well normal DSS & SE samples.
				  ◦ Inter-stage samples did not indicated high O/A in Aqueous streams or high A/O in organic streams.
				  ◦ Hydraulic performance was normal, no indications of solids (weir) pluggage.
				Parsons did not visually inspect contactors upon completion of testing. Contactors were acid cleaned and the acid was disposed of without analysis.	

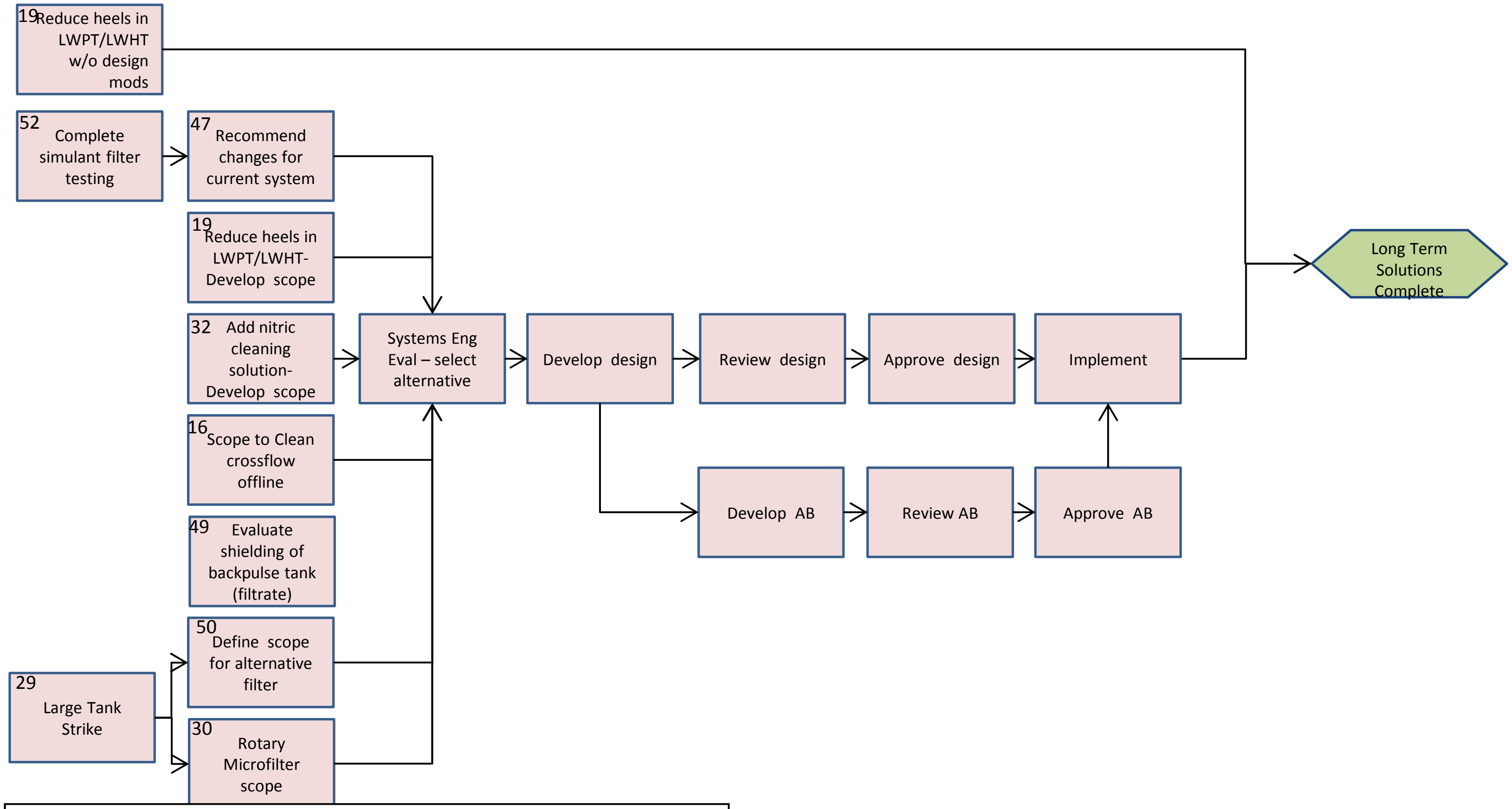
#	Potential Cause	Data needed to Evaluate	Expected Result if Cause is Real	Actual Result	Date Completed
7. Equipment Malfunction					
7a	Inadequate mixing in SPA-100 causes precipitation	Observe solids buildup in SPA-100 Model partial mixing (Cases 7-8)	SPA-100 will show signs of solids	The modeling results also indicated that minimal impact to solids precipitation with respect to partial mixing in SPA-100	6/3/2014
		If SPA-100 has solids, then mockup SPA-100 in SRNL and observe results of tests	Tests will show inadequate mixing causes solids	N/A	
7b	Drain Line valve is closed along with chronic buildup	Plant observation	Valve is closed	Valve operated properly per video inspection	5/16/2014
8. 512-S Filter Change					
8	512-S filter change from 0.1 to 0.5 micron allowed solids to pass through	Develop process timeline including 512-S filter changes	Review the amount of material processed since the change	Only 3 hours of material was processed after the filter was changed	5/20/2014

