Chemical Sludge Heel Removal At The Savannah River Site F-Tank Farm Closure Project – 8183

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ABSTRACT

Chemical Sludge Removal (CSR) is the final waste removal activity planned for some of the oldest nuclear waste tanks located at the Savannah River Site (SRS) in Aiken, SC. In 2008, CSR will be used to empty two of these waste tanks in preparation for final closure. The two waste tanks chosen to undergo this process have previously leaked small amounts of nuclear waste from the primary tank into an underground secondary containment pan.

CSR involves adding aqueous oxalic acid to the waste tank in order to dissolve the remaining sludge heel. The resultant acidic waste solution is then pumped to another waste tank where it will be neutralized and then stored awaiting further processing. The waste tanks to be cleaned have a storage capacity of 2.84E+06 liters (750,000 gallons) and a target sludge heel volume of 1.89E+04 liters (5,000 gallons) or less for the initiation of CSR. The purpose of this paper is to describe the CSR process and to discuss the most significant technical issues associated with the development of CSR.

INTRODUCTION

The Savannah River Site (SRS) is in the process of removing waste from some of the 1950s vintage carbon steel waste tanks that do not meet current containment standards. Waste Removal activities, which include mechanical and chemical cleaning, are currently in progress for Tanks 5 and 6 at SRS.

Mechanical cleaning activities have been completed for Tank 6 and have been initiated for Tank 5. 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 waste into a slurry. The slurried waste is pumped into other waste tanks for further processing. Mechanical cleaning effectiveness has been limited due to numerous interferences from cooling coils and other equipment obstructions within the tanks (see Figure 1). Mechanical cleaning has been completed for several tanks at SRS with varying degrees of success. The final sludge heel volume for Tank 6 at the completion of mechanical cleaning is approximately 2.27E+04 liters (6,000 gallons).

The completion of mechanical cleaning is declared when the amount of sludge waste removed during each cleaning evolution becomes marginal (typically, less than 5%). Graphing of the sludge heel over time is a tool that is used to aid with this decision. The sludge heel volume usually falls rapidly during the first few cleaning cycles. The amount of sludge removed during each cycle decreases over time and the slope of the graph flattens. Once this occurs, mechanical cleaning is declared to be complete if the remaining sludge volume is less than 2.84E+04 liters (7,500 gallons), which is currently the maximum sludge volume allowed at mechanical cleaning completion per contract with the Department of Energy.

