Corrosion Control during Closure Activities at the Savannah River Site – 13514

Bruce J. Wiersma*, Karthik H. Subramanian** and Keisha B. Martin**
* Savannah River National Laboratory, Aiken, SC, bruce.wiersma@srnl.doe.gov
** Savannah River Remediation, Aiken, SC, karthik.subramanian@srs.gov

ABSTRACT

Liquid radioactive wastes from the Savannah River Site (SRS) separation process are stored in large underground carbon steel tanks. Until the waste is removed from storage, transferred, and processed, the materials and structures of the tanks must maintain a confinement function by providing a barrier to the environment and by maintaining acceptable structural stability during normal service and design basis events (e.g., earthquake conditions). A corrosion control program is in place to ensure that degradation of the steel does not impact the structural and leak integrity functions of these waste tanks.

The SRS is currently retrieving waste from older waste tanks and processing the waste through the vitrification for long term stabilization. The retrieval processes prepare the tanks for ultimate closure (i.e., grouting) by removing sludge by mechanical and/or sluicing methods, dissolving salt cake by adding water, and chemical cleaning of the residual sludge with oxalic acid. Each of these retrieval methods will result in waste chemistry that does not meet the requirements of the current corrosion control program. Given the short-term exposure and limited remaining service life for the tanks in which retrievals are being performed, an assessment of the need for corrosion controls in these tanks was performed. The assessment reviewed the corrosion rates in the more aggressive environments and the postulated loads on the structure during the closure activities. The assessment concluded that the current corrosion control program may be suspended for a short period of time while final retrieval of the waste is performed.

INTRODUCTION

The SRS Tank Farm Facility is in the initial stages of closing the sixteen older style double shell tanks (DST), which were constructed during the 1950's, and the four remaining single shell tanks (SST). While the tanks were utilized for interim storage of radioactive waste, a rigorous corrosion control program was in place to minimize corrosion of the carbon steel tank and components. Corrosion control was accomplished by meeting requirements for minimum inhibitor concentration levels and maximum temperature limits. In order to ensure that the program requirements were met, routine waste sampling and temperature monitoring were performed. As the tanks proceed from waste removal up to eventual grouting, they will experience a number of environments that do not meet the requirements of the program. However, given the anticipated short time periods for the closure activities, an evaluation was performed to determine the impact of removing these requirements while closure activities proceed.

The facility consists of many process areas that perform specific, independent functions to accomplish the closure mission. The activities in these process areas are performed independently and thus separate mode designations are given to each area. During the process of closing a tank there are seven modes that the tank may pass through depending on the tank type: Gas Release, Operation, Acidic Chemical Cleaning, Non-Acidic Chemical Cleaning, Mechanical Cleaning, Closure, and Removed From Service. Table I shows the anticipated time frames for each mode and process as well as the likely corrosion mechanisms.

The table also includes the anticipated corrosion mechanisms during each closure activity. General corrosion is possible during all modes of operation. General corrosion uniformly decreases the wall thickness of a plate. Pitting corrosion will likely be the dominant mechanism during Acidic Chemical

Cleaning of HM Sludge, Operation (Bulk Sludge Removal or BSR), Closure and Removed From Service modes. Pitting corrosion would likely be isolated to liquid-air interfaces and beneath any deposits on the tank wall or cooling coils during Operation, Closure and RFS modes. However pitting can become an issue during Acidic Chemical Cleaning at high temperature and oxalic acid (OA) concentrations. The Bulk Salt Dissolution (BSD) process, which is performed in either Gas Release or Operation mode, can create an environment that could result in stress corrosion cracking (SCC) of the carbon steel tanks. Since these tanks were not stress-relieved, SCC may occur near the seam welds, weld repairs and weld attachments [1]. The crack lengths (i.e., on the order of 6 inches or less) are not expected to extend significantly due to the localized nature of the residual stresses near these welds. The risk of unstable crack growth (i.e., tank unzipping) has been shown to be minimal for cracks of this size under both normal and seismic loading [2]. Another mitigating factor is temperature. If the temperatures are less than 40 °C and the exposure times are short, the risk of SCC is significantly reduced.

As mentioned above general corrosion will affect the tank wall thickness, and hence the allowable fill capacity for the DST. The carbon steel liner for the SST does not provide structural stability; hence the wall thickness does not determine the allowable fill capacity for these tanks. Localized corrosion mechanisms, i.e., pitting and SCC, may impact the leak integrity of the tank wall. The facility has procedures in place to manage leakage into the annulus of the Type I and Type II tanks during waste tank closure activities. Therefore the presence of a through-wall pit or crack would not hinder closure activities. On the other hand, pitting of the carbon steel liner for the SST is critical given that it provides containment for the contents of the tank. Thus, general corrosion will be considered the limiting corrosion mechanism for the DST, while pitting corrosion will be considered the limiting corrosion mechanism for the SST [3].

