Status Of Chemical Cleaning Of Waste Tanks At The Savannah River Site – F-Tank Farm Closure Project – 9114

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ABSTRACT

Chemical Cleaning is currently in progress for Tanks 5 and 6 at the Savannah River Site. The Chemical Cleaning process is being utilized to remove the residual waste heel remaining after completion of Mechanical Sludge Removal. This work is required to prepare the tanks for closure.

Tanks 5 and 6 are 1950s vintage carbon steel waste tanks that do not meet current containment standards. These tanks are 22.9 meters (75 feet) in diameter, 7.5 meters (24.5 feet) in height, and have a capacity of 2.84E+6 liters (750,000 gallons).

Chemical Cleaning adds 8 wt % oxalic acid to the carbon steel tank to dissolve the remaining sludge heel. The resulting acidic waste solution is transferred to Tank 7 where it is pH adjusted to minimize corrosion of the carbon steel tank. The Chemical Cleaning flowsheet includes multiple strikes of acid in each tank. Acid is delivered by tanker truck and is added to the tanks through a hose assembly connected to a pipe penetration through the tank top. The flowsheet also includes spray washing with acid and water.

This paper includes an overview of the configuration required for Chemical Cleaning, the planned flowsheet, and an overview of technical concerns associated with the process. In addition, the current status of the Chemical Cleaning process in Tanks 5 and 6, lessons learned from the execution of the process, and the path forward for completion of cleaning in Tanks 5 and 6 will also be discussed.

INTRODUCTION

The Savannah River Site (SRS) is in the process of removing waste from several 1950s vintage carbon steel waste tanks that do not meet current containment standards. Mechanical cleaning activities are complete for Tanks 5 and 6 and Chemical Cleaning activities are currently in progress.

Mechanical cleaning utilizes either long shafted slurry pumps or, as is the case for Tanks 5 and 6, submersible mixing pumps (SMPs) to suspend the sludge as a slurry. The slurry is pumped into other waste tanks for further processing. Mechanical cleaning effectiveness is limited due to numerous interferences from cooling coils and other equipment obstructions within the tanks. Mechanical cleaning has been completed for several tanks at SRS with varying degrees of success. The final sludge heel volumes for Tank 5 and Tank 6 at the completion of mechanical cleaning were approximately 1.32E+04 liters (3,500 gallons) and 2.27E+04 liters (6,000 gallons), respectively [1,2]. The difference in the final sludge volumes is due to using three SMPs for mixing in Tank 5 versus two SMPs in Tank 6 [3].

The Chemical Cleaning process will add 8 wt % oxalic acid to the waste tank in order to dissolve the remaining sludge heel. The resulting acidic waste solution will be transferred to Tank 7 where it will be pH adjusted to meet existing corrosion control requirements and then stored awaiting further processing.

CHEMICAL CLEANING FLOWSHEET AND CONFIGURATION

Prior to the first acid strike, well water was added to each tank to dilute the liquid supernate heel. The heel is approximately 30,300 liters (8,000 gallons) and was diluted using 1.7E+5 liters (45,000 gallons) of well water. The purpose of the dilution is to lower the sodium molarity of the heel to reduce the formation of sodium oxalate precipitate as the oxalic acid reacts with the supernate.

The planned flowsheet for Chemical Cleaning includes three acid strikes in each waste tank. The first strike adds acid at a 20:1 volume ratio of acid to sludge and mixing is provided for a minimum of 24 hours using two SMPs to aid in dissolution and suspension of the sludge. It is recognized that the pumps may be stopped or slowed down in response to process variables such as HEPA filter loading, tank temperature increases, purge ventilation flow reduction, or due to problems with pump performance. Many of these parameters are established by the safety analyses.

Subsequent acid strikes utilize a 13:1 volume ratio of acid to sludge with no mixing since the resulting liquid level in the tank is expected to be too low to support operation of the SMPs. One week of soak time is planned for each acid strike with the start of the soak being defined as the start of acid addition. Oxalic acid (8 wt %) at 50ºC is delivered by tanker truck and added to the tanks using an unloading manifold and hose connections to a pipe penetration (or “downcomer”) through the tank top.