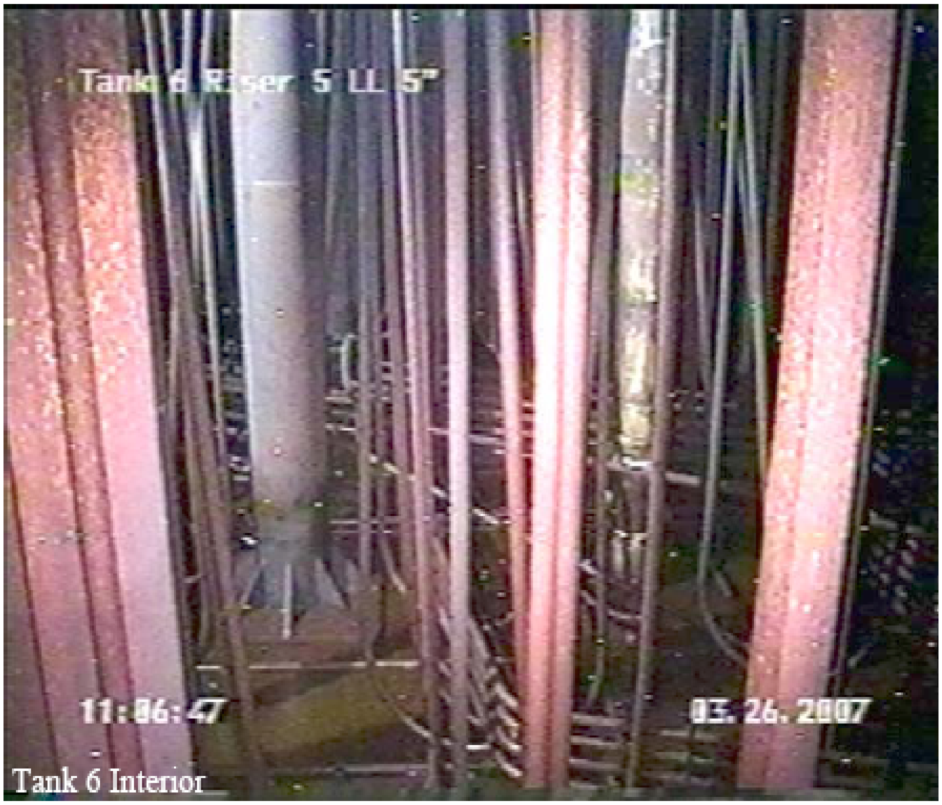

Fig. 1. Tank 6 interior showing numerous cooling coil and equipment interferences.

If the sludge heel graph flattens prior to reaching 2.84E+04 liters (7,500 gallons), then additional mechanical cleaning activities (e.g., installation of additional or more powerful mixing pumps) are performed. A target value for completion of mechanical cleaning is established at 1.89E+04 liters (5,000 gallons) based upon the past history of waste tank mechanical cleaning effectiveness at the Savannah River Site.

The final phase of waste removal is Chemical Sludge Removal (CSR). The CSR process will add 8 weight-percent 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 neutralized to meet existing corrosion control requirements and then stored awaiting further processing.

The current plan for CSR includes three acid strikes in each waste tank. The first strike will add acid at a 20:1 volume ratio of acid to sludge and mixing will be provided to aid in dissolution and suspension of the sludge. Subsequent strikes will utilize a 13:1 volume ratio of acid to sludge with no mixing (the liquid level in the tank will be too low to support operation of mixing devices). Acid will be delivered by tanker truck and will be added to the tanks by hose(s) via a pipe penetration through the tank top. The final acid strike will be added via a spray wash nozzle to clean the entire interior of the waste tank.

The final steps for CSR will include a well water spray wash followed by a final mechanical-mixing cleaning evolution (using well water) to rinse and remove residual acid from the tank and to remove any remaining insoluble solids from the tank that are capable of being slurried. Completion of CSR will prepare the tanks for closure which includes filling the tanks with grout.

HISTORY OF THE CHEMICAL SLUDGE HEEL REMOVAL PROCESS AT SRS

Chemical cleaning of a waste tank using oxalic acid has been previously performed in Tank 16 at SRS in the late 1970s. Acid cleaning was utilized in combination with mechanical cleaning to remove 99.9% of the original waste volume from Tank 16 [1]. This evolution was performed as a demonstration of potential waste removal techniques.

Phase 1 of the demonstration used various combinations of long shafted slurry pumps to remove 99% of the original waste volume. At the completion of the first phase, 5.22E+03 liters (1,380 gallons) of sludge remained in the tank. Phase 2 of the demonstration included an additional mechanical cleaning step, two water washes, three acid washes, and a final water rinse. At the completion of the second phase, no significant sludge deposits were observed on the tank floor.

A 7.62 cm (3 inch) diameter sample pan was installed on the tank bottom prior to the final water rinse. The tank bottom was allowed to dry after the completion of Phase 2 and the sample pan was retrieved to determine if residual waste remained in the tank. A thin layer of solids was observed to be coating the sample pan. Analysis of the solids showed that the majority of the activity remaining in the tank was due to Sr-90 at 87 mCi/g. Other radioisotopes found in the residue material were Cs-137 at 0.004 mCi/g and Pu-238/Pu-239 at 0.006 mCi/g [1].

During the water washes and acid washes, oxalic acid and water were added to the tank via spray nozzles at a temperature of 90^{o}C. The elevated temperatures and the spray addition resulted in rapid expansion of the gases in the vapor space of the tank. This lead to pressurization of the tank (the tank is normally operated at a slight vacuum), release of a small amount of contamination at tank top riser plugs, and several instances where ventilation system HEPA filters became wetted.

TECHNICAL ISSUES AND RESOLUTION

The Tank 16 demonstration as well as a variety of technical studies have identified several technical issues associated with oxalic acid cleaning of carbon steel waste tanks [1,2]. These technical issues include HEPA filter wetting, pressurization of the tank, formation of a floating solids layer that could trap hydrogen, accelerated corrosion of the carbon steel tank walls, and increased hydrogen generation due to the corrosion reaction. Additionally, process planning discussions identified potential nuclear criticality concerns.

