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Calculation of the Amount of Corrosion Product in HLW Tank 19

Summary

Calculations are being performed to estimate the residual radionuclides present in the iron oxide present on the sidewalls and bottom of Tank 19. SRTC/MTS estimates that approximately 497 pounds of rust has accumulated in the tank in the zone exposed to the waste. The key event during the service history of the tank that prevented a significant build-up of corrosion product was the waste removal operations performed in 1980. The calculations of metal loss, and the videotape of the interior wall, support the conclusion that corrosion of the wall has been minor. Thus the overall structural integrity of the tank has not been compromised.

Background

HLW Tank 19, a Type IV waste tank, in F-Area is in the process of being closed. Prior to immobilizing the interior by filling the space with grout, it is necessary to characterize the residual waste. Corrosion products (or rust) have accumulated on the sidewall and bottom of the carbon steel tank during its 40-year operating history. SRTC/MTS has been requested to estimate the weight of this rust. This activity will be accomplished by reviewing videotape of the interior walls of Tank 19 and by calculation of the metal loss based on tank dimensions, historical tank levels, literature values for the corrosion rate, and properties of the oxide film.

Review of Videotape

A visual inspection of the interior of Tank 19 was performed on September 27, 2001. From the videotape there appears to be a historical high liquid level watermark at approximately the 30-foot level (Note: The total height of the steel liner is approximately 34 feet). This level is consistent with the historical liquid level data (see Liquid Level History section below). Due to the presence of what appears to be salt deposits on the wall, it was difficult to assess the volume of rust present. However, it did appear from the patches of metal visible that the corrosion had been light and general. The layer appeared typical for carbon steel exposed to either an alkaline aqueous or an ambient vapor space environment. There was no evidence of extensive pitting corrosion.

Calculation Steps

Review of Liquid Level History

Figure 1 shows the liquid level for the service life of Tank 19 [1]. Essentially the tank was at two levels during its service history. Between June 1961, when waste was initially introduced, and January 1981, the first stage of waste removal, the volume of waste was approximately 1.3 million gallons. Given that there are 3540 gallons for every inch of tank level, the liquid level was approximately 30.6 feet. From January 1982 through December 2001, the final stage of waste removal, the volume of waste was approximately 300,000 gallons. Therefore, the liquid level during this time was approximately 7.1 feet.

Prior to 1981, the level history shows that there were several transfers into and out of the tank. Due to these transfers, oxygen would have been replenished in the upper region of the tank (above ~ 15 foot level). The bottom portion of the tank, however would have remained oxygen depleted, and as will be discussed, would not have corroded significantly.

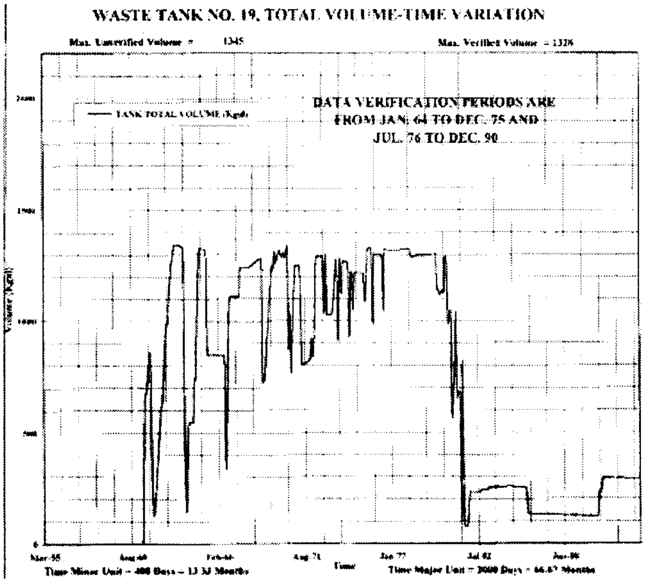

Figure 1. Tank Level History from 1960-1994. Tank Level did not change significantly after 1994.

From the standpoint of rust accumulation on the carbon steel, the most significant event was the waste removal operations during 1980. Two slurry pumps were operated during the salt dissolution operations. As a result the movement of the liquid would likely have stripped most of the loose iron oxide from the sidewalls and bottom of the tank. For purposes of this calculation, it is assumed that the corrosion product accumulated between 1961 and 1980 was removed from the wall during the waste removal. Hose washing of the walls followed the waste removal. Therefore, the tank wall is covered essentially and only with corrosion developed and accumulated since 1981. Additionally the liquid level data indicates that elevation of waste has not exceeded 7.1 feet since then, so that only 7.1 feet of the tank has been exposed to the waste. Hence, only corrosion product accumulated in this space should be considered in the residual radionuclide calculations.

