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Flammable Gas in Tank 43-H Leak Detection Boxes (U)

B. J. Wiersma
Savannah River Technology Center
Strategic Materials Technology Department
Materials Technology Section

Harold Peacock
Savannah River Technology Center
Strategic Materials Technology Department
Materials Technology Section

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Westinghouse Savannah River
Savannah River Site
Aiken, SC 29808

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B. J. Wiersma

Harold Peacock

SRTC Savannah River Technology Center, Aiken, SC 29808
Westinghouse Savannah River Company
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Approvals

____ Date:______________________

B. J. Wiersma, Co-Author
Materials Applications and Corrosion Technology Group
Materials Technology Section

____ Date:______________________

H. B. Peacock, Co-Author
Materials Applications and Corrosion Technology Group
Materials Technology Section

____ Date:______________________

P. E. Zapp, Reviewer
Materials Applications and Corrosion Technology Group
Materials Technology Section

____ Date:______________________

G. T. Chandler, Manager
Materials Performance and Corrosion Technology Group
Materials Technology Section

____ Date:______________________

N. C. Iyer, Manager
Materials Technology Section
Strategic Materials Technology Department

____ Date:______________________

William M. Barnes, Manager
WPT & East Hill Tank Farm Engineering
Materials Technology Section

Introduction and Summary

Flammable gases were discovered in leak detection box LDB-3 of High Level Waste Tank 43 from gas samples drawn during October 2001. The gas was discovered during routine gas sampling prior to camera inspection of the LDB. Later, hydrogen gas was also found in other LDBs associated with the waste tank. Analysis of the original gas sample indicated a level of about 60 % of the lower flammable limit (LFL) for hydrogen. The LFL limit is about 4-volume percent (v/o) hydrogen in air. Additional samples were analyzed by SRTC; only hydrogen gas was identified in the LDB samples. It is suspected that the drain lines from the LDBs to the H-Area Diversion Box (HDB-7) may be a primary source and/or storage repository for hydrogen gas. The High Level Waste Division (HLWD) requested that SRTC evaluate corrosion of carbon steel to determine if sufficient quantities of hydrogen gas could be generated in the LDB and associated piping to rationalize the existence of the flammable gas.

A Kepner-Tregoe problem analysis team performed an analysis to identify potential mechanisms for hydrogen generation.(1) The mechanisms that were considered included general corrosion of carbon steel, radiolysis of water and biological activity. The final evaluation indicated that general corrosion of carbon steel was the most likely contributor to the hydrogen gas build-up in the LDB.

This report focuses on corrosion of carbon steel for the LDB and transfer line jacket as well as for the drain line header. The report describes calculations made to estimate hydrogen gas generation due to carbon steel corrosion and calculations made to estimate the pipe wall thickness after corrosion. Results demonstrate that hydrogen gas generation in the LDB and associated piping is consistent with that estimated from the corrosion of carbon steel. The LFL limit within the LDB and transfer line jacket may be reached in 10 to 465 days based on acidic or basic environmental conditions, respectively. Acid conditions are expected due to radiolysis of moist air/water within the transfer line jacket and/or seepage of acidic ground water into the drain line system.

Background

Leak detection boxes and associated piping were constructed using carbon steel pipe, likely schedule 40 ASTM A106. The LDB is located adjacent to the waste Tank 43-H about 8 feet under ground and is connected to the jacket surrounding the waste transfer line from Tank 43 to the 2H evaporator. The volume of the transfer line jacket is approximately 14 gallons (1.87 ft^3).(2) Liquid that accumulates in the transfer line jacket tends to drain to the LDB-3, and when the LDB fills to the overflow pipe, the liquid drains to H-Area Diversion Box (HDB-7) sump though the drain piping system. The LDB construction is schematically shown in Figure 1.

The detection of flammable gases in the LDB is not a new phenomenon. In 1989, during the connection of the Low Point Drain Tank to Waste Tank 50, HP (Health Protection) reported a flammable gas measurement within the jacket vapor space of 80% LFL using a MSA-260 probe.(3) The system was purged first with argon and then with nitrogen for a total of about 28 hours before a 0% LFL reading was obtained. Operations personnel stated that in the past high LFL readings were often obtained for closed-jacketed lines.

Videotapes of the LDB show a moist environment with liquid present. The drainpipe is generally capped, and the over flow pipe extends about 7 inches above the bottom of the box. The conductivity probe detects liquid in the LDB, but it is about ¼ inch off the bottom, so it could possibly contain ¼ inch of liquid and not be detected by the probe.

Corrosion evaluation of Tank 40 LDB using destructive metallography was done in 1999.(4) This Tank had been in service approximately 18 years. Both general corrosion and microbiological corrosion were evaluated. Visual examination of the exterior surface did not reveal any significantly corroded areas where its integrity was impaired. The LDB exhibited mild general corrosion that was characterized as typical of carbon steel corrosion in soils and mild aqueous environments. The microbiological assessment revealed only limited microbial activity. The analysis also indicated that sulfate-reducing bacteria (SRB), commonly associated with microbial corrosion of carbon steel, was not present in significant numbers. Sections through the LDB wall are shown in Figures 2, 3 and 4. Corrosion products are evident on the inside surface of the pipe. The wall thickness at the bottom of the LDB was measured from the 8X photograph shown in Figure 4. This data allowed calculation of an estimated corrosion rate for carbon steel for waste tank environments.

