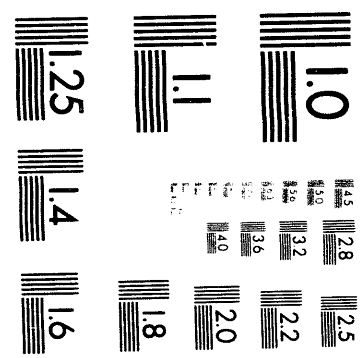
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WASTE TANK CORROSION PROGRAM AT SAVANNAH RIVER SITE

by

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DISCLAIMER

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ABSTRACT

The Savannah River Site (SRS) has approximately 30 million gallons of high level radioactive waste stored in 51 underground tanks. SRS has maintained an active corrosion research and corrosion control and monitoring program throughout the operating history of SRS nuclear waste storage tanks. This program is largely responsible for the successful waste storage experience at SRS. The program has consisted of extensive monitoring of the tanks and surrounding environment for evidence of leaks, extensive research to understand the potential corrosion processes, and development and implementation of corrosion chemistry control. Current issues associated with waste tank corrosion are primarily focused on waste processing operations and are being addressed by a number of active programs and initiatives.

INTRODUCTION

The Savannah River Site (SRS) has 51 large underground tanks for storing and processing aqueous high-level radioactive waste. The wastes were primarily produced during the reprocessing of spent nuclear fuel at SRS. SRS has had a long history of corrosion research programs, and the recommendations resulting from these efforts have largely eliminated corrosion concerns. Still, SRS maintains an active program to refine corrosion chemistry control requirements and to further understand the corrosion process. This paper describes the SRS corrosion program for high-level waste storage tanks. A related paper, "Corrosion Inhibition in Radioactive Waste Tanks Through Chemistry Control," discusses measures implemented as a result of past SRS studies.

Each tank holds about one million gallons. All of the tanks are constructed of carbon steel and reinforced concrete. Forty-three of the tanks have forced cooling systems (primarily water) and either double steel walls or single steel walls with secondary steel containment pans. The remaining eight tanks have single steel walls. This latter design has no forced cooling and is only used to store low-heat waste.

As produced during fuel reprocessing, the wastes are acidic. Before transfer to the underground waste tanks, the wastes are neutralized to high alkalinity ($[NaOH] \geq 1M$). As fresh waste ages, solid material settles. The insoluble material forms a layer of sludge at the bottom of the tank. This sludge consists of oxides and hydroxides of manganese, iron, and some aluminum; small amounts of uranium, plutonium and mercury; and most of the longer-lived fission products. The supernatant solution formed during this settling process contains dissolved salts, including radioactive cesium and strontium. The supernate is transferred to a continuous evaporator. Concentrate from the evaporator is transferred to a cooled waste tank where the salts crystallize and settle as the liquid cools. The remaining supernate is returned to the evaporator for further concentration. This process continues until the liquid is converted to a damp salt cake.

SRS has a program to remove wastes from underground tanks and solidify them for final disposal. The salt cake will be redissolved and pumped to the In-Tank Precipitation (ITP) facility for decontamination. The sludge will be washed in the Extended Sludge Processing (ESP) facility. The products of ITP and ESP will be incorporated into borosilicate glass in the Defense Waste Processing Facility (DWPF). The vitrified waste will be sent to a repository off-site for final disposal.

As part of the comprehensive Waste Tank Structural Integrity Program, a Corrosion Technology Program was instituted. The primary purpose of this program is to develop an understanding of factors which influence corrosion of waste tanks and hence develop methodologies to mitigate potential corrosion. The SRS corrosion technology program is essentially centered on the following areas:

- Corrosion technology and inhibiting methodologies;
- Corrosion monitoring and surveillance;
- Potential for cooling coil failure and repair;
- Development of alternate inhibitors;
- Kinetics of pit initiation and propagation.

Resources for the program include personnel from Waste Management operations and engineering organizations, and personnel and testing facilities at the Savannah River Technology Center (SRTC).

DISCUSSION

SRS Corrosion Technology Program

The Waste Tank Corrosion Working Group (COWOG) was formed in the mid-1980's as the key to implementing SRS corrosion technology strategy. The COWOG is a multi-disciplinary committee comprised of personnel from High Level Waste Engineering (HLWE), the engineering organization which directly supports waste tank operations, and SRTC. The COWOG meets on a monthly basis or by special request of Waste Management. The Group serves as a resource to discuss corrosion-related issues and is involved in developing corrosion control policies. The COWOG also recommends and guides corrosion research programs in SRTC.