Determination of Corrosion Rate and Formation of Corrosion Products

The primary corrosion reactions in an aqueous environment are [2]:

$Fe = Fe^{2+} + 2 e^-$ (anodic reaction)

$O_2 + 2 H_2O + 4 e^- = 4 OH^-$ (cathodic reaction)

The iron cations further react with water to form the corrosion product or rust. The corrosion products are actually a very complex mixture of various iron oxides. For the purposes of this calculation it will be assumed that the primary component of rust is γ - FeOOH or lepridocite [2].

For this application, there are three regions of the tank to consider: the vapor space, the oxygen rich region that is just below the vapor-liquid interface and the oxygen depleted region of the liquid. The corrosion rate in the vapor space will be assumed to be equivalent to that in a humid environment, 0.18 mpy [3]. For the oxygen rich regions it was assumed that oxygen will be able to diffuse to the carbon steel surface that is approximately 1 foot beneath the vapor-liquid interface. Thus, corrosion would continue at a relatively constant rate in this region. Laboratory and field test data indicate the general corrosion rate in alkaline waste solutions is less than 1 mil per year [4]. Ultrasonic (UT) inspection results that the wall loss due to general corrosion is minor [5]. Data for Tank 15 (reference 5, Figure 14), indicates that all the wall thickness measurements overlap, and the spread in the data for the period between 1972 and 1984 is typically less than 0.0045 inches. UT measurement error actually exceeds ± 0.002 inches, such that an upper bound on the wall loss for the 12 year period is 0.002 inches. Thus, the corrosion rate calculated from these measurements would be 0.00017 inch/yr (or 0.17 mpy). Therefore, for a bounding calculation, and to simplify the calculations it was assumed that the corrosion rate in the vapor space and the oxygen rich solution were the same, 0.18 mpy. This corrosion rate is very low and would be expected to produce minor general corrosion. Investigations in Tank 23, another Type IV tank, confirmed that the amount of general corrosion that occurs in the alkaline waste environments and the ambient air is not significant [6].

As shown by the corrosion reactions, oxygen and moisture are required for corrosion of iron in neutral to alkaline solutions [7]. Both are necessary, because oxygen alone or water free of dissolved oxygen does not corrode iron significantly. Iron corrodes in neutral waters at a rate that is proportional to the concentration of dissolved oxygen. Water in contact with iron will continue to cause corrosion until the dissolved oxygen is consumed. Calculations showed that if all the dissolved oxygen in neutral water saturated with dissolved oxygen were utilized to corrode iron, the depth of metal corroded would be approximately 0.0006 inches per square inch of iron surface per gallon of water. Given that the corrosion rate of iron in alkaline environments is a factor of 4 less than that in water [8], the value that may be assumed for Tank 19 is 0.00015 inches per square inch of iron surface per gallon of waste in the oxygen depleted region of the alkaline waste (e.g., along the bottom of the tank).

Determination of Metal Loss

The liquid level history can be utilized to determine how long these various environmental conditions existed. The level history suggests that there have been 3 periods of time: 1) 1981-1985, 2) 1985-1990, and 3) 1990-2001. Table 1 identifies the regions of the tank that were exposed to each of the environments during each period of time. The distances listed in the table are the height above the tank bottom. Corrosion of the tank bottom was also considered during the initial time period. No significant corrosion of the tank bottom occurred after the initial dissolved oxygen was depleted. The table also identifies the corrosion rate, or in the case of oxygen depleted zones, the amount of metal loss given that the dissolved oxygen has been consumed during that time. The region of oxygen depletion is also shown in Figure 2. Figures 3 to 5 show the cumulative metal loss profile at the end of each of these periods of time. The results show that for the submerged portion of the tank the average corrosion rate for the entire time interval is less than would be expected in the oxygenated atmosphere. Example calculations are included in the Appendix.

Table 1. Summary of Tank Wall Exposure from 1981-2001

Regions	Years		
	1981-1985	1986-1990	1990-2001
Oxygen rich liquid	Sidewall from 4.7 to 5.9 feet (0.18 mpy)	Sidewall from 1.75 to 2.94 feet (0.18 mpy)	5.88 to 7.1 feet
Oxygen depleted liquid	Tank Bottom and Sidewall from 0 to 4.7 feet (0.75 mils wall loss)	Tank Bottom and Sidewall from 0 to 1.75 feet (0 mils wall loss)	Sidewall from 1.75 to 5.88 feet (0.13 mils wall loss) Tank Bottom and Sidewall from 0 to 1.75 feet (0 mils wall loss)
Vapor space	Sidewall from 5.9 feet to 34 feet (0.18 mpy)	Sidewall from 2.94 feet to 34 feet (0.18 mpy)	Sidewall from 7.1 feet to 34 feet (0.18 mpy)

