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Characterization of the Corrosion Behavior of the Carbon Steel Liner in Hanford Site Single-Shell Tanks

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After an extensive literature review, it has been determined that uniform corrosion, hydrogen embrittlement and microbiologically influenced corrosion are not relevant mechanisms for single-shell tank failure.

Based on the above analysis, the ranking of failure mechanisms for Hanford single-shell tanks in order of decreasing importance is:

- Stress corrosion cracking
- Pitting/crevice corrosion
- Uniform corrosion
- Hydrogen embrittlement
- Microbiologically influenced corrosion.

Other failure mechanisms such as radiation damage, liquid metal embrittlement, galvanic corrosion, intergranular corrosion, creep, erosion corrosion, caustic cracking, selective leaching, wear, and thermal embrittlement were not considered.

RECOMMENDATIONS

To control or mitigate corrosion, the methods usually employed are material selection, application of coatings, environment modification, and cathodic protection. It is too late for all these options for Hanford single-shell tanks except for environment modification (chemistry adjustment).

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The following specific recommendations are made to control corrosion and to assist in the resolution of outstanding unreviewed safety questions. These recommendations are discussed in more detail in Section 5.0; they are specific to the tanks indicated. The tanks are listed in decreasing order of priority for the action under consideration.

1. Remove as much liquid as possible by expediting stabilization, then by forced evaporation (if possible) from tanks that are sound and are suspected of having waste that is much more aggressive than the tanks listed below. Options to reduce condensation should also be considered. (Tanks BY-109, BY-102, BX-106, C-102, C-105, C-103, and C-106.)

2. Add a corrosion inhibitor (e.g., sodium hydroxide) to tanks that are sound and will not be interim stabilized in the near future and are suspected of having liquids that do not meet tank waste specifications. (Tanks U-103, U-102, U-111, U-106, U-105, U-107, U-108, U-109, S-102, S-111, S-106, S-109, S-108, S-110, S-112, S-103, S-101 and S-107.)

3. Install corrosion monitoring probes and/or coupons (stress corrosion cracking) in tanks that are sound but are suspected of having liquids that do not meet tank waste specifications. These tanks are on a lower priority for adding inhibitors because their wastes are not as aggressive as the tanks categorized for inhibitor addition.

(Tanks SX-105, SX-106, SX-102, SX-101, SX-103, T-110 and T-104.)

in 14 different solutions that simulated various steps in the sludge washing cycle. The pH was adjusted between 9.5 and 10.2 to simulate equilibrium with airborne carbon dioxide. There was a concern that pH at the air/liquid interface would decrease in time by reacting with carbon dioxide in the air with the result the pitting inhibition of hydroxide would be lost. Nitrite at several concentrations was added to each of the solutions until the potentiodynamic tests demonstrated that pitting inhibition was achieved. Four month coupon immersion tests were then carried out at 30, 50, and 60 °C to confirm the potentiodynamic results. A statistical analysis yielded the following equation for nitrite concentration to inhibit nitrate-induced pitting at pHs of 9.5 to 10 for the temperature range of 23 to 60 °C:

$$[\text{NO}_2^-] = 0.038 * [\text{NO}_3^-] * 10^{0.041T} \quad (\text{Equation 3})$$

Where

T = Temperature, C

$[\text{NO}_2^-], [\text{NO}_3^-]$ = concentration, moles/liter

Table A-2 shows the nitrite/nitrate ratios required to inhibit pitting as calculated from Equation 3.

Table A-2. Calculated Nitrite/Nitrate Ratios for Pitting Inhibition for pH ~ 10.

$[\text{NO}_2^-]/[\text{NO}_3^-]$	Temperature, °C
0.33	23
1.6	40
11.0	60

Coupon tests were run in simulated and actual sludge supernate. The pH was periodically measured throughout the four-month tests. The sludge composition was 0.76 M nitrate, 0.63 M nitrite, <0.0056 M chloride, 0.5 M free hydroxide, and other minor constituents. Over a four month period, the pH decreased from 13 to 11 for the concentrated supernatant. The pH was still decreasing when the test was terminated. For the test using a 25X dilution of supernate with a nitrite addition, the pH decreased from approximately 12 to a steady-state value of 9.5. These data show that carbon dioxide causes the pH to decrease with time, and the pH enters a regime (pH \approx 10) where the carbon steel will pit.

Elmore (1993) carried out the corrosion testing of carbon steels in simulated tank 8D-2 wash solutions for West Valley Nuclear Services. The major chemical components of the simulated waste are listed in Table A-3.

Table A-3. Target Composition of Tank 8D-2, Third-Stage Wash Simulant.

Component	Concentration, ppm
Nitrate	5600
Nitrite	4700
Sulfate	1900
Chloride	80
Hydroxide	pH > 12

Uniform and localized corrosion testing of carbon steel tank materials was carried out at 65.6 and 87.8 °C. After six months vapor phase exposure, pits 12 mils deep were found on coupons. A few pits were observed on the fully submerged specimens; one pit was ~3 mils deep.

To support sludge washing activities, Danielson and Bunnell (1994) carried out a statistically designed waste composition study of carbon steel corrosion behavior in the dilute waste environment. Incipient or shallow pits were usually observed in the vapor phase. One deep pit growing at 40 mpy was discovered. No pitting was observed in the liquid phase.

A.2 CREVICE CORROSION

Crevices are formed whenever there is a gap between the underlying metal and an overlying structure exposed to the solution. Examples of crevice-formers include the following: bolted flanges, gaskets, weld splatter, grinding laps, salt crusts, and the meniscus region of a vapor/liquid interface. Crevice corrosion has many similarities to pitting (Claiborne et al. 1985). In particular, the growth stages are believed to be alike. Consequently, environments that result in pitting are also likely to result in crevice corrosion. In practice, the general environment is usually oxygenated while the solution within the crevice gap is depleted in oxygen. As a result, the electrochemical potential in the crevice becomes less anodic (less positive). Since the exterior and interior of the crevice are electrically connected to each other through the metal and the ionically-conducting solution, the exterior electrochemical potential polarizes the crevice anodically; that is, drives the crevice cell into a potential regime that increases the crevice corrosion rate. The local chemistry in the crevice region gradually becomes more aggressive with time and, in turn, supports an even higher corrosion rate. It is the conditions of anodic polarization and

presence of sulfur, phosphate, and irregular regions of attack, identification of MIC is difficult. In the case of carbon steel, sulfur and phosphorus are always present as tramp elements, making this characteristic difficult to interpret. Tubercles on carbon steel are also strong indicators of MIC. A key observation for differentiating the mechanisms is that increasing the temperature decreases the corrosion kinetics associated with MIC while at the same time increasing the corrosion rate from non-MIC causes. The presence of microorganisms in the solution is not indicative of a MIC problem since they are always present. It is the attached, but usually out of sight, colonies that are the most dangerous. Definitive identification of MIC is usually accomplished by duplicating the process in the laboratory. Control of MIC is usually accomplished by cleaning the system followed by the use of biocides such as ozone, chlorine, hydrogen peroxide or surfactants.

The effect of ionizing radiation upon MIC is largely unknown, and it is often assumed that radiation fields that are dangerous to human life would also strongly inhibit or stop microbial growth. However, there is a famous case (Katonak and Hofstetter 1987) of a microbiological bloom (which seriously obscured the water clarity and hampered the cleanup) in the melted core of the Three Mile Reactor, Unit 2. Hydraulic fluid was accidentally leaked into the cooling and shielding water when a hydraulic hose burst, and the microbes used the oil as a nutrient. The radiation levels (TMI 1979) in the recirculating water were determined to be approximately 200 $\mu\text{Ci/ml}$ gross activity (predominantly Cs-137). Although radiation levels adjacent to the broken core elements must have been extremely high, no reference can be found supporting the existence of such high radiation levels. The microbes were not identified because most of the effort was devoted to determining the optimal biocide (hydrogen peroxide proved most efficacious) and filter techniques. Microbiologically influenced corrosion was not observed during the period of active microbe growth. Clearly, microbiological growth is possible under ionizing radiation conditions, but the propensity for MIC is completely unexplored.

Danielson and Bunnell (1994) carried out a statistically designed waste composition study of the corrosion behavior of carbon steel in the dilute waste environment to support sludge washing activities. Coupons with evidence of pitting and crevice corrosion were submitted to scanning electron microscopy to evaluate whether certain metabolic products characteristic of microbial life were present (i.e., sulfur and phosphorus). Only one case of localized attack occurred in which MIC might have been involved.

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