HEPA filter wetting and tank pressurization were observed problems during the Tank 16 demonstration and can result in radiological contamination and airborne releases. Pressurization in Tank 16 was due to; 1) expansion of the tank vapor space gases during spray washing with hot acid and water; and 2) gas generation from the reaction of acid with sludge and carbon steel.

Laboratory studies have shown that oxalic acid will accelerate corrosion of carbon steel and that this reaction can result in the generation of hydrogen. Accelerated corrosion can weaken the structural integrity of the tank which must maintain its ability to contain the waste until waste removal activities are complete. Excessive hydrogen generation can lead to a waste tank explosion.

The formation of a floating solids layer during neutralization is a phenomenon that was observed during sludge heel removal using oxalic acid at the DOE Hanford site during 2004 [3]. This layer, which is estimated to be 10 to 30 inches thick, could trap gases that form during the neutralization and subsequent waste storage. Trapped gas is considered a technical issue due to the possibility of an uncontrolled release of these gases leading to tank pressurization or a waste tank explosion.

Nuclear criticality was a concern because it was not known whether the dissolution process or precipitation during the neutralization process would preferentially separate the fissile material from the abundant poisons (e.g., neutron absorbing poisons such as iron and manganese) found in the sludge waste.

To address these issues, extensive laboratory experiments were performed at the Savannah River National Laboratory (SRNL) using both simulated and real nuclear waste material [4,5]. The experiments were performed at three different temperatures (25^{o}C, 50^{o}C, and 75^{o}C) and at two different mixing conditions. Some of the corrosion tests using simulant included irradiation to determine if radiolysis affected the corrosion rate. Additional parameters evaluated included the effect of light on the acid reactions and the effect of oxygen on the acid reactions. These experiments were designed to determine bounding values for the carbon steel corrosion rate, the hydrogen generation rate, and the overall gas generation rate (including determination of the principle gases produced). The experiments also examined the efficiency of the process at various temperature and mixing conditions, evaluated the potential for preferential dissolution or precipitation of fissile material and poisons, and evaluated the potential to form floating solids during neutralization and whether these solids would trap gas. Completion of this experimental work provided data that allowed calculations to be performed that; 1) demonstrated that the structural integrity of the tank could be maintained during CSR, and 2) that waste tank explosions could be prevented using the existing credited purge ventilation systems for the waste tanks. The data also supported the completion of a Nuclear Safety Criticality Evaluation that showed that criticality was not credible during CSR.

The experimental work also provided a total gas generation rate that allowed for the proper sizing of a supplemental ventilation system to prevent tank pressurization. The supplemental ventilation system will include a demister to help prevent HEPA filter wetting during CSR. Calculations have been performed to ensure that this system can maintain the tank at a slight vacuum during the heated acid spray washing that is planned as part of the CSR process.

The formation of a floating solids layer during neutralization of the acid waste solution was confirmed by the experiments. However, these solids were found to be easily mixed and quickly settled to the bottom of the tank after mixing. Additionally, gas bubbles injected into the solution below the solids layer were not trapped by the solids.

SEQUENCE OF OPERATIONS DURING CSR

The sequence of operations during CSR is described in this section [6]. CSR will begin after mechanical cleaning activities have been completed. Mechanical cleaning is complete for Tank 6 and the final sludge waste inventory at completion is approximately 2.27E+04 liters (6,000 gallons). This represents the starting point for CSR. The final phase of mechanical cleaning for Tank 5 is planned for early 2008. Three SMPs will be used in Tank 5 while only two SMPs were used in Tank 6. Because of the additional mixing energy available in Tank 5, it is expected that the final sludge waste inventory at the completion of mechanical cleaning in Tank 5 will be less than 2.27E+04 liters (6,000 gallons). The sequence of CSR operations described below will be stated in generic terms for a single tank. The general process is expected to be identical for both tanks.

The first step in CSR will be dilution of the approximate 3 inch supernate heel (aqueous salt waste) in the tank. 5.13E+04 liters (13,550 gallons) of water will be added and allowed to diffuse into the supernate. The diluted supernate will then be pumped out to Tank 7. This dilution process will be repeated. Each dilution will reduce the sodium molarity of the remaining supernate heel by approximately 62.5%. Therefore, the two phase dilution process will reduce sodium molarity to a seventh of the original value. Reducing sodium molarity is important to minimize the reaction of the oxalic acid with sodium which forms new sodium oxalate solids. SRNL experiments have shown that these solids are difficult to slurry for removal from the tank.

