

Determining Migration of Vapor Corrosion Inhibitors Using Corrosion Potential Data

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ABSTRACT

Hanford stores millions of gallons of high-level waste in 27 carbon-steel double shell, underground tanks. A secondary shell surrounds the primary shell, where the bottom plate of the secondary shell rests on a channeled concrete pad. There have been instances of metal loss on the secondary shell bottom plates in contact with the concrete basemat where groundwater accumulation in the channels may have caused corrosion. In addition, uneven contact between the basemat and shell could create occluded areas where localized corrosion is possible. In previous studies, vapor corrosion inhibitors (VCIs) were tested for their ability to mitigate concrete-basemat side corrosion of the secondary shell bottom. The previous study indicated that VCIs are effective in mitigating corrosion in both immersed and vapor space conditions. However, the tanks being large with approximately 70-ft bottom, it is important to understand VCI distribution rate after VCIs are injected. Experiments were conducted with VCI injection in the groundwater along with coupons positioned at several locations with respect to the ground water. Coupons' potentials were monitored, and corrosion rate data were analyzed. It was determined that corrosion potential is a good indicator of VCI concentration in the simulated groundwater solution. The paper presents result and analysis of the experimental data.

Key words: Vapor Corrosion Inhibitors, Hanford, Double Shell Tanks, Bottom Plate, Pitting Corrosion.

INTRODUCTION

High-level radioactive waste generated during reprocessing of spent nuclear fuel at Hanford has been stored in several single- and 27 double shell tanks (DSTs). Each DST consists of a primary shell (inner) surrounded by secondary (outer) liner. The secondary liner rests on a concrete foundation. Rainwater may seep in and accumulate in the drain slots and may corrode the exterior of the secondary liner. Evidence of wall thinning has been detected via ultrasonic inspections of the annulus floor between the primary and secondary tank shells. Since the inspection is confined to this region, there is a concern that corrosion is widespread on the underside of the bottom plate. Since the rainwater level can vary in the drain slots based on accumulation, corrosion could be caused by direct contact with the accumulated water; when the leak detection pit (LDP) water level is below the structural limit, vapor space corrosion (VSC) could also occur. Accumulated water is drained through the sumps in the LDP. The LDP water

was analyzed for its constituents, and two simulants were developed considering the chemical composition range of the accumulated water. The simulants are identified as leak detection pit and ground water (GW); compositions are listed in Table 1. A previous study established that GW simulant is more corrosive than the leak detection pit, therefore GW was used in the VCI effectiveness study.¹

Laboratory experiments were conducted to address the concerns of both immersed-phase corrosion and VSC of the tank steel exposed to GW simulant. VCIs were also tested to determine their efficacy in mitigating the corrosion on pre-corroded surfaces. VCIs' application for above ground storage tank bottom corrosion control is recent, and several studies have documented effectiveness of VCIs for tank bottom plate corrosion control.^{2,3,4} One of the key questions regarding VCIs' delivery is their migration rates. A previous study with VCI focused on tank bottom application has indicated that corrosion potential values provide an indication of the migration of the VCIs.⁴ This study was focused on understanding the coupons' corrosion potentials in immersed and vapor space coupons as a function of VCI concentration.

Table 1
Composition of the Leak Detection Pit and Ground Water Simulants

Source chemical	Concentration (M)	
	Leak Detection Pit	Ground Water
Sodium bicarbonate	1.12×10^{-3}	1.75×10^{-3}
Calcium hydroxide	1.21×10^{-4}	1.50×10^{-3}
Potassium nitrate	6.75×10^{-5}	2.40×10^{-4}
Magnesium Nitrate, 6hydrate	1.52×10^{-5}	–
Strontium Nitrate	4.04×10^{-6}	2.87×10^{-6}
Sodium sulfate	1.83×10^{-6}	–
Ferric sulfate	–	6.25×10^{-4}
Sodium Metasilicate, 5hydrate	4.57×10^{-5}	6.00×10^{-4}
Ferric chloride	2.67×10^{-6}	7.67×10^{-5}
Manganese Chloride	–	3.100E-04
Acetic Acid	3.00×10^{-4}	3.000E-04
Adjusted pH	7.6	7.6

EXPERIMENTAL

Several experiments were set up using GW simulant as electrolyte. The first experiment was a control experiment, and no VCI was added to this experiment, and the coupons were not monitored for their corrosion potentials. A second test was conducted with a commercially available VCI, and the recommended dosage of the VCI was used. The VCI was added to the GW simulant at the start of the test. The coupons in the second test were monitored for their corrosion potential. A third test was conducted in parallel to the second test. In this test, the coupons were immersed in the GW simulant only without VCI, and coupons corrosion potentials were monitored.

Disk coupons, machined from a legacy carbon steel plate, were used in the experiments. The legacy carbon steel is based on specifications of Association of American Railroads⁽¹⁾ Tank Car (AAR TC 128) steel, and its chemistry and microstructure are similar to the vintage steel from which the tanks were fabricated UNS K02401 (i.e., American Society for Testing and Materials (ASTM)⁽²⁾ A515 Grade 60 carbon steel). The chemical composition of the legacy carbon steel is listed in Table 2. All elemental compositions except for Mn and Si meet the ASTM A515 Grade 60 specification. The coupons were 25 mm (1 inch) diameter with a thickness of 3 mm (0.125 inch) and polished to a 600-grit finish. The coupons

⁽¹⁾ American Association of Railroads, 425 3rd Street SW, Washington, DC 20024

⁽²⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959

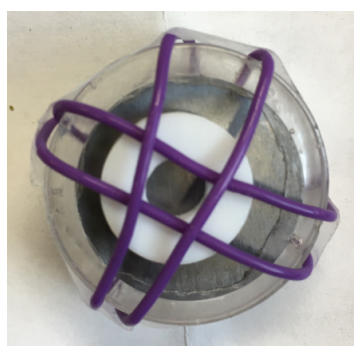
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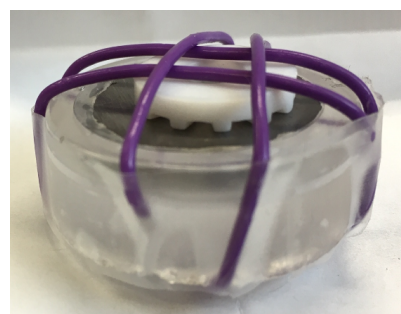
were potted in a mold prepared with a two-part transparent epoxy mold, such that that one face of the coupon was exposed to the test electrolyte. The coupons' exposed surfaces were modified to simulate crevice corrosion. A crevice former was attached to each coupon surface using tape and wire. The crevice formers partially covered coupons' surfaces, which created conditions for localized corrosion under the crevice formers. An image of the coupon with the crevice former is presented in Figure 1; these coupons were used in the first experiment. For the second and third experiments, the coupons with the crevice former were slightly modified. A platinum (Pt) wire was added to the coupon assembly as shown in Figure 2. The Pt-wire was connected to the metal surface through an interconnecting Nafion™ film which was cured as per the procedure detailed in Hsu and Wan⁵ before using it to connect the Pt wire with the metal surface. The use of Pt wire was needed to ensure electrical continuity between the coupon surface and Pt wire on each coupon assembly, especially needed for the vapor phase coupons to be able to measure coupons' metal surface potential with respect to the Pt-wires. Additional experimental details are in Shukla et al.⁶

Table 2
Chemical Composition of AAR TC 128 Steel (wt.%)

	C	Mn	P	S	Si	Fe
Specification	0.24 (max.)	0.9 (max.)	0.035 (max.)	0.04 (max.)	0.13 to 0.33	Balance
Measured	0.212	1.029	0.012	0.013	0.061	Balance



(a) Top view



(b) Side View

Figure 1. (a) Top, and (b) Side views of the partially covered coupon. The coupon's surface is partially covered with a crevice former, which is held in place using purple wire and tape

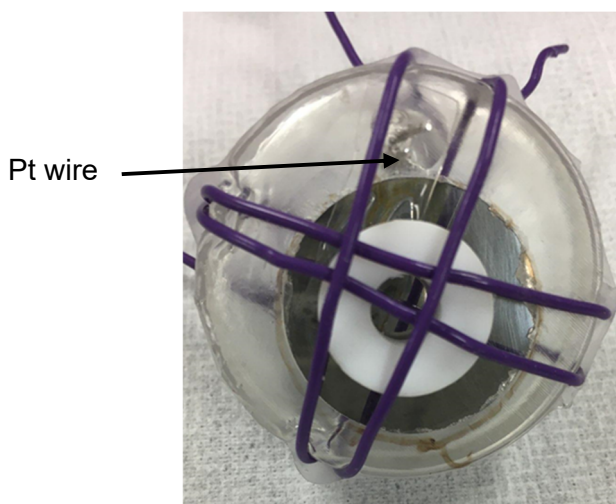


Figure 2. Top view of the partially covered coupon with platinum wire and Nafion™ film interconnecting the Pt-wire with the metal surface.

A glass vessel of dimensions 1.0 m (3.3 ft) tall and 14 cm (5.5 inch) diameter was used for each experiment. Approximately 1.25 L of GW simulant was added to a vessel for each experiment. Each vessel has a water jacket around the simulant holding area which was used to circulate warm water to maintain the simulant temperature at 45 ± 2 °C. Each vessel also has several ports, which were used to insert thermocouples and electrical resistance (ER) probes. An image showing the three vessels used is presented in Figure 3. Coupons were exposed to the electrolyte and vapors of the electrolyte in each experiment by suspending them using rods. The coupons were suspended such that the exposed surfaces of the vapor space coupons were facing the electrolyte. The rods holding the coupons were placed inside the vessels. Several coupons were immersed in each vessel, and coupons were also placed in vapor space of each vessel. The vapor space coupons were placed at several height levels with respect to the electrolyte using the rods. The coupons' positions, with respect to electrolyte in each vessel, simulated different vapor space conditions and water levels in the drain slots. These levels, representing the drain slot characteristics and its position with respect to the bottom, are described:

Level 1: Bottom or low level. Coupons were dipped in the simulant for five minutes prior to testing. The coupons were hung at the bottom fixed ring of the rod. These coupons were suspended approximately 25 mm (1 inch) above the liquid level of the simulant. Every two weeks, the coupons were lowered into the simulant for 5 minutes. This level is representative of the situation when the secondary liner bottom plate experienced periodic wetting/drying.

Level 2: Intermediate or middle level. Coupons were dipped in the simulant for five minutes prior to testing. The coupons were hung at the middle-fixed ring approximately 46 cm (18 inch) above the liquid simulant in each vessel. This level is representative of a vapor space region of the secondary liner bottom that at one time was exposed to water but has infrequent or no contact with the water. However, this region is exposed to the humidified air.

Level 3: Top or high level. This set of coupons was not exposed to the solution prior to testing. The coupons were suspended approximately 92 cm (36 inch) above the simulant. This level is representative of the secondary liner bottom plate region that is only exposed to the humidified air and any volatile species from the solution.

A description of the vessels for each electrolyte is provided in Table 3. Electrical Resistance (ER) probes were placed in Vessels 1, 2, and 3; placement positions are detailed in Table 3. ER probe data were collected periodically. Coupons were removed after several months of exposure, cleaned with Clarke's solution⁷ to remove corrosion products, and weighed to determine the mass loss of each coupon.

Table 3
Electrolyte Description, Vessel Identification, and Coupons and ER Probe Information

Electrolyte	Corrosion Cell	Notes
GW simulant only, exposure time of six months	Vessel 1	6 coupons each in immersed, Level 1, Level 2, and Level 3 positions, total 24 coupons. - ER probes at each level. Cylindrical element probes at immersed, Levels 1 and 3, and wire element probe at Level 3.
GW simulant mixed with the VCI as per the VCI-vendor recommended concentration	Vessel 2	6 coupons each in immersed, Level 1, Level 2, and Level 3 positions, total 24 coupons. - Each coupon had Pt-wire in its assembly; vapor space coupons' potentials were measured with respect the Pt-wire. The immersed phase coupons'