VAPOR SPACE AND LIQUID/AIR INTERFACE CORROSION TESTS

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1.0   Summary

The phenomena of vapor space corrosion and liquid/air interface corrosion of carbon steel in simulated liquid waste environments have been investigated. Initial experiments have explored the hypothesis that vapor space corrosion may be accelerated by the formation of a corrosive electrolyte on the tank wall by a process of evaporation of relatively warmer waste and condensation of the vapor on the relatively cooler tank wall. Results from initial testing do not support the hypothesis of electrolyte transport by evaporation and condensation. The analysis of the condensate collected by a steel specimen suspended over a 40 °C simulated waste solution showed no measurable concentrations of the constituents of the simulated solution and a decrease in pH from 14 in the simulant to 5.3 in the condensate.

Liquid/air interface corrosion was studied as a galvanic corrosion system, where steel at the interface undergoes accelerated corrosion while steel in contact with bulk waste is protected. The zero-resistance-ammeter technique was used to measure the current flow between steel specimens immersed in solutions simulating (1) the high-pH bulk liquid waste and (2) the expected low-pH meniscus liquid at the liquid/air interface. Open-circuit potential measurements of the steel specimens were not significantly different in the two solutions, with the result that (1) no consistent galvanic current flow occurred and (2) both the meniscus specimen and bulk specimen were subject to pitting corrosion.

2.0   Introduction

A structural integrity program is in place to ensure the safe operation of the high level waste tanks. A key element of maintaining structural integrity is the corrosion control program [1]. Based on the results of extensive laboratory testing, minimum concentrations of nitrite and hydroxide have been specified in the corrosion control program to prevent or mitigate corrosion of the tanks by their waste contents. The concentrations of the inhibitor nitrite and hydroxide anions depend mainly on the concentration of nitrate in the bulk aqueous phase of the waste. Nitrate is the principal corrosive, or aggressive anion, although the chloride and sulfate ions may become significant aggressive species in wastes with low nitrate concentration. Historically the corrosion modes of concern have been, first, stress corrosion cracking (SCC) initiating in steel in contact with high-nitrate ($\geq$ 1.0 M concentration) bulk waste and, second, pitting in steel in contact with the interface between low-nitrate (< 1.0 M concentration) bulk waste and the vapor space above the waste. SCC was discovered in many of the site's older Types I and II waste tanks, which were constructed without post-fabrication heat treatment to relieve the corrosion-driving weld residual stresses. Through-wall pitting was discovered in a cooling coil of a tank whose waste was highly diluted with well water used in that instance to slurry the waste for transfer out of the tank [2]. Pitting has been particularly associated with the metal exposed to the liquid-air interface because of the depletion of hydroxide by reaction with absorbed atmospheric carbon dioxide to form bicarbonate and carbonate. These reactions in the interface solution and in an aqueous layer or film that is believed to form on the steel wall immediately above the interface are thought to proceed more rapidly than the diffusion rate of hydroxide from the bulk waste, resulting in orders of magnitude decrease in the hydroxide concentration [3]. Thus, the focus of waste tank corrosion research and the corrosion control program has been on steel in contact or very near contact with the bulk waste. Corrosion of the steel walls and ceiling of the

tanks has historically not been of concern because ultrasonic measurements of wall thickness have shown no reportable degradation [4].

Recent experience has shown that steel in contact with the vapor space above the bulk waste may be vulnerable to the initiation and propagation of SCC and pitting.   Photographs of Tank 15 taken between 1994 and 2000 revealed the apparent growth of a through-wall crack near the middle girth weld that was well above the sludge waste level then stored in this tank. Ultrasonic testing subsequently confirmed the through-wall crack [4]. In other instances of possible vapor space corrosion (VSC), previously unknown but probably pre-existing leak sites in Tanks 5 and 6 became evident by leakage into the annulus immediately after new transfers of waste into those tanks.   These Tank 5 and 6 leak sites were also well above the pre-transfer waste level. The Tank 5 and 6 leak sites have been attributed to nitrate-induced SCC, but visual examination alone of these painted Type I tanks cannot rule out pitting corrosion as another possible mechanism [5].

