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AGING MECHANISMS FOR STEEL COMPONENTS OF HIGH-LEVEL WASTE STORAGE TANKS

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ABSTRACT

High-level waste storage tanks in service at the present time were fabricated from either carbon steel or low-carbon stainless steel, in each case surrounded by a concrete vault. A variety of potential degradation mechanisms may affect these steel tanks, including corrosion, stress-corrosion cracking, fatigue, radiation, erosion, and hydrogen embrittlement. Historically, some of the non-stress-relieved carbon steel tanks have leaked; in the only failure analysis performed to date, stress corrosion cracking in the heat-affected zone (HAZ) of the weld was identified as the cause.

Potentially significant aging mechanisms include general corrosion, pitting and/or crevice corrosion, stress-corrosion cracking, microbiologically-induced corrosion, concentration cell attack, and corrosion of external tank surfaces by in-leakage of ground water. Aging mechanisms which are deemed non-significant include thermal and radiation embrittlement, creep and stress relaxation, fatigue, erosion and erosion/corrosion wear, and hydrogen embrittlement. Justification for the potential significance or non-significance for each mechanism is provided, based on the current understanding of these processes and the environments to which the tanks are exposed.

INTRODUCTION

High-level waste storage tanks in service at the present time were fabricated from either carbon steel or low-carbon stainless steel, in each case surrounded by a concrete vault.

As a tank ages, a variety of aging mechanisms may become operative that impact either or both of the functions of the tanks as described by Bandyopadhyay, et al., (1995), i.e., leak tightness and structural stability. The physical and chemical characteristics of the waste as well as the environment surrounding the tank structure can accelerate the aging process. Based on experience gained from operation of the tank farms, a number of possible aging mechanisms have been identified. However, not all of them are expected to be operative in a specific tank structure or tank farm.

A variety of degradation mechanisms may potentially affect both the steel shell and liner. These include corrosion-based mechanisms: general corrosion, (bulk, uniform), pitting/crevice corrosion, stress-corrosion, microbiologically-induced corrosion (MIC), and concentration cell/waterline corrosion; and other mechanisms: fatigue, erosion, and erosion-corrosion, wear, and hydrogen embrittlement.

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The discussions below review the potential significance of each of these mechanisms to aging degradation of the steel components of high-level nuclear waste storage tanks, and the justification for classifying each as "potentially significant" or "potentially insignificant."

POTENTIALLY SIGNIFICANT AGING MECHANISMS

The aging degradation mechanisms deemed to be potentially significant are corrosion-based.

General Corrosion

General or bulk corrosion may be a concern for ferritic steels in an oxidizing environment where rates may reach many mils per year [Madihara, 1992a; ASM, 1987]. This rate will decrease with an increase in pH, provided that the pH does not exceed 14.0. Above pH 14.0 the FeO_2^- ion becomes stable, and corrosion of carbon steel could increase. Thus, a pH of ~14 is considered the top of the safe operating range for carbon steel tanks from the standpoint of general corrosion. In practice, there are tanks that have contained HLW at pH up to about 14.5 for many years, without reported leaks, although the loss of wall thickness is not known.

In-situ coupons and experiments using synthetic wastes yielded very low general corrosion rates that differed little among various carbon steels [Madihara, 1992a and b; Dacres, 1993; Lini, 1975]. Values were less than one mil per year in bismuth phosphate waste solutions.

Pitting and/or Crevice Corrosion

Pitting corrosion can occur on either carbon or stainless steels. Basically, an electrochemical cell is formed, consisting of a small anodic (corroding) area surrounded by a larger cathodic (non-corroding) surface region that stimulates the localized dissolution at the anode. Once started, pits may continue to grow autocatalytically. Crevice corrosion is associated with geometries where a localized area is occluded, setting up local anode/cathode relationships on the steel, closely related to conditions just described for pitting corrosion.