Gas Sampling and Analysis

After the initial gas sample from LDB-3 showed a high LFL value, several more samples were taken by HLWD Operations to verify the results. They were sent to SRTC for analysis. The samples were analyzed on an Agilent M200 micro GC (Gas Chromatograph) that has two columns each with thermal conductivity detectors. One column is a 10 meter 5A° molecular sieve column used mostly for analyzing He, H_2, O_2, N_2, and CH_4. The other column is an 8-meter OV1 column for analyzing volatile organic compounds (VOCs).

Gas samples were taken in 6-liter canisters that had been evacuated to 0.05 Torr. To assist in transfer of the sample to the GC instrument, the canisters were back-filled with argon to 1000 Torr. The GC was calibrated with traceable standards prior to analyzing the samples. (5)

Results of sample analysis are shown in Table 1. Flammable gases averaged 0.75 volume % hydrogen with no methane gas or volatile organic compounds detected in the LDB. Oxygen levels were only slightly lower than atmospheric values and the nitrogen levels tended to be somewhat less than atmospheric. Lower oxygen values indicate corrosion reactions with some dissolved oxygen in the corroding medium expected.

A gas sample was taken from the LDB when the HDB-7 drain line was open. Analysis gave a value of 0.146 v/o hydrogen. The drain line was recapped, the LDB was purged, and a gas sample was taken 3 hours later. The analysis gave a value of zero v/o hydrogen. This led the site to believe that the drain line was a major contributor to hydrogen build-up in the LDB.

Table 1. Analysis of Gas Samples from LDB-3 of Tank 43-H*

Sample Date	Sample No.	Vol % H2	Vol % O2	Vol % N2	Vol % CH4
Dry Air Values	--	5×10^{-5}	20.95	78.09	14×10^{-5}
11/09/01	LDBS1	1.77	14.82	80.78	0
	LDBS2	400ppm	20.07	75.60	0
11/15/01	LDB-3	0.243	19.42	78.46	0
11/20/01	Sample 1	0.576	19.28	76.56	0
	Sample 2	0.410	18.82	74.50	0
11/19/01	HDB-7 Drain line open	0.146	--	--	--
11/19/01	HDB-7 Drain Line closed	0	--	--	--

+ Analyzed by SRTC, Tommy Sessions

Additionally, HLWD Operations sampled the LDB-3 using the Mine Safety Appliance instrument (MSA 241) at 1-hour intervals for about 9 hours. The gas samples were sent to SRTC for Gas Chromatograph/Mass Spectroscopy (GC/MS) analysis. The top of the vent pipe was taped with the sampling line inside the upper 1-foot of the vent pipe. Gas samples were taken every hour and after 2 minutes and 10 minutes in some instances. The results are shown in Figure 5. When these samples were taken, the LDB was connected to the HDB-7 drain line through the overflow pipe.

The initial hydrogen content was found to be about 30% of the LFL. The concentration of measured hydrogen increased after the second sample and remained at high LFL values, up to 90% LFL, at each initial 1-hour reading. Two-minute samples always showed significantly lower values (10-20% of LFL). After 10 minutes, all samples showed even lower values (5-8% of LFL).

The data show that the flammable gas content in the upper part of the vent pipe is reduced with time during sampling, and after 1-hour it builds up to approximately its original concentration. The decrease in hydrogen content with time (2 and 10 minutes) appears to be the result of sample space dilution with outside air from the vent-cap area. During the 1-hour interval between sampling, diffusion increases the hydrogen content to almost it original value. The data shown in Figure 5 also shows that there is a tendency for the initial hydrogen gas values to decrease with time indicating depletion of the flammable gas mixture within the LDB system as gases are removed for analysis . That is, the upper vent pipe is partially purged during the sampling process.

Corrosion Reactions

The basic reactions for uniform corrosion of carbon steel are: (6)

$Fe^o \rightarrow 2e^- + Fe^{+2}$ anodic reaction (1)

$2H^+ + 2e^- \rightarrow H_2$ (gas) cathodic reaction (low pH) (2)

$2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O$ cathodic reaction (neutral to high pH) (3)

General corrosion is controlled by the cathodic reaction and is rapid in low pH (acid) environments, but generally slow in alkaline or neutral media. Hydrogen generation shown in equation 2 takes place especially in deaerated solutions where the rate depends on low hydrogen overvoltage. Impurities in steel tend to lower the hydrogen overvoltage potential; thus, leading to greater H_2 production compared to pure iron. From equations 1 and 2, it can be seen that corrosion of carbon steel in an acidic environment could produce as much as 1 mole of hydrogen for each mole of iron corroded.

In neutral conditions, the governing equation for the reaction is equation 3, which shows the formation of water. However, Speller indicates that even in this environment about 3% of the total corrosion reactions produce hydrogen gas. (7) The reaction rate for equation 3 increases with dissolved oxygen concentration via a process known as depolarization. In these environments, the corrosion rate is proportional to the diffusion of the dissolved oxygen to the metal surface. It is known that neither equation (2) nor equation (3) can completely explain the corrosion process for steel but requires a combination of the two for a complete analysis. Thus, hydrogen generation will always take place for normal corrosion of carbon steel.

The effect of pH on corrosion of iron in aerated soft water and at room temperature is shown in Figure 6. The corrosion rate appears independent of the solution pH between 10 and 4. Whitman et. al. reported a corrosion rate within this pH range of about 10 mil/yr for iron.(9) At a pH< 4, the corrosion rate increases very rapidly, and the reaction rate is the sum of hydrogen evolution and oxygen depolarization. For low pH conditions, the surface oxide dissolves exposing the metal to fresh acid and accelerating corrosion and hydrogen generation.

