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Calculation of the Amount of Corrosion Product on the Wall of Tank 19

Summary

Calculations were performed to estimate the iron oxide present on the sidewalls and bottom of Tank 19. It is estimated that approximately 87 pounds of corrosion product accumulated on the tank walls in the zone exposed to the waste between 1981and 2001. The calculations of metal loss and visual inspection 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

Tank 19, a Type IV waste tank in F-Area, is in the process of being closed. Prior to filling the interior of the tank with grout, it is necessary to characterize the residual waste and estimate the weight of the accumulated corrosion products on the sidewall and bottom of the carbon steel tank during its operating history. The weight of the corrosion products was estimated by reviewing videotape of the interior walls of Tank 19 and calculating 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 performed on September 27, 2001 revealed a historical high liquid level watermark at approximately the 30-foot level consistent with the historical liquid level data, as shown in Figure 1. (Note: The total height of the steel liner is approximately 34 feet). Although difficult to visually estimate the volume of rust present due to the presence salt deposits on the wall, visual inspection concluded that 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.

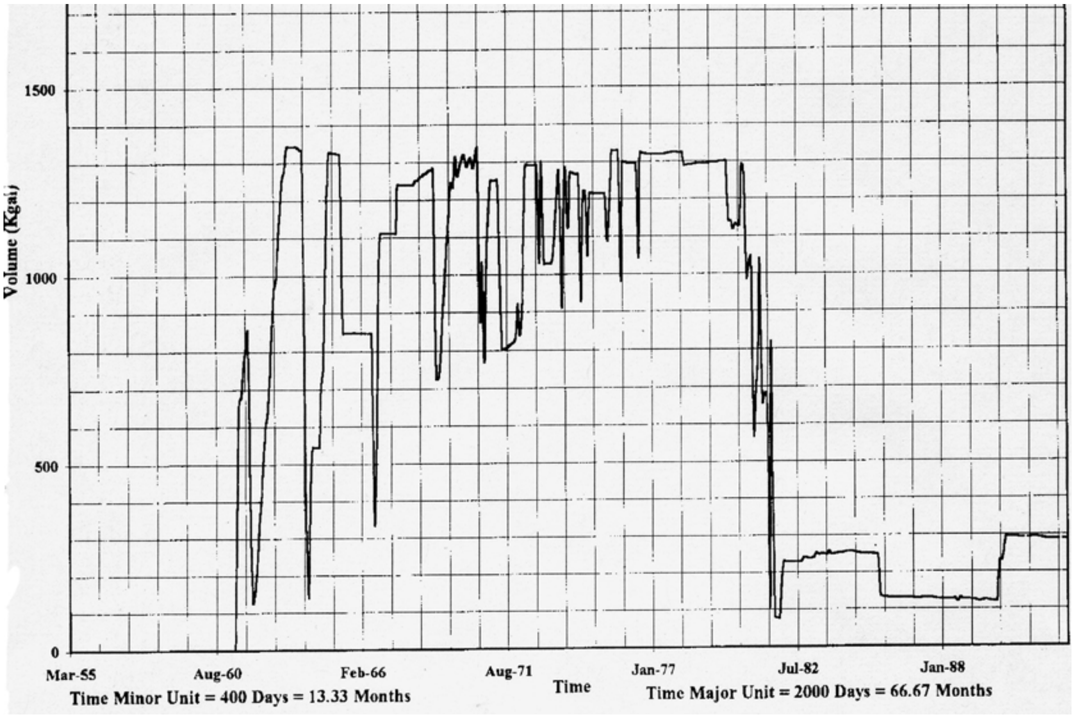

Figure 1. Tank Level History from 1960-1994. Tank Level did not change significantly between 1994 and 2001.