Attachment D. Logic Diagram Equilibrium/Kinetics of Oxalates in Salt Solutions



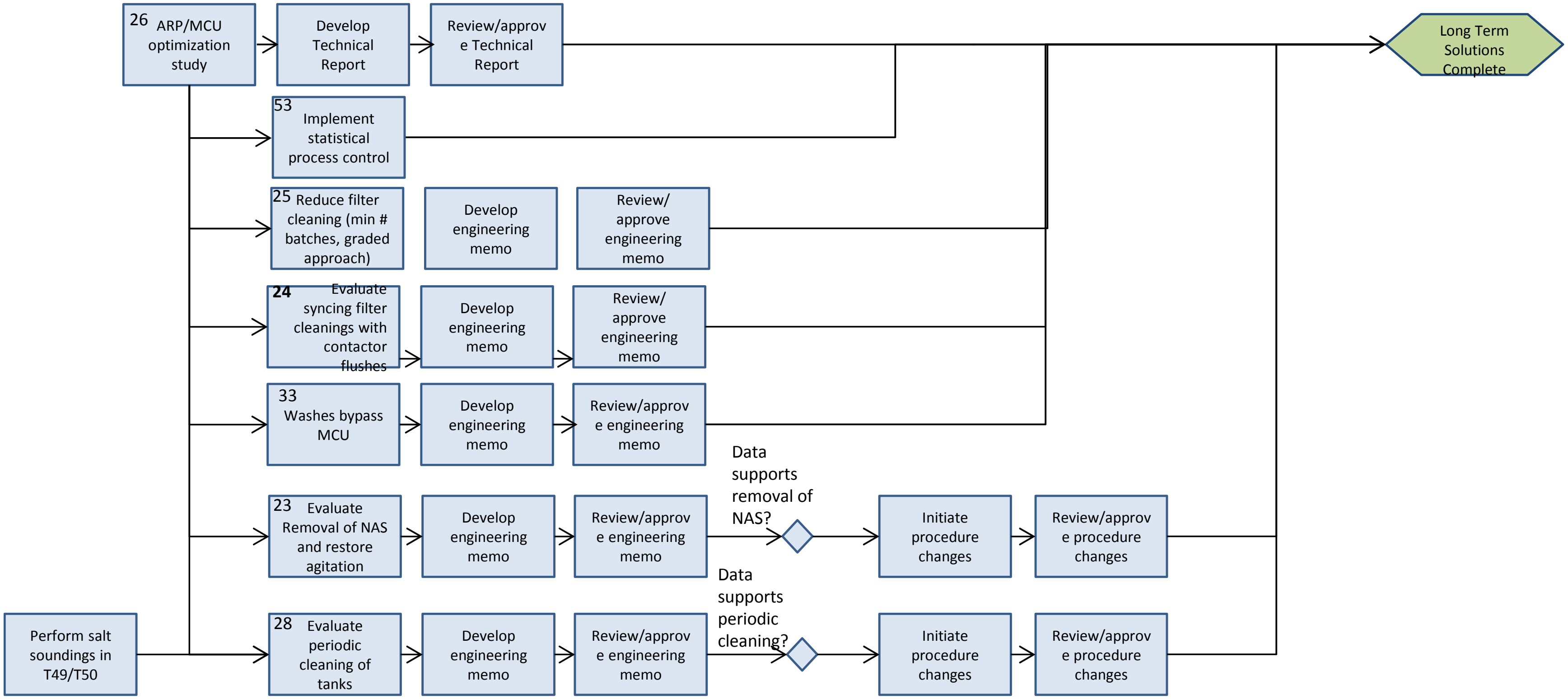
Numbers in the boxes match the recommendation number

Attachment E. General Filtration Performance



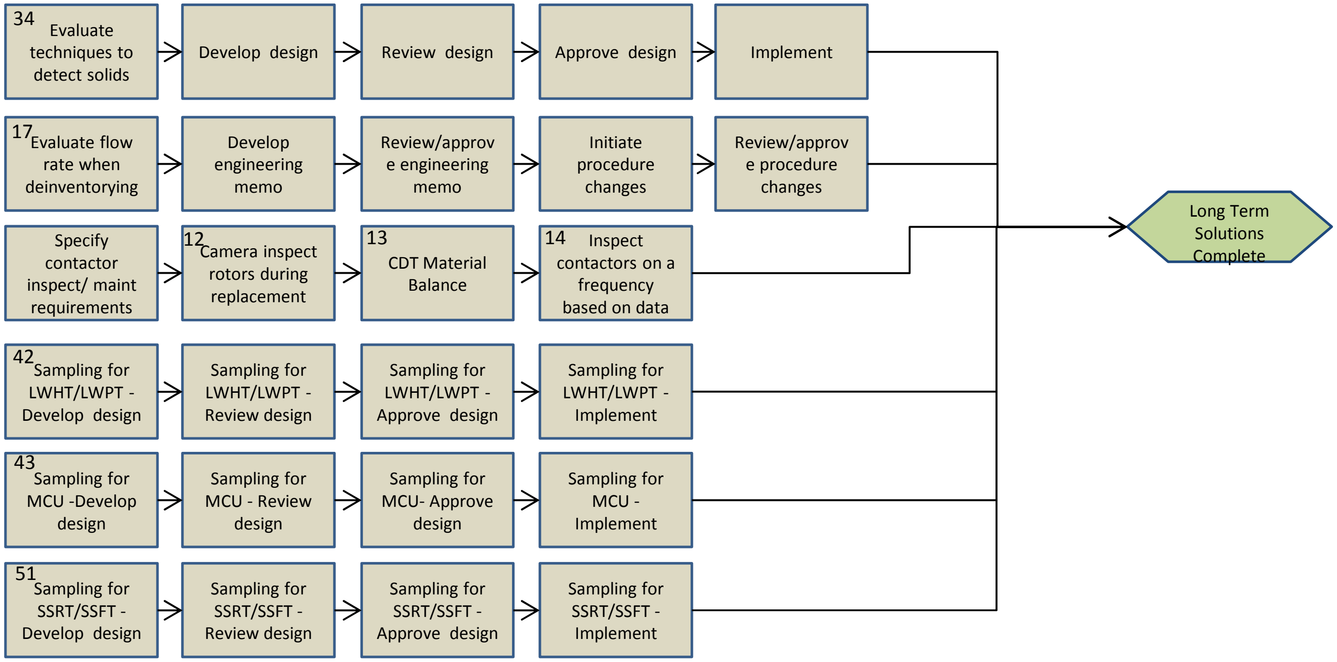
Numbers in the boxes match the recommendation number