An oxalic acid spray wash is performed for each tank and is allowed to be performed in conjunction with an acid strike. The spray wash is accomplished using a modified downcomer with a rotating Gamajet Model IV-GT dual ~11mm (7/16 in) spray nozzle at the discharge end of the downcomer. During spray washing, acid continues to be delivered by tanker truck and unloaded via hoses. However, a skid mounted booster pump is connected between the tanker truck and the downcomer to raise the pressure and flow of acid to the Gamajet to approximately 5.86E+5 N m^{-2} (85 psi) and 380 liters per minute (100 gpm). The spray wash tool has a range of approximately 13.7 m (45 ft) and will be used in two risers on opposite sides of each tank (See Figure 1) in order to wet all interior surfaces and components in the tanks.

At the completion of each acid strike, the acid waste solution is transferred to Tank 7 to await further processing. Caustic and/or supernate is added to Tank 7 (if needed) prior to each acid waste transfer to ensure that the Tank 7 chemistry is maintained to minimize corrosion of the

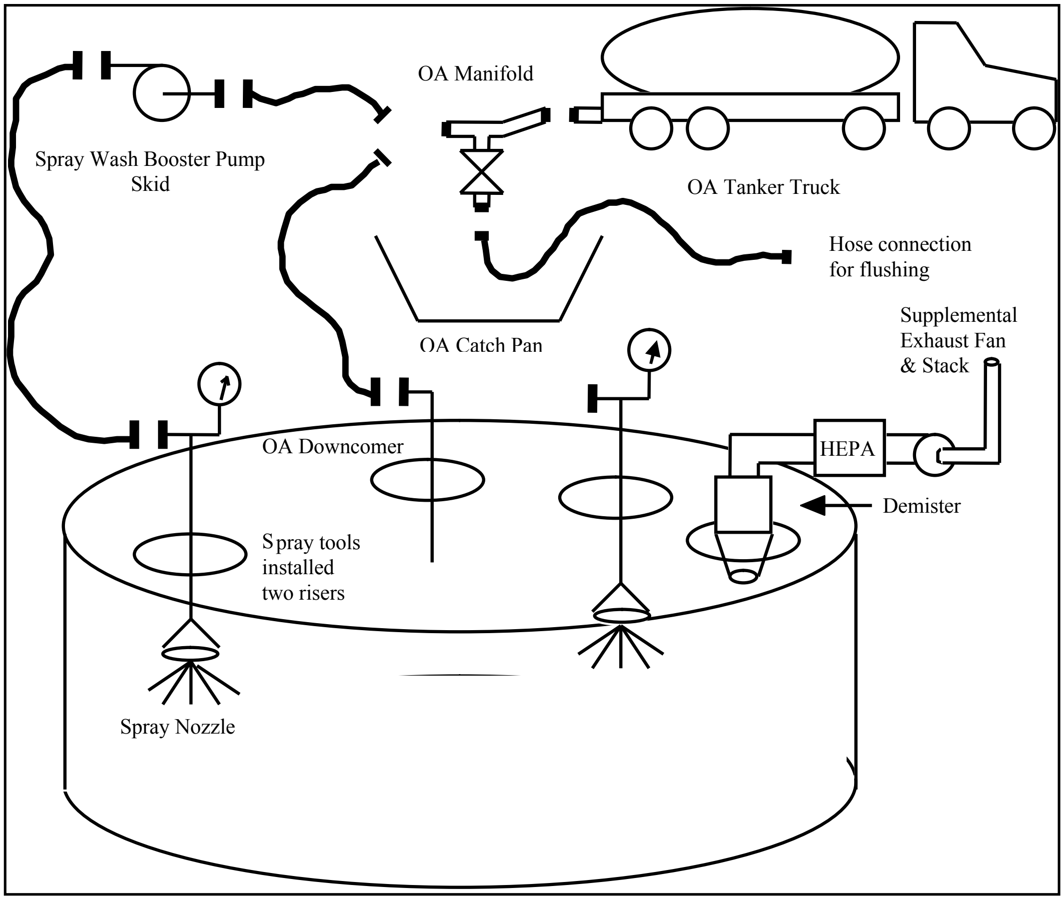

Figure 1. Tank Configuration for Chemical Cleaning

carbon steel tank. Slurry pump(s) are operated in Tank 7 during the transfer to promote mixing and prevent the formation of a floating acid layer in the tank.

The planned flowsheet assumes that 70% of the sludge heel will be removed in the first strike, 50% of the remaining solids will be removed in the second strike and 30% of the remaining solids will be removed in the third strike.