From the standpoint of rust accumulation on the carbon steel, the most significant event was the waste removal operations during 1981. The waste removal operations in 1981 most likely removed all corrosion products from the tank wall due to agitation from slurry pumps and subsequent spray washing. As such, it was assumed that the corrosion product accumulated between 1961 and 1980 was removed from the wall during the waste removal, and the tank wall is covered with corrosion products accumulated only since 1981. Additionally the liquid level data indicates that elevation of waste did not exceed 7.1 feet until 2000, so that only 7.1 feet of the tank was exposed to the waste. Hence, only corrosion product accumulated in this space should be considered in the residual radionuclide calculations. In 2000-2001, waste removal operations were performed again in order to remove the remaining zeolite [2]. Flygt mixer pumps were utilized to agitate the solution and multiple slurry/transfer/recycle batch processes between Tank 19 and Tank 18 were performed. The effect of the mixers was to remove nearly all the corrosion products on the tank bottom and mix them into the sludge. Some of the wall corrosion products were also probably dislodged due to the agitation. Although difficult to quantify, it was assumed that 50% of the corrosion product on the 7.1 foot region of the tank wall has sloughed off during the removal. This is a qualitative assessment, but is based on mechanistic understanding.

> a) Sloughing of the oxide film occurs if the Pilling-Bedworth ratio (volume oxide:volume metal) is not equal to 1 [3]. This ratio for the different iron oxides that may form is between 2 and 6. The larger the ratio, the more likely it is to slough off.
> b) Iron oxides may transform as the surface is alternately wetted and dried, or the pH of the solution changes. This transformation involves changes in the crystal structure. As a result the corrosion product layer is typically a mixture of different oxides (e.g., magnetite, lepidocrocite, goethite, etc.). Discontinuities form at the interfaces between these oxides, which causes cracking and spalling of the oxide film.
> c) Figure 2 shows corrosion of steel in a de-aerated, quiescent alkaline solution [4]. A considerable amount of corrosion product, hydrated magnetite, has sloughed off the metal and collected at the bottom of a test tube. Certainly if the solution is agitated even more corrosion product would slough off.

Figure 2. Corrosion of steel in a de-aerated quiescent alkaline solution [4].

Thus this evaluation considered the tank wall exposure between 1981-2001 (i.e., from the end of the first waste removal campaign until the end of the second waste removal campaign. Since 2001, the tank has been quiescent with approximately 4 inches of alkaline waste on the bottom [1]. The waste is also dilute with respect to radionuclides [5]. Therefore it will be assumed that there has been negligible incorporation of radionuclides into the corrosion products since 2001.

Determination of the Corrosion Products Formed and the Corrosion Rate

The primary corrosion reactions in an alkaline aqueous environment are [6]:

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

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

The iron cations further react with water and oxygen to form the corrosion products or rust. The corrosion products may be a very complex mixture of various iron oxides. The predominant oxide present at the surface depends upon the conditions of exposure. For example, in de-aerated, alkaline conditions the primary oxide present is magnetite [4]. In aerated solutions and vapor space conditions, the primary component of rust is γ - FeOOH or lepidocrocite [6]. A third exposure condition that can occur is a dry-wet cycle [7]. As the dry surface becomes wet, reduction of ferric ions in the lepidocrocite to ferrous ions occurs, and the lepidocrocite partially transforms to magnetite (Fe_3O_4). Metal ion dissolution (i.e., corrosion) occurs simultaneously during this process. On the other hand, during the drying stage as more oxygen becomes available, the ferrous ions in the magnetite re-oxidize back to lepidocrocite. For this calculation it will be assumed that if a section of the wall experiences a dry-wet cycle, the oxide will be assumed to be lepidocrocite if the most recent exposure was a drying stage or an aerated solution, while for a de-aerated solution the oxide will be assumed to be magnetite. Thus, a mixture of oxides will be assumed to be present on the wall. However, the transformation from one oxide form to another will be neglected.

The corrosion rates in the vapor space, the oxygen rich region that is just below the vapor-liquid interface and the oxygen depleted region of the liquid were determined. The corrosion rate in the vapor space will be assumed to be equivalent to that in a humid environment, 0.18 mpy [6]. For the oxygen rich regions, it was assumed that sufficient oxygen diffuses to the carbon steel surface that is approximately 1 foot beneath the vapor-liquid interface in order to maintain a relatively constant corrosion 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 [9]. Ultrasonic (UT) inspection results indicate that the wall loss due to general corrosion is minor [10]. Data for Tank 15 [10], shows that all the wall thickness measurements overlap, and the spread in the data for the period between 1972 and 1984 is typically less than 0.00045 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 [11].