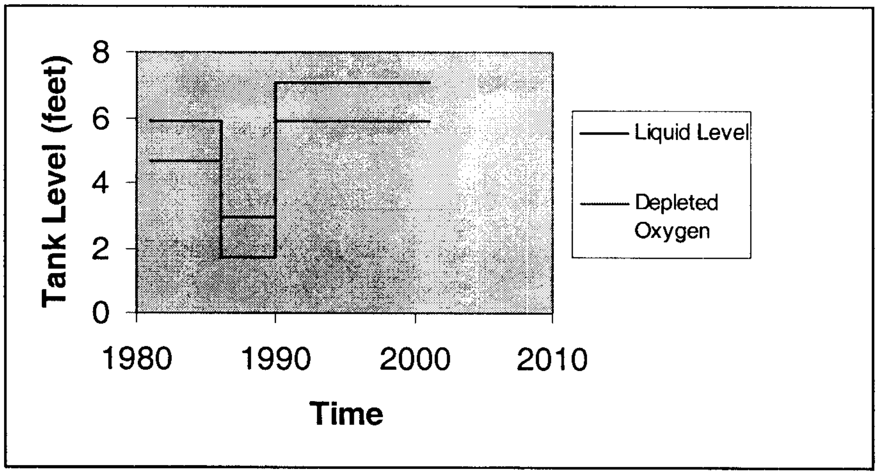

Figure 2. Tank 19 Liquid Level History Since 1981

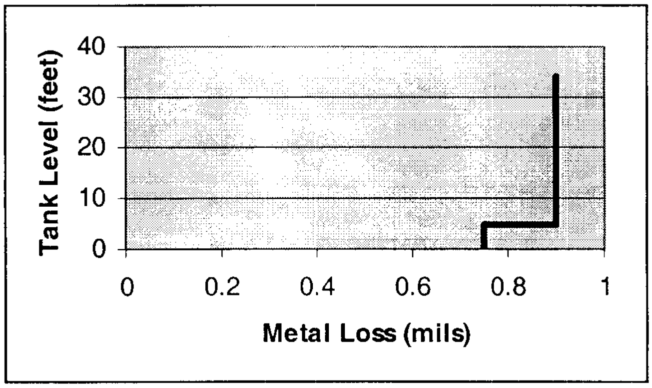

Figure 3. Cumulative metal loss between 1981-1985

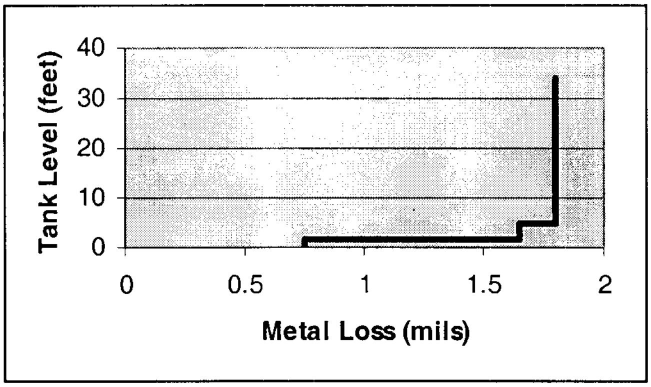

Figure 4. Cumulative Metal Loss Between 1981-1990

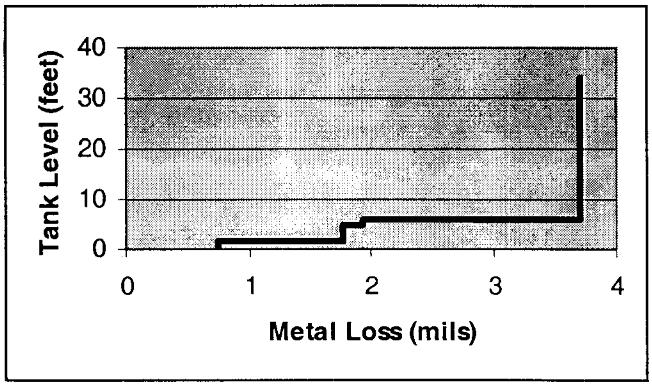

Figure 5. Cumulative Metal Loss Between 1981-2001

Calculation of Oxide Accumulated on Tank Bottom and Sidewalls

The volume of metal lost due to corrosion is calculated by multiplying the surface area by the metal loss (see Appendix for example calculation). From the stoichiometry, it is observed that for every mole of iron that is dissolved one mole of corrosion product is formed. The ratio of the volume of oxide formed (Vo) to the volume of metal dissolved (Vm) can be calculated in the following manner:

Vo/Vm = ((moles of γ - FeOOH * Molecular Weight of γ - FeOOH)/ density of γ - FeOOH) / ((moles of Fe * Molecular Weight of Fe)/density of Fe)

Inputs for this equation include:

density of Fe = 7.86 g/cm^3
Molecular Weight of Fe = 56 g/mole
density of γ - FeOOH = 4.09 g/cm^3
Molecular Weight of γ - FeOOH = 89 g/mole

Vo/Vm = ((1 * 89)/ 4.09)/((1 * 56)/7.86) = 3.05

Therefore the total volume of oxide produced is approximately 3 times the volume of the metal lost.

The pounds of iron oxide are then calculated by multiplying the volume of the oxide by its density (see Appendix for example calculation). Table 2 shows the weight of the corrosion product in each region of the tank as well as the total corrosion product. For the calculations of the residual radionuclides, the corrosion products on the tank bottom and the first 7.1 feet of the wall should be considered. **The final weight of accumulated corrosion product is 497 pounds.** It should also be taken into account that for the past year heel removal operations using Flygt mixers have occurred, thus again perhaps disturbing the oxide. Therefore, this number is likely an upper bound.

Table 2. Cumulative Corrosion Product in Tank 19

Height of Tank	Pounds of Iron Oxide
0 (tank bottom)	270
0 to 1.75 feet	22
1.75 to 4.7 feet	89
4.7 to 5.9 feet	39
5.9 to 7.1 feet	77
Total	497

Conclusions

An estimate has been made of the weight of the corrosion product (rust) accumulated on the walls and bottom of HLW Tank 19 during its service history. Approximately 497 pounds of rust is estimated to have been generated and to possibly remain accumulated in the tank in the zone exposed to the alkaline radioactive waste for the past 20 years. The key event in the past that prevented additional significant build-up of corrosion product was the waste removal operations performed during 1980.

References

1. P. Daneshvar, "A Survey of Historical Waste Tank Temperatures", T-CLC-G-00027, April 4, 1995.
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3. R. P. Anantatmula and P. C. Ohl, "DST Remaining Useful Life Estimates", WHC-SD-WM-ER-585, June 28, 1996.
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7. H. H. Uhlig, **Corrosion Handbook**, pp. 125-126.
8. H. H. Uhlig, **Corrosion and Corrosion Control**, p. 99.

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Appendix

Calculation of Metal Loss Example

Depleted Oxygen Region Example

Tank Bottom and sidewall up to 4.7 feet
Tank Data:
Tank diameter is 85 feet.
3540 gallons/inch of level

Surface Area $= 2 \Pi r h + \Pi r^2$
$= (2 \Pi (42.5 \text{ feet}) (4.7 \text{ feet}) + \Pi (42.5 \text{ feet})^2)\ 144 \text{ inch}^2/\text{foot}^2$
$= 998{,}208 \text{ inch}^2$

Volume = (4.7 feet) (12 inches/foot) (3540 gallons/inch) = 200,000 gallons

Metal Loss $= (0.00015 \text{ inches/inch2/gal}) (998{,}208 \text{ inch}^2)/ (200{,}000 \text{ gallons})$
$= 0.00075$ inches
$= 0.75$ mils

Oxygen Rich Liquid or Vapor Space Example

Time = 5 years

Metal Loss = (0.00018 inch/year) * 5 years = 0.0009 inch = 0.9 mils

Calculation of Volume of Metal Loss Example

1981-2001
Tank Bottom

Metal Loss = 0.75 mils

Volume of Metal Loss $= \Pi r^2$ (Metal Loss)
$= \Pi (42.5 \text{ feet})^2 (0.00075 \text{ inch}) \; 144 \text{ inch}^2/\text{foot}^2$
$= 613 \text{ inch}^3$

Calculation of Volume of Iron Oxide Example

Volume of Oxide = 3 (Volume of Metal Loss)
$= 3 (613 \text{ inch}^3) = 1839 \text{ inch}^3$

Calculation of Pounds of Iron Oxide Example

Density of Iron Oxide = 4.09 g/cm^3

Pounds of Iron Oxide = (Volume of Oxide) (Density of Oxide)
$= (1839 \text{ inch}^3) (4.09 \text{ g/cm}^3)(16.39 \text{ cm}^3/\text{inch}^3)(1 \text{ pound}/454 \text{ g})$
= 270 pounds