Austenitic stainless steels often pit severely, particularly in the presence of chlorides. Pitting has not been reported to date in stainless steel tanks storing nitrate solutions. Experiments with synthetic wastes often yield high pitting growth rates on carbon steels above the liquid level. Cases of in-situ pitting have been limited to cooling coils where the apparent cause was reaction of NaOH with CO_2 during air sparging, or the radiolysis of organic compounds leading to a local increase in the acidity [Madihara, 1992a]. Pitting by reaction of NaOH with CO_2 to reduce the pH locally in the meniscus at the waste-vapor interface is a potential mechanism for water-line attack; no instances of this occurring in service have yet been identified.

Since the water-lines in these tanks vary with time, due to waste removal, evaporative losses and/or additions of waste solutions or replacement water, the 'water-line' attack, if present, may be spread over a wide band.

Stress-Corrosion Cracking

Stress-corrosion cracking (SCC) requires a susceptible material as well as the simultaneous presence of a sustained tensile stress and an aggressive environment. Both carbon and stainless steels are susceptible to SCC in certain environments. Welding causes residual tensile stress (which is sustained unless a stress-relieving treatment is performed); the heat from welding also causes changes in the material adjacent to the weld, which may make it more susceptible to some forms of SCC. Tensile stresses from occasional short-lived loads are not of concern. Intergranular and transgranular cracking (IGSCC and TGSCC) are possible in both materials.

Carbon Steel

Two environmental causes of SCC that could apply to carbon-steel HLW tanks are hot nitrate and hot caustic solutions. The ratio of hydroxide and nitrate ions determine whether or not SCC is likely to occur. Nitrite has been found to act as an inhibitor of nitrate SCC. In service, SCC has been identified in non-stress-relieved carbon steel tanks with nitrates providing the aggressive environment [Madihara, 1992a; Dacres, 1993; Girdler, 1965; Ondrejcin, 1979]. There has been no reported leakage in stress-relieved tanks, particularly when the tanks have had sufficient caustic and a nitrite inhibitor added, nor has additional leakage developed to date in non-stress-relieved tanks after nitrite inhibitors were added. However, there is no assurance that SCC will never occur, particularly when tanks contain no inhibitor and may have localized regions of cold work or stresses due to local buckling.

Extensive studies have shown that SCC of carbon steel tanks can be reduced or eliminated by implementing the following [Madihara, 1992a]:

- Heat treating the inner tank at 590°C (1100°F) followed by controlled slow cooling to relieve stresses in and adjacent to the welded joints, and

- Controlling the pH and caustic/nitrate ratio and adding nitrite to the high level wastes.

Stainless Steel

For stainless steels with carbon levels greater than 0.015%, a non-stress-relieved welded region can contain residual tensile stresses near the yield point as well as chromium depletion (sensitization). In these areas IGSCC may occur. TGSCC is associated with a tensile stress and exposure to a hot, oxidizing, chloride-containing solution. TGSCC becomes more severe as temperature and chloride content increase. Stainless steel tanks could be susceptible to either form of SCC.

DISCLAIMER

TGSCC is not confined to a particular pH, but appears to be worst under acid conditions. Even low chloride levels can lead to cracking in crevices or at points of evaporation where concentrations can build up.

The only high-level waste tanks at DOE sites that are made of stainless steel are used to contain low-pH nitrate waste solutions at the Idaho site. These tanks were fabricated of 304L stainless steel which minimizes sensitization, temperatures are maintained below 51°C (and usually below 35°C) with cooling coils, and chloride levels in the waste solutions are low. In over 40 years of service, no leaks attributed to SCC have developed in these tanks. SCC remains a potentially significant degradation mechanism for these tanks, however.

Microbiologically-Induced Corrosion

Microbiologically-induced corrosion (MIC) has been a problem with buried piping and it has been necessary to install cathodic protection to minimize such attack. A remote possibility is attack of the outer wall of the secondary tank due to water being trapped in the interface between the concrete containment and the secondary tank. Stagnant water often contains aerobic bacteria that can cause chemistry changes and lead to attack of the tank wall. This scenario assumes that water can enter the interface, and, once there, does not leak out rapidly.

Concentration Cell Attack

A condition very similar to MIC or crevice corrosion also can arise when an oxygen gradient exists near the vapor/liquid interface in stagnant water. If the situation continues for an extended period, severe localized corrosion is a possibility. This is a form of attack that could penetrate the wall and not be detected readily before leakage develops.