It should be noted that while three acid strikes are planned, the actual number performed will be determined by the effectiveness of the process and the actual volume of remaining sludge after each acid strike evolution. Sludge mapping will be performed after each strike to determine the volume of the remaining sludge heel. Mapping is performed using video camera inspection of the tank interior and estimating sludge mound dimensions by comparison to known dimensions of the tank interior and tank internal components (e.g., cooling coils and coil supports). The height of sludge mounds can be determined by the tank liquid level observed as the mound is uncovered during a transfer out of the tank. Mapping can not be performed accurately unless the initial liquid level is high enough to completely cover the sludge mounds.

At the completion of the acid strikes, failed cooling coils are flushed into the tank to remove any waste that has migrated to the interior of the coils. Additionally, a water spray wash is performed to rinse residual acid from the tank interior surfaces and components.

The final step for Chemical Cleaning is a mechanical-mixing cleaning evolution (using well water) to rinse and remove residual acid from the bottom of the tank and to remove as much of the remaining solids as possible. SMPs are used during this cleaning evolution. Completion of Chemical Cleaning will prepare the tanks for closure which includes filling the tanks with grout.

A supplemental ventilation system (SVS) is installed on each tank to ensure that the tank remains under vacuum for contamination control. The SVS is needed to handle the large volumes of carbon dioxide that are expected to form as the acid reacts with the sludge heel. Previous bench scale process testing at the Savannah River National Laboratory (SRNL) provided data that supported this requirement. Additionally, the SVS is designed to handle the vapor space volume expansion that occurs during spray washing.

The SVS includes a skid mounted HEPA filtered blower with dampers, a Variable Frequency Drive to adjust unit flow rate, a shielded riser connection to the tank vapor space, a demister with dampers, and an elevated vertical stack to ensure that carbon dioxide and other hazardous chemical vapors are dispersed so that their concentrations remain within regulatory limits in personnel breathing areas. Flexible duct was used to connect the various components together.

TECHNICAL CONCERNS DURING CHEMICAL CLEANING

Several technical issues were identified based upon oxalic acid cleaning of Tank 16 during the late 1970s and recent bench scale process testing at SRNL. The most significant issues identified include loss of tank vacuum resulting in the spread of contamination, corrosion of the carbon steel tanks walls, formation of new solids in the treatment tanks, and effectiveness of the process at removing all of the residual heel material. The bases for these issues are discussed in more detail in the remainder of this section.

Loss of tank vacuum was discussed earlier in this paper. This could result from large volumes of carbon dioxide generated during the reaction of the oxalic acid with the sludge or due to tank vapor space expansion when warm acid (at 50ºC) or water is sprayed into the tank. The generation of large volumes of carbon dioxide was observed during the SRNL bench-scale process testing and loss of tank vacuum due to vapor space expansion was observed during oxalic acid cleaning of Tank 16. The supplemental ventilation system was designed to accommodate these challenges.

During SRNL testing, new solids (i.e., oxalates) formed as the acid reacted with the sludge and with carbon-steel coupons simulating the tank walls and cooling coils. Some of these solids proved difficult to suspend and remove in the laboratory tests.

The SRNL process testing also provided a bounding corrosion rate for the carbon steel tank walls in contact with the oxalic acid. The bounding rate was determined to be 1.5 mm per year (60 mils per year). This rate of corrosion was evaluated for effect on tank structural integrity. The evaluation confirmed that the waste tank would remain intact for the case where the tank remains in Chemical Cleaning for a full year.

CURRENT STATUS OF TANKS 5 AND 6 CHEMICAL CLEANING

The following parts of the flowsheet have been completed for Tanks 5 and 6:

- Liquid supernate heel dilution
- First Acid Strike with SMP operation
- Second Acid Strike
- Acid Spray Washing
- Water Spray Washing

See Table 1 for a timeline which provides dates, addition volumes, and heel volumes for each of these evolutions for each tank.

Table I. Chemical Cleaning Timeline

Tank 5 Evolutions	Date	Heel Volume (liters x 10^3 (gallons))	Addition Volumes (liters x 10^3 (gallons))	Comments
MSR Complete	May 9, 2008	23.2 (3,500)		
Heel Dilution	June 7, 2008		170 (45,000)	Date Completed
First Acid Strike	June 10-17, 2008		255 (67,500)	Acid Addition Phase
Well Water Addition	June 18, 2008		163 (43,000)	
SMP Operation & Transfer to Tank 7	June 19-23, 2008	10.4 (2,750)		
Second Acid Strike	August 18-21, 2008		52.2 (13,800)	Acid Addition Phase
Transfer to Tank 7	October 10-11, 2008	13.6 (3,600)		
Acid Spray Wash	October 22, 2008		36.5 (9,650)	
Water Spray Wash	November 10-11, 2008		37.9 (10,000)	
Transfer to Tank 7	November 20, 2008			