The second step in CSR will be the addition of oxalic acid at a 20:1 volume ratio of acid to sludge. The oxalic acid will be added at a temperature of approximately 50^{o}C via tanker trucks. The acid will be unloaded through a valve manifold and hoses which will be attached to a downcomer pipe that penetrates through the tank top to discharge the acid into the tank.

Once the acid addition is complete, water will be added if needed to reach a tank level of at least 114.3 cm (45 inches). This is the minimum operating level for the SMPs. When the tank reaches 114.3 cm (45 inches), SMPs will be operated for several days to ensure that fresh acid remains in contact with the sludge. It is expected that the acid will also reduce the particle size of any solids that are not dissolved. This may allow the SMPs to suspend sludge that was not previously removed during mechanical cleaning.

After several days of SMP operation, the slurried acid waste solution will be pumped out to Tank 7. SMPs will continue to operate during the pump out until they reach a minimum operating level of about 76.2 cm (30 inches). Pump out will continue until the transfer pump loses suction at a tank level of approximately three inches. At this point, the remaining sludge contents in the tank will be mapped to estimate the volume of sludge present. This volume will be used to determine the volume of acid needed for the next acid strike. This completes the first acid strike.

The second acid strike (step 3) will follow the same process sequence as the first except that the SMPs will not be operated and the acid will be added at a 13:1 acid to sludge volume ratio. The SMPs will not be operated after this strike because the tank level is expected to be too low to allow SMP operation. A graphical representation of the supernate dilution and the first two acid strikes is provided in Figure 2.