In addition to this and other SRS experience, both VSC and liquid/air interface corrosion (LAIC) at static waste levels have been of concern in the double-shell waste tanks at Hanford. This common interest at SRS and Hanford motivated the organization of two expert panel workshops on VSC and LAIC in 2002 and 2006 [6, 7]. The panelists of the two workshops endorsed continued research into VSC and LAIC especially to understand the formation and compositions of the corrosive electrolytes involved. The two phenomena of VSC and LAIC are often discussed together because they are both considered to be localized corrosion forms that occur under thin layers of electrolyte in contrast to corrosion under bulk waste. Certain chemical reactions in the thin layers, especially reactions involving dissolved gases, may proceed with different rates and results than those that may occur in the bulk waste. As noted above the relatively rapid absorption and reaction of carbon dioxide is believed to lead to the increased corrosion susceptibility of steel at the LAI. VSC and LAIC differ in certain ways that require different experimental approaches. In the case of potential VSC the thin electrolyte layer may form by (1) dissolution of dry nitrate-bearing salts left on the tank wall by humid air or (2) the transport of nitrate from the bulk waste to the tank wall by evaporation or aerosolization [8]. The volume of electrolyte in either concept would form as a thin layer of water condensed on the tank wall. As in the Hobbs and Wallace model of the LAI, atmospheric gases could dissolve into a thin layer and react rapidly. LAIC differs from VSC in that its electrolyte is a continuous extension of the aqueous phase of the bulk waste. The LAI chemical composition should be similar to that of the bulk waste except for the effects of dissolved gases in the interface solution. While VSC may take place anywhere on a tank wall that is covered with condensed electrolyte, LAIC is limited to the steel in contact with the meniscus formed by the waste. Along with carbon dioxide, the effect of dissolved oxygen may be especially important for LAIC, where the interface solution may have a higher oxygen content than the bulk waste. A higher oxygen content could change the electrochemical potential of the steel under the interface versus that of the steel immediately below, which is in contact with the bulk waste.

Preliminary results are presented here on experiments to investigate both VSC and LAIC [9]. The first experiment was conducted to test the hypothesis of formation of a corrosive electrolyte by evaporation and condensation (*vapor space corrosion tests*).   The second experiment was conducted to evaluate the electrochemical potential difference and resulting

current flow between a carbon steel specimen in contact with the bulk liquid and a specimen in contact with the LAI or meniscus liquid (*zero-resistance ammeter tests*).

3.0 Vapor Space Corrosion Tests

As discussed above, one hypothesis for the formation of a corrosive electrolyte on a tank wall above the level of the liquid waste is the evaporation of waste and the subsequent condensation of the vapor on the cooler tank wall. The focus of vapor space corrosion testing in FY09 was the laboratory-scale simulation of this process and the collection and analysis of the condensate. A specially designed glass condensation collection cell was fabricated for the testing (Figure 1a). The cell allowed the collection of condensate formed on the surface of an approximately 4-inch-square steel sheet specimen without the necessity of opening the cell and thus altering the vapor environment. The cell consisted of a 16-inch tall, 6-inch diameter glass vessel equipped with a condensate collection tube which extended outside the cell to a 3-way valve. The valve permitted the condensate to be taken for chemical analysis or recycled into the cell. The specimen was supported in the cell about 8 in. above the test solution. As Figure 1b shows, the steel sheet specimen was formed into a shallow funnel shape in a manual press, with the downward-facing surface at the location of condensation. The shallow funnel shape was selected to give the condensate some residence time on the steel surface before dripping under gravity into the collection tube. The cell was heated on a hot plate to raise the simulated waste solution to 40 °C. The cell was equipped with a chilled reflux condenser and thermocouple with temperature controller.