Attachment F. Flowsheet Optimization



Numbers in the boxes match the recommendation number

Attachment G. Improve Diagnostic Capability



Numbers in the boxes match the recommendation number

Attachment H. Priority 4 Recommendations

Priority	Number	Recommendation
⊟ 4	⊟ 36	Reduce T of strip
	⊟ 38	Evaluate salt dissolving process
	⊟ 39	Dedicated transfer path from SSFT to Tank 50
	⊟ 40	Reduce MST
	⊟ 41	Tertiary filter
	⊟ 44	Perform testing in SRNL to compare NGS and Bob performance with high salt feeds
	⊟ 45	Add mixing capabilities back to Tank 49 to mix the feed to ARP-MCU and to increase filter flux by transferring insoluble solids that will act as filter aid
	⊟ 48	Make WAC/WCP paperwork to complete 512-S cleaning more efficient – bounding versus counting every penny

Attachment I. Estimate of Oxalates Transferred from 512-S to MCU

The majority of the oxalate solids discovered at MCU are theorized to have precipitated at 512-S and transferred to MCU during the MST/sludge solids washing step performed prior to transferring the LWPT to the LPPP-PPT (DWPF). SRNL recently simulated the 512-S filtration process in OLI ESP™ in order to better understand the potential causes of poor filter performance. The evaluation of solid precipitates in the simulated LWHT shows solids, primarily sodium oxalate. The source of most of the sodium oxalate in the LWHT comes from the LWPT during MST/sludge solids washing in the LWPT. The material balance resulting from the steady-state simulation of the solids washing operation shows a substantial fraction of the precipitated solids in the LWPT transfers with the wash solution. The source of sodium oxalate in the LWPT is precipitated sodium oxalate from the Salt Batch feed material and from sodium oxalate formed in the LWPT from residual oxalic acid cleaning of the primary filter.[I-1]

The purpose of this calculation is to estimate the amount of sodium oxalate that may have accumulated at 512-S and subsequently transferred to MCU in the period leading up to the MCU process upset in April 2014.

Inputs

1. The molecular weight of sodium oxalate is 134.0 g/mol. The molecular weight of the oxalate ion is 88.05 g/mol [I-2].
2. The oxalate concentration in Salt Batch 6D is 304 mg/L [I-3].
3. Seven primary filter cleaning/flushing evolutions took place in 512-S in the months leading up to the process upset at MCU. Filter cleanings/flushes are associated with a MST/sludge solids washing step that would have solubilized oxalates in the LWPT that had precipitated prior to the primary filter cleaning (See Assumptions 1, 2, and 3). Four of the six primary filter cleanings also added additional oxalate ions to the LWPT since they were oxalic acid filter cleaning evolutions.

Table 13. Filter Cleanings from August 2013 to April 2014

Filter Cleaning	Type	Notes
8/15/2013	Oxalic Acid Addition	MST/Sludge solids Wash prior to cleaning. The oxalates solubilized prior to cleaning would have been processed through MCU prior to the 9/30/2013 NGS outage.
8/30/2013	Oxalic Acid Addition	MST/Sludge solids Wash prior to cleaning.
12/2/2013	Oxalic Acid Additions	No MST/Sludge solids Wash prior to cleaning.
1/7/2014	Caustic Cleaning	MST/Sludge solids Wash prior to cleaning.
2/7/2014	Oxalic Acid Addition	MST/Sludge solids Wash prior to cleaning.
3/1/2014	Caustic Cleaning	No MST/Sludge solids Wash prior to cleaning. Volume added to filter/LWPT assumed to solubilize oxalates in heel (Assumption 6)
3/18/2014	Filter Flush	No MST/Sludge solids Wash prior to cleaning. Volume added to filter/LWPT assumed to solubilize oxalates in heel (Assumption 6).

4. The volume of oxalic acid added to the 512-S system from the Oxalic Acid Filter Cleanings and the corresponding LWPT volumes are provided in the table below. Filter cleaning process start dates are based on process knowledge based on PI level information.

Table 14: Oxalic Acid Storage Tank Volumes and LWPT Volumes from PI

Oxalic Acid Filter Cleaning Completion Dates	**Oxalic Acid Storage Tank Volume (\\hlwpi3\DLI7087)**		**LWPT Volume (\\hlwpi3\DLI7189)**	
	Initial Volume Prior to Oxalic Acid Cleaning addition [gal]	**Final Volume Post Oxalic Acid Cleaning [gal]**	**Volume of LWPT prior to transfer of cleaning material to DWPF [gal]**	**Volume of LWPT heel post transfer of cleaning material to DWPF [gal]**
8/15/2013	8/16/2013 15:00	8/16/2013 17:00	8/16/2013 22:30	8/17/2013 2:00
	1620	1085	2727	730
8/30/2013	8/29/2013 14:42	8/29/2013 17:30	8/30/2013 3:24	8/30/2013 4:00
	4476	3858	3385	593
12/2/2013*	11/19/2013 16:24	11/19/2013 17:12	11/30/2013 12:30	11/30/2013 14:24
	3833	3543		
	11/20/2013 15:18	11/20/2013 15:48	2752	566
	3543	3442		
2/7/2013†	2/3/2014 12:00	2/3/2014 12:42	2/5/2014 21:36	2/5/2014 22:12
			3980	1819
	3462	2949	2/6/2014 10:54	2/6/2014 12:24
			1819	621

*The 12/2/2013 filter cleaning was an extended soak that involved the addition of oxalic acid twice.
†The LWPT contents were transferred to the LPPP-PPT (DWPF) in two transfers.

5. The number of batches of salt solution processed at 512-S in between filter cleanings leading up to the April 2014 process upset at MCU (SW4-15.116 – 8.1, Batch Calculation Data Sheet) are listed below in Table 15.

Table 15: 512-S Batches Processed prior to Filter Cleanings

Filter Cleaning Dates/Types	**Number of Batches Prior to Cleaning**	**Cycle Number**
8/15/2013 Oxalic Acid Primary Filter	*	5
8/30/2013 Oxalic Acid Primary Filter Cleaning	16	6
12/2/2013 Oxalic Acid Primary Filter Cleaning	0	6
1/7/2014 Caustic Primary Filter Cleaning	10	7
2/7/2014 Oxalic Acid Primary Filter Cleaning	3	7
3/1/2014 Caustic Primary Filter Cleaning	14	8
3/18/2014 Primary Filter Flush	8	8

*Oxalates from the salt batches in Cycle 5 prior to the 8/15/2013 would have been processed through MCU prior to the MCU NGS outage (8/30/2013) and are not thought to have contributed to the excess of sodium oxalate solids found at MCU in the 4/6/2014 process upset.