However, at depths greater than 1 foot beneath the liquid-air interface it is assumed that diffusion of oxygen to the surface is limited by both the low solubility of dissolved oxygen as well as the presence of the magnetite film. Thus, it will be assumed that in this region corrosion occurs until the dissolved oxygen in this layer is depleted. After that, the solution is essentially de-aerated and corrosion essentially ceases. As shown by the corrosion reactions, oxygen and moisture are required for corrosion of iron in alkaline solutions [12]. Iron corrodes in alkaline solutions at a rate that is proportional to the concentration of dissolved oxygen. The dissolved oxygen concentration is a function of the temperature and salinity (i.e., salt content of the liquid) [13]. Based on historical temperatures and concentrations of the waste in Tank 19, the dissolved oxygen concentration was determined to be 1.9 mg/l or 5.94×10^{-5} moles O_2 /l (See Appendix for calculation). For the formation of magnetite, three moles of iron must be consumed along with 2 moles of oxygen. Therefore, 8.91×10^{-5} moles Fe/literr 4.97×10^{-3} g Fe/liter is dissolved before the oxygen is consumed. The volume of iron corroded, 6.31×10^{-4} cm^3/liter, is calculated by dividing the last value by the density of iron (7.87 g/cm^3). The total penetration is determined by multiplying the volume of iron corroded by the ratio of the volume of solution to the surface area of the steel (See Appendix for calculation).

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 3. Tables 2 to 4 show the metal loss for each period of time between 1981 and 2001. 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 shown 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)	5.9 to 7.1 feet
Oxygen depleted liquid	Tank Bottom and Sidewall from 0 to 4.7 feet (0.029 mils wall loss)	Tank Bottom and Sidewall from 0 to 1.75 feet (0 mils wall loss)	Sidewall from 1.75 to 5.9 feet (0.16 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 7.1 feet (0.18 mpy)	Sidewall from 2.94 feet to 7.1 feet (0.18 mpy)	Sidewall from 7.1 feet to 34 feet (0.18 mpy)

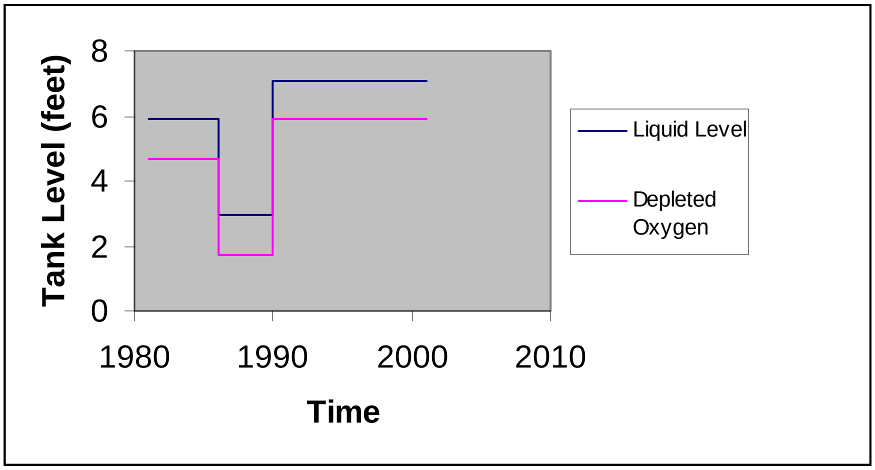

Figure 3. Tank 19 Liquid Level History Since 1981

Table 2. Metal Loss and Oxide Build-up 1981-1985

Tank Level (ft)	Environment	Corrosion Loss (mils)	Magnetite (lbs.)	Lepidocrocite (lbs.)
0-4.7[a]	Oxygen Depleted	0.029	11.4	-
4.7-5.9	Oxygen Rich	0.9	-	18.7
5.9-7.1	Vapor	0.9	-	18.7