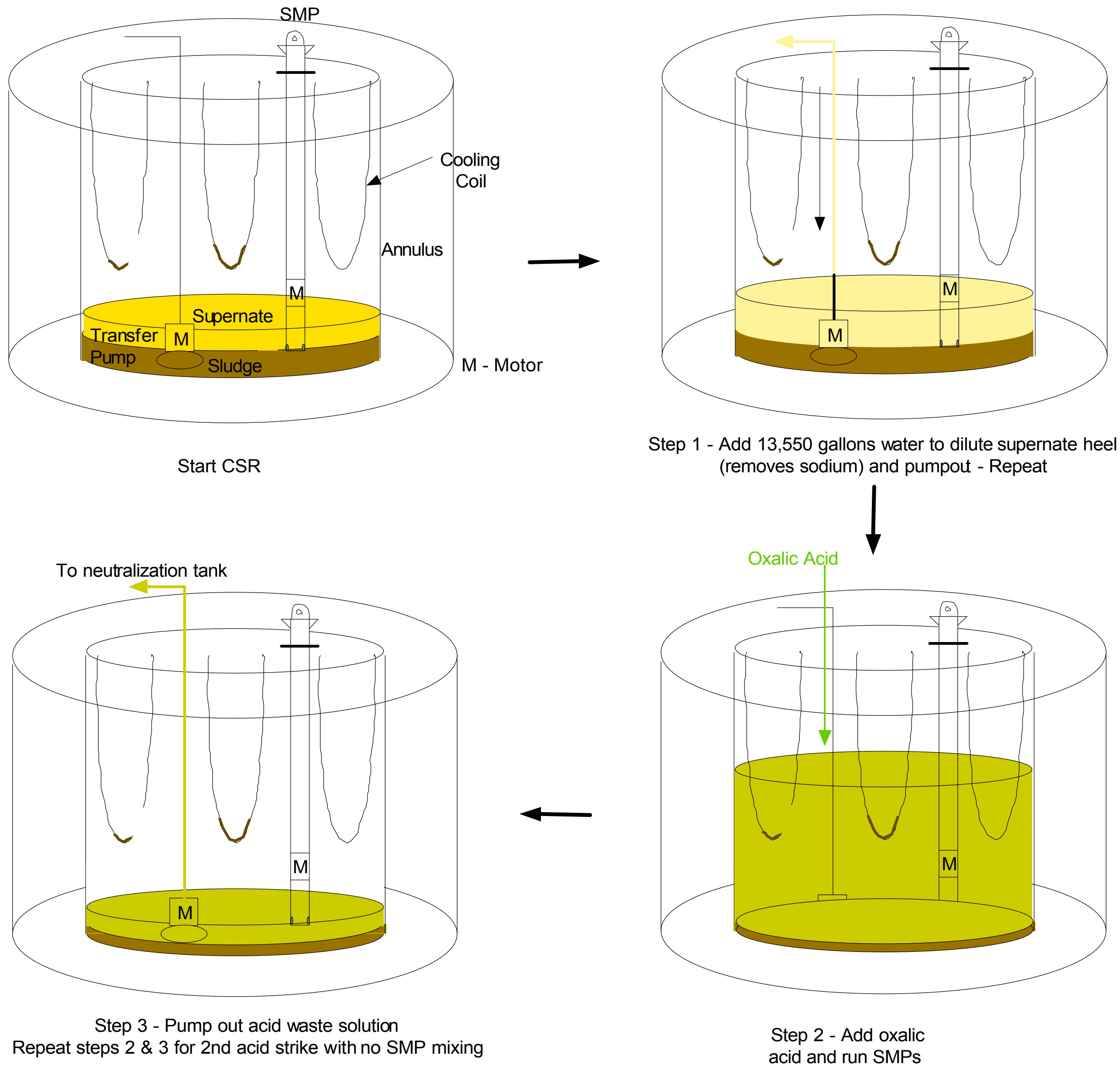

Figure 2. CSR Process Sequence – Dilution of supernate heel and first two acid strikes

Step 4 of CSR will be to flush the contents of any failed cooling coils into the tank. The purpose of this step is to remove any sludge waste that may be contained in the coils so that it can be dissolved in the remaining acid strike.

Steps 5 will be the third and final planned acid strike for CSR. Oxalic acid during the final strike will be added at a 13:1 volume ratio via a spray wash nozzle so that the entire tank internal surface is wetted and cleaned with acid. This will help remove any dried waste residue from the waste tank walls, cooling coils, and installed equipment. Step 6 will pump out the acid waste solution to Tank 7. Graphical representation of failed cooling coil flushing and the final acid strike is provided in Figure 3.

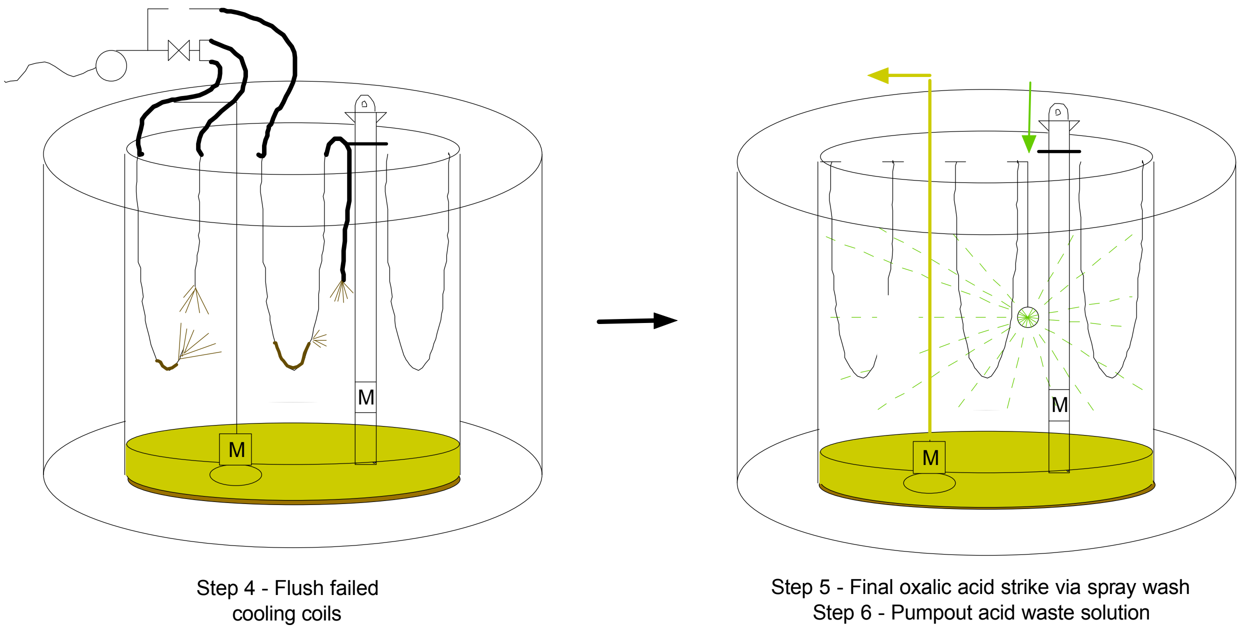

Figure 3. CSR Process Sequence – Cooling coil flush and final oxalic acid strike via spray wash

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).