Concentration cell attack is also a possibility under sludge that accumulates at the bottom, acting as a shield to oxygen supply. This is sometimes referred to as deposit corrosion. Chelating or complexing species could also affect the anodic reaction of metals by lowering the local concentration of corrosion products.

Another type of concentration cell could develop where foreign objects (i.e., tools) are inadvertently dropped into the tank during loading, or other operating procedures.

Corrosion of External Tank Surfaces by In-leakage of Ground Water

In tank farms where the water table is high, or excessive soil moisture is occasionally present following heavy rains, ground water leakage into the annulus between the inner and outer carbon steel tanks is possible. This water contains some dissolved ionic impurities, concentration of which, by evaporation, can cause local corrosion cells to develop on the external surfaces of tanks. Also, excess humidity in the annulus can cause external corrosion of the steel surface. The presence of aerobic bacteria in this water can accelerate attack on the external surface, especially at or near the bottoms of the tanks. In some areas, the pH of the ground water may be slightly acidic and increase the corrosion rate. No known leakage of waste materials has developed to date by this mechanism.

POTENTIALLY NON-SIGNIFICANT AGING MECHANISMS FOR STEEL SHELL AND LINER

Aging mechanisms considered to be potentially non-significant for carbon or stainless steel shells and liners during their design and extended life cycles include the following:

- Thermal Embrittlement
- Radiation Embrittlement (neutron and gamma)
- Creep and Stress Relaxation

Aging mechanisms normally considered to be non-significant, but which may occur under special circumstances include the following:

- Fatigue
- Erosion and Erosion-Corrosion
- Wear
- Hydrogen Embrittlement

Generally, the conditions present in the double-shell tanks do not favor the occurrence of any of these mechanisms; however, it is possible that a given tank may have a unique set of conditions that could promote one of the them. Thus, while they can be dismissed generically, it may be necessary to consider them on a case-by-case basis.

Thermal Embrittlement

Stress-relieved carbon steel is not prone to embrittlement even during long periods of holding in the temperature range of interest for waste storage tanks (300-600°F, i.e., 149-316°C maximum). The steels will undergo a ductile to brittle transition if cooled to low enough temperatures. However, it is difficult to conceive of any scenario in which these underground tanks filled with heat-generating waste would be cooled to such a low temperature. The other way in which such steels can lose ductility and toughness requires cold working and then aging in the range of 200°F to 300°F (93°C to 149°C) and is called strain aging. The degree of embrittlement only becomes severe in regions that undergo strains of approximately 10% or greater, and/or quenching from elevated temperatures (> 1000°F, > 538°C) [Baird, 1971]. Such conditions would not occur in the stress-relieved steels of interest here. It has also been shown that repair welds (made after the stress relief treatment) also demonstrate acceptable structural integrity [EPRI, 1984].

For those tanks made of stainless steel, thermal embrittlement is not expected.

Radiation Embrittlement
Radiation embrittlement of ferritic steels arises from displacement of atoms in the steel by high energy (> 0.1 MeV) neutron and very high energy gamma radiation.

In an attempt to estimate the combined effects of the delayed neutrons and high energy gamma irradiation, Caskey [1992] has calculated the possible displacements per atom (dpa) under a number of potential situations.

Even considering the high energy gamma flux in "fresh canyon waste," Caskey estimated the maximum dpa to be 4×10^{-7}, which is more than 20-fold lower than the most conservative threshold values for radiation embrittlement. Therefore, radiation embrittlement of the carbon steel tanks is concluded to be a non-significant aging mechanism.

Stainless steel tanks are expected to be at least as resistant as carbon steel to radiation embrittlement.

Creep and Stress Relaxation
Creep is the time-dependent inelastic deformation of a metal subjected to a stress that is typically below the elastic limit. It is not a concern for steels below a temperature of 800°F (427°C). Neither is stress relaxation likely to occur below 800°F. Therefore, these phenomena should not occur even in non-stress-relieved waste storage tanks during operation. Indeed, the apparent instances of stress-corrosion cracking developing in heat-affected zones of welds in such tanks many years after fabrication suggests that residual stresses are not relieved under tank operating conditions.