Table I. Anticipated Exposure Times and Corrosion Mechanisms for Closure Waste Tanks During Different Modes

Mode	Anticipated Process Time (years)	Corrosion Mechanisms
Gas Release or Operation	Bulk Sludge Removal (BSR): 3 Bulk Salt Dissolution (BSD): 2[a]	BSR: Pitting and General Corrosion BSD: Stress Corrosion Cracking and General Corrosion
Chemical Cleaning	1	Pitting and General Corrosion
Mechanical Cleaning	2	Pitting and General Corrosion
Closure	10[b]	Pitting and General Corrosion
Removed From Service	10[b]	Pitting and General Corrosion

[a] In some waste tanks both salt dissolution and sludge removal will be required to accomplish bulk waste removal. However, the total time for both activities will not exceed 3 years. In the case where both are performed, for the calculations it will be assumed that salt dissolution will require 2 years, sludge removal will require 1 year, and chemical cleaning will require 1 year.

[b] The total combined time a tank will be in Closure and Removed From Service Mode is anticipated to be less than 10 years. These are not sequential times (i.e., a maximum of 20 years).

Two cases were evaluated: a) bounding case and b) anticipated operations scenario. The bounding case applied conservative assumptions for the environment and exposure times to estimate the type and extent of corrosion damage. The results of the bounding case will be utilized to assess the length of time that the requirements of the corrosion control program may be suspended. The anticipated operations assessment will utilize the proposed operating plans for each waste removal stage, assuming an expected exposure time for each given step. These exposure times give the anticipated estimate of the type and extent of corrosion damage that might be expected during waste removal operations.

ACCELERATED CORROSION RATES FOR BOUNDING CASE ANALYSIS

For Gas Release or Operations mode during BSR, neutral pH water was assumed to be the corrosive medium. The bounding general corrosion rate for water at a pH between 4 and 10 and at a temperature of 25 °C is 0.25 mm/year [4]. Higher temperatures will increase the corrosion rate in an exponential fashion. When corrosion is controlled by diffusion of oxygen, as in this case, the corrosion rate will double for every 30 °C rise in temperature [4]. The relationship between the general corrosion rate and temperature is:

$$\text{Corrosion Rate (mm/y)} = 0.14\, e^{(0.0231\, T)} \qquad \text{(Eq. 1)}$$

where T is the temperature in °C.

Pitting corrosion may also occur during sludge removal. Pit depth has been shown to increase in an exponential fashion with respect to time according to the following equation:

$$\text{Pit depth (mm)} = k\, t^{n} \qquad \text{(Eq. 2)}$$

where t is the time in days and k and n are constants [5]. Corrosion experiments performed in simulated uninhibited dilute wastes at 50 °C determined that the values for k and n were 3.6 and 0.45, respectively [6]. Thus Equation 2 has the following form:

$$\text{Pit Depth (mm)} = 0.091\, A\, t^{0.45} \qquad \text{(Eq. 3)}$$

A similar temperature dependence for pitting corrosion that was observed for general corrosion was assumed. The temperature dependence was incorporated into Equation 2 by normalizing to the corrosion tests performed at 50 °C, as shown in Table II. Table II also shows the pitting corrosion rate as a function of temperature. For example, since the maximum expected temperature is 60 °C, the pitting rate and hence pit depth will be multiplied by a factor A equal to 1.26.

General corrosion will also occur to a limited degree in tanks in Operation mode that experience BSD. For dissolved salt solutions at temperatures of 25 and 50 °C the corrosion rates were 0.02 and 0.035 mm/yr, respectively [7]. Salt dissolution in the Type I and II tanks may be performed utilizing pumps or by a density gradient method. For salt dissolution with a pump technique, the general corrosion rate for 50 °C is appropriate for a bounding case, while the lower temperature corrosion rate is appropriate if a density gradient technique is utilized. For Type I and II tanks the bounding case will initially assume that pumps will be utilized for the tank. Pitting corrosion is expected to be insignificant during this stage unless there is a stagnant interface for a significant period of time.

Table II. Pitting Corrosion Rate as a Function of Temperature for Bulk Waste Removal

Temperature (°C)	Pitting Rate (mm/yr)	A
20	0.64	0.5
30	0.78	0.63
40	1.02	0.79
50	1.27	1.00
60	1.60	1.26
80	2.54	2.00

The current baseline for the Chemical Cleaning mode utilizes OA to dissolve residual sludge solids heel (< 10,000 gallons) that remain in the tank so final closure activities (i.e., grouting of the tank) may proceed. Oxalic acid maximum concentration up to 8 wt.% is added to a treatment tank followed by water to dilute the solution to ≤ 4 wt.%. Laboratory tests were conducted [8, 9] to correlate the impact of oxalic acid sludge dissolution of PUREX and HM sludge on waste tank corrosion and the propensity for corrosion induced hydrogen generation. Tests were performed with a 20:1 volume ratio of OA to sludge for acid concentrations of 8 wt.%, 4 wt.%, and 2.5 wt.% with and without agitation. The tests also varied temperatures between 25-75°C. From Reference 8, corrosion rates were observed during a simulated waste test of 8 wt.% OA in contact with PUREX sludge. Testing used vertical coupons to simulate the primary tank wall. For tests with agitation of the solution, an average of the maximum instantaneous corrosion rates measured 1.14 mmpy, 1.83 mmpy and 3.78 mmpy for the 25, 50 and 75 °C tests, respectively and stagnant conditions at these temperatures measured 0.051 mmpy, 0.28 mmpy, and 0.91 mmpy respectively. The average maximum instantaneous corrosion rate measured on the vertical coupons at each temperature was calculated. A least squared fit of these data yielded the following exponential equation for the corrosion rate under agitated conditions as a function of temperature:

$$\text{Corrosion Rate (mmpy)} = 0.60\ e^{(0.024T)} \qquad \text{(Eq. 4)}$$

The corresponding relationship for stagnant conditions was:

$$\text{Corrosion Rate (mmpy)} = 0.013\ e^{(0.058\ T)} \qquad \text{(Eq. 5)}$$

Laboratory tests were recently performed on an HM simulant at four conditions representative of the anticipated maximum operating conditions that may occur during the chemical cleaning process [9]. The tests were performed with a 20:1 volume ratio of OA and sludge in contact with 8 wt.%, 4 wt.%, and 2.5% wt.% acid concentration with and without agitation at 60 and 75°C. Test results from coupon immersion in 2.5 and 4 wt.% OA at 60 ºC with mixing indicated that general corrosion was the dominant corrosion mechanism at these conditions. Time averaged general corrosion rates decreased over the test interval. The maximum time- averaged corrosions rates measured 0.74 mmpy and 1.14 mmpy respectively.

At 8 wt.% OA and 60 ºC with mixing, tests results indicate that both general corrosion and pitting occur. The time averaged general corrosion rates increased with each time interval for the test at 60 ºC with mixing from 0.51 mmpy at day 1 of testing to 2.36 mmpy at day 28.

At 8 wt.% OA and 75 ºC stagnant tests results indicate that both general corrosion and pitting occur.

The time averaged general corrosion rates decreased with time from 3.56 mmpy at day 1 to 2.18 mmpy at day 28.

General corrosion rate and the average pitting corrosion rate for each testing condition were utilized to determine the total corrosion rate as shown in Table III for HM simulant testing.

Table III. Total Corrosion Rate for HM Waste

Condition: OA wt.%, °C	Maximum General Corrosion Rate (mm/day)	Average Pitting Corrosion Rate (mm/day)	Total Corrosion Rate (mm/day)
8wt%, 75°C *	0.0099	0.05	0.06
8wt%, 60°C	0.0064	0.025	0.031
4wt%, 60°C	0.003	0.0064	0.0094
2.5wt%, 75°C	0.006	0.051	0.057
2.5wt%, 60°C	0.002	0.005	0.007
2.5wt%, 50°C	0.0015	No Pitting	0.0015

*Stagnant Condition

Table IV provides a similar summary for PUREX Simulant.

Table IV. Total Corrosion Rate for PUREX Waste

Condition: OA wt.%, °C	Maximum General Corrosion Rate (mm/day)	Average Pitting Corrosion Rate (mm/day)	Total Corrosion Rate (mm/day)
8wt.%, 75°C	0.01	No Pitting	0.01
8wt.%, 50°C	0.005	No Pitting	0.005
8wt.%, 25°C	0.003	No Pitting	0.003
2.5wt.%, 75°C	0.002	No Pitting	0.002
2.5wt.%, 50°C	0.004	No Pitting	0.004

Usually, wall loss determinations consider only general corrosion rates. By utilizing the Total Corrosion Rate, which effectively applies the sum of the localized pitting rate and the general corrosion rate to the entire submerged tank surface, a more conservative value is obtained. The total corrosion rate for HM Sludge is bounding for PUREX Sludge and will be utilized to determine bounding wall case.

CALCULATION OF CORROSION DAMAGE

General corrosion damage was expressed in terms of wall thickness loss. The equation for determining wall thickness loss is:

Wall Thickness Loss = Corrosion Rate x Exposure Time (Eq. 6)

Pitting corrosion damage for tanks in Normal Operation Life Cycle will be expressed in terms of total penetration. A model developed by the Tank Waste Expert Panel was used to determine total penetration [10].

Total penetration (T) can be represented by the following equation:

T = General Corrosion Depth + Pitting Corrosion Depth (Eq. 7)

A pitting factor (PF) was defined by the following formula:

PF = Maximum Initial Pit Depth/ Initial General Corrosion Depth (Eq. 8)

The pitting factor is assumed to be constant for the life of the tank, and for the purposes of this calculation the worst case will be applied to all tanks. Typically a Type III tank has seen approximately 35 years of service. If a general corrosion rate of 0.025 mm/year is assumed, the initial general corrosion depth is 0.88 mm. Given that the maximum initial pit depth is 1.75 mm, the pitting factor for the primary wall of the waste tanks is estimated to be 1.98. This ratio is indicative of the development of broad shallow pits. Substitution of Equation (8) into Equation (7) results in:

$$T = (PF+1)(\text{Maximum Pit Depth})/PF \quad \text{(Eq. 9)}$$

From Equation 3 above:

$$\text{Maximum Pit Depth} = (1.26)(0.091)\ t^{0.45} \quad \text{(Eq. 10)}$$

where t is days of service and k is a constant with units of mm/yr$^{0.45}$. The constant, 1.26, accounts for a temperature of 60 °C.

The total penetration, T, is thus:

$$T = 2.97\ [1.26 \times 0.091 \times t^{0.45}]/1.97 \quad \text{(Eq. 11)}$$

or

$$T = 0.17 \times t^{0.45} \quad \text{(Eq. 12)}$$

CALCULATION OF REMAINING WALL THICKNESS AND THROUGH-WALL PENETRATION FOR BOUNDING CASE

General corrosion rates were utilized to calculate the remaining wall thickness for each Type I, II, and IV waste tank. However for Chemical Cleaning, pitting corrosion is accounted for in the total corrosion rate. The remaining wall thickness was calculated from the following equation.