Assumptions

1. The volume salt solution/MST slurry transferred from 241-96H to the LWPT for each batch is approximately 3700 gallons [I-1].
   Basis: The volume of the waste transferred to the LWPT is tracked by operations in an Batch Calculation Data Sheet (SW4-15.116-8.1). The average LWPT batch volume (Salt

Solution/MST slurry) during the period investigated (associated with cycles 6, 7, and 8) was 3818 gallons. A conservatively low value of 3700 gallons was chosen to account for instrument uncertainty and/or variances in precipitation rate over the batch accumulation process.
Sensitivity: One gallon of salt solution is anticipated to precipitate approximately 0.1754 g of sodium oxalate (assuming a concentration of 304 mg/L). An increase or decrease in the average batch size would have an associated increase or decrease in the estimate of sodium oxalate generated. Utilizing the methodology outline in Equation I-1, if the average salt batch volume were increased to 3818 gallons, the amount of sodium oxalate generated from salt batch accumulation would be expected to increase to 222 kg.

2. Every batch received from 241-96H precipitates 197.9 mg of oxalate/L of MST/salt solution slurry in LWPT.
   Basis: SRNL sample results for Salt Batch 6D in the LWPT indicated that the oxalate concentration in the feed decreased to 97.7 mg/L in LWPT [I-1]. 97.7 mg/L of oxalate corresponds to the LWPT-1 sample. LWPT-1 samples were collected from the LWPT after receiving the last batch of material from 241-96H (SB 6D Cycle 6 Batch 16), but before filtration of the last batch has taken place. The 97.7 mg/L is the lowest aqueous concentration for oxalate for the two normal batch samples taken at that time (LWPT-2 taken after filtration had taken place indicated 104 mg/L of oxalate in solution). If no precipitation were occurring this sample would be expected to be consistent with the Salt Batch 6D aqueous oxalate concentration with dilution at 241-96H. The average salt batch volume for cycles 6, 7, and 8 for Salt Batch 6D, transferred from 249-96H was 3713 gallons without assuming the addition of 105 gallons of MST and water. The MST and water addition represents a 2.75 % dilution of the Salt Batch 6D feed. As a result the MST/Salt Solution slurry would be expected to have a 2.75% reduction in oxalate concentration (304 mg/L – (304 mg/L * 2.75%)) or 295.6 mg/L of oxalate. Therefore, each batch of salt solution/MST slurry for Salt Batch 6D is expected to precipitate 197.9 mg of oxalate for each liter of salt solution/MST slurry (295.6 mg/L – 97.7 mg/L).
   Sensitivity: The incoming feed material contains a maximum of 304 mg/L. The maximum sodium oxalate that could precipitate from the 512-S batches would be 304 mg for each liter of salt solution fed to 512-S if no dilution were to take place at 241-96H. Utilizing the methodology outline in Equation I-1, if each 512-S batch precipitated 304 mg per liter of material transferred into the LWPT, the amount of sodium oxalate generated from salt batch accumulation would be expected to increase to 330 kg.
3. All oxalate solids that have accumulated in LWPT throughout the cycle are solubilized during the solids washing step prior to filter cleaning/flushing and are transferred to LWHT.
   Basis: Modeling shows that the washing step associated with the batch MST/sludge solids washing/oxalic acid cleaning solubilizes the oxalates that have accumulated in the LWPT heel [I-1].
   Sensitivity: If less oxalates are solubilized during the MST/sludge solids washing then fewer oxalate solids would be anticipated in MCU. For example, if only 90% of the sodium oxalate in the LWPT is solubilized the estimate for sodium oxalate found in the LWHT would be 90% of the current estimate.
4. All the oxalate from oxalic acid filter cleaning remaining in the LWPT heel after transfer to the LPPP-PPT (DWPT) are assumed to precipitate out in the form of sodium oxalate after the next MST/salt solution slurry batch is introduced into the LWPT.

Basis: Modeling shows that oxalates precipitate in the form of sodium oxalate upon contact of the next batch of MST/salt solution slurry transferred to the LWPT [I-1].

5. The molarity of oxalic acid added during the filter cleaning process is 0.5 M.
   Basis: This is a nominal value. The DWPF DSA allows a maximum oxalic acid concentration of 0.6 M [I-4].
   Sensitivity: Higher oxalic acid concentration could result in more oxalate to precipitate in the LWPT, and subsequently more oxalate would be solubilized during the next filter cleaning evolution. Utilizing the methodology outlined in Equation I-2, an oxalic acid concentration of 0.6 M utilized during filter cleanings would result in an estimated 99 kg of sodium oxalate generated from all oxalic acid filter cleanings in the period leading up to the process upset at MCU.
6. Filter flush/caustic cleaning added enough volume to effectively solubilize the sodium oxalate in the LWPT and transfer them with the next batch of CSS to the LWHT.
   Basis: The OLI ESP™ simulation recently created for 512-S assumes the addition of 3250 gallons of wash water during the MST/sludge solids washing step. This wash water solubilized the majority of precipitated oxalate solids. The caustic cleaning evolution and filter flush on 3/1/2014/ and 3/18/2014, respectively, each added approximately 1200 gallons of water and 1200 gallons of dilute caustic to the LWPT. This could have provided enough sodium dilution for oxalate solids in the LWPT to solubilize and remain soluble after the addition of the next batch of MST/salt solution slurry. Because the purpose of this calculation is to determine the mass of oxalates that could have accumulated and been subsequently transferred to MCU, the oxalates accumulated in the batches leading up to the 3/1/2014 and 3/18/2014 caustic cleaning and flush are included.
   Sensitivity: If none of the oxalate was solubilized and transferred to the LWHT after the 3/1/2014 and 3/18/2014 cleanings, the sodium oxalate mass associated with the 14 batches prior to the 3/1/2014 caustic cleaning and the 8 batches prior to the 3/18/2014 filter flush would not have contributed to the mass of sodium oxalate at MCU.