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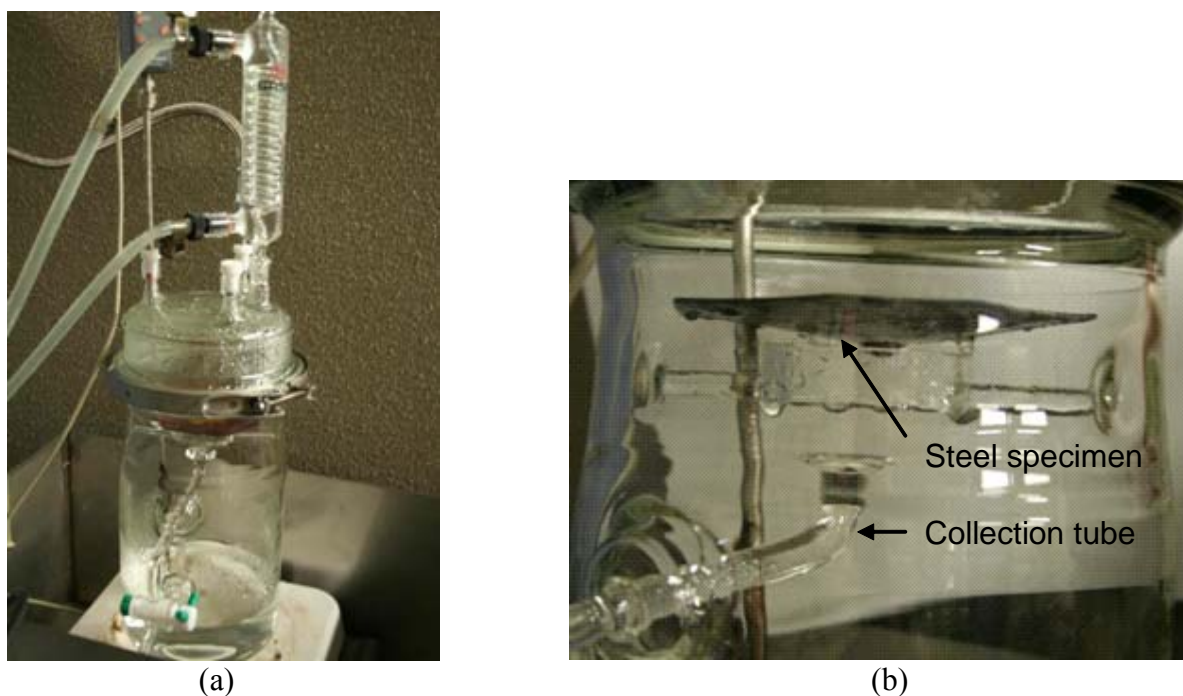<tr><td>(a)</td><td>(b)</td></tr>
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Figure 1. (a) Condensate collection cell on hot plate. (b) Configuration of steel sheet

The sheet specimens were cut by wire electro-discharge machining from 1-inch-thick plate of ASTM A285 steel. Specimens were approximately 4 in. by 4 in. by 0.05 in. before the

corners were trimmed as shown in Figure 2(a). The specimens were formed into the funnel shape using a manually operated hydraulic press, with the convex mill-scale surface of the plate as the tested surface in the condensate cell. A thermocouple was spot-welded to the upward-facing surface of the specimen.

A comprehensive, non-radioactive simulant of the aqueous phase of high-level radioactive waste was used in this experiment. Its composition is shown in Table 1. The compound concentrations are shown in the table in moles per liter, and the equivalent anion concentrations are give in parts per million (ppm) for ease of comparison with the results of the chemical analyses. The simulant was representative of stored liquid waste and was based on chemical analysis of actual waste [10]. In preparing the test solution, the weight of sodium hydroxide was calculated to account for the formation of the $Al(OH)_4^-$ ion (that is, to account for the reaction of four OH^- ions with each Al^{+3} ion in aluminum nitrate). The resulting nitrate ion concentration is 1.1 M, as each aluminum nitrate contributes three NO_3^- ions per molecule. Approximately 970 mL of test solution was added to the cell, and the solution was heated to 40 °C with a temperature-controlled hot plate. With the test solution at 40 °C, the steel specimen thermocouple measured 32 °C.

Two funnel specimens have been tested this year. Funnel F5 was exposed in the cell in the as-machined condition for 71 days. Funnel F6 was pre-coated with the salts evaporated from the Table 1 test solution. Salt was built up to a visible thickness by repeated deposition of solution and evaporation in a drying oven at 50 °C (Figure 3). Funnel F6 was prepared to replicate the development of an electrolyte on a tank wall with residual salt deposits. This specimen is currently being exposed in the condensation cell.