Remaining Wall (in.) = Estimated Wall Thickness from 2015 – Wall Loss from Salt Dissolution – Wall Loss from Sludge Removal –Wall Loss from Chemical Cleaning (Eq. 13)

Table V presents a summary of the calculations and results for the tank wall. Note that for Mechanical Cleaning it was assumed that the tank walls were predominantly exposed to a humid vapor atmosphere. The wall loss for each mode was determined by multiplying the corrosion rate for each mode by the anticipated process time (Table I) applicable to each tank. The applied corrosion rate for Bulk Salt Dissolution at 50 ºC and Bulk Sludge Removal at 60 ºC was 0.036 mmpy and 0.56 mmpy, respectively. The applied total corrosion rate for chemical cleaning at 4 wt.% OA and 60°C for HM waste is 3.43 mmpy.

The estimated remaining wall thickness for the Tanks 1-12 ranged between 7.1 to 8.5 mm, i.e., approximately 58-68% of the nominal wall thickness is projected to remain prior to entering the Final Stabilization Life Cycle. The estimated remaining wall thickness for Tanks 13-15 ranged between 10.5 to 11.7 mm or approximately 67-74% of the nominal wall thickness. The estimated remaining wall thickness for the SST was 6.5 mm or approximately 79% of the nominal wall thickness.

LEAK INTEGRITY

The pit depth equation was utilized to calculate the total through-wall penetration of the primary wall for the DST and SST. The total penetration during closure operations was calculated by the following equation. The initial pit depth accounts for pitting corrosion during the Normal Operation Life Cycle.

Total Penetration (inches) = Initial pit depth + Pit depth from sludge removal + Total Corrosion loss during chemical cleaning (Eq. 14)

The initial pit depth was assumed to be the maximum observed via an ultrasonic inspection. The initial pit depth was based on the tolerance limit calculation and was 1.75 mm. The equation assumes that the bottom of the deepest pits corrode uniformly during chemical cleaning. Pitting in neutral water is assumed to resume during Closure/Remove From Service modes. The wall loss due to general corrosion is given in Table V.

Table VI presents a summary of the calculations and results for penetration of a pit through the tank wall. The results indicate that pitting would not reach 50% through-wall for the DST during sludge removal. Thus, the likelihood of leakage due to pitting corrosion is minimal during this time. The pitting remains localized and has no impact to structural or leak integrity based upon the low pressures applied to the tank wall. Due to Chemical Cleaning for Tanks 1-12, pits may penetrate between 61 to 75% through-wall, while for Tanks 13-15 they are estimated to penetrate between 48 to 59%. For SST, the calculations indicate that a pit would penetrate approximately 71% through-wall.

FILL LIMITS FOR CLEANING ACTIVITY LIFE CYCLE

A calculation was performed to determine the fill limits for a Type I tank given a certain wall loss due to general corrosion [11]. The calculation assumed a nominal wall thickness of 12.7 mm. A fill limit based on the specific gravity of the waste and the wall loss was calculated. These limits were calculated under normal operating and seismic conditions. Table VII is a summary of the results of the wall loss and fill limit calculations for Operation and Chemical Cleaning modes. The fill limit for each stage is based on the cumulative wall loss at the end of each stage of the process from Table V. The cumulative wall loss for sludge removal also includes the wall loss from the salt dissolution stage. Likewise, the cumulative wall loss for chemical cleaning includes the wall loss from the previous stages. The fill limit for Bulk Salt Dissolution was extrapolated from the current and 1.27 mm wall loss at a specific gravity of 1.3. The fill limit for Bulk Sludge Removal was bound by the 1.27 and 2.54 mm wall loss at a specific gravity of 1.1. The fill limit for Chemical Cleaning was extrapolated and bounded by the 4.45 and 5.72 mm wall loss at a specific gravity of 1.2. The results indicate that even with the conservative bounding assumptions; fill limits for the tanks during closure activities will not be exceeded.

Table V. Remaining Wall Thickness Estimates for the DST and SST: Bounding Case During Cleaning Activity Life Cycle. Note: Tanks 1-15 are DST, while Tanks 21-24 are SST.

	Gas Release/Operation Mode		Chemical Cleaning Mode	Mechanical Cleaning Mode		
Tank	Wall Loss during BSD (mm)	Wall Loss during BSR (mm)	Wall Loss with 4 wt.% Oxalic Acid (mm)	Humid, Vapor Exposure (mm)	Total Wall Loss (mm)	Remaining Wall Thickness (mm)
1	0.08	0.56	3.43	NA	4.07	8.48
2	0.08	0.56	3.43	NA	4.07	8.33
3	0.08	0.56	3.43	NA	4.07	8.28
4	NA	1.68	3.43	NA	5.11	7.34
5	NA	1.68	3.43	NA	5.11	7.29
6	NA	1.68	3.43	NA	5.11	7.21
7	NA	1.68	3.43	NA	5.11	7.37
8	NA	1.68	3.43	NA	5.11	7.34
9	0.04	0.56	3.43	NA	4.03	8.43
10	0.08	0.56	3.43	NA	4.07	8.43
11	NA	1.68	3.43	NA	5.11	7.14
12	NA	1.68	3.43	NA	5.11	7.24
13	NA	1.68	3.43	NA	5.11	10.54
14	3	0.56	3.43	NA	4.07	11.73
15	NA	1.68	3.43	NA	5.11	10.69
21	NA	1.68	NA	0.01	1.7	6.48
22	NA	1.68	NA	0.01	1.7	6.48
23	NA	1.68	NA	0.01	1.7	6.48
24	NA	1.68	NA	0.01	1.7	6.48