Mass of Oxalate Accumulated in LWPT with Each Batch:

Assuming 3700 gallons of salt solution is transferred from 241-96H with each batch (Assumption 1), and that 197.9 mg/L of oxalate precipitates with each batch (Assumption 2):

Equation I-1:

$$\boldsymbol{m_{NaOx}} = (\boldsymbol{V_B})(\boldsymbol{N})\left(\frac{\mathbf{3.7854}\boldsymbol{L}}{\mathbf{1}\boldsymbol{gal}}\right)(\boldsymbol{C_{Ox}})\left(\frac{\mathbf{1}\boldsymbol{g}}{\mathbf{1000}\boldsymbol{mg}}\right)\left(\frac{\boldsymbol{mol\ oxalate}}{\mathbf{88.05}\ \boldsymbol{g\ oxalate}}\right)\left(\frac{\mathbf{1}\ \boldsymbol{mol\ sodium\ oxalate}}{\mathbf{1}\ \boldsymbol{mol\ oxalate}}\right)\left(\frac{\mathbf{134}\ \boldsymbol{g\ sodium\ oxalate}}{\boldsymbol{mol\ sodium\ oxalate}}\right)\left(\frac{\mathbf{1}\ \boldsymbol{kg}}{\mathbf{1000}\ \boldsymbol{g}}\right)$$

$$\boldsymbol{m_{NaOx}} = \mathbf{3700}\boldsymbol{gal} * \mathbf{51} * \left(\frac{\mathbf{3.7854}\boldsymbol{L}}{\mathbf{1}\boldsymbol{gal}}\right)\left(\frac{\mathbf{197.9}\ \boldsymbol{mg}}{\boldsymbol{L}}\right)\left(\frac{\mathbf{1}\boldsymbol{g}}{\mathbf{1000}\boldsymbol{mg}}\right)\left(\frac{\boldsymbol{mol}}{\mathbf{88.05}\ \boldsymbol{g}}\right)\left(\frac{\mathbf{134}\ \boldsymbol{g}}{\boldsymbol{mol}}\right)\left(\frac{\mathbf{1}\ \boldsymbol{kg}}{\mathbf{1000}\ \boldsymbol{g}}\right)$$

$$\boldsymbol{m_{Ox,C}} = \mathbf{215}\ \boldsymbol{kg}$$

Where:

m_{NaOx}= Mass of sodium oxalate potentially sent to MCU after a cycle [kg]

V_B= Average Volume of one batch transferred to the LWPT [gal] (Assumption 1)
N = Number of batches [unitless] (51 total)
C_{Ox} = Oxalate concentration in the LWPT batch that precipitates [mg/L] (Assumption 2)

Mass of Oxalate Contributed from Oxalic Acid Cleaning:

Equation I-2:

$$C_{Ox,OA} = \frac{\left[V_{OA}\left(\frac{3.7854L}{1gal}\right)(C_{OA})\left(\frac{1\,mol\,oxalate}{1\,mol\,oxalic\,acid}\right) + X_{ox}\right]}{V_{LWPT,i}\left(\frac{3.7854\,L}{gal}\right)}$$

$$C_{Ox,OA\_12.2.13} = \frac{\left[391\,gal\left(\frac{3.7854L}{1gal}\right)\left(\frac{0.5\,mol\,oxalic\,acid}{L\,solution}\right)\left(\frac{1\,mol\,oxalate}{1\,mol\,oxalic\,acid}\right) + 205\,mol\,oxalate\right]}{2752\left(\frac{3.7854\,L}{gal}\right)}$$

$$C_{Ox,OA\_12.2.13} = 0.091\,M$$

Where:

$C_{Ox,OA}$= Concentration of oxalate ions in the LWPT heel during cleaning [M]
V_{OA} = Volume of oxalic acid added to the LWPT based on Oxalic Acid Storage Tank depletion (or the initial Oxalic Acid Storage Tank volume minus the final Oxalic Acid Storage Tank volume given in Input 4) [gal]
$C_{OA\,=}$ Concentration of oxalic acid [M]
$X_{OA\,=}$ Oxalates from previous cleaning. This value is only applicable for 12/2/2013 cleaning, as no material was processed from the LWPT from the 8/30/2013 cleaning to the 12/2/2013 cleaning [mol]. XOA for 12/2/2013 is equal to the number of moles left in the LWPT following the methodology in Equation I-2 for the 8/30/2013 cleaning.
$V_{LWPT,i}$ = Maximum volume of the LWPT after oxalic acid addition but prior to any transfers (Input 4) [gal]

Equation I-3:

$$m_{NaOx,OA} = C_{Ox,OA}V_{LWPT,f}\left(\frac{3.7854\,L}{gal}\right)\left(\frac{1\,mol\,sodium\,oxalate}{1\,mol\,oxalate}\right)\left(\frac{134\,g\,sodium\,oxalate}{1\,mol\,sodium\,oxalate}\right)\left(\frac{1\,kg}{1000\,g}\right)$$

$$m_{NaOx,OA\_12.2.13} = (0.091\,M)\,(2752\,gal)\left(\frac{3.7854\,L}{gal}\right)\left(\frac{134\,g}{1\,mol}\right)\left(\frac{1\,kg}{1000\,g}\right)$$

$$m_{Ox,OA\_12.2.13} = 26\text{ kg}$$

Where:

$m_{NaOx,OA}$ = Mass of sodium oxalate generated from oxalic acid addition during chemical cleaning [kg]
$C_{Ox,OA}$= Concentration of oxalate ions in the LWPT heel during cleaning (calculated in Equation I-1) [M]
$V_{LWPT,f}$ = Volume of the LWPT after transfer to the LPPP-PPT (Input 4) [gal]

Results

An estimate of the sodium oxalate accumulated and transferred to the LWHT from salt batch precipitation is provided in Table 16 below.

Table 16: Estimate of Sodium Oxalate Precipitated from Salt Batches

Filter Cleaning Dates/Types	**Number of Batches of Salt Solution Prior to Filter Cleaning**	**Volume of Salt Solution Processed Prior to Filter Cleaning [gal]**	**Volume of Salt Solution Processed Prior to Filter Cleaning [L]**	**Oxalate Accumulation from Salt Batch Prior to Filter Cleaning [mg]**	**Oxalate Accumulation from Salt Batch Prior to Filter Cleaning [mol]**	**Sodium Oxalate Accumulation from Salt Batch Prior to Filter Cleaning [kg]**
8/15/2013 Oxalic Acid Primary Filter Cleaning	0	-	-	-	-	-
8/30/2013 Oxalic Acid Primary Filter Cleaning	16	59,200	224,096	4.44E+07	504	67.5
12/2/2013 Oxalic Acid Primary Filter Cleaning	0	-	-	-	-	-
1/7/2014 Caustic Primary Filter Cleaning	10	37,000	140,060	2.77E+07	315	42.2
2/7/2014 Oxalic Acid Primary Filter Cleaning	3	11,100	42,018	8.32E+06	94	12.7
3/1/2014 Caustic Primary Filter Cleaning	14	51,800	196,084	3.88E+07	441	59.1
3/18/2014 Primary Filter Flush	8	29,600	112,048	2.22E+07	252	33.7
Total	**51**	**188,700**	**714,305**	**1.41E+08**	**1606**	**215**

An estimate of the sodium oxalate accumulated and transferred to the LWHT from oxalic acid cleanings is provided in Table 17 below.

Table 17: Estimate of Sodium Oxalate accumulated from Oxalic Acid Filter Cleaning

Oxalic Acid Filter Cleaning	**Oxalic Acid added to the LWPT (Input 4)* [gal]**	**Oxalic Acid added to the LWPT (Input 4)* [gal]**	**Oxalic Acid Conc. [M]**	**Oxalate added to the LWPT [mol]**	**Residual Oxalate ** [mol]**	**LWPT Initial Vol. [gal]**	**LWPT Initial Vol. [L]**	**Conc. Oxalate in LWPT [M]**	**LWPT heel [gal]**	**LWPT heel [L]**	**Oxalate in LWPT [mol]**	**Mass of Sodium Oxalate [kg]**
8/15/13	535	2025	0.5	1013	0	2727	10323	0.098	730	2763	271	36.3
8/30/13	618	2339		1170	0	3385	12814	0.091	593	2245	205	***
12/2/13	391	1480		945	205	2752	10417	0.091	566	2143	194	26.0
2/7/14	513	1942		971	0	3980	15066	0.064	621	2351	151	20.3
Total												**83**

* The volume of oxalic acid added to the LWPT is calculated by subtracting the initial and final volumes of the oxalic acid storage tank.

**This value X_{ox} in Equation I-2. The only non-zero value applies to the 12/2/2013 cleaning, because the residual oxalates generated in the 8/30/2013 cleaning remained in the LWPT until the next cleaning with no solids washing in between.

***The mass of sodium oxalate from the 8/30/2013 cleaning is part of the calculated value for 12/2/2013.

Conclusions

It is estimated that 297 kgs of sodium oxalate were generated at 512-S via precipitation from the salt batch feed and addition from oxalic acid filter cleanings. These results are summarized in the table below.

Table 18: Estimate of Sodium Oxalate from 512-S

Filter Cleaning Dates/Types	**Sodium Oxalate Accumulation from Salt Batch Prior to Filter Cleaning [kg]**	**Sodium Oxalate Generated from Oxalic Acid Cleaning [kg]**
8/15/2013 Oxalic Acid Primary Filter Cleaning	Not applicable. All oxalates that would have accumulated prior to this cleaning would have been solubilized and processed through MCU prior to NGS Outage and Restart at MCU	36.3
8/30/2013 Oxalic Acid Primary Filter Cleaning	67.5	Included in 12/2/2013 cleaning
12/2/2013 Oxalic Acid Primary Filter Cleaning	0.0	26.0
1/7/2014 Caustic Primary Filter Cleaning	42.2	not applicable
2/7/2014 Oxalic Acid Primary Filter Cleaning	12.7	20.3
3/1/2014 Caustic Primary Filter Cleaning	59.1	not applicable
3/18/2014 Primary Filter Flush	33.7	not applicable
Sodium Oxalate Mass Subtotal [kg]	*215*	*83*
Sodium Oxalate Mass Total [kg]	***297***	

References

[I-1] SRNL-STI-2013-00700, Revision 0,"Actinide Removal Process Sample Analysis, Chemical Modeling, and Filtration Evaluation," 2014.
[I-2] CRC Handbook of Chemistry and Physics, http://www.hbcpnetbase.com/ Accessed August 7, 2014-D," 2013.
[I-3] X-ESR-H-00501, Revision 0, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 6
[I-4] WSRC-SA-6, Revision 32, "Final Safety Analysis Report Savannah River Site Defense Waste Processing Facility"

Attachment J. Estimate of Oxalates Recovered From MCU

The purpose of this calculation is to estimate the mass of sodium oxalate solids in MCU at the time of the process upset in April 2014. An estimate of the sodium oxalate solids in the contactors will be made based on contactor volume. An estimate of the sodium oxalate solids in the SSFT and SSRTs will be made based on the concentration of oxalate in the DSSHT during the clean out process.

Solids in the SSFT/SSRTs

As part of the recovery effort at MCU, the SSFT and SSRTs were deinventoried of any residual CSS (bypassing the CSSX process, sending the waste to the DSSHT and then Tank 50). The tanks were then cleaned using a series of deionized (DI) water flushes followed by 2.7 M caustic adjustment to the heels. The DI water was used to dissolve the sodium oxalate solids. Each SSFT/SSRT flush was agitated for a minimum of 4 hours and then transferred to the DSSHT with the source tank agitator running.

The first flushes were done in the SSFT. The first flush was a full SSFT volume DI water flush (approximately 6000-7000 gallons). The second flush and each subsequent flush was approximately 3000-3500 gallons. After each flush of the SSFT, the tank was camera inspected to monitor the progress of the solids removal.

The SSFT flushes were transferred to the DSSHT, and sampled once the transfer was near completion (within approximately 500 gallons) to ensure the sample was representative of the material transferred, and then the DSSHT contents were transferred to Tank 50.

Solids in the Contactors

During the trouble shooting efforts to identify and resolve the April 2014 MCU process upset, oxalate solids were identified in Extraction Contactors 401 and 402 and Scrub Contactors 501 and 502. The drain line to Extraction Contactor 401 was also found to be plugged with sodium alumina silicate (NAS) solids. Solids were not found in Extraction Contactor 403 or Strip Contactor 607. Solids were also not found in the SPA-100 or the extraction aqueous heat exchanger, although flushing completed prior to the observation could have removed oxalate solids.

Inputs

1. The volume of the V-10 contactor rotor is 6 gallons [J-2].
2. The volume of the V-05 contactor rotor is 0.6 gallons [J-2].
3. The density of sodium oxalate is 2.34 g/mL [J-3].
4. The DSSHT Volumes before and after receipt of clean out material from the SSRTs and SSFTs are taken from PI (PI Tag: \\hlwpi3\MCU-278LI3030PV2) and provided in the table below:

Table 19: DSSHT Volumes from PI Associated with MCU Cleaning Efforts

Tank Cleaned	DSSHT Maximum Clean Out Volume (gal)	Date associated with DSSHT Maximum Clean Out Volume	DSSHT Volume Post Transfer to Tank 50 (gal) Heel Volume	Date associated with DSSHT Volume Post Transfer to Tank 50
DSSHT Heel	-	-	288	6/21/2014 17:10
SSFT	6340	6/22/2014 8:10	278	6/22/2014 14:20
SSFT	2995	6/22/2014 23:00	256	6/23/2014 6:40
SSRT #2	3173	6/23/2014 21:20	245	6/23/2014 23:50
SSRT #2	3229	6/24/2014 10:30	451	6/24/2014 12:10
SSRT #2	3850	6/25/2014 8:50	502	6/25/2014 13:40
SSRT #1	6584	6/26/2014 5:00	484	6/26/2014 7:00
SSRT #1	3497	6/26/2014 19:10	466	6/26/2014 20:50
SSRT #1	3524	6/27/2014 2:30	484	6/27/2014 9:00

5. The DSSHT oxalate sample results from F/H Lab, taken before and after receipt of flush material from the SSRTs and SSFT are provided in the table below. The DSSHT volume at the time the sample was taken is also provided in the table below. DSSHT volumes are taken from PI (PI Tag: \\hlwpi3\MCU-278LI3030PV2).

Table 20: DSSHT Oxalate Sample Results from F/H Lab Associated with MCU Cleaning Efforts

Sample Date	Tank Cleaned	LIMS # (Sample Taken in the DSSHT)	DSSHT Volume at Time of Sample [gal]	Oxalate Concentration [mg/L]
6/20/2014 14:16	DSSHT Heel	200655233	2653	≤100
6/22/2014 7:47	SSFT	200655246	6239	2806
6/22/2014 21:20	SSFT	200655269	2312	436
6/23/14 16:51	SSRT #2	200655384	2723	2989
6/24/14 8:27	SSRT #2	200955518	2754	1049
6/25/14 8:25	SSRT #2	200655527	3850	413
6/26/2014 4:30	SSRT #1	200655547	6275	1498
6/26/2014 17:05	SSRT #1	200655550	3173	292
6/27/2014 2:07	SSRT #1	200655555	3317	≤100

6. The molecular weight of sodium oxalate is 134.0 g/mol. The molecular weight of the oxalate ion is 88.05 g/mol [J-3].

Assumptions

1. The DSSHT aqueous sample is representative of the contents of the DSSHT and the material transferred to the DSSHT during the flushing process (i.e., solids do not precipitate in the DSSHT and the flush material from the source tanks doesn't increase in concentration after the sample was taken.
Basis: The DSSHT was sampled once the transfer was near completion (within approximately 500 gallons) to ensure the sample was representative of the material transferred. The natural mixing of the dilute flush material transfer should allow for adequate mixing in the DSSHT. The gradual decrease in oxalate concentration (refer to Table 20) as the clean out progressed

suggests that solids were adequately removed from the source tanks and did not accumulate in the DSSHT.

2. The sodium oxalate solids found in the contactors are assumed to occupy the equivalent volume of one full V-10 rotor and one full V-05 rotor.
   Basis: Solids were found in Extraction Contactors 401 and 402 (V-10 contactors) and Scrub Contactors 501 and 502 (V-05 contactors). Visual inspection of the contactors occurred after cleaning of the extraction contactor, so some solids may have been removed. During the process upset, material exited with the DSS and the SE, which indicates that the blockage in the contactors was only partial (full rotor blockage would have led to a significant disparity in expected volumes). This implies that no one contactor had a rotor completely filled with solids. In addition, the solids analyzed indicated the presence of a significant amount of aluminum hydroxide compounds, amorphous nitrates (likely present as a result of contactor cleaning), titanium, and sodium aluminum silicate. The oxalate solids are estimated to be at least 40 – 50 wt. % of the solids in the contactor rotors (likely closer to 60 wt. %) [J-4].
   Sensitivity: If the entire rotor volume associated with all four contactors where solids were found (two V-10s and two V-05s) was assumed to be completely filled with sodium oxalate the sodium oxalate estimate would increase to approximately 117 kgs. If sodium oxalate were assumed to be 60 wt.% of the solids occupying the four full contactors, the estimate of oxalates would be 70 kgs (this assumes the density of all the solids in the contactor are approximately the same as sodium oxalate).

Estimate of Solids in the SSFT/SSRTs

The mass of oxalate added to the DSSHT is calculated for each transfer of flush material from the clean out effort by using sample data to establish the concentration of oxalate before and after each transfer. These concentration can be used to determine the moles of oxalate added by taking into account the oxalates remaining the DSSHT heel from the previous cleaning evolution.