a - Includes tank bottom and tank wall

Table 3. Metal Loss and Oxide Build-up 1981-1990

Tank Level (ft)	Environment	Corrosion Loss (mils)	Magnetite (lbs.)	Lepidocrocite (lbs.)
0-1.75[a]	Oxygen Depleted	0.029	10.06	-
1.75-2.94	Oxygen Rich	0.93	0.52	18.5
2.94—4.7	Vapor	0.93	0.86	27.39
4.7-5.9	Vapor	1.8	-	37.4
5.9-7.1	Vapor	1.8	-	37.4

a - Includes tank bottom and tank wall

Table 4. Metal Loss and Oxide Build-up 1981-2001

Tank Level (ft)	Environment	Corrosion Loss (mils)	Magnetite (lbs.)	Lepidocrocite (lbs.)
0-1.75[a]	Oxygen Depleted	0.03	10.06	-
1.75-2.94	Oxygen Depleted	1.09	3.39	18.5
2.94—4.7	Oxygen Depleted	1.09	5.1	27.39
4.7-5.9	Oxygen Depleted	1.96	2.9	37.4
5.9-7.1	Oxygen Rich	3.78	-	78.5

a - Includes tank bottom and tank wall

Calculation of Oxide Accumulated on Tank Bottom and Sidewalls

The volume of metal lost due to corrosion is calculated by multiplying the surface area of the region by the metal loss. The ratio between the volume of metal loss and the volume of oxide formed is referred to as the Pilling-Bedworth ratio [14]. For magnetite this ratio is 2.1, while for lepidocrocite the ratio is 3.05 [3, 14]. The volume of oxide is then calculated by multiplying the volume of metal loss by the Pilling-Bedworth ratio.

The pounds of iron oxide are then calculated by multiplying the volume of the oxide by its density (see Appendix for example calculation). Tables 2-4 also show the weight of the corrosion product in each region of the tank as well as the total corrosion product. The total oxide, before accounting for waste removal in 2001 and slough off of loosely adherent corrosion product, is shown in Table 5.

Table 6 shows the cumulative corrosion product on the Tank 19 walls assuming that the corrosion product on the tank bottom was removed during waste removal in 2000-2001 and approximately 50% of the corrosion product has sloughed of the walls. **The estimated weight of accumulated corrosion product is 87 pounds.** The table also shows the approximate thickness of the corrosion product. This thickness was calculated by dividing the weight of oxide by the density of the oxide and the surface area of the region of the tank (see Appendix for example calculation). The depth of corrosion product ranges from 0.03 to 5.8 mils assuming a tightly packed oxide. This amount of rust is consistent with the light general corrosion that was observed visually on the tank wall.

Table 5. Cumulative corrosion product on Tank 19 walls, not accounting for slough off and waste removal.

Tank Level (ft)	Magnetite (lbs.)	Lepidocrocite (lbs.)	Iron Oxide (lbs.)
0 (tank bottom)	9.29	-	9.29
0-1.75	0.77	-	0.77
1.75-2.94	3.39	18.5	21.89
2.94-4.7	5.1	27.39	32.49
4.7-5.9	2.9	37.4	40.3
5.9-7.1	-	78.5	78.5
Total	21.45	161.79	137.23

Table 6. Cumulative corrosion product on Tank 19 walls.

Tank Level (ft)	Magnetite (lbs.)	Lepidocrocite (lbs.)	Iron Oxide (lbs.)	Thickness of Oxide (mils)
0 (tank bottom)	0	-	0	
0-1.75	0.39	-	0.39	0.03
1.75-2.94	1.7	9.3	11	1.6
2.94-4.7	2.6	13.7	16.3	1.6
4.7-5.9	1.5	18.7	20.2	2.9
5.9-7.1	-	39.3	39.3	5.8
Total	6.19	81	**87.19**	

Conclusions

An estimate of the weight of the corrosion products accumulated on the Tank 19 walls and bottom during its service history was made. It was estimated that 87 pounds of corrosion product accumulated on the tank walls in the zone exposed to the waste between 1981-2001.