Table VI. Remaining Tank Wall Thickness until Penetration for the DST and SST: Bounding Case

		Gas Release/Operation Mode	Chemical Cleaning Mode	Mechanical Cleaning Mode		
Tank	Initial Pit Depth (mm)	Penetration during BSR (mm)	Penetration during 4 wt.% Oxalic Acid (mm)	Penetration during humid, vapor (mm)	Total Penetration (mm)	Remaining Wall Thickness (mm)
1	1.75	2.46	3.43	NA	7.64	4.90
2	1.75	2.46	3.43	NA	7.64	4.75
3	1.75	2.46	3.43	NA	7.64	4.70
4	1.75	4.03	3.43	NA	9.21	3.23
5	1.75	4.03	3.43	NA	9.21	3.18
6	1.75	4.03	3.43	NA	9.21	3.10
7	1.75	4.03	3.43	NA	9.21	3.25
8	1.75	4.03	3.43	NA	9.21	3.23
9	1.75	2.46	3.43	NA	7.64	4.83
10	1.75	2.46	3.43	NA	7.64	4.85
11	1.75	4.03	3.43	NA	9.21	3.02
12	1.75	4.03	3.43	NA	9.21	3.12
13	1.75	4.03	3.43	NA	9.21	6.43
14	1.75	2.46	3.43	NA	7.64	8.15
15	1.75	4.03	3.43	NA	9.21	6.58
21	1.75	4.03	NA	0.4	5.82	2.36
22	1.75	4.03	NA	0.4	5.82	2.36
23	1.75	4.03	NA	0.4	5.82	2.36
24	1.75	4.03	NA	0.4	5.82	2.36

ANTICIPATED OPERATIONS SCENARIOS

The impact of Cleaning Activity Life Cycle processes on tank integrity was also calculated using inputs and assumptions consistent with the current baseline. The operating plans for salt dissolution [12], bulk sludge removal [13], chemical cleaning [14], and mechanical cleaning [15] were used as a base case. The results of this analysis can be used to approximate the margin between a more realistic case and the calculations based on the bounding condition assumptions.

The inputs were very conservative for the bounding case studies. For example during anticipated operations, the submersible mixer pumps will not run continuously during bulk sludge removal at a slurry temperature of 60 ºC. The temperature during most of the activity will remain in the 30 to 40 °C range. Similarly, it is unlikely that the pumps will run continuously during salt dissolution. Additionally, the presence of residual inhibitors in the waste or the use of supernate, which contains excess corrosion inhibitors, during bulk sludge removal, would make the conditions less corrosive than those assumed in Table I.

Table VII. Fill limits[a] at each Stage of the Cleaning Activities Life Cycle

Tanks	Cumulative Wall Loss for Salt Dissolution (mm)	Fill Limit for Salt Dissolution assuming pumps operated (cm)	Cumulative Wall Loss for Bulk Sludge Removal (mm)	Fill Limit for Bulk Sludge Removal (cm)	Cumulative Wall Loss for Chemical Cleaning (mm)	Fill Limit for Chemical Cleaning (cm)
1	0.23	505	0.79	523	4.22	318
2	0.38	498	0.94	523	4.37	318
3	0.43	495	0.99	523	4.42	318
4	NA	NA	1.93	460	5.36	267
5	NA	NA	1.98	460	5.41	267
6	NA	NA	2.06	460	5.49	267
7	NA	NA	1.91	460	5.33	267
8	NA	NA	1.93	460	5.36	267
9	0.28	503	0.84	523	4.27	318
10	0.28	503	0.84	523	4.27	318
11	NA	NA	2.13	460	5.56	267
12	NA	NA	2.03	460	5.46	267

a Fill limit is the maximum liquid volume that may be added based on stress evaluation. The actual fill height during operations such as chemical cleaning is much lower.

Another significant change from Table I is the anticipated exposure times at these worst case conditions. For example, with bulk sludge removal the exposure time to wastes at temperatures of 60 °C is expected to be four to six weeks rather than 3 years. During chemical cleaning with oxalic acid the exposure time is reduced from 1 year to approximately 1 month.

The accelerated corrosion rates were essentially the same with a couple of minor differences. The general corrosion rate for carbon steel exposed to 4 wt.% oxalic acid while the tank is being agitated and is at 60 °C (i.e., 1.9 mmpy) is calculated by taking an average of the rate at 8 wt.% and 60 ºC (2.5 mmpy) and 2.5 wt.% and 50 ºC (1.3 mmpy) since it was not experimentally determined for the current baseline case. The temperature of the waste during bulk removal will oscillate between 30 and 60 °C. An assumption is made that the tank wall will be near the average of these two temperatures for the duration of the process (i.e., 45 °C). Therefore the general corrosion rate was reduced to 0.4 mmpy. The temperature constant for the pit depth was also reduced from 1.26 to 0.89.
During the 6 month delay prior to chemical cleaning that was assumed to occur after BSR or BSD, the temperature of the remaining liquid was assumed to be 30°C. General corrosion and pitting corrosion for carbon steel exposed to well water at this temperature were assumed. This scenario is conservative as it is likely that only the tank bottom will be completely exposed to the well water.

The results for BSD indicated that 90% of the wall loss could occur during the six month exposure to well water. The wall loss prior to that stage was less than 1 mil. Salt dissolution operations have been performed in Tank 41 for the past several years. These operations were at low temperature (i.e., 25 °C) and utilized no pumps. Ultrasonic wall thickness measurements were recently made in Tank 41 during 2006 and 2010 [16]. There was no discernible wall thinning observed in Tank 41 during this time. Thus, the corrosion rate was consistent with the laboratory results (i.e. less than 0.025 mmpy) and the results of the calculations.

The results of the wall loss and penetration calculations for the BSR process indicate that approximately 0.05 mm of wall loss is anticipated and that the 1.75 mm deep pit would grow to 2.46 mm. The greater amount of wall loss and pitting projected compared to BSD was due to the higher temperatures and the exposure to well water. As with BSD, greatest percentage of wall loss and pit growth was predicted to occur during the six month period after the completion of BSR.

Bulk sludge removal operations were performed in Tank 6 utilizing supernate rather than well water. Ultrasonic measurements were taken in Tank 6 prior to performing chemical cleaning [17]. Not surprisingly, the wall thickness loss was less than what would have been anticipated, which assumed well water was utilized. In the case of Tank 6 supernate from Tank 7, which was well inhibited, was utilized to remove the sludge solids.

Calculations indicate that approximately 0.2 mm of wall loss is anticipated during the chemical cleaning process. Ultrasonic (UT) measurements were made on the primary wall of Tank 6 before and after chemical cleaning with oxalic acid [17]. The results from this inspection provided the opportunity to verify that significant wall loss did not occur as well as validate the corrosion rates and corrosion models that were assumed in this analysis. The results showed that only portions of the wall that were immersed in the oxalic acid exhibited significant wall loss (0.25 to 0.30 mm). No significant wall loss was observed in the vapor space above the oxalic acid or in areas that had been spray washed with the acid (0.0 to 0.1 mm). Limited attack was expected in these areas. The results show that the corrosion models slightly under estimate the actual corrosion rate.

All the predicted wall loss estimates are within this uncertainty ultrasonic measurements (i.e., 0.14 mm) [16]. Therefore, the corrosion models appear to be a good means for evaluating the degree of corrosion that occurs during chemical cleaning. It should be noted however, that the corrosion rates for carbon steel during chemical cleaning that were utilized apply to an 8 wt.% oxalic acid solution. If different acid concentrations are utilized for chemical cleaning, corrosion rates for carbon steel at these compositions should be utilized in the analysis. The corrosion rates for 4 wt.% oxalic acid were noted earlier in this report.

The process was revised to reflect the current baseline, general assumptions, and methodology for calculating tank wall loss applied for the DST using corrosion rates for PUREX Waste. As seen in Table VIII the Total wall loss using the current baseline is comparable with that of the previous Chemical Cleaning process utilized for Tanks 5 and 6.

Table IX provides the anticipated wall loss for acidic chemical cleaning of tanks containing HM waste reflecting the nominal flow sheet. The wall thickness that results in acceptable structural stresses such that the tank remains seismically qualified based on fill limits. A wall thickness of 7.1 mm for Tanks 1-12, and 10.5 mm for Tanks 13-16, resulted in acceptable stresses of the tank wall. Cumulative corrosion damage for waste tank walls are shown in Table X considering process activities applicable in the Cleaning Activities Life Cycle of the Corrosion Control Program in addition to waste tanks in Final Stabilization Preparation Life Cycle designated as Closure and Removed From Service Mode (RFS) tanks to show that the remaining primary wall and tank bottom thickness results in acceptable structural stresses.

Table VIII. Calculated Wall Loss during Chemical Cleaning Process Steps for PUREX Waste Reflecting Nominal Flow Sheet Case

	time (days)	time (yr)	Corrosion Rate (mmpy)	Wall loss (mm)
Strike 1 Acid Add	5.3	0.014	3.8	0.055
Strike 1 Water Add	0.9	0.003	2.5	0.006
Strike 1 Well Mixed Run SMPs	0.3	0.001	2.5	0.002
Strike 1 Mixing	6.0	0.016	1.9	0.032
Strike 1 Transfer	3.8	0.010	1.9	0.020
Strike 2 Acid Add	1.1	0.003	3.8	0.011
Strike 2 Water Add	0.2	0.001	2.5	0.001
Strike 2 Well Mixed	0.3	0.001	2.5	0.002
Strike 2 Mixing	6.0	0.016	1.9	0.032
Strike 2 Transfer	0.8	0.002	1.9	0.005
Strike 2 Neutralize/mixing	0.8	0.002	0.3	0.001
Neutral 2 Transfer	2.3	0.006	0.3	0.002
Strike 3 Acid Add	1.0	0.003	3.8	0.010
Strike 3 Water Add	0.2	0.000	2.5	0.001
Strike 3 Well Mixed	0.3	0.001	2.5	0.002
Strike 3 Mixing	6.0	0.016	1.9	0.032
Strike 3 Transfer	0.4	0.001	1.9	0.002
Strike 3 Neutralize/mixing	0.8	0.002	0.3	0.001
Neutral 3 Transfer	2.3	0.006	0.3	0.002
Total	38.8			0.219

For Table X the wall loss during Acidic Chemical Cleaning for waste tanks containing PUREX sludge accounted for general corrosion and for the DST containing HM sludge accounted for general and pitting corrosion based on anticipated operations.