Equation J-1:

$$\begin{aligned} m_{NaOx} &= \left[\left((V_{DSSHT,f}) \left(\frac{3.7854\ L}{gal} \right) \left[C_{ox\_f} \left(\frac{1\ g}{1000\ mg} \right) \left(\frac{1\ mol\ oxalate}{88.05\ g\ oxalate} \right) \right] \right) \right. \\ &\quad \left. - \left((V_{DSSHT,i}) \left(\frac{3.7854\ L}{gal} \right) \left[C_{ox\_i} \left(\frac{1\ g}{1000\ mg} \right) \left(\frac{1\ mol\ oxalate}{88.05\ g\ oxalate} \right) \right] \right) \right] \left(\frac{1\ mol\ sodium\ oxalate}{1\ mol\ oxalate} \right) \left(\frac{134\ g\ sodium\ oxalate}{1\ mol\ sodium\ oxalate} \right) \end{aligned}$$

$$\begin{aligned} m_{NaOx\_SSFT1} &= \left[\left((6340\ gal) \left(\frac{3.7854\ L}{gal} \right) \left[2806\ mg/L \left(\frac{1\ g}{1000\ mg} \right) \left(\frac{1\ mol}{88.05\ g} \right) \right] \right) \right. \\ &\quad \left. - \left((288\ gal) \left(\frac{3.7854\ L}{gal} \right) \left[100\ mg/L \left(\frac{1\ g}{1000\ mg} \right) \left(\frac{1\ mol}{88.05\ g} \right) \right] \right) \right] \left(\frac{134\ g}{1\ mol} \right) \end{aligned}$$

$$m_{NaOx\_SSFT1} = \mathbf{102\ kg}$$

Where:

m_{NaOx}= Mass of sodium oxalate [kg]

$V_{DSSHT,i}$ = Volume of DSSHT heel prior to receiving the next cleanout flush material [gal]
$V_{DSSHT,f}$ = Maximum Volume of DSSHT cleanout flush material [gal]
$C_{Ox,i}$ = DSSHT oxalate sample concentration for the heel prior to receiving the next cleanout flush material [mg/L]
$C_{Ox,f}$ = DSSHT oxalate sample concentration after receiving the cleanout flush material [mg/L]

Estimate of Solids in the Contactors

The mass of oxalates for each contactor is estimated as follows:

Equation J-2:

$$m_{NaOx\_Contactors} = V_{V-10}\left(\frac{3.7854\,L}{gal}\right)\rho_{NaOx}\left(\frac{1000\,mL}{1\,L}\right)\left(\frac{1\,kg}{1000\,g}\right) + V_{V-05}\left(\frac{3.7854\,L}{gal}\right)\rho_{NaOx}\left(\frac{1000\,mL}{1\,L}\right)\left(\frac{1\,kg}{1000\,g}\right)$$

$$m_{NaOx\_Contactors} = 6\,gal\left(\frac{3.7854\,L}{gal}\right)2.34\frac{g}{mL}\left(\frac{1000\,mL}{1\,L}\right)\left(\frac{1\,kg}{1000\,g}\right) + 0.6\,gal\left(\frac{3.7854\,L}{gal}\right)2.34\frac{g}{mL}\left(\frac{1000\,mL}{1\,L}\right)\left(\frac{1\,kg}{1000\,g}\right)$$

$$m_{NaOx\_Contactors} = 58\,kg$$

$m_{NaOx\_Contactors}$= Mass of sodium oxalate from the contactors [kg]
V_{V-10} = Volume of V-10 rotor [gal]
V_{V-05} = Volume of V-05 rotor [gal]
ρ_{NaOx} = Density of sodium oxalate [g/mL]

Results

An estimated 58 kg of sodium oxalate was assumed to be present in the contactors prior to cleaning. Results for the estimate of sodium oxalate removed from the SSRTs and SSFT are provided in the table below. In total 297 kg of sodium oxalate solids were estimated to be present in MCU prior to cleanup.

Table 21: Estimated Mass of Sodium Oxalate Removed during Clean Out of SSRTs and SSFT

Tank Cleaned	DSSHT Maximum Clean Out Volume (gal)	DSSHT Volume Post Transfer to Tank 50 (gal) Heel Volume	Volume Added to DSSHT (gal)	Volume Added to DSSHT (L)	Oxalate Conc. [mg/L]	Oxalate Conc. [mol/L]	Oxalate Content of DSSHT Maximum Clean Out Volume [mol]	Oxalate Content of DSSHT Heel Volume [mol]	Oxalate Added From Cleaned Tank [mol]	Mass of Sodium Oxalate added from the Cleaned Tank [kg]
DSSHT Heel	-	288	-	-	≤100	1.14E-03	-	1.24E+00	-	
SSFT	6340	278	6062	22946	2806	3.19E-02	7.65E+02	3.36E+01	7.64E+02	102.32
SSFT	2995	256	2739	10367	436	4.95E-03	5.61E+01	4.80E+00	2.26E+01	3.02
SSRT #2	3173	245	2928	11082	2989	3.39E-02	4.08E+02	3.15E+01	4.03E+02	53.99
SSRT #2	3229	451	2778	10517	1049	1.19E-02	1.46E+02	2.03E+01	1.14E+02	15.30
SSRT #2	3850	502	3348	12672	413	4.68E-03	6.83E+01	8.91E+00	4.80E+01	6.43
SSRT #1	6584	484	6100	23089	1498	1.70E-02	4.24E+02	3.12E+01	4.15E+02	55.61
SSRT #1	3497	466	3031	11475	292	3.32E-03	4.40E+01	5.85E+00	1.28E+01	1.71
SSRT #1	3524	484	3039	11505	≤100	1.14E-03	1.51E+01	2.08E+00	9.30E+00	1.25
Total										**239**

References

[J-1] SRR-LWE-2014-00088, Revision 1, “Path Forward for the cleanout of the SSFT and SSRTs in the MCU,” June 2014.

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[J-3] CRC Handbook of Chemistry and Physics, http://www.hbcpnetbase.com/ Accessed August 7, 2014

[J-4] SRNL-L3100-2014-00128, Revision 0, “Results of Further Analyses of Solids Removed from MCU,” June 2014.