References

1. P. Daneshvar, “A Survey of Historical Waste Tank Temperatures”, T-CLC-G-00027, April 4, 1995;LWDP Morning reports 1995-2001.
2. B. J. Wiersma, “Monitoring of Supernate Temperature and Composition During Waste Removal from Tank 19”, HLW-STE-2000-00083, Rev. 1, July 13, 2000.
3. L.S. McNeill and M. Edwards, “The Importance of Temperature In Assessing Iron Pipe Corrosion in Water Distribution Systems”, *Environmental Monitoring and Assessment*, Vol. 77, no.3, August 2002, pp. 229-242.
4. http://www.corrosion-doctors.org/Experiments/iron-products.htm
5. R. F. Swingle, “Characterization of the Tank 19F Closure Grab and Core Samples and the Tank 18F Dip Sample”, WSRC-TR-2002-00107, March 6, 2002.
6. K. R. Trethewey and J. Chamberlain, **Corrosion**, Longman Scientific and Technical, Essex, UK, 1988.

7. C. Leygraf and T. E. Graedel, **Atmospheric Corrosion**, The Electrochemical Society, Pennington, NJ, 2000, pp. 148-152.
8. R. P. Anantatmula and P. C. Ohl, "DST Remaining Useful Life Estimates", WHC-SD-WM-ER-585, June 28, 1996.
9. R. L. Sindelar and B. J. Wiersma, "SRS High Level Waste Tank and Piping Systems – Structural Integrity Program and Topical Report", WSRC-TR-95-0076, June 1995.
10. B. J. Wiersma and P. E. Zapp, "Structural Dimensions, Fabrication, Materials and Operational History for Types I and II Waste Tanks", WSRC-TR-98-00373, October 1998.
11. P. S. Bird and C. F. Jenkins, "Dye Penetrant Inspections of Internal Walls, Waste Tank 17, 20, and 23", DPSPU 85-11-4, March-July 1984.
12. H. H. Uhlig, **Corrosion Handbook**, pp. 125-126.
13. J. E. Sherwood, F. Stagnitti, M. J. Kokkinn, and W. D. Williams, "Dissolved Oxygen Concentrations in Hypersaline Waters", Limnol. Oceanogr., Vol. 36, No. 2, 1991, pp. 235-250.
14. http://www.corrosionsource.com/technicallibrary/corrdoctors/Modules/HotCorrosion/Pilling.htm
15. SRS Database on \\WG08\WASTE8\SAMPLES\HLWTankChemistry\NTANK19.

Appendix

Calculation of Dissolved Oxygen Concentration

Step 1: Estimate the salt concentration in Tank 19 waste between 1981-2001.

The waste sample results for Tank 19 showed relatively consistent results during this 20 year period [15]. The primary constituents were sodium hydroxide, sodium nitrite, sodium nitrate, and sodium carbonate. The average concentration for each of these components and the average solution density was calculated (see Table A1). The average solution density was 1.21 g/cm^3.

Table A1. Average Salt Concentrations for Tank 19 between 1981-2001.

Constituent	Concentration (M)	Concentration (g/liter)
Sodium Hydroxide	0.93	37
Sodium Nitrate	1.55	132
Sodium Nitrite	1.17	80.5
Sodium Carbonate	0.37	36

Step 2: Determine the Salinity of the Solution

The salinity is simply the g per kg of solution. This may be calculated by taking the total g/l of salt and dividing by the average density. In this case:

Salinity = (285.5 g/l)/(1.21 kg/liter) = 236 g salt/kg solution

Step 3: Use an empirical relationship to determine the dissolved oxygen concentration as a function of temperature and salinity.

The average temperature in Tank 19 between 1981-2001 was approximately 25 °C [1] and the salinity calculated from step 2 was 236 g salt/kg salt. The empirical relationship for the dissolved oxygen concentration is [13]:

$$\ln (DO) = a_0 + a_1/T + a_2 \ln T + a_3T + a_4T^2 + S(a_5 + a_6T + a_7T^2) + a_8S^2$$

where:

DO = Dissolved oxygen concentration (mg/l)
a_i = Empirical constants shown in Table A2
T = Temperature (K)
S = Salinity (g/kg)

The dissolved oxygen concentration in Tank 19 supernate was calculated to be 1.9 mg/liter.