Carbon steel pipes also contain manganese sulfide inclusions that form into stringers in the microstructure during fabrication. Manganese sulfide reacts with nitric acid solution to produce hydrogen sulfide gas (H_2S). SRTC tests have shown that in a nitric acid solution H_2S gas is a measurable off-gas product of the corrosion reaction.(8) About 12 ppm was generated in a pH1 nitric acid solution in about 30 minutes. Hydrogen sulfide gas smell has been reported, but samples have not been analyzed for the gas by SRTC.

Radiolysis Reactions

Waste solution from Tank 43 is transferred continuously to the 2H evaporator during operations through a 3-inch diameter stainless steel pipe. The waste is radioactive and could produce both hydrogen and nitric acid by radiolysis of moist air and/or liquid inside the carbon steel jacket. Calculations indicate that about 5.5 x 10^{-6} moles of nitric acid in the gas phase could be produced per year inside the transfer line from the interaction of Cs-137 gamma rays with air provided the supernate is continually transferred through the line.(10,11) The gas would be adsorbed by liquids present in the pipe annulus. To obtain a pH of 4 solution, about 55 ml of water would be needed in the transfer line pipe per year. This assumes no leakage of ground water into the system. The pH of ground water in H-Area varies from 2.6 to 11 with an average value of 5.8. Given the potential generation of nitric acid, the LDB environment as well as any liquid films absorbed on steel surfaces may become acidic. Thus, the controlling corrosion reaction might be expected to follow more closely equation (2) with hydrogen generation becoming dominant. Liquid/vapor from the LDB could get into the HDB-7 drain line creating an acid environment in the drainpipes.

Calculated Corrosion Rate

The corrosion rate of steel varies depending on its corroding environment. For example, published corrosion rates for carbon steel show values ranging from 1.8 to about 10 mils/yr. The LDB for Waste Tank 40 was examined destructively in 1999 to determine the extent of corrosion after 18 years of service. An average corrosion rate was estimated from a photograph of the wall cross section at the bottom of the LDB, shown in Figure 4. The original wall thickness of the 8-inch diameter schedule 40 pipe is 0.322 inch. The measured wall thickness was 0.25 inch. Over a period of 18 years, this gives an estimated average corrosion rate of 4 mils/yr. This value is used as the representative corrosion rate for LDB-3 in Waste Tank 43 H and for the drain lines in this report.

Results and Discussion

The generation of hydrogen in the LDB was determined as a function of corrosion rate for carbon steel. The hydrogen generation rate (G_r) was derived from the definition of the corrosion rate, and from the fact that corrosion of carbon steel always produces hydrogen gas. The equation becomes,

$$G_r = 3.8 \times 10^{-5}\,(K)\,(S_A)(F) \quad \text{moles } H_2/\text{hr} \qquad (4)$$

where K is the corrosion rate in mil/yr, S_A is the surface area that is corroding in square feet and *F* is the fraction of total corrosion generating hydrogen gas. For low pH acidic environments, it is assumed that *F* would be 1 whereas for neutral/basic conditions the value of *F* would be 0.03. These values should bracket the generation of hydrogen gas due to corrosion reactions for carbon steel.

The surface area for the LDB and piping and for 50 feet of the transfer line jacket was determined to be approximately 3.8 ft^2 and 52.5 ft^2. The volumes were calculated to be 0.52 and 1.87 ft^3, respectively. The generation of hydrogen by corrosion was calculated using equation (4) along with the appropriate surface area and corrosion fraction, while the moles of hydrogen (N) needed to give a 4 v/o hydrogen mixture were calculated using the perfect gas law. The time in days to develop the LFL limit was calculated using:

$$t = 4.2x10^{-2}(N/G_r) \qquad (5)$$

where t is time in days, N is moles of hydrogen, and Gr is the hydrogen generated, in moles/hour, from the corrosion reaction. Calculations assume the corrosion of carbon steel is governed by anodic and cathodic reactions given in (1) and (2) and with *F* equal to 1 for low pH conditions and 0.03 for near neutral/basic conditions.

The time needed to reach a 4 v/o mixture of hydrogen gas in the LDB and the transfer line jacket is shown in Figure 7. For an acid environment, it shows that the lower flammability limit could be reached in the LDB and transfer line jacket in about 15 days at a corrosion rate of 4 mils/yr. If the conditions approach a neutral or basic environment, it would take longer, up to ~465 days to reach the LFL. The actual time is expected to be somewhere between these values, and it depends on the environmental conditions for corrosion in the LDB and associated piping. It is not unreasonable to expect that it could take up to about one year.

Nitric acid may form in the transfer line jacket due to radiolysis so that hydrogen build-up may be attributed to corrosion of the carbon steel in an acid environment. This is consistent with gas data presented for LDB. Radiolysis of water or moist air also generates hydrogen gas but at a much slower rate. This additional hydrogen could decrease the time needed to buildup to the LFL from corrosion alone.

The drain line from LDB-7 to HDB-7 has a large surface area and volume. The area provides large surface for hydrogen gas generation, and assuming stagnant conditions, the volume provides storage area for hydrogen gas. The drain line could be a source of hydrogen gas and could reduce the time to build-up to the LFL when the drain line is opened to the LDB. As shown in Figure 8, corrosion of the carbon steel drainpipe and the LDB could generate the LFL in about 7 days considering a closed system and an acid environment.