Less than three acid strikes will be used if all of the sludge is dissolved during either the first or second strike. Additional strikes of acid beyond the third will be considered if each successive strike is still dissolving sludge.

Step 7 of CSR will be annulus cleaning. Small amounts of waste (estimated to be 30.3 liters (8 gallons) in Tank 5 and 348 liters (92 gallons) in Tank 6 [7]) have leaked into the annuli of Tanks 5 and 6 in the past. This waste will be cleaned from the annulus by; 1) scraping and/or dissolving any dried solids on the outer primary tank walls and allowing the loosened/dissolved material to collect at the bottom of the annulus, and 2) adding a few inches of water to the annulus to dissolve any remaining dried solids that have collected in the bottom of the annulus. After allowing sufficient soak time to dissolve the waste, the resulting liquid waste solution will be pumped back into the primary tank.

Step 8 of CSR will be a water wash using the spray wash nozzles. This will rinse residual acid from the acid spray wash (i.e., final strike) from the tanks walls, cooling coils, and equipment. Additional water will be added to the tank in Step 9 of CSR to reach a level of 114.3 cm (45 inches). At this point, SMPs will be operated to suspend any insoluble solids remaining in the tank. While the SMPs are still operating, a transfer of the wash water to Tank 7 will be initiated (Step 10). SMPs will be shut down when their minimum operating level is reached and the transfer will be shutdown when the transfer pump loses suction.

Step 11 of CSR will include removal of the transfer pump and installation of a new dewatering pump. The dewatering pump will be operated to remove as much as possible of the residual wash water in the tank (to a target level of 1.27 cm (0.5 inch) or less). This completes the CSR process. Graphical representation of annulus cleaning, the final acid strike (via spray washing), and dewatering is provided in Figure 4.