During sludge removal approximately 3.35 mm of penetration may occur (i.e., this includes the initial 1.75 mm deep pit). Thus, the remaining wall until penetration is approximately 9.34 mm for Tanks 1-12 or 12.3 mm for Tanks 13-15. The likelihood of through-wall pitting would be negligible at this stage. The wall loss due to general corrosion during the chemical cleaning of PUREX and general and pitting corrosion during chemical cleaning of HM Sludge was 0.46 mm and 1.47 mm, respectively. Thus, it is unlikely that through-wall penetration of the DST would occur if chemical cleaning occurs for short period of time. Cumulative wall loss for process operations up to chemical cleaning is well below the allowable remaining wall thickness requirement. The assumption that pitting continues during this lay-up time is conservative, but not unrealistic as pitting corrosion beneath residual damp deposits has been observed [18].

Pit depths in the SST would also decrease due to the lower temperatures and shorter contact times. For mechanical cleaning in SST, no slurry pumps were used. High pressure hydro-lancing coupled with an eductor will be used to accomplish sludge removal. The liquid level in the tank will be extremely low during this time. For the anticipated scenario it was be assumed that water has accumulated on the tank bottom and is at 25 °C for 1 year. Equation 10 modified for the lower temperature of 25 °C is:

$$T = 2.97x\ [0.56 \times 0.091 \times t^{0.45}]/1.97 \quad \text{(Eq. 15)}$$

or

$$T = 0.077 \times t^{0.45} \quad \text{(Eq. 16)}$$

Assuming an initial pit depth of 1.75 mm, the total penetration would then be 2.8 mm. Thus, the maximum pit depth would be less than 50% through-wall and the likelihood of through-wall pitting is minimal for the SST as well.

Table IX. Calculated Wall Loss during Chemical Cleaning Process Steps for HM Waste Reflecting Nominal Flow Sheet Case

	time (days)	time (yr)	Corrosion Rate (mmpd)	Wall loss (mm)
Strike 1 Acid Add	5.3	0.014	0.060	0.316
Strike 1 Water Add	0.9	0.003	0.031	0.029
Strike 1 Well Mixed Run SMPs	0.3	0.001	0.031	0.010
Strike 1 Mixing	6.0	0.016	0.009	0.056
Strike 1 Transfer	3.8	0.010	0.009	0.036
Strike 2 Acid Add	1.1	0.003	0.060	0.065
Strike 2 Water Add	0.2	0.001	0.031	0.006
Strike 2 Well Mixed	0.3	0.001	0.031	0.010
Strike 2 Mixing	6.0	0.016	0.009	0.056
Strike 2 Transfer	0.8	0.002	0.009	0.008
Strike 2 Neutralize/mixing	0.8	0.002	0.001	0.001
Neutral 2 Transfer	2.3	0.006	0.001	0.002
Strike 3 Acid Add	1.0	0.003	0.060	0.059
Strike 3 Water Add	0.2	0.000	0.031	0.005
Strike 3 Well Mixed	0.3	0.001	0.031	0.010
Strike 3 Mixing	6.0	0.016	0.009	0.056
Strike 3 Transfer	0.4	0.001	0.009	0.004
Strike 3 Neutralize/mixing	0.8	0.002	0.001	0.001
Neutral 3 Transfer	2.3	0.006	0.001	0.002
Total	38.8			0.732

Table X. Remaining Wall Thickness Estimates for the DST for Anticipated Case

Tank	Bulk Salt Dissolution - Realistic (mm)	Bulk Sludge Removal - Realistic (mm)	Chemical Cleaning (mm)	Closure / Removed From Service Mode (mm)	Total Wall Loss (mm)	Remaining Wall Thickness (mm)
1	0.025	0.05	0.46	0.05	0.58	12.0
2	0.025	0.05	0.46	0.05	0.58	11.8
3	0.025	0.05	0.46	0.05	0.58	11.8
4	N/A	0.05	0.46	0.05	0.56	11.9
5	N/A	0.05	0.46	0.05	0.56	11.8
6	N/A	0.05	0.46	0.05	0.56	11.8
7	N/A	0.05	0.46	0.05	0.56	11.9
8	N/A	0.05	0.46	0.05	0.56	11.9
9	0.025	0.05	1.47	0.05	1.60	10.9
10	0.025	0.05	1.47	0.05	1.60	10.9
11	N/A	0.05	1.47	0.05	1.57	10.7
12	N/A	0.05	0.91	0.05	1.02	11.3
13	N/A	0.05	1.47	0.05	1.57	14.1
14	0.025	0.05	1.47	0.05	1.60	14.2
15	N/A	0.05	1.47	0.05	1.57	14.2

CONCLUSIONS

Given the expected short time periods for the closure activities, an evaluation was performed to assess the impact of eliminating the requirements of the corrosion control program while closure activities proceeded for the older style DST and SST. The results of the bounding case study indicate that even with suspension of the corrosion chemistry requirements, sufficient tank wall thickness remains to complete closure operations. A realistic operations scenario was also evaluated. The results indicated that the bounding case is very conservative and that short contact times will limit the amount of corrosion damage. In both cases, the most vulnerable region of the tank will be the bottom floor.