Using the estimated average corrosion rate of 4 mils/yr, the wall thickness for the LDB and for 1-1/2 inch diameter drainpipe was calculated as a function of time. Figure 9 shows the wall thickness for inside corrosion only using the estimated corrosion rate of 4 mils/yr. After 20 years, the wall thickness of the LDB decreased from 0.322 to 0.242 inch leaving about 75 % of the original wall thickness. For the 1-1/2 inch drain lines, the remaining wall thickness, assuming the same conditions, is calculated to be 0.065 inch or about 45 % of its original wall thickness. Only corrosion of the pipes inside diameter was considered in the calculations because the outside diameter was coated with bitumastic insulation. However, corrosion of the pipes from the outside in is possible if poor coating techniques were used. Even though calculations show that the pipes have not corroded through-wall, they may have been perforated from the outside if there are places where the bitumastic coating is not present.

Conclusions

The data in this report demonstrates that corrosion of carbon steel can produce hydrogen gas in quantities that are consistent with the flammable gas content of samples taken from the LDB. In low pH environments, the LFL limit could be produced in about 10 days while in neutral or high pH environments, it may require over a year. Radiolysis of water and moisture within the transfer line jacket creates both hydrogen and NOx gases but at a slow rate. Hydrogen generated by radiolysis will add to the amount of hydrogen generated by corrosion of the carbon steel. Additionally, a steam leak in the vicinity of Waste Tank 43H could have increased the corrosion rate and may have increased the hydrogen generation rate due to corrosion. Based on the estimated corrosion rate, uniform corrosion is expected to decrease the wall thickness of the LDB and drain line pipes to approximately 75% and 45% of their original thickness after 20 years, respectively.

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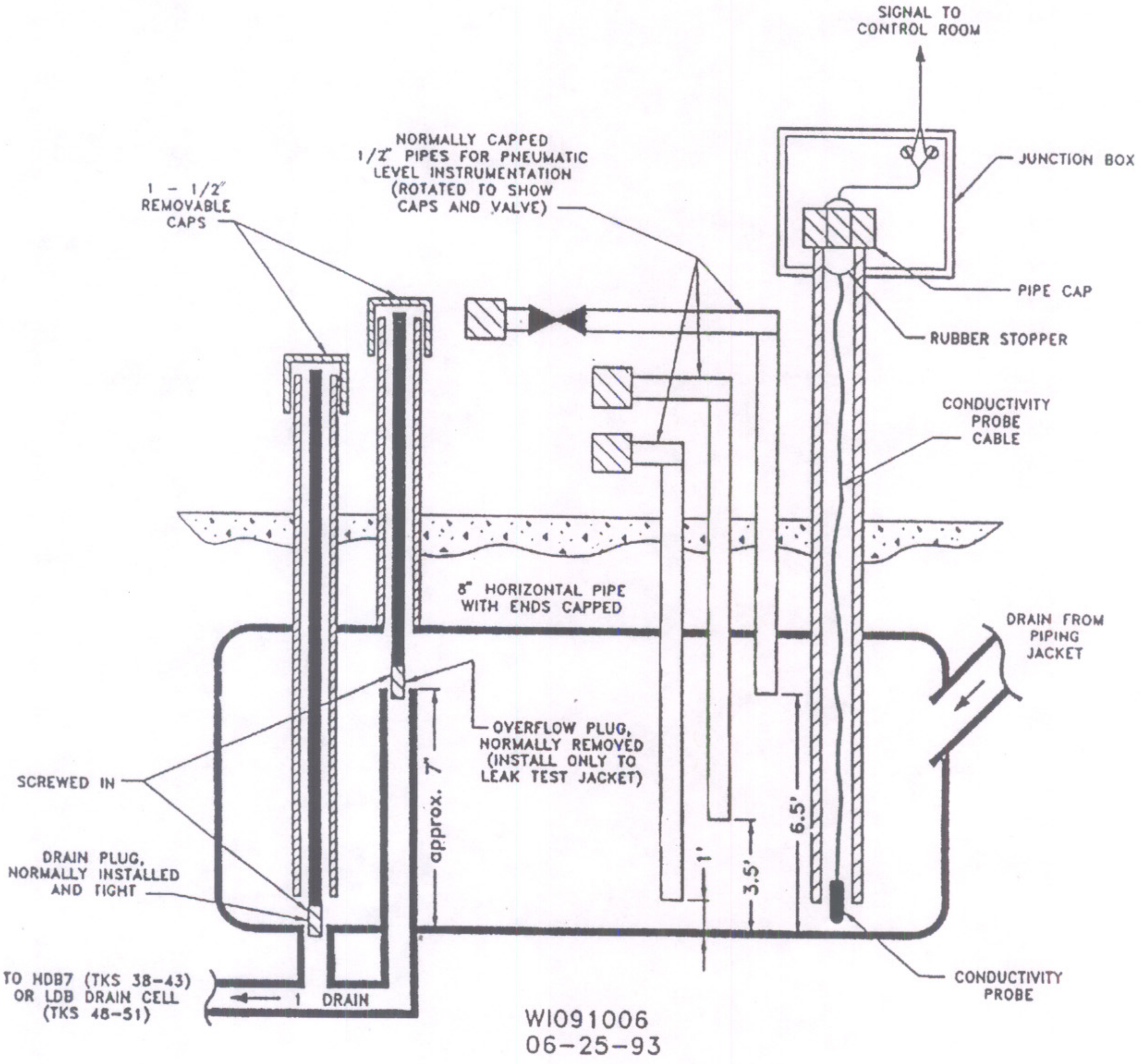