Tank 6 Evolutions	Date	Heel Volume (liters x 10^3 (gallons))	Addition Volumes (liters x 10^3 (gallons))	
MSR Complete	August 5, 2007	22.7 (6,000)		
Heel Dilution	June 8, 2008		170 (45,000)	Date Completed
First Acid Strike	June 18-27, 2008		420 (110,900)	Acid Addition Phase
SMP Operation	July 3-6, 2008			
SMP Operation & Transfer to Tank 7	July 13-14, 2008	9.09 (2,400)		
Second Acid Strike	August 27-September 2, 2008		110 (29,000)	Acid Addition Phase
Transfer to Tank 7	October 11, 2008	12.3 (3,250)		
Acid Spray Wash	November 5, 2008		36.5 (9,650)	
Water Spray Wash	November 12-13, 2008		37.9 (10,000)	
Transfer to Tank 7	November 21, 2008			

Additional details associated with the completed work are provided below.

During the first acid strike, all sludge solids in Tank 5 were covered by acid one day prior to the completion of acid unloading. As soon as acid unloading was completed, well water additions to the tank were initiated in order to bring the liquid level to 114.3 cm (45 inches) which is the minimum level required to start SMPs due to minimum suction head. All sludge solids in Tank 6 were covered by acid four days prior to the completion of acid unloading. The amount of acid added to Tank 6 was sufficient to meet the minimum liquid level required for SMP operation. Therefore, no well water additions were required for the first acid strike for Tank 6. Two SMPs were operated during the first acid strikes.

During the first acid strike in each tank a liquid dip sample was taken of the acid waste solution during the transfer after the SMPs were stopped. The SMPs were stopped at a tank level of

76.2 cm (30 inches) to prevent spraying of the waste into the tank vapor space which is a safety basis requirement to prevent aerosolization of the waste in the tank.

Sludge mapping was performed during and after each acid waste transfer to estimate the volume of solids remaining in the tank. SRNL analysis of the dip samples has indicated that some of the remaining solids may be oxalate precipitates that formed in the tank during the cleaning evolution. The pH of the acid waste solution at the end of each cleaning cycle was expected to be less than or equal to 2. The pH of the solution at the end of the Tank 5 first acid strike was 4. An SRNL evaluation concluded that the most likely cause for this higher than expected pH condition is higher than expected concentrations of base ions in the Tank 5 sludge heel. The pH of the Tank 6 acid waste solution sample was approximately 2 as expected. Dip samples for both tanks taken at the completion of the second acid strike and after the spray washing were also found to have a pH of approximately 2.

The second acid strikes for each tank were added using a modified downcomer designed to improve the contact of the acid with the sludge. The modified downcomer had a 90º reducing elbow at the discharge end so that the acid stream was directed horizontally to the top of the main sludge mound. The reducing elbow also caused a slight expansion of the flow stream. The effect on the main sludge mound in Tank 5 from this modification was to lower the peak of the mound from 56 centimeters (22 inches) to 41 centimeters (16 inches) and to lower its overall profile. Flow into Tank 6 was throttled during the second acid strike to minimize the impact to HEPA differential pressure and tank vacuum. Because of this, the acid stream did not reach the solids mound and, therefore, the modification had no impact to the size or shape of the main sludge mound.

During the second acid strikes, the transfer of the acid waste solutions out of each tank after the minimum soak time was reached was delayed five to six weeks due to equipment problems in Tank 7. At the completion of the second strikes in both tanks, the total solids volume had increased. The increase in solids volume is attributed to oxalate precipitation and is shown graphically in Figure 2. The formation of additional solids is detrimental to the overall cleaning effort, and therefore, the third acid strike was combined with the acid spray wash and the total volume of acid to be added was reduced to the minimum amount needed to complete the spray wash. This change from the original flowsheet was made after consultation with SRNL.

Oxalic acid spray washes were completed in both tanks. Two tankers of acid (36,500 liters total (9,650 gallons)) were used for the spray wash in each tank. One tanker of acid was unloaded through each of the spray nozzles at riser 2 and riser 7. These risers are located 180 degrees apart so that maximum coverage of the tank interior is obtained (refer to Figure 1). Mapping was not performed at the completion of acid spray washing because the liquid level in the tank was not sufficient to cover the solids mounds to support the mapping process.