Note: This equation was developed from experiments which utilized sodium chloride as the salt present in solution. It is assumed that the presence of other salts in solution will have a similar effect on the dissolved oxygen concentration.

Table A2. Empirical constants for dissolved oxygen concentration.

Constant	Value
a_0	-6.85693750E+04
a_1	1.28038367E+06
a_2	1.32716777E+04
a_3	-4.59371240E+01
a_4	2.65097198E-02
a_5	-4.29122353E-02
a_6	2.06161380E-04
a_7	-2.68767762E-07
a_8	-3.60557809E-06

Calculation of Metal Loss Example

Depleted Oxygen Region Example

Step 1: Calculate the exposed surface area and volume.

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

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

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

Step 2: Calculate the moles of dissolved oxygen present initially.

There were 1.9 mg/liter of dissolved oxygen present initially.

Moles of DO $= (1.9 \text{ mg/liter}) (1/(32 \text{ g/mole } O_2))(1\text{g}/1000 \text{ mg})$
$= 5.94 \times 10^{-5} \text{ moles } O_2/\text{l}$

Step 3: Calculate the moles of iron consumed during the formation of magnetite.

The formula for magnetite is Fe_3O_4. Therefore, 3 moles of iron are consumed for every 2 moles of O_2 in the formation of this oxide.

Moles of Fe consumed = (3 moles Fe/2 moles O_2)* 5.94 x10^{-5} moles O_2/liter
= 8.91 x 10^{-5} moles Fe/liter

Step 4: Calculate the volume of metal loss

The volume of metal loss is calculated from the weight of metal loss divided by the density of the metal. In this case:

Volume of metal loss = (8.91 x 10^{-5} moles Fe/liter)(55.8 g Fe/mole Fe)(1/(7.87 g Fe/cm^3))
= 6.31 x 10^{-4} cm^3 Fe/liter

Step 5: Calculate the depth of penetration

The depth of penetration is calculated by taking the volume of metal loss and multiplying by the volume to surface area ratio. In this case:

Depth of penetration = (6.31 x 10^{-4} cm^3 Fe/liter)(200,000 gal)(3.785 liter/gal)(1/998,208 in^2)(1 in^3/16.37 cm^3)
= 0.000029 inches
= 0.029 mils

<u>Oxygen Rich Liquid or Vapor Space Example</u>

Time = 5 years

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

Calculation of Volume of Metal Loss Example

Tank Bottom

Metal Loss = 0.029 mils = 0.000029 inches

Volume of Metal Loss = $\prod r^2$ (Metal Loss)
= $\prod$ (42.5 feet)^2 (0.000029 inch) 144 $inch^2/foot^2$
= 23.7 $inch^3$

Calculation of Volume of Iron Oxide Example

Tank Bottom

The Pilling-Bedworth ratio for magnetite is 2.1.

Volume of Oxide = 2.1 (Volume of Metal Loss)
= 2.1 (23.7 $inch^3$) = 49.77 $inch^3$

Calculation of Pounds of Iron Oxide Example

Tank Bottom

Density of Magnetite = 5.18 g/cm^3

Pounds of Iron Oxide = (Volume of Oxide) (Density of Oxide)
= (49.77 $inch^3$) (5.18 g/cm^3)(16.39 cm^3/$inch^3$)(1 pound/454 g)
= 9.3 pounds

Calculation of Thickness of Oxide

Tank wall from 5.9 to 7.1 feet

Surface Area = 2∏ rH = 2 ∏ (42.5 ft)(7.1-5.9 ft) 144 $inch^2$/$foot^2$
= 46,144 in^2

Density of Lepidocrocite = 4.09 g/cm^3

Oxide Thickness = (78.5 lbs of lepidocrocite)(1/4.09 g/cm^3)(454 g/lb)/((46,144 in^2)(16.39 cm^3/in^3))
= 0.0115 inches
=11.5 mils

Assume 50% slough-off:

Oxide Thickness = 0.5 (11.5 mils)
= 5.75 mils