Figure 1. Leak Detection Box (LDB) for Waste Tanks

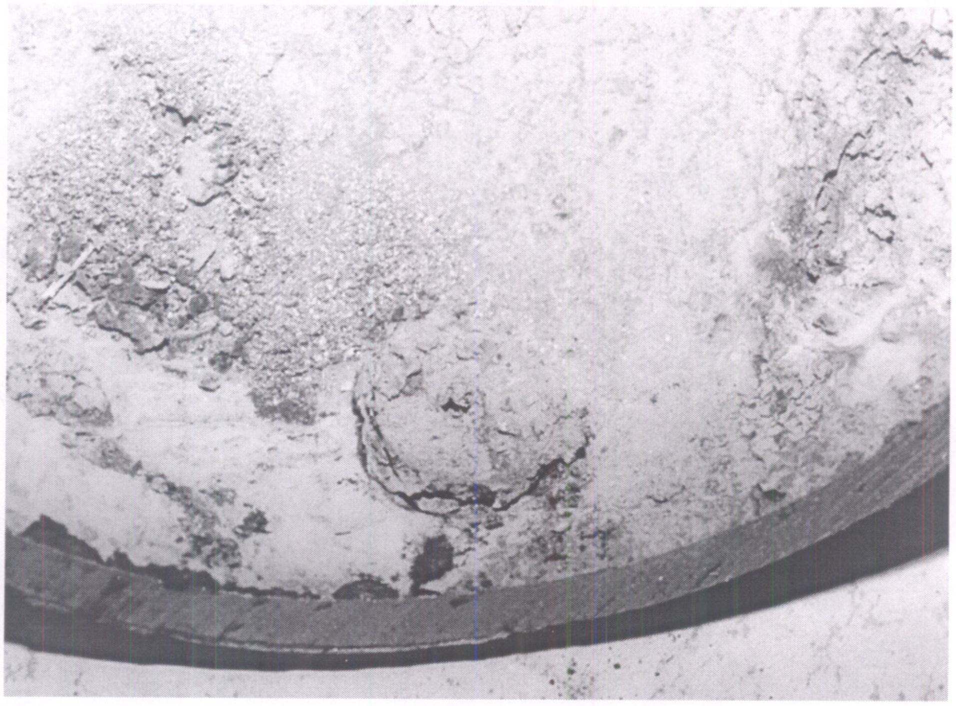

Figure 2. Wall section from Leak Detection Box #1 of Waste Tank 40 showing corrosion products on the inside diameter of the box. ***Reference: WSRC-TR-99-00200(U)***

Figure 3. Section from Leak Detection Box #1 of Waste Tank 40
Reference:WSRC-TR-99-00200(U)

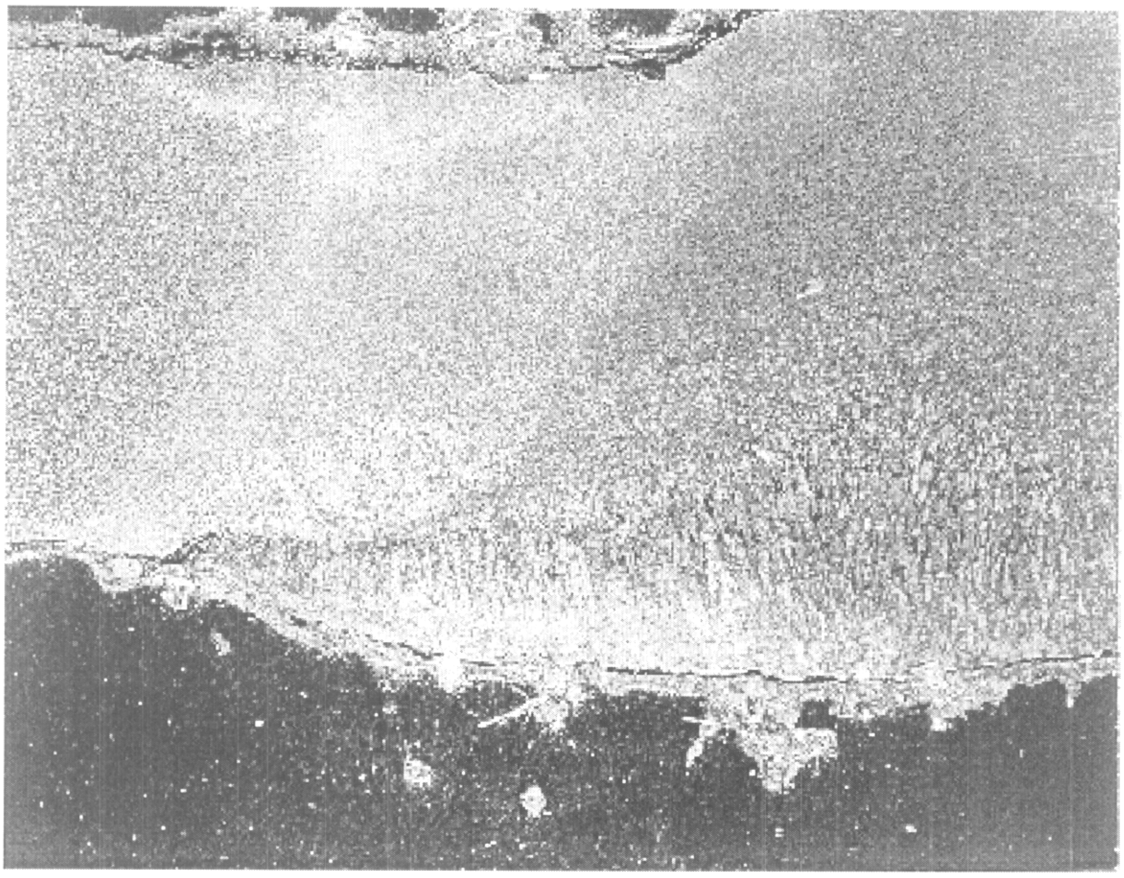

Figure 4. Photograph showing wall thickness at the bottom of LDB #1 of Waste Tank 40 (8x magnification)

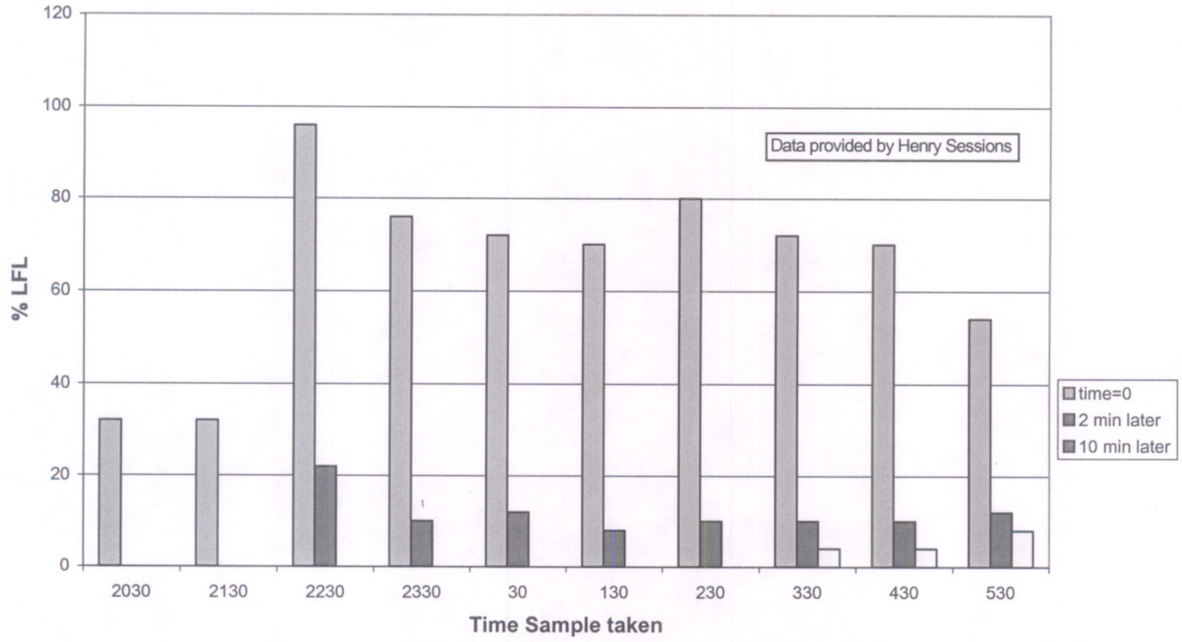

Figure 5. Hydrogen Content for Waste Tank 43 LDB-3 as a function of time.

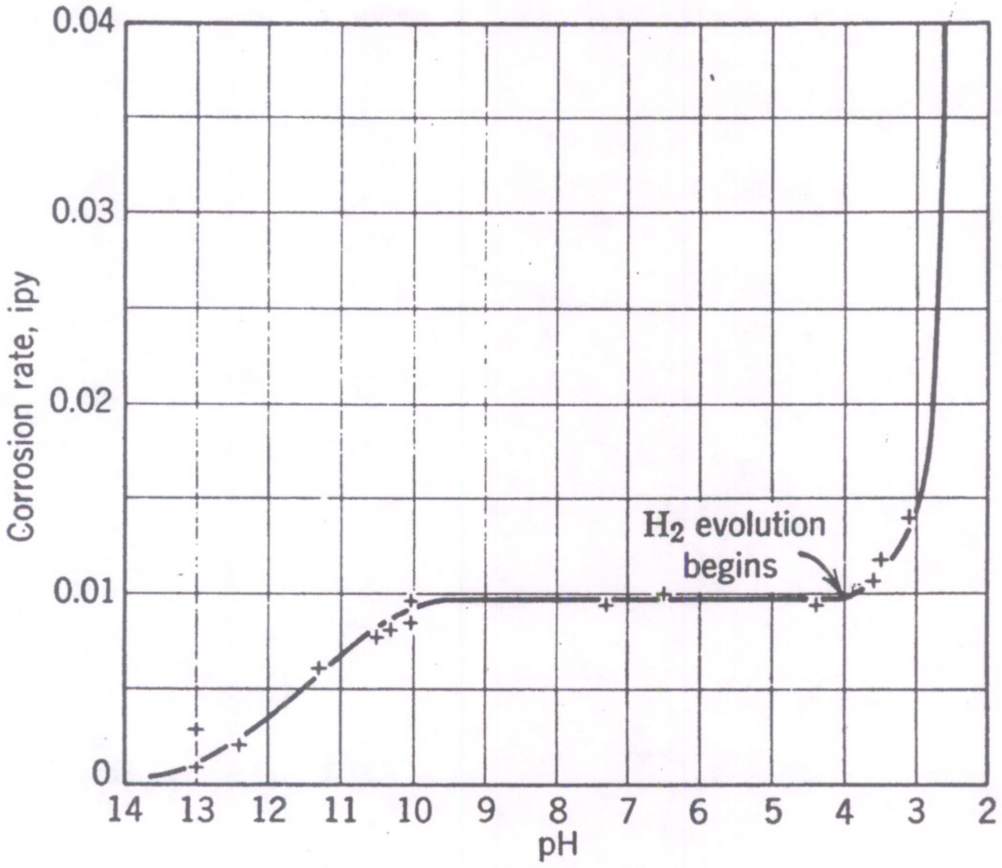

Figure 6. Effect of pH on corrosion of iron in aerated soft water at room temperature.(8)