Stainless steel is equally resistant to creep and stress relaxation at tank operating temperatures.

Fatigue
Fatigue is an aging process of metals exposed to alternating stress loads. The number and intensity of alternating stress cycles due to loading/unloading of wastes in the tanks are both sufficiently small so that mechanical fatigue can be classified as a non-significant aging mechanism.

Fatigue stresses due to thermal cycling, however, could be a potential aging concern. These need to be treated on a case-by-case basis. They may be a function of how cooling water is added to the tank.

Erosion and Erosion-Corrosion
Erosion and erosion-corrosion are potential age-related degradation mechanisms for carbon steel but not for stainless steel where flowing waste slurries impinge on the steel surface.

In general, the low temperature, high pH, and high oxygen content of the waste solutions are all beneficial factors in minimizing the risk of degradation by erosion/corrosion processes. The only areas where these processes could occur would be in the vicinity of pumps.

Erosion and erosion-corrosion may, however, affect transfer piping systems.

Wear
Wear is an age-related degradation mechanism resulting from relative motion of two solids against each other. In these massive tanks, with their largely static loads, there is little reason for wear to develop. During addition of hot waste (or cold water) thermal expansion or contraction of the inner tank may also cause some relative motion. The number of such cycles, however, is small, and no leaks are known to have developed by this mechanism.

Hydrogen Embrittlement
Two types of hydrogen embrittlement effects need to be considered in assessing aging-related materials degradation of carbon steel tanks:

In the first, hydrogen diffuses into the steel from the solution (where it is produced by radiolysis) and reacts with carbon in the steel to form methane gas, resulting in loss of strength and ductility of the steel. This tends to be a high-temperature, high-pressure phenomenon, and should not occur at tank operating temperatures and pressures. The American Petroleum Institute has published curves [1977] delineating safe zones of operation to avoid this phenomenon. They show that, for a carbon steel such as those used in the tanks, at temperatures below 500°F, pressures of several hundred psi lie in the safe range for an indefinite period of operation. Therefore, this type of hydrogen embrittlement should be a non-significant age-related degradation process.

The second type of hydrogen embrittlement results from the presence of interstitial hydrogen in the steel lattice. The embrittlement is exhibited only at low temperatures, i.e., below 200°F (93°C), and the effect is most pronounced at or below room temperature and in high strength steels. It is usually attributed to electrochemical feeding of hydrogen into the steel by an active corrosion process. The absorption of hydrogen by the steel can be drastically increased by the presence of "poisons," such as cyanide and arsenic, which are present in some single-shell tanks. For the double-shell tanks, at the temperature experienced with hot waste (up to 600°F or 316°C) the hydrogen produced by the limited corrosion occurring in these tanks readily diffuses out of the steel and the concentration required for embrittlement on cooling cannot accumulate. It is hard to imagine how such embrittlement (reduced ductility) could cause any problems in the steel waste storage tanks because:

a) the hydrogen will diffuse out before the tank cools to a temperature where embrittlement can occur, and

b) the stress-relieved carbon steel tank is sufficiently soft that even if a high concentration of hydrogen did accumulate the steel would undergo substantial strains (> 10%) before it would fracture.

Experience to date has shown that steel samples removed from an existing tank after exposure to waste solutions retained normal ductility in bend tests [Girdler, 1965]. This suggests hydrogen embrittlement should be considered a non-significant degradation mechanism. Stainless steels used as tank material are resistant to hydrogen embrittlement.

SUMMARY AND CONCLUSIONS

Potential degradation mechanisms for steel components for high-level nuclear waste storage tanks have been reviewed and evaluated for their significance.

Potentially significant mechanisms include several forms of corrosion: general-, pitting-, crevice-, microbiological-, and concentration-cell corrosion, as well as stress-corrosion cracking. These require management and control by the tank farm operators.

Potentially non-significant aging mechanisms include thermal-, radiation-, and hydrogen embrittlement, creep and stress-relaxation, fatigue, erosion, wear, and erosion-corrosion. In special cases where one or more of these may be deemed applicable, management options or inspections may be required.

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