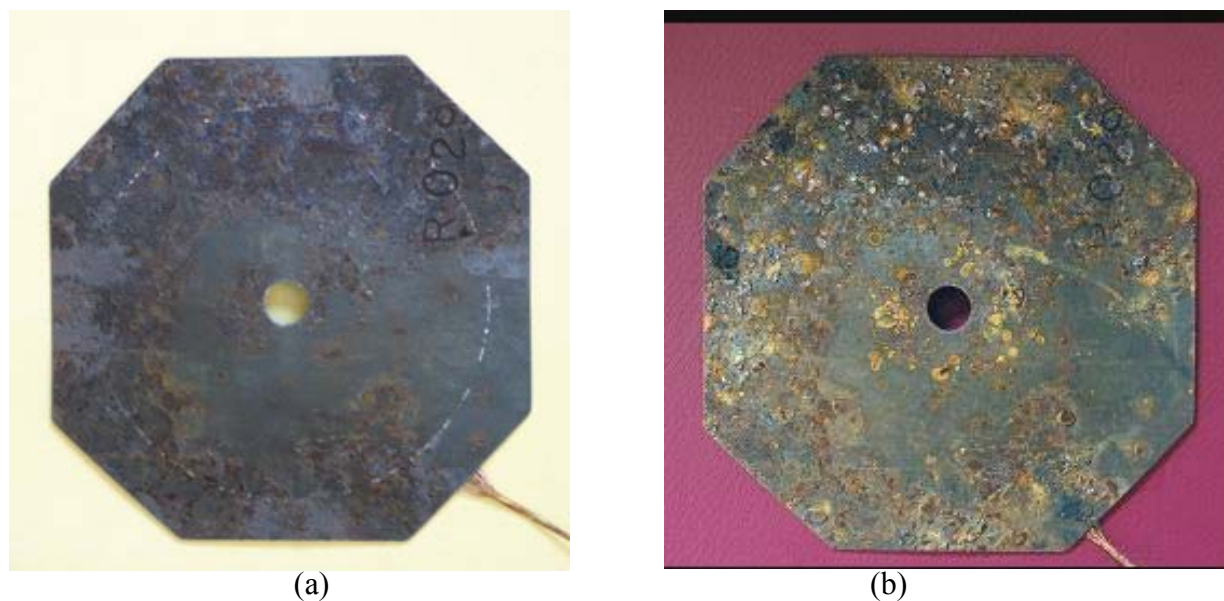(a)   (b)

Figure 2. (a) ASTM A285 steel specimen F5 before exposure in the
condensate cell and (b) after exposure.

Table 1. Composition of Simulated Waste Solution for Condensate Tests

Compound	Concentration (M)	Equivalent Anion Concentration (ppm)
Sodium Carbonate	0.100	6,000
Sodium Chloride	0.010	350
Aluminum Nitrate	0.366	68,100
Sodium Nitrite	0.096	4,400
Sodium Phosphate	0.010	950
Sodium Sulfate	0.020	1,900
Sodium Hydroxide	1.120	not calculated

Figure 3. ASTM A285 steel specimen F6 with salt deposits
before exposure in the condensate cell.

The condensate cell, when operated at a solution temperature of 40 °C, yielded condensate at a rate of between 5 and 10 mL per day. Table 2 shows the series of sample analyses from the exposure of steel specimen F5. The chemical analyses that are most relevant in this experiment are anion concentrations, free hydroxide, and pH. The anion concentrations were determined by ion chromatography. The condensate analyses show that there was no detectable presence of the anions in the condensate samples, and the pH was mildly acidic at 5.3. The difference in sensitivity among the condensate samples derived from different dilution levels in the analytical preparation.

Table 2. Analyses of Specimen F5 Solutions
(Anion concentrations in ppm and free hydroxide in moles/liter)

Anion	Bulk 1	Bulk 2	Bulk 3	Condensate 1	Condensate 2	Condensate 3
Chloride	522	497	521	<50	<1	<2.5
Nitrate	65,400	65,400	66,700	<50	<1	<2.5
Nitrite	4,550	4,390	4,510	<50	<1	<2.5
Phosphate	130	740	812	<50	<1	<2.5
Sulfate	3,340	3,230	3,610	<50	<1	<2.5
Free OH	1.08	1.05	1.12			
pH	14	14	14	5.3	5.3	5.3
Sample Date	4/15/2009	5/20/2009	6/25/2009	4/21/2009	5/20/2009	6/25/2009

Analytical results to date from the salt-coated steel specimen F6 are shown in Table 3. The sample for the initial condensate 1 was collected continuously for about 24 hours from the beginning of the placement of specimen F6 in the cell. Anion concentrations in condensate 1 were similar to those of the bulk 1 values, which reflects the dissolution of the salt coating into the condensed liquid. Condensate 2 was collected four days after condensate 1. During that interval the condensate was recycled back to the bulk liquid, and the analysis of condensate 2

indicates that the recycling of condensed liquid had dissolved and removed the deposited salt coating. For example the nitrate concentration fell substantially from 71,100 ppm in condensate 1 to 140 ppm in condensate 2. The analysis of condensate 3, which was collected after 27 days of exposure, is similar to the condensate analyses of the F5 specimen, showing essentially complete removal of deposited salts and no transport of anions from bulk solution to steel specimen.