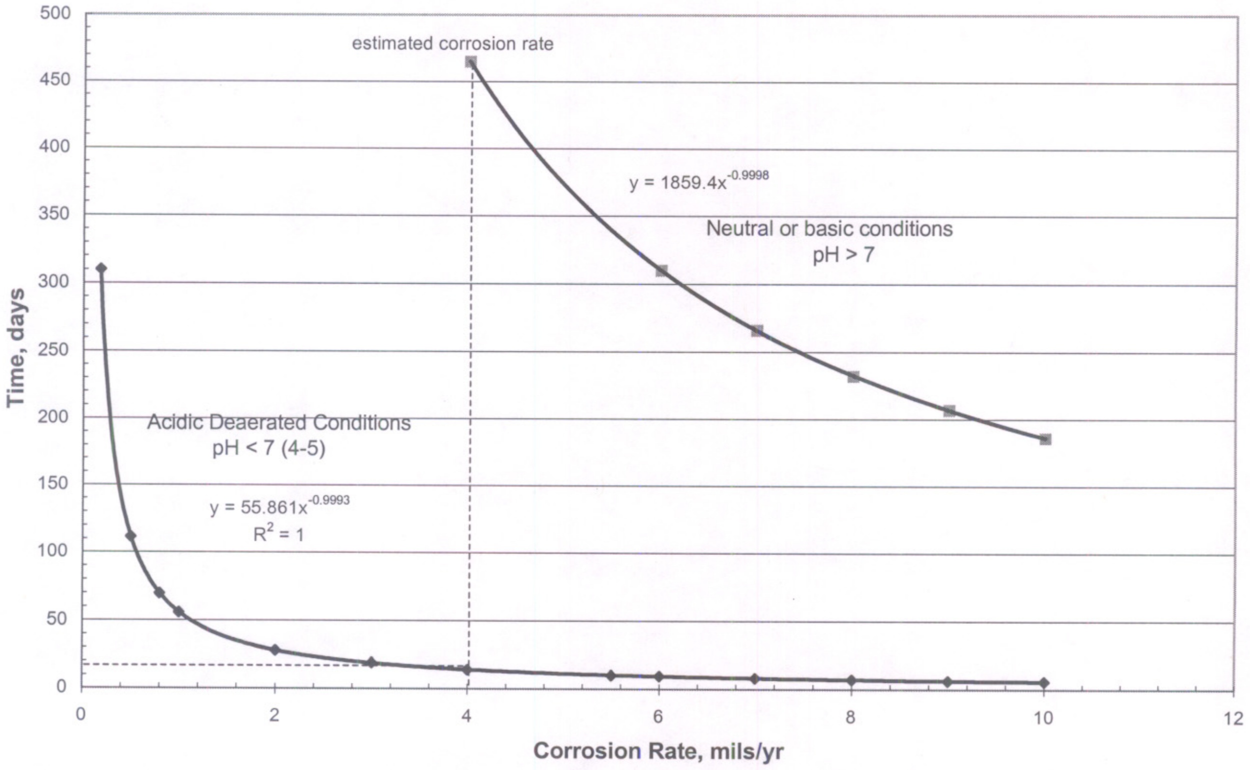

Figure 7. Time to Reach 4 v/o Hydrogen in LDB-3 & Transfer-Line Jacket

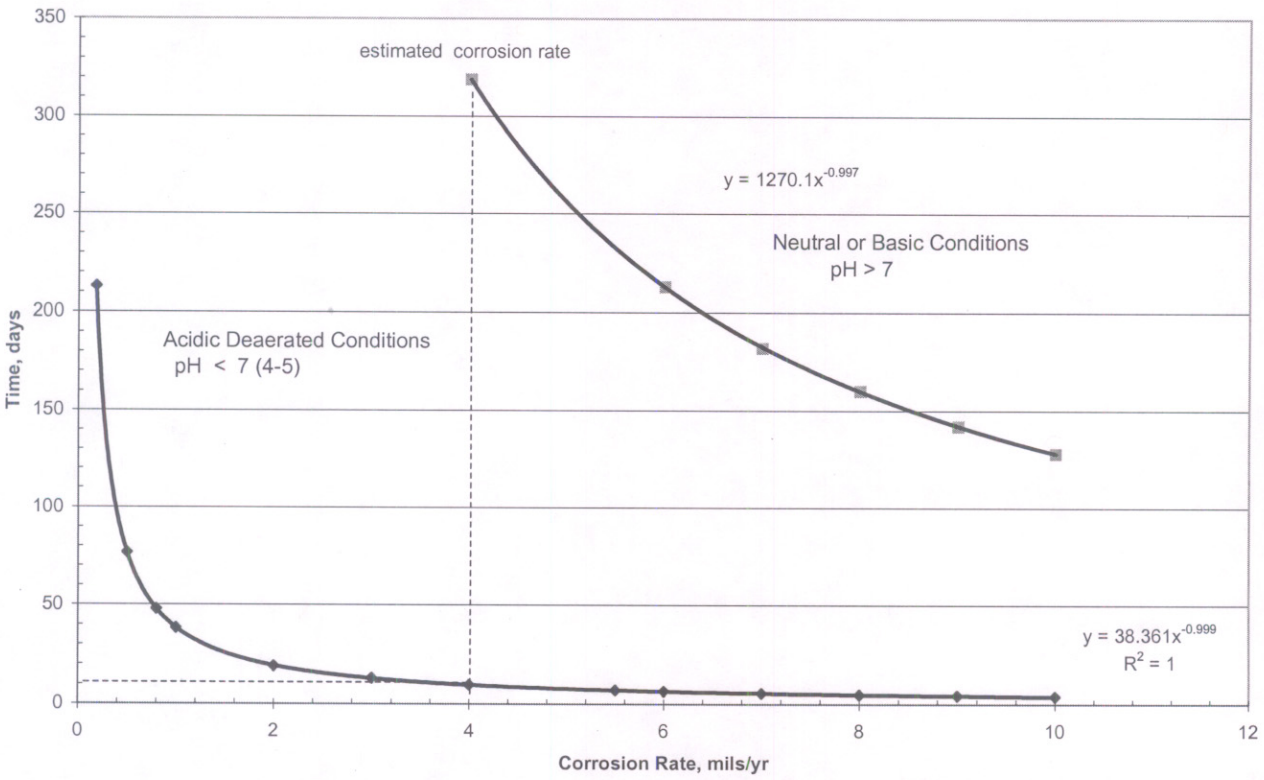

Figure 8. Time to Reach 4 v/o Hydrogen in Waste Tank 43 Drain Lines

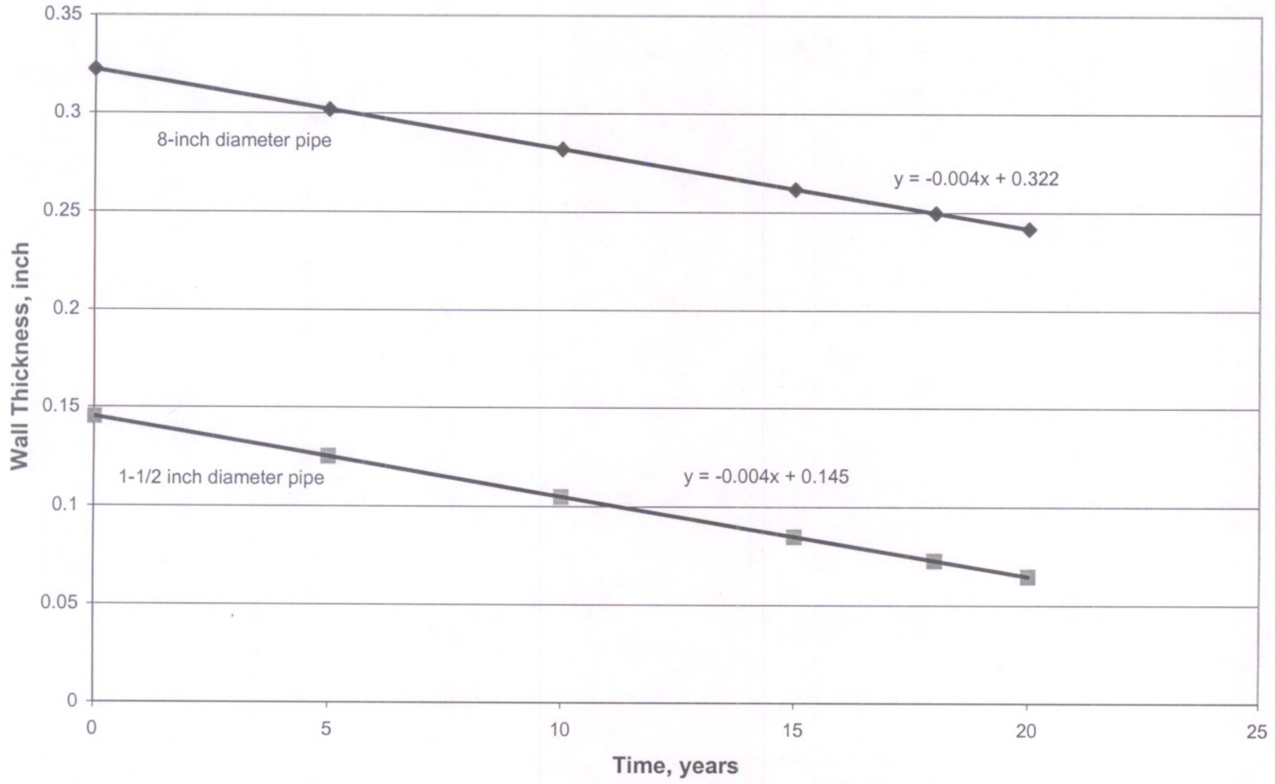

Figure 9. Wall Thickness for Schedule 40 Pipe after Corrosion
(estimated corrosion rate 4mils/yr)

Distribution:

T. J. Lex, 703-H
J. P. Morin, 703-H
M. S. Miller, 703-H
W. M. Barnes, 704-56H
D. Krementz, 241-119H
E. M. Tshishiku, 241-152H
G. J. Hutchens, 703-H
D. J. Martin, 703-H
J. L. England, 773-54A
W. L. Tamosaitis, 773-A
Natraj Iyer, 773-41A
H. B. Peacock, 773-A
G. T. Chandler, 773-A
B. J. Wiersma, 773-A
P. E. Zapp, 773-A