SRTC maintains state-of-the-art corrosion testing facilities. These facilities are staffed by full-time corrosion engineers and engineering aides (technicians). Although the laboratory supports a variety of site programs, the majority of the current focus is related to waste management programs.

Facilities are available for conducting corrosion tests on slightly contaminated and "clean" samples. In addition, corrosion tests on actual waste streams or contaminated materials can also be conducted in the High-Level Caves (HLC) of SRTC. To simplify operations, tests are normally conducted on clean samples using non-radioactive simulants of actual waste compositions. These simulants have been shown to closely match the electrochemical behavior of actual waste solutions.

The corrosion laboratory contains several computer-controlled potentiostats for conducting electrochemical corrosion tests. Among the many electrochemical tests routinely conducted in the laboratory are cyclic potentiodynamic polarization, linear polarization, electrochemical impedance spectroscopy (EIS), and electrochemical potentiokinetic reactivation (EPR). Tests can be run at temperatures ranging from 0 to approximately 130 °C. In addition to the electrochemical test facilities, the corrosion laboratory contains several controlled atmosphere ovens and temperature baths for coupon immersion testing. These tests are often conducted to confirm the more rapid electrochemical tests and are performed under conditions which more closely simulate the anticipated environment. The laboratory also contains several computer-controlled tensile test frames which are used to conduct slow-strain rate tensile (SSRT) and constant extension rate tensile tests (CERT) to determine a material's susceptibility to stress-corrosion cracking (SCC).

SRTC also maintains metallography and characterization facilities [including optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning Auger microanalysis (SAM)] necessary to prepare and analyze corrosion test samples.

Waste Tank Corrosion Monitoring and Surveillance

SRS has an active program for monitoring waste tank chemistry to control corrosion, as well as a historically strong program for monitoring and surveillance of leaks, evidence of corrosion, and other general conditions of the waste tanks and ancillary equipment. This program has been largely successful and the number of tanks that have degraded throughout the years of service has been minimal. The ITP and ESP waste tanks are being transformed from their initially intended use as long-term storage tanks. There is a practical need to ensure that these tanks do not leak. In order to achieve this goal, a program is currently underway to develop comprehensive, state-of-the-art corrosion monitoring techniques for SRS nuclear waste tanks. This multifaceted program includes the following:

- A survey of current industrial corrosion monitoring practices;
- Implementation of coupon immersion test racks for the ITP and ESP tanks;
- Evaluation and development of an electrochemical polarization resistance probe for ITP;
- Continued development of electrochemical impedance spectroscopy;
- Evaluation and development of advanced electrochemical noise techniques.

Waste Tank Cooling Coil Failure Mechanisms

Some waste tanks are equipped with cooling coils to remove the decay heat generated by radioactive wastes. Cooling is achieved by running chromate-inhibited water at a temperature of approximately 60°F (15°C) through the coils. The coils are 2 in. ID, schedule 40 pipes fabricated from either ASTM A53 (A53) or ASTM A106 (A106) carbon steel.

Recently, several cooling coils were found to be leaking. A leaking coil is blanked off, which results in a reduction in cooling capacity for the waste tank. If additional coils fail, a subsequent increase in the waste temperature could occur. The increase in temperature would require additional nitrite inhibitor for corrosion prevention. Additional inhibitor is undesirable because of additional chemical costs and the deleterious effects on the waste vitrification process.

In response to the cooling coil failures, a program was developed by SRTC to better understand the possible degradation and failure mechanisms. Past cooling coil failures have been attributed to pitting corrosion which occurred in dilute waste solutions. The precise location and mechanism by which the recent coil failures occurred has not been determined. Three possible corrosion mechanisms have been proposed to explain the failures:

- Pitting corrosion in the section of coil embedded in concrete;
- Pitting corrosion of the section of coil in the vapor space region above the waste;
- Pitting corrosion due to the depletion of the chromate inhibitor within the coil.

<u>Concrete Corrosion Tests.</u> Concrete generally provides a protective environment for embedded metals. During cement hydration a passive oxide film is formed on metals which prevents corrosive attack. This passive film is maintained by the alkaline solution (pH ~12-13) present in the pore matrix of the concrete. However, chloride ions from the environment may penetrate the concrete matrix, via the "pore water", and breakdown this passive oxide film thereby initiating localized attack. The literature suggests that there is a threshold $[Cl^-]/[OH^-]$ level for the pore water above which embedded iron will begin to depassivate.

Analyses results indicate that the threshold ratio for $[Cl^-]/[OH^-]$ is approximately 0.3. This value converts to a pore water chloride level of 9000 ppm, but this is significantly higher than the 10 ppm measured in a concrete sample from a tank top. The literature suggests that other carbon steels, such as concrete reinforcement bar, have a similar threshold chloride level. These results suggest that the chloride level in the concrete is not sufficient to initiate pitting. This conclusion however, assumes that the chloride concentration is uniform throughout the concrete matrix which may or may not be the situation. In fact, the valve house, where the concrete sample was taken, is protected from the environment and would probably show little change between the initial chloride content of the concrete and the present chloride content. There may be other areas of the tank roof which are exposed to chloride containing environments. Also, the severity of attack is controlled by the ability of water and oxygen to diffuse through the concrete matrix. More information on the environment and quality of the concrete exposed to the elements is necessary to make a complete assessment.

Tests are being planned which will attempt to simulate the permeability of the concrete matrix. Coupons of A106 material will be embedded in sand. Pore water, with given chloride levels (i.e., similar to those used in the electrochemical tests), will then be poured over the sand. These tests will simulate the diffusion of chloride, water and oxygen to the cooling coil surface and hence the possibility of attack.

Vapor Space Corrosion Tests. Vapor space corrosion of the carbon steel tank walls has been observed in tanks containing uninhibited dilute waste. The attack occurs when condensate seeps beneath precipitate particles. The precipitate, and eventually the corrosion products, form a crevice where broad, shallow pits may form. A long segment of the cooling coil runs along the top of the tank and may be particularly susceptible to attack.

Coupons of A106 carbon steel were sectioned from failed cooling coils that were extracted from three tanks. Tests are currently being run in simulants.

Chromate Inhibitor Tests. The sodium chromate/dichromate inhibitor is referred to as a passivator or "dangerous" inhibitor. Passivators limit uniform corrosion by shifting the corrosion potential several tenths of a millivolt in the anodic direction. This potential shift initially increases the current density (i.e., corrosion rate) at the anodic sites. However, iron rapidly reduces Cr^{6+} to Cr^{3+}, and the resulting adsorbed oxygen layer (see reaction below) decreases the corrosion rate by passivating the iron surface.

$$Cr_2O_7^{=} + 8H^+ \xrightarrow{Fe} 2Cr^{3+} + 4H_2O + O_2 + O_{ads}$$

Once the surface is passivated, chromate continues to be consumed at a much lower rate in order to repair localized breakdown of the oxide film. A critical concentration of chromate is required to maintain a continuous oxygen layer. Below the critical concentration, the chromate removes the oxygen layer at localized sites and pitting may initiate.

Electrochemical tests, linear polarization, and cyclic potentiodynamic polarization are being used to determine the resistance of the cooling coil material to uniform and localized corrosion in cooling water at different levels of chromate inhibitor.

Cooling Coil Inspection Program. In order to fully understand the mechanism by which the cooling coils are failing, the information gathered in the experimental program must be compared to the failures experienced in the field. However, due to the complexity of the cooling coil geometry and the difficulty associated with remote inspections, only one observation of a failed cooling coil has been made. Recently, a number of attempts have been made to visually locate the leaks in the failed cooling coils using remote equipment. These efforts have been largely unsuccessful, however, due to the limited visibility within the tank (each tank contains over twenty thousand feet of cooling coils). Therefore, in order to locate the existing leaks, the inspection must be performed from inside the cooling coil. The current program is aimed at such an inspection using two different concepts.

Visual inspection will utilize equipment that is currently available at SRS. This will be accomplished using a 100-ft video probe to look for leaks or large flaws from the interior of the cooling coil. The video probe should provide visual access to the cooling coil run across the tank top. Five failed coils in one tank are clustered in the same general location and make entry into the tank primary at a point approximately 180 degrees from the cooling coil valve house. This seems to suggest, although it remains to be proven, that the long run through the concrete may be contributing to the coil failure.

The geometry and length of the cooling coil run makes it difficult to employ commercially available techniques for full non-destructive examination (NDE) inspection of the cooling coils. SRTC has developed a second concept for inspecting the failed cooling coils. The second concept uses a remote field Eddy current technique married to a hydraulic rabbit system for delivery. The development of this inspection technique has been initiated and a "proof-of-principle" test has been completed. A second technique to be utilized with the hydraulic rabbit system is measurement of hydraulic pressure changes during rabbit movement through a coil. SRTC has demonstrated that pressure transducers, mounted at the entrance and exit of a cooling coil, can detect pressure changes due to movement of the rabbit past a hole in the coil. Further development is continuing.

Repair of Failed Cooling Coils. Once the location and mechanism of cooling coil failures have been determined, attempts will be made to repair the failed coils to return them to service. Two distinct repair strategies are currently being pursued. The first is a "local repair," in which a leak site (identified and located by a suitable inspection technique) is repaired with a patch or some other means of local repair. The second technique is a "global repair," in which the entire interior of the coil is treated with a liquid that can effectively seal any leaks that may exist. The programs currently underway are discussed below.

The SRTC rabbit inspection concept also includes provisions for local repair. The concept provides for sleeving the cooling coil at the leak site with a "shape-memory metal." An alloy of nickel and titanium is said to have "shape-memory" because it experiences a phase transition at a specified temperature and reverts to its original undeformed shape. By controlling the alloy composition, this concept proposes delivery of a deformed sleeve of the alloy to the leak location and then allowing the alloy to revert to its initial undeformed shape (i.e., a tube). The sleeve would cover the existing flaw and allow the coil to be returned to service. This technique is currently used in both air conditioning systems and hydraulic systems on aircraft to repair failed tubing. Its application in a remote delivery system and to applying a sleeve to the interior of piping/tubing has not been fully demonstrated. However, the patch is believed to possess adequate strength to produce a "leak-tight" repair. Development of this technique is planned to follow rabbit development.

Global repair methods offer the benefit of not requiring location of the leak. Effectively the global repair involves exposing the entire piping/tubing interior to a solution containing the repair solution, allowing the solution to penetrate any cracks or flaws, and then draining the excess solution. The material that has deposited on the coil interior then cures and plugs any leaks. SRTC has been developing a sol-gel repair system which may be applicable to the waste tank cooling coils. This system was originally developed for repair of the C-Reactor tank and has been previously used to repair the exterior surfaces of cracked piping in separations facilities. A program is currently underway with Ames Laboratory to further develop this application for piping repair. Several piping test stations have been developed and are being used to assess the durability of the repair. This work has been expanded to include interior patching which will be more directly applicable to the repair of cooling coils. Preliminary feasibility tests have been completed on two commercially available sealants and an SRTC-developed sol-gel composite (SGC). Results from these tests indicate that one brand of commercial sealant and the SGC successfully sealed the controlled leaks (a 1 mm hole and a joint simulating a stress-corrosion crack). Based on these results, a more comprehensive program is being developed to better understand the sealing process and to determine limits on the size of the flaws that can be effectively sealed.

Alternate Inhibitors

Concentrations of nitrite and hydroxide to prevent pitting have been established for In-Tank Precipitation (ITP) and Extended Sludge Processing (ESP). Still there is continued interest in examining alternative inhibitors and inhibitor systems. The combination of nitrite and hydroxide has been proven effective, however, there are disadvantages associated with each. The addition of NaOH adds increased sodium to the feed for DWPF. At significantly high levels, sodium can result in glass quality (i.e., glass durability) problems. The use of $NaNO_2$ also creates problems in the DWPF. High levels of nitrite in the DWPF feed can lead to undesirable levels of NO_x and the possible formation of ammonium nitrate.

As a result of these concerns, a program is being established to evaluate a number of inhibitors and combinations of inhibitors that may not produce the undesirable effects of hydroxide and nitrite.

Kinetics Of Pit Initiation and Propagation

The criteria used to establish inhibitor levels for the SRS waste tanks have been traditionally very conservative. Levels were set based on laboratory studies and were developed based on the criterion that no degradation (either by stress-corrosion cracking or pitting) was initiated. Safety factors accounting for laboratory tests with non-radioactive waste simulants, sampling frequency, and analytical uncertainty are added to the laboratory values to further increase the conservatism.

There is little information available on the kinetics of tank corrosion, particularly pitting corrosion in diluted alkaline solutions. Several questions regarding such examinations have recently been raised, including:

- How long can a tank remain in an uninhibited state before pit initiation occurs?
- After a pit forms, what is the time necessary for it to propagate through a tank wall or cooling coil?

Typically, it is difficult to develop such information since pitting is a random process that is controlled by localized chemistry conditions. However, a program is being established to determine the kinetics of pit initiation and propagation in a variety of environments. This program will include long-term coupon exposure in conditions known to cause pitting as well as in inhibited systems. Coupons will be periodically removed and examined for evidence and extent of pitting. Using extreme value statistical analysis the rate of pitting will be deduced.

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