The following recommendations are made for engineering risk evaluations and revisions to the corrosion control program.

1) The corrosion control program description document currently allows for the suspension of corrosion inhibitor, sample frequency, and annulus ventilation requirements during the Cleaning Activity Life Cycle (bulk sludge removal, salt dissolution, mechanical, and chemical cleaning) for a specified time limit. Namely, the requirements of the corrosion control program may be suspended a total of 1460 days (i.e., 4 years) for the Cleaning Activity Life Cycle, which accounts for the tank being exposed to 4 wt.% oxalic acid at 60 ºC for 365 days for chemical cleaning activities. Revised temperature requirements will still be in effect while operating submersible mixer pumps. These temperatures were considered for the bounding analysis case and are 60°C for sludge removal and chemical cleaning, and 50°C for salt dissolution. It is recommended that these be maintained.
2) Revise the remediation actions for the corrosion control program description document to address the situation when the time limits are exceeded. An engineering risk evaluation shall be performed to estimate the amount of wall loss present. The approach to the evaluation may be similar to that of the realistic scenario calculations. Actual exposure time, liquid levels, temperature, and corrosive

environment should be considered.

3) If the tank is returned to Operation mode after being in Closure mode it is recommended that an engineering risk assessment and an ultrasonic inspection be performed to determine the remaining wall thickness prior to changing modes.

REFERENCES

1. R. M. Girdler, "Leaks in Radioactive Waste Tanks", DP-990, December 1965.
2. C. A. McKeel, "Fracture Evaluation of Type I and Type II High Level Waste Tanks", T-CLC-G-00159, March 11, 2002.
3. B. J. Wiersma, "Estimation of High Level Waste (HLW) Tank Remaining Service Life", WSRC-TR-2006-00196, May, 2005.
4. H. H. Uhlig, *Corrosion and Corrosion Control*, 2nd Ed., John Wiley and Sons, New York (1971).
5. Z. Szklarska-Smialowska, *Pitting Corrosion of Metals*, National Association of Corrosion Engineers, Houston (1986).
6. P. E. Zapp, "Pitting Growth Rate in Carbon Steel Exposed to Simulated Radioactive Waste", WSRC-TR-96-0024, June, 1996.
7. B. J. Wiersma and J. I. Mickalonis, "Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations", WSRC-STI-2006-00029, September, 2007.
8. D. T. Herman, B. J. Wiersma, F. F. Fondeur, J. C. Wittkop, J. M. Pareizs, K. P. Crapse, M. S. Hay, M. R. Poirier, and S. D. Fink, "Investigating Hydrogen Generation and Corrosion in the Treatment Tank and the Potential Formation of a Floating Layer in the Neutralization Tank during Waste Tank Heel Chemical Cleaning", WSRC-STI-2007-00209, April 30, 2007.
9. B. J. Wiersma, "Treatment Tank Corrosion Studies For The Bulk Oxalic Acid Cleaning Process In H-Tank Farm", SRNL-STI-2012-00305 Rev. 0, May 2012.
10. M. Terry, et.al. "Expert Panel Workshop for Hanford Site Double-Shell Tank Waste Chemistry Optimization", RPP-RPT-22126, November 10, 2004.
11. M. E. Maryak, "Type I Tank Liner Integrity Under Oxalic Acid Induced Corrosion", T-CLC-F-00383, Rev. 1, August 22, 2012.
12. J. A. Pike, "Flowsheet and Physical Property Estimation for Tank 25 Salt Dissolution", CBU-PIT-205-00081, March 28, 2005.
13. T. C. Baughman, "Tank 5 Waste Removal and Closure Operating Plan", U-ESR- F-00024, Rev. 3, September 12, 2007.
14. T. C. Baughman, "Tank 5 and 6 Closure Strategy Sequence of Events", LWO- LWE-2007-00104, July 17, 2007.
15. J. P. Hyche, "Tanks 18 and 19 Waste Removal Operating Plan", U-ESR-F-00025, Rev. 2, July 2, 2007.
16. J. B. Elder, "Tank Inspection NDE Results for Fiscal Year 2006 Including Waste Tanks 27, 29, 33, 39, 40, 41 and 43", WSRC-TR-2006-00002, September, 2006.
17. J. B. Elder, "Tank Inspection NDE Results Tank 6, Including Summary of Waste Removal Support Activities in Tanks 5 and 6", SRNL-STI-2009-00560, February, 2010.
18. C. F. Jenkins, "HLW Evaporator Tube Bundle: Evaluation of Corrosion Failure Modes", SRT-MTS-2002-40070, May 21, 2002.