Following the acid spray washes, spray washing with de-ionized water (DIW) was performed to rinse the acid from the tank roof, walls, and components. DIW was used to minimize the formation of new solids that could form through reaction of dissolved or suspended minerals in well water with the acid waste solution left in the tanks after the acid spray washes.

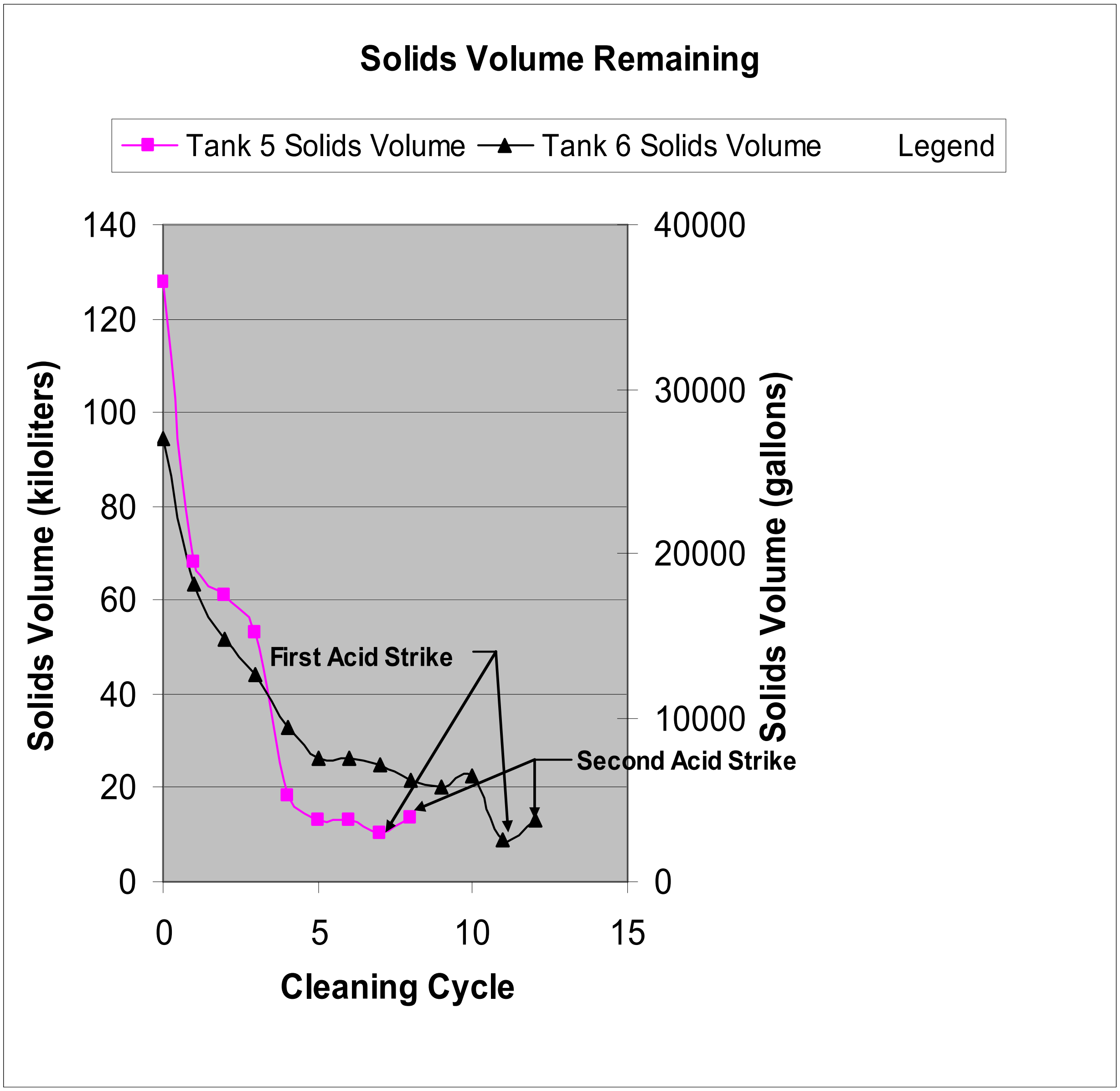

Figure 2. Solids Volume Remaining After Each Cleaning Cycle

Visual examination of the tank interior revealed no significant changes in the shape or configuration of the solids mounds at the end of the spray washing. However, the tank walls and coils appeared cleaner with original construction markings visible.

The combined acid and DIW spray wash solutions were transferred to Tank 7. Failed cooling coils were flushed in Tank 5 and the final water wash with SMP operation was completed in December, 2008. Preparations are in progress for failed coil flushing in Tank 6 followed by the final water wash with SMP operation.

LESSONS LEARNED

Lessons learned thus far in the execution of the Chemical Cleaning process for Tanks 5 and 6 will be discussed in this section.

Loss of tank vacuum due to high overall gas generation rate (primarily carbon dioxide) has not been observed. Tank vacuum did not significantly change during bulk acid addition or while the acid was soaking, mixing, and being transferred out of Tanks 5 and 6. Tank vacuum and HEPA filter differential pressure were affected during acid spray washing and when bulk addition (during the second acid strikes) was performed in each tank using the modified downcomer with a 90º reducing elbow. The supplemental ventilation system was found to be capable of handling the effects of the spray washing and the use of the modified downcomer, although, flow through the modified downcomer was reduced during Tank 6 acid addition.

Operational limits for tank vacuum and HEPA filter differential pressure were changed prior to spray washing to reduce the likelihood of an unnecessary shut down of the spray wash system. The low tank vacuum alarm setpoint was changed from 0.187 mm-Hg (0.1 in-wc) to 0.093 mm-Hg (0.05 in-wc) and the high HEPA differential pressure alarm setpoint was changed from 2.8 mm-Hg (1.5 in-wc) to 3.5 mm-Hg (1.9 in-wc). The change to the limits proved to be effective as there were no inadvertent shutdowns caused by these alarms.

Visual inspections of the tank interiors have been performed during the cleaning process. Figure 3 is a photograph of Tank 5 prior to the fourth cycle of mechanical cleaning and is provided as an example of tank cleanliness prior to Chemical Cleaning. Inspections during Chemical Cleaning have not revealed evidence of severe corrosion since no large accumulations of corrosion products on tank walls and components have been observed (See Figure 4). These inspections have also shown that the majority of the tank is in a clean condition. Ultrasonic testing of the waste tank side walls was performed prior to Chemical Cleaning to measure wall thickness. This testing will be repeated at the completion of Chemical Cleaning to determine actual corrosion rates for the carbon steel walls in contact with the oxalic acid.

Condensation occurred in the stack and blower of the supplemental ventilation system during cold weather. Leakage of the condensation from the SVS was controlled using containment pans. The demister was not effective in preventing the condensation as it is designed to remove entrained moisture not water vapor.

During the unloading of the first acid tankers into Tank 5 and Tank 6, fumes were seen exhausting from the waste tank purge ventilation exhaust stack and the supplemental ventilation system stack. The fumes were generally described by personnel as being a faint brownish yellow color. It is believed that the fumes are NO_x gases. Off-gassing is expected during the Chemical Cleaning process due to the chemical reaction of the oxalic acid with the sludge. Industrial Hygiene (IH) has periodically monitored the stacks and the tank top area for mercury, carbon dioxide (CO_2), NO_x, and ammonia and has found no elevated vapor concentrations except for carbon dioxide emissions from the ventilation stacks. This was confirmed with additional vapor sampling with SRNL sample analysis via gas chromatography. As acid unloading continued, the colored fumes faded until they were no longer noticeable. IH monitoring will continue for the duration of the Chemical Cleaning process.

Figure 3. Tank 5 prior to completion of mechanical cleaning.

Figure 4. Tank 5 after the second Chemical Cleaning acid strike.

The formation of new solids in the treatment tanks has proven to be a significant issue during the Chemical Cleaning process. This phenomenon was observed in the bench-scale process testing at SRNL. Inspections and solids mapping confirmed that new solids formed in Tanks 5 and 6 during the Chemical Cleaning process. However, it will not be possible to determine if the remaining solids in the tanks are new oxalate precipitates, un-reacted sludge, or a combination of the two until solids samples are obtained and analyzed.

PATH FORWARD

The planned flowsheet for Chemical Cleaning has been modified based upon the formation of additional solids in Tanks 5 and 6. The third acid strike was combined with the acid spray wash and the total volume of acid to be added was reduced to the minimum amount needed to complete the spray wash.

Planning is underway to obtain a sample of the residual solids (if any) at the completion of Chemical Cleaning. Sample analysis will be performed by SRNL to determine the make-up of the residual solids. A path forward will be developed based upon whether the amount of radionuclides remaining in the tank meets regulatory requirements for tank closure. The sample analysis will also provide the data needed to develop a flowsheet for future cleaning if required.

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