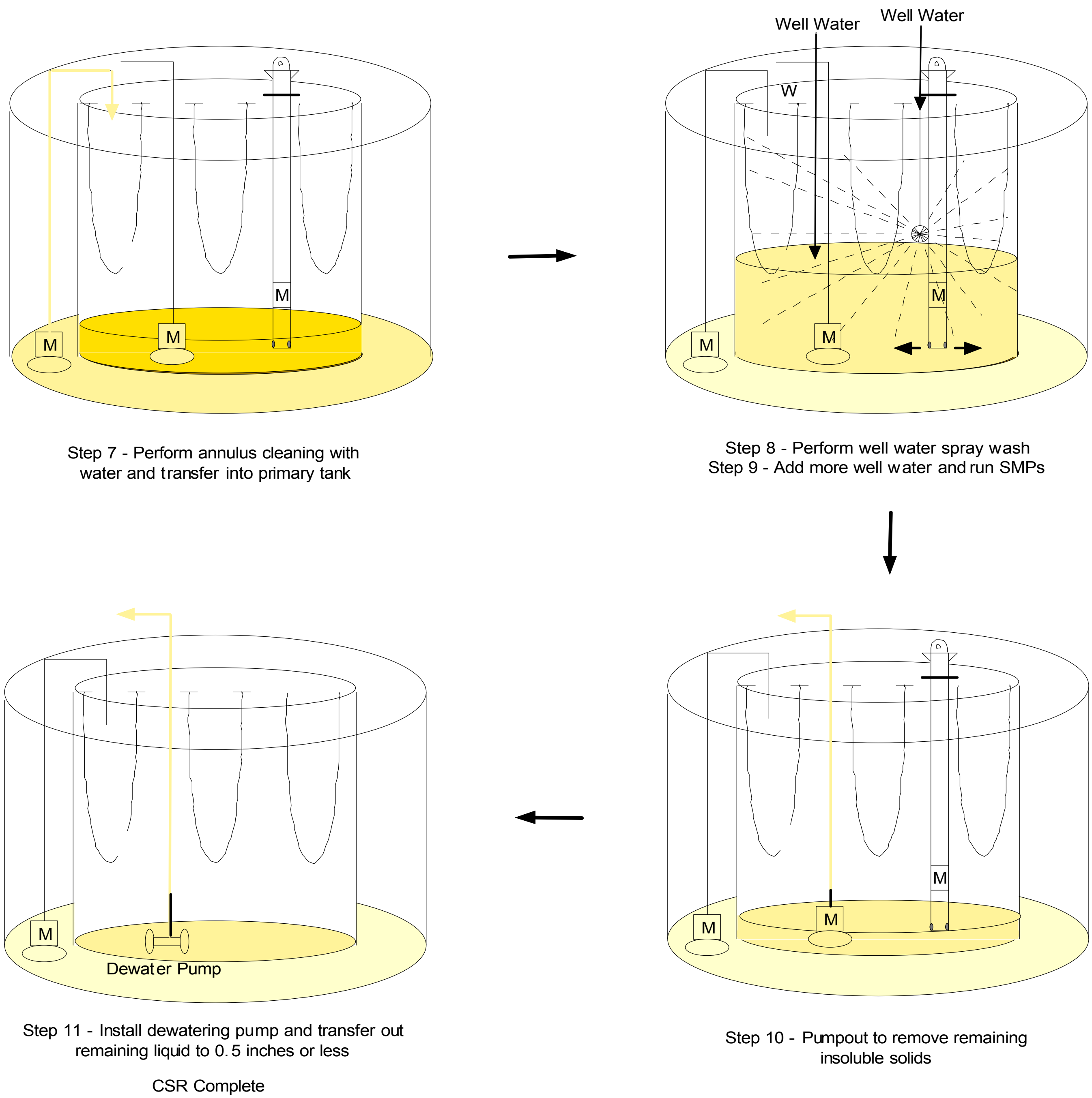

Figure 4. CSR Process Sequence – Annulus cleaning, well water spray wash, final wash with SMP agitation, and dewatering

PATH FORWARD

Chemical Sludge Heel Removal is planned for Waste Tanks 5 and 6 at the Savannah River Site during 2008 to support grouting and closure of these tanks prior to Federal Facility Agreement commitments in 2010. Technical issues associated with the chemical cleaning process using oxalic acid have been resolved and a Safety Analysis has been developed and approved by the Washington Savannah River Company and the Department of Energy. The objective of this process will be to remove all visible sludge from the waste tanks (to the maximum extent practical) to allow for closure of the tanks.

REFERENCES

1. W.L. WEST, "Tank 16 Demonstration – Water Wash and Chemical Cleaning Results," DPSP-80-17-23, Savannah River Site (1980)
2. B.J. WIERSMA, "Corrosion Mechanisms and Rates for Carbon Steel and Stainless Steel Materials Exposed to Oxalic Acid Solutions (U)," WSRC-TR-2004-00109, Savannah River National Laboratory (2004)
3. K. ADU-WUSU, B.J. WIERSMA, S.D. FINK, "TASK TECHNICAL AND QUALITY ASSURANCE PLAN TO INVESTIGATE HYDROGEN AND CORROSION IN THE TREATMENT TANK AND THE POTENTIAL FORMATION OF A FLOATING LAYER IN NEUTRALIZATION TANK DURING HIGH LEVEL WASTE TANK HEEL CHEMICAL CLEANING," WSRC-STI-2006-00035, Savannah River National Laboratory (2006)
4. D.T. HERMAN, B.J. WIERSMA, et.al., "INVESTIGATING HYDROGEN GENERATION AND CORROSION IN THE TREATMENT TANK AND THE POTENTIAL FORMATION OF A FLOATING LAYER IN NEUTRALIZATION TANK DURING WASTE TANK HEEL CHEMICAL CLEANING," WSRC-STI-2007-00209, Savannah River National Laboratory (2007)
5. M.S. HAY, K.P. KRAPSE, S.D. FINK,and J.M. PAREIZS, "CHARACTERIZATION AND ACTUAL WASTE TESTS WITH TANK 5F SAMPLES," WSRC-STI-2007-00192, Savannah River National Laboratory (2007)
6. T.C. BAUGHMAN, "Tank 5 & 6 Closure Sequence of Events," LWO-LWE-2007-00104, Savannah River Site (2007)
7. R.S. WALTZ, "SRS High Level Waste Tank Leaksite Information," C-ESR-G-00003, Savannah River Site (2006)