Table 3. Analyses of Specimen F6 Solutions
(Anion concentrations in ppm and free hydroxide in moles/liter)

Anion	Bulk 1	Condensate 1	Condensate 2	Condensate 3
Chloride	412	645	<10	<1
Nitrate	83,300	71,100	140	4
Nitrite	5,510	4,950	<25	<1
Phosphate	1,070	3,330	<10	<1
Sulfate	2120	794	22	2
Free OH	1.08			
pH	14	13	11	6.5
Sample Date	8/20/2009	8/20/2009	8/24/2009	9/16/2009

The corroded, mill-scale starting surface of specimen F5 was further corroded by exposure in the condensate collection cell, as shown in Figure 2(b). Additional light brown rust deposits are prominent in the figure. X-ray diffraction analysis of specimen F5 showed that the starting surface of naturally weathered mill-scale was composed of the fully oxidized (all Fe^{+3} oxidation state) iron oxide hydroxide phase lepidocrocite (γ FeOOH). Exposure in the condensate cell resulted in the formation of mixed-valence (Fe^{+2} and Fe^{+3}) magnetite Fe_3O_4. Prominent formation of magnetite has been noted in steel exposed in a marine atmosphere [11], which bears similarity to the moist atmosphere over the salt solution in the condensate cell.

4.0 Zero-Resistance Ammeter Testing in LAIC Environments

The purpose of this testing was to investigate liquid/air interface corrosion as an example of galvanic corrosion, in which an electrochemical current flows between the steel in contact with the meniscus of the waste and the steel in contact with the bulk waste, such that the former is corroded and the latter protected. The experimental apparatus consisted of two one-liter glass reaction vessels connected by a salt bridge (containing 0.1 M sodium nitrate solution) for ionic current flow (Figure 4). One vessel contained solution simulating the relatively low pH meniscus environment while the other vessel contained the relatively high pH bulk waste simulant. Identical ASTM A537 carbon steel specimens (0.62-inch-diameter discs purchased from Metal Samples, Inc., Munford AL) were immersed in each vessel and connected to one another through a Gamry Reference 600 Potentiostat/Galvanostat operating in the mode of zero-resistance ammeter (ZRA). Thus electrical current in the system is completed by the electronic current flowing through and measured by the ZRA and by the ionic current flowing through the test solutions and the salt bridge.

Silver/silver-chloride reference electrodes were installed to measure the open-circuit potential of each specimen prior to connection for ZRA measurements. Solutions were heated to 40°C on temperature-controlled hot plates. The vessels were equipped with reflux condensers and gas purge tubes for carbon dioxide-free air purges of the test solutions.

Figure 4. Zero-resistance ammeter measurement apparatus.

LAIC is a concern particularly in steel contacted by dilute waste solutions (nitrate concentration < 1.0 M), such as may be seen in waste removal as well as in waste prepared for vitrification. The test solutions used in the initial tests reported here were simple simulants of waste supernate containing 0.5 M sodium nitrate and 0.1 M sodium nitrite.   The meniscus solutions contained sodium bicarbonate and sodium carbonate at concentrations that resulted in a buffered pH of 9, a value representing a liquid/air interface layer highly depleted in the corrosion-inhibiting hydroxide ion concentration. The bulk solutions contained 0.1 M sodium hydroxide, which corresponds to pH 13. The tests with these solutions were designed to disclose whether significant current would flow between a steel specimen at pH 9 and a specimen at pH 13. Two-liter volumes of the solutions were mixed to provide solution for 3 replicate tests.

The specimens were polished to a fresh 800-grit finish immediately before being immersed in heated, air-purged solutions and allowed to reach steady-state open circuit potentials. Figure 5 shows the open circuit potentials recorded over 2 hours for 3 bulk solution replicates using the same steel specimen and fresh solution for each replicate. Figure 6 shows the corresponding meniscus open circuit potentials. Both figures show reasonably steady potentials after 2 hours' immersion. However, there was significant variation from replicate to replicate, especially in the bulk solution measