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Effects of Vapor Corrosion Inhibitors on Corrosion of Secondary Liner in Double Shell Tanks at Hanford

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ABSTRACT

High level radioactive waste is stored in 28 double shell tanks (DSTs) at Hanford. Each DST consists of two distinct tank shells: primary and secondary, with primary shell inside the secondary. The secondary shell rests on a concrete pad that has drain slots. The slots provide a flow path for detection of the tank fluid in case of a leak. It is known that water can accumulate in the slots and needs to be drained out periodically. Ultrasonic inspections have determined that there is thinning of the bottom plate of the secondary liner and is suspected to be caused by general and localized corrosion in the vapor space due to accumulation of water that contains chloride and nitrate ions. A set of experiments were conducted with commercially available vapor corrosion inhibitors (VCIs) to test their efficacy in mitigating general and vapor space corrosion (VSC) corrosion when it is applied at the surface of carbon steel and when added to the water. Electrical resistance (ER) probes were also utilized to measure VCIs' efficacy at a level close to the liquid air interface and being complete submerged. Experimental studies indicate that VCIs mitigate general and localized corrosion of the tank steel in the vapor space and when in direct contact with the water treated with VCI.

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

INTRODUCTION

There are 28 double shell tanks (DSTs) at Hanford. Each DST consists of a primary shell (inner) surrounded by secondary (outer) shell. The secondary shell rests on a concrete pad. The schematic diagram, which shows the concrete foundation and drain slots, is presented in Figure 1.

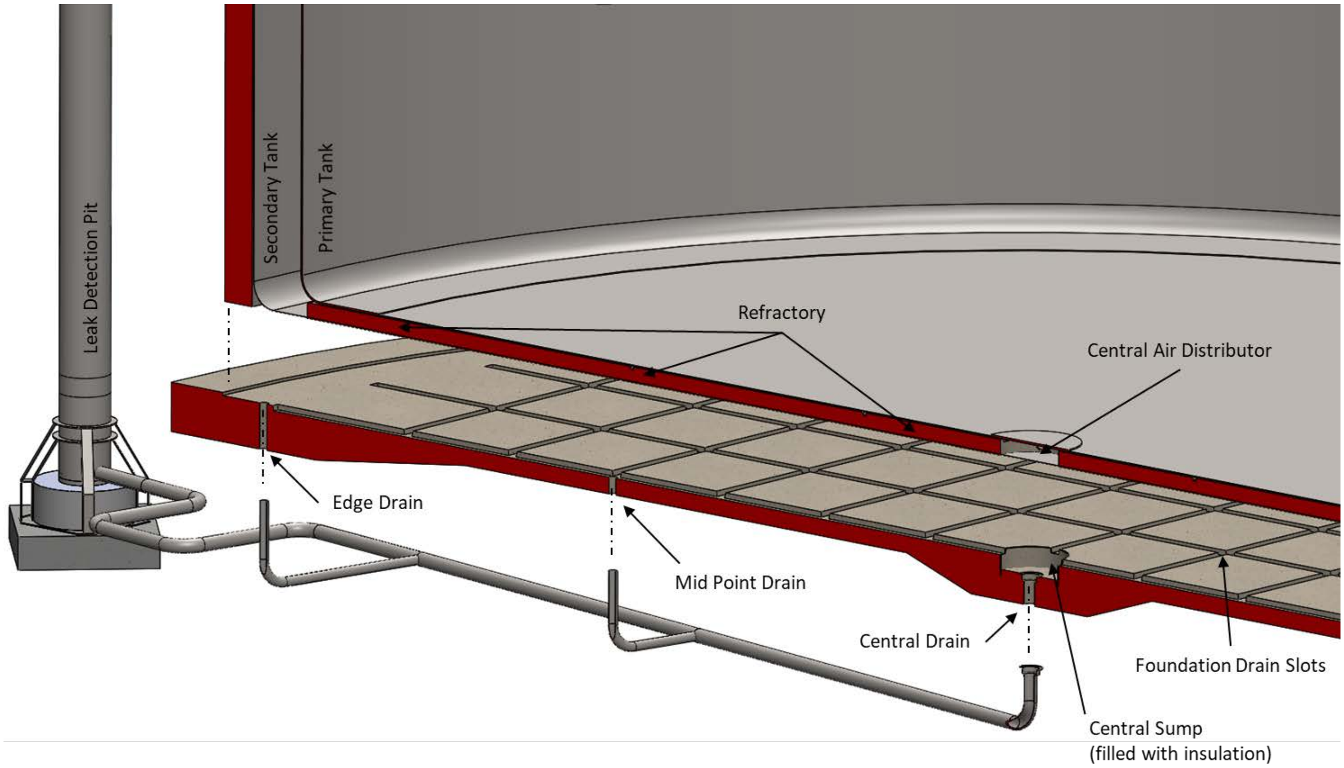

Figure 1. Schematic of a double shell tank depicting primary and secondary tank shells, concrete foundation, and drain slots.

Water is known to accumulate in the drain slots, and cause corrosion on the exterior of the bottom plate. Evidence of corrosion has been detected during ultrasonic inspections of the bottom plate. The inspection is confined to the annular space between the primary and secondary tanks; there is a concern that corrosion is widespread on the underside of the bottom plate. Since the water level can vary in the drain slots based on accumulation, corrosion could be caused by direct contact with the accumulated water; when water level is below the underside of the tank bottom, vapor space corrosion (VSC) could also occur. Accumulated water is drained through the sumps in the leak detection pits. The drained 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 (LDP) and ground water (GW). Their compositions are listed in Table 1. The pH of both simulants was adjusted using sodium carbonate and acetic acid to 7.6 after preparation.

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

Source chemical	**Concentration (M)**	
	Leak Detection Pit	**Ground Water**
Sodium bicarbonate	1.120E-03	1.750E-03
Calcium hydroxide	1.210E-04	1.500E-03
Potassium nitrate	6.750E-05	2.400E-04
Magnesium Nitrate, 6hydrate	1.520E-05	–
Strontium Nitrate	4.040E-06	2.874E-06
Sodium sulfate	1.830E-06	–
Ferric sulfate	–	6.250E-04
Sodium Metasilicate, 5hydrate	4.570E-05	6.000E-04
Ferric chloride	2.670E-06	7.667E-05
Manganese Chloride	–	3.100E-04
Acetic Acid	3.000E-04	3.000E-04
pH adjusted using sodium	7.6	7.6

carbonate and acetic acid		

Laboratory scale experiments were conducted to address the concerns of both general corrosion and VSC of the tank steel exposed to LDP and GW simulants. Vapor corrosion inhibitors (VCIs) were also tested to determine their efficacy in mitigating the corrosion. VCIs have been used for corrosion mitigation in numerous applications for decades. However, VCIs' application for above ground storage tank bottom corrosion control is recent, and several studies have documented effectiveness of using VCIs for tank bottom plate corrosion control.[1] [2] [3] [4]Details of the present experiments, experimental data, and results are discussed below.

EXPERIMENTAL

Several experiments were setup with LDP and GW simulants as electrolytes. The experiments included (i) as-prepared LDP and GW simulants, (ii) coupons treated with a commercially available VCI identified as VCI-A and exposed to as-prepared LDP and GW simulants, and (iii) GW simulant treated with two commercially available VCI mixture identified as VCI-B.

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 presented in Table 1. All elemental compositions except for Mn and Si meet the ASTM A515 Grade 60 specification. The coupons were 0.625 inch diameter with a thickness of 0.125 inch and polished to a 600 grit finish. The coupons were potted in a mold prepared with a two-part clear epoxy solution (EpoKwick® from Buehler) so that one face of the coupon was exposed to the test electrolyte. An image showing two test coupons is presented in Figure 2. A wire was attached to the potted face of each coupon; the coupons hanged at various heights with the aid of the attached wires.

Table 1. 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

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

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

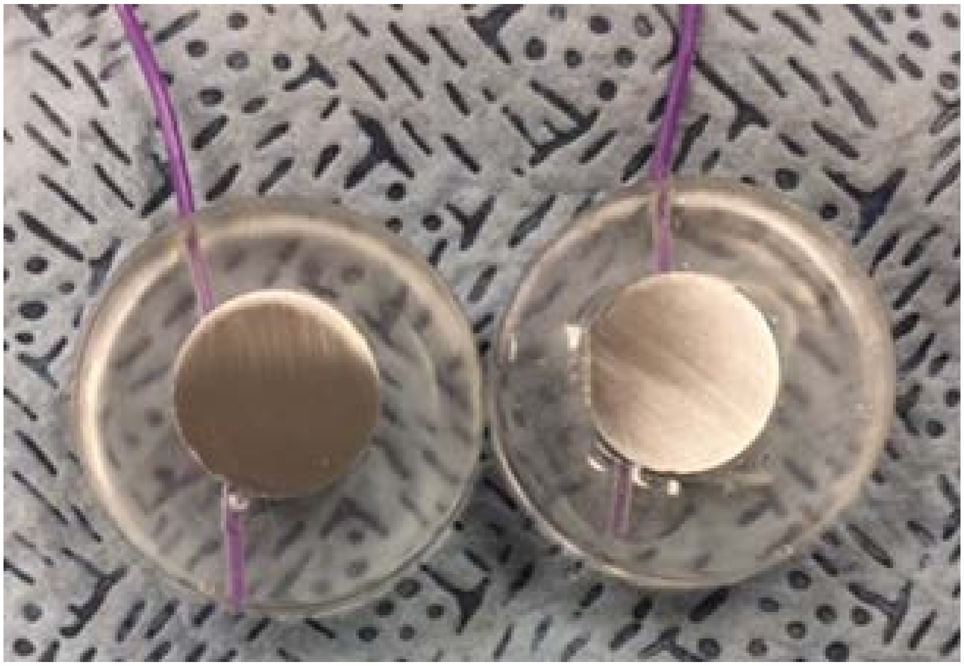

Figure 2. Image of the coupons used in the study. A purple wire was attached to each coupon, and coupons were suspended above the liquid interface using the wires.

A glass vessel of dimensions 3.3 ft tall and 5.5 inch diameter was used for each experiment. Approximately 1 L of either treated or untreated simulant was added to a vessel for each experiment; treated simulated refer to mixture of prepared simulant plus VCI, and untreated simulant refer to as prepared simulant 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 two vessels used is presented in Figure 3(a). Coupons were exposed to the electrolyte and vapors of the electrolyte in each experiment by suspending them through a rod shown in Figure 3(b). The rods holding the coupons were placed inside the vessels. 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 are described as follows.

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 shown in Figure 3(b). These coupons were suspended approximately 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 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 18 inches 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 36 inches 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) (b)

Figure 3. Images of the (a) experimental configuration, and (b) steel rod to suspend the coupons inside the vessel containing electrolyte.

ER probes were placed in each vessel near the coupons at Level 1. ER probe data was collected periodically. Coupons were removed after several months of exposure, cleaned with Clarke's solution[5] to remove corrosion products and report accurate weight losses.

EXPERIMENTAL DATA AND RESULTS

Images of the coupons exposed to the LDP and GW simulants are presented in Figures 4 and 5, respectively Coupons that were treated with VCI-A[3] are marked with an asterisk next to the number. Treatment was applied by immersing the coupons in VCI-A for 5 minutes before placing them in the experimental chambers.

Coupons were weighed before and after exposure and mass-loss data were used to estimate surface average corrosion rates. The corrosion rate data is listed in Table 2. Visually, the photographs displayed a higher degree of corrosion for coupons exposed to GW than LDP simulants. Level 1 coupons demonstrated the highest degree of VSC, as expected. Corrosion rates did not seem to be affected by the presence of the VCI as corrosion rates were on average similar to the non-VCI treated coupons. The coupon immersed in the LDP and GW simulants exhibited greater corrosion rates than the coupons in the vapor space.

Electrical resistance (ER) probes was used to assess the corrosion environment and effect of VCI. The ER probes were placed at Level 1 positions. In using ER probes, corrosion rates are obtained by measuring resistance of the probe element, which changes over time, as metal loss occurs. The reduction in cross-sectional area of the element, fabricated of 1080 carbon steel, will increase in electrical resistance as it corrodes. The ER-probe derived metal loss versus time data are presented in Figures 6(a) and 6(b) for LDP and GW, respectively; corrosion rates were estimated using the initial and end values for all cases and are noted next to the curve in the

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(3) VCI-A was VpCI-337 manufactured by Cortec Corporation.

same color as the metal loss data points of the curve. Additional corrosion rates were calculated [in black on Figures 6(a) and 6(b)] every two months for the VCI treated probes exposed to LDP and GW simulant electrolytes. The two corrosion rates were compared to determine if the VCI-treated ER probe experienced less corrosion.

As shown in Table 2, VSC in the GW environment is generally more aggressive compared to the LDP vapor space environment. Similarly, the coupon immersed in GW experienced more corrosion compared to the coupon immersed in LDP. The effectiveness of VCI-A was not clear from the coupons. The results from the inhibited ER probes indicate that metal loss began to increase after 30 days. The uninhibited ER probes, on the other hand, began to corrode immediately. Additionally, initially uninhibited probes, when dipped in the VCI, and placed in solution again after two months exposure, had a short period of stability of metal loss that lasted approximately 10 days. The corrosion rates for the second part of the experiment decreased slightly. However, the ER data shows that applying VCI-A by dipping the metal into VCI-A for inhibition has a short-lived effectiveness.

It was established that the GW environment is more corrosive compared to the LDP, and that the VCI treatment method, i.e., dipping the coupons in the electrolyte, was ineffective. Another set of experiments were conducted with new treatment method: that is, VCI-A and VCI-B were directly added to GW simulants. Experiments were repeated using the vessels described above. The VCI' doses were as per the manufacturer's recommendation. The ER probes were placed in the vessels; with one ER probe immersed in the solution and another one at Level 1 in each vessel. The ER probe data and corresponding corrosion rates are presented in Figures 7(a), and 7(b) for VCI-A and VCI-B,(4) respectively.

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(4) VCI-B was a mixture of VpCI-645 and VpCI-609, both manufactured by Cortec Corporation.

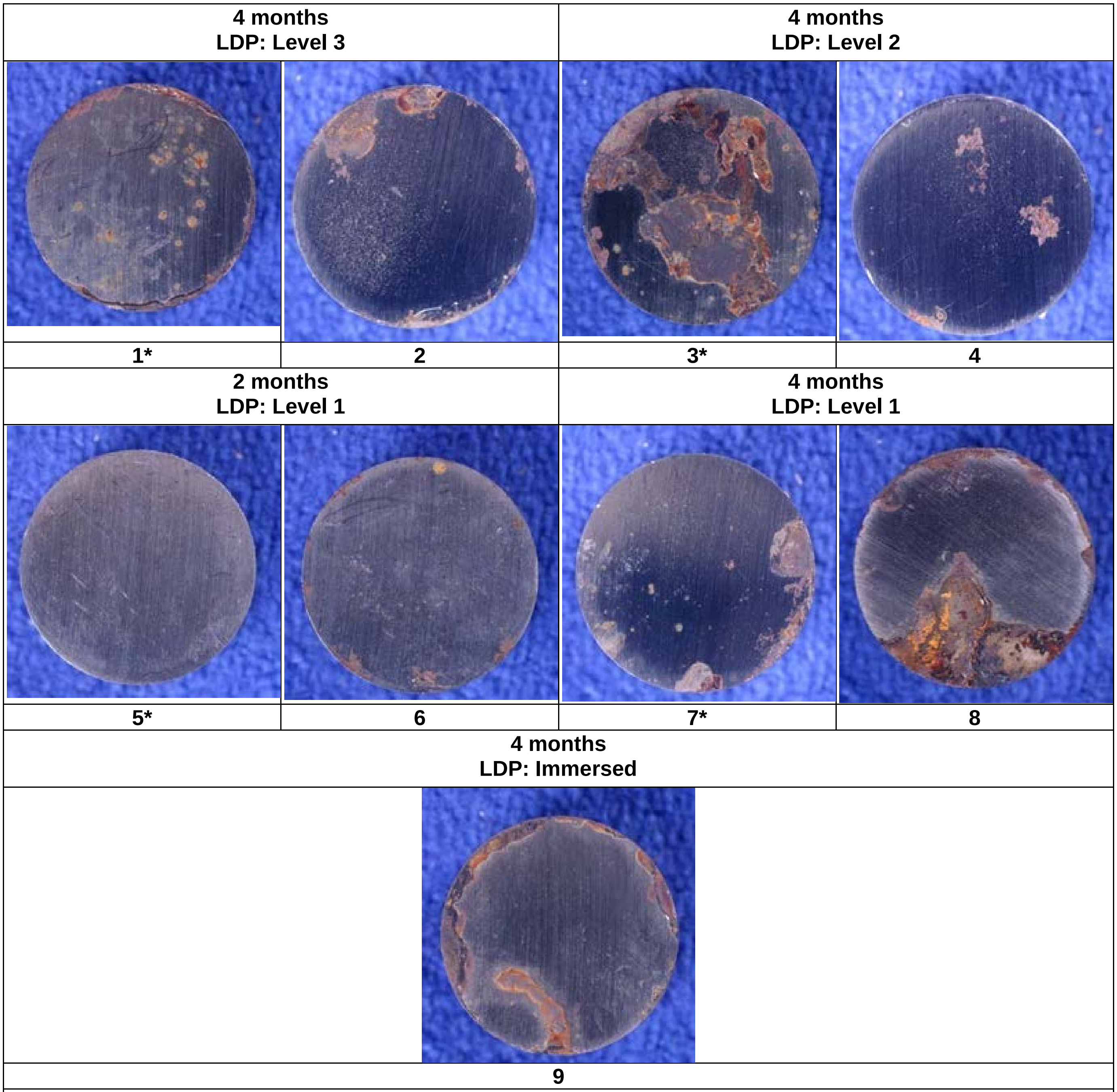


Figure 4. Images of the coupons exposed to LDP simulant, at various levels and immersed in the simulant. Exposure time and level is identified above each coupon, and coupon identification number below each coupon. (The asterisks next to a number implies that the coupon was dipped in VCI-A)

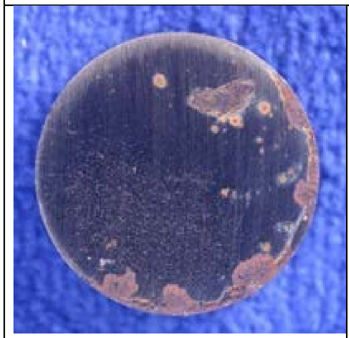
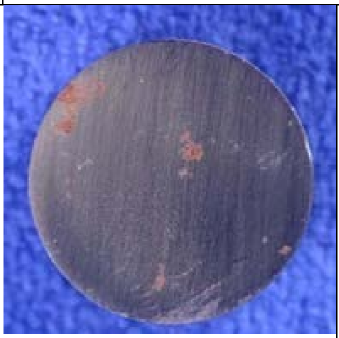
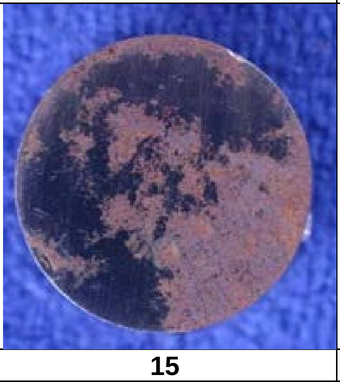
<table>
<tr><td colspan="2">4 months
GW: Level 3</td><td colspan="2">4 months
GW: Level 2</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>10*</td><td>11</td><td>12*</td><td>13</td></tr>
<tr><td colspan="2">2 months
GW: Level 1</td><td colspan="2">4 months
GW: Level 1</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>14*</td><td>15</td><td>16*</td><td>17</td></tr>
<tr><td colspan="4">4 months
GW: Immersed</td></tr>
<tr><td colspan="4"></td></tr>
<tr><td colspan="4">18</td></tr>
</table>

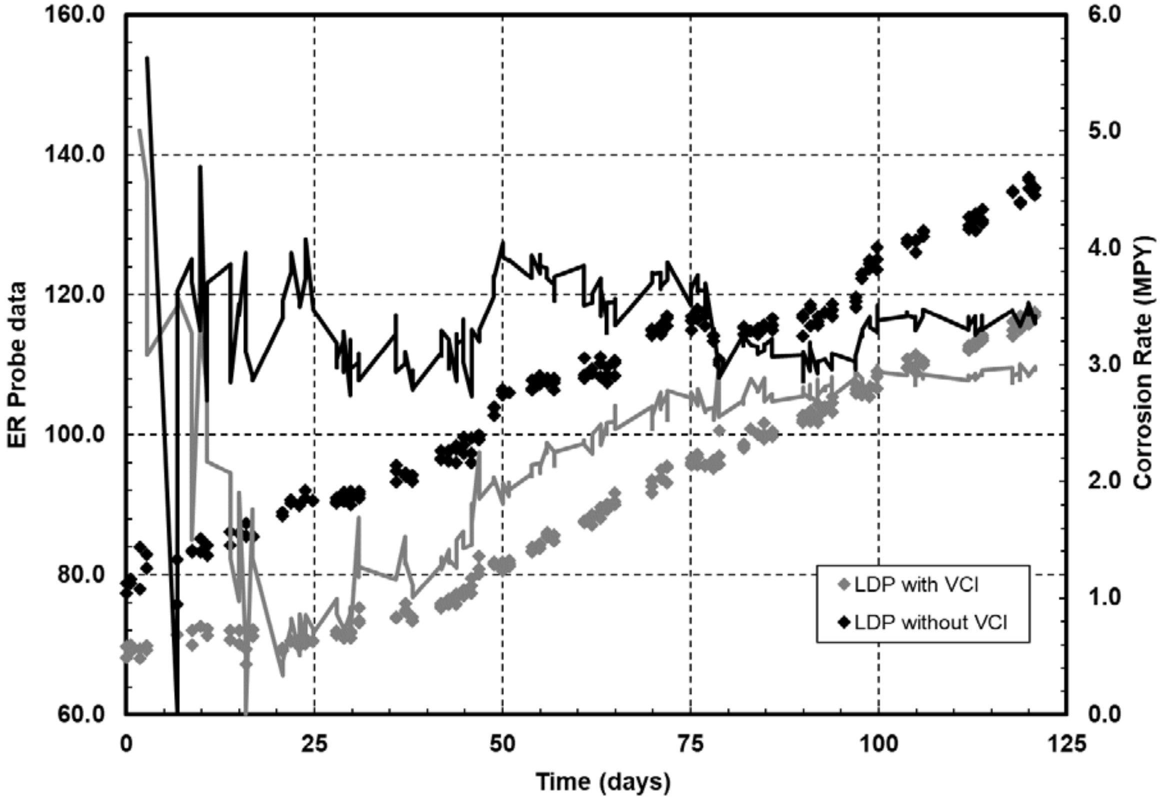
Figure 5. Images of the coupons exposed to GW simulant, at various levels and immersed in the simulant. Exposure time and level is identified above each coupon, and coupon identification number below each coupon. (The asterisks next to a number implies that the coupon was dipped in VCI-A)

Table 2. Corrosion rates of the coupons exposed to as-prepared LDP and GW simulants

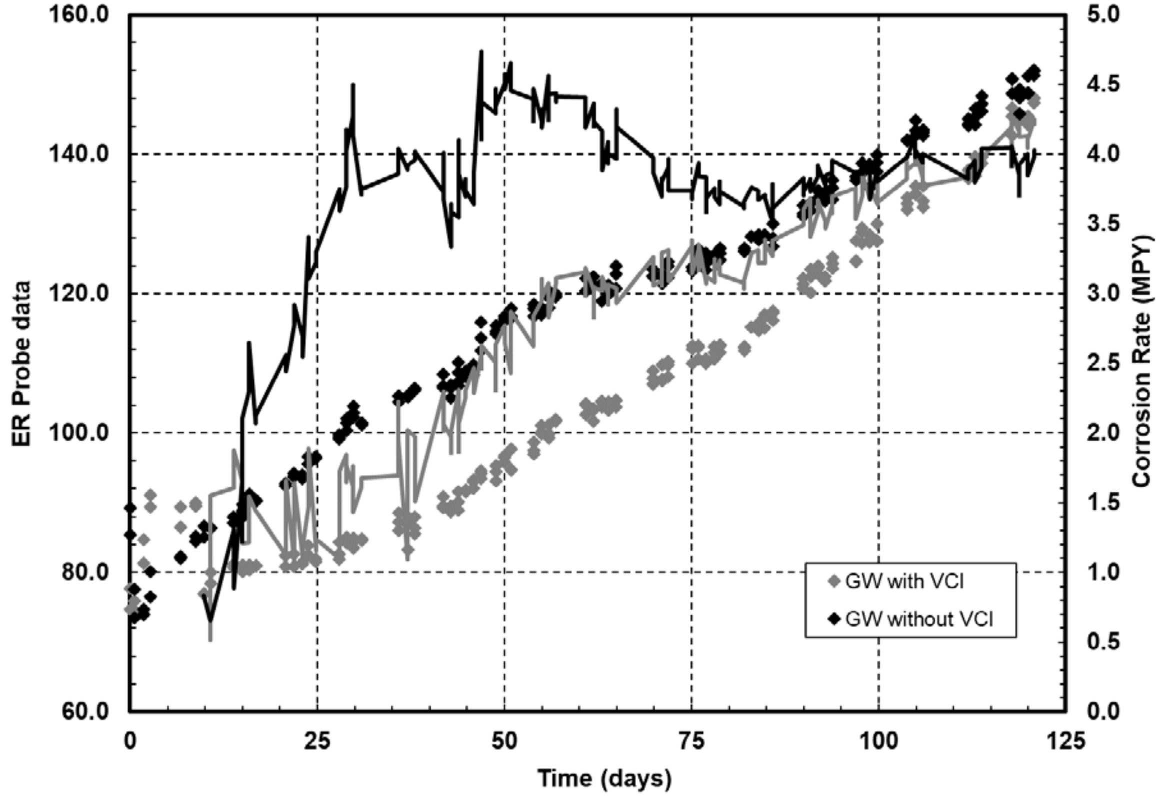
Electrolyte	Coupon number	Level in vessel	Exposure Time (month)	mass loss (g)	Corrosion rate (mpy)
LDP	1*	High (Level3)	4 months	0.0012	0.10
	2	High (Level3)	4 months	0.0016	0.13
	3*	Middle (Level 2)	4 months	0.0029	0.24
	4	Middle (Level 2)	4 months	0.0000	0.00
	5*	Low (Level 1)	2 months	0.0000	0.00
	6	Low (Level 1)	2 months	0.0001	0.02
	7*	Low (Level 1)	4 months	0.0021	0.17
	8	Low (Level 1)	4 months	0.0071	0.59
	9	Immersed	4 months	0.0161	1.33
GW	10*	High (Level3)	4 months	0.0009	0.07
	11	High (Level3)	4 months	0.0059	0.49
	12*	Middle (Level 2)	4 months	-0.0001	-0.01
	13	Middle (Level 2)	4 months	0.0021	0.17
	14*	Low (Level 1)	2 months	0.0008	0.13
	15	Low (Level 1)	2 months	0.0020	0.33
	16*	Low (Level 1)	4 months	0.0053	0.44
	17	Low (Level 1)	4 months	0.0090	0.74
	18	Immersed	4 months	0.0917	7.57

*denotes coupons treated with VCI-A

The effectiveness of VCI-A and VCI-B are presented in Figures 7(a) and 7(b), respectively. ER probe data and corresponding corrosion rates for GW + VCI-A are presented in Figure 7(a). The data points are presented by filled circles, and corrosion rates by solid lines. The data for immersed and vapor space ER probes are in blue and orange color, respectively. As seen in Figure 7(a), the corrosion rate of the ER probes both immersed and vapor space are effectively zero. Few non-zero corrosion rate values are observed for the vapor space ER probe, but the corrosion rates are calculated using the ER probe data which fluctuated daily. The fluctuation in the ER probe data also resulted in negative corrosion rates, but these values are set to zero in Figure 7(a). Similarly, ER probe data and corresponding corrosion rates for GW + VCI-B are presented in Figure 7(b). The colors and symbols used in Figure 7(b) are same as ones in Figure 7(a). When compared to GW + VCI-A electrolyte, the corrosion rate of the ER probes both immersed and vapor space had positive values. Specifically, initial values of corrosion rates for both immersed and vapor phase ER probes are several MPY. These high values are due to the short time duration between measurements, and the upward trend in the ER probe data immediately after initiating the test. Eventually the long-term corrosion rates stabilized, and trended downward. Specifically, the corrosion rates are less than 2 MPY after 10 days of exposure. This analysis does not account for random error in the ER data measurement. Even though ER probe is a plug and play technology, the probe data is known to vary between measurements which are just few minutes apart. For example, two measurements conducted 7 days after start on the GW + VCI-A ER probe are 140 and 142 units. The measurements are just few minutes apart, and the same is observed with other measurements. These experiments are continuing for an additional 3 months.



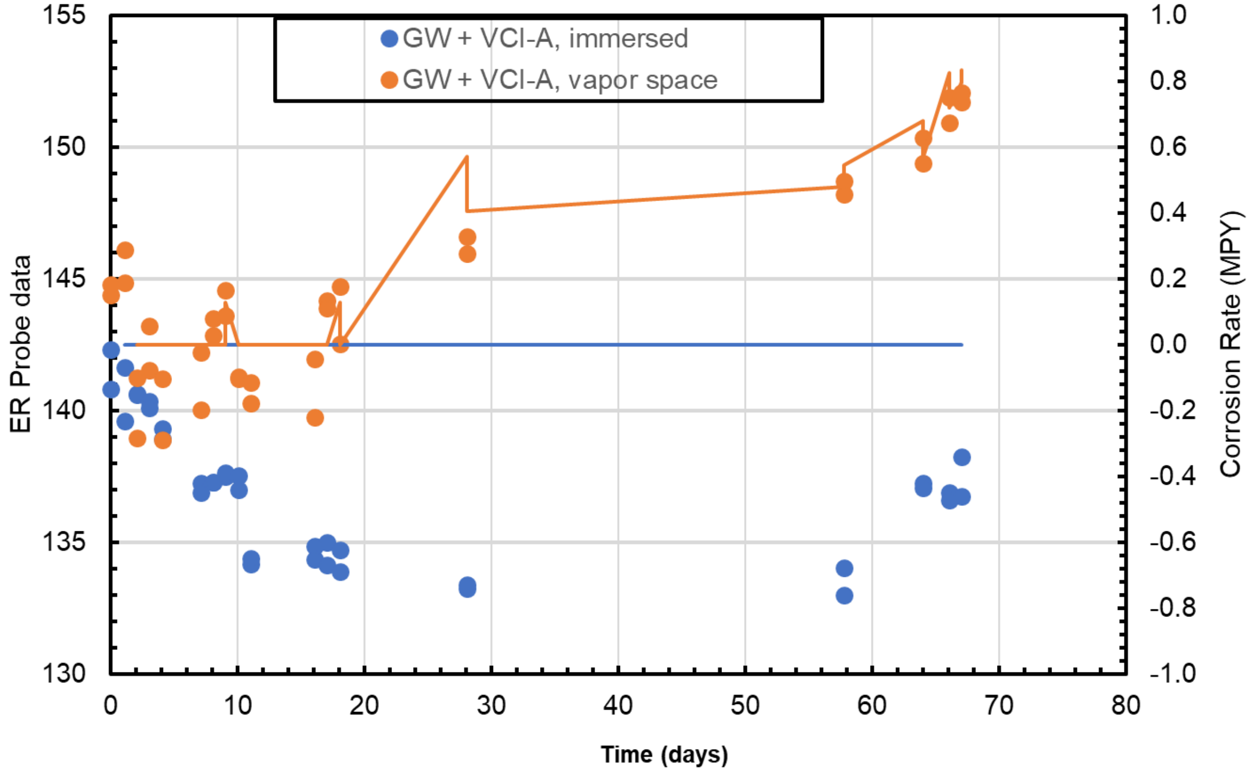
(a) LDP



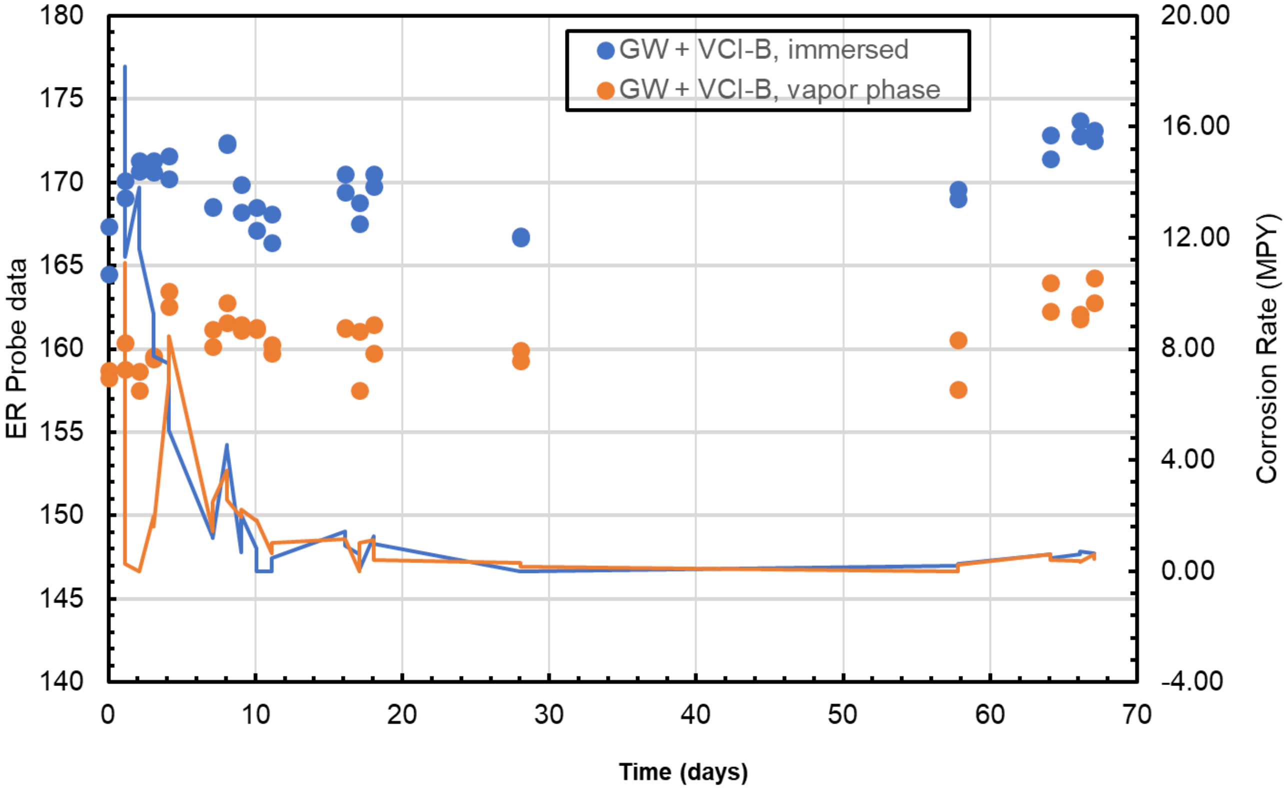
(b) GW

Figure 6. ER data showing metal loss vs. time for probes placed close to Level 1 in (a) LDP and (b) GW

simulant electrolytes. Two ER probes were placed in each vessel: one inhibited with VCI-A and one without inhibitor.



(a) GW + VCI-A



(b) GW + VCI-B

Figure 7. ER probe data and corresponding corrosion rates for (a) GW + VCI-A, and (b) GW + VCI-B.

SUMMARY

High-level waste storage double shell tanks at Hanford are experiencing corrosion on the exterior of the secondary liner, which rests on a concrete pad having the drain slots. Water accumulates in the slots, and is suspected tocause general and pitting corrosion when in direct contact with the plate, and vapor space corrosion when water levels are below the plate. Two simulants, leak detection pit (LDP) and groundwater (GW), were utilized to represent the accumulated water. Experimental studies were conducted to determine corrosivity of the simulants, and to determine the effectiveness of vapor corrosion inhibitors (VCIs) for mitigation of the corrosivity of LDP and GW simulants. Commercially available VCIs were identified as VCI-A and VCI-B. The second VCI, i.e., VCI-B, is a mixture to separate VCIs. The VCI dosages were as per the manufacturer's recommendations. Two VCI treatment methods were adopted. In the first treatment, coupons were dipped in VCI-A for five minutes and then exposed to simulant environment. In the second application method, VCIs were directly added to the simulants. For the first treatment, corrosion rates of the coupons that were exposed for 4 months with VCI-A were unaffected by the VCI application as corrosion rates of the treated coupons were similar to the untreated coupons. ER probe measurements, used to assess the corrosion environment and its effects with VCI, showed that the GW vapor space environment was more aggressive than LDP vapor space. The ER probes, treated with VCI in the first treatment, and exposed to the simulants were protected for approximately 30 days, while untreated probes started corroding immediately. The corrosion rates of the unprotected ER probe increased after the first 30 days, increased to the corrosion rate of the unprotected ER probe. The ER probe data suggested that the first treatment method is short lived and will not significantly reduce carbon steel corrosion in LDP and GW simulant environments. VCI effectiveness experiments using the second treated method, i.e., VCIs directly added to the simulants, have showed promising results. No significant corrosion was observed on the coupons, and ER probe data also indicate a low corrosion rate in the second treatment method. This study showed that the second treatment method, i.e., directly adding the VCIs to the simulants, provide increased protection against corrosion compared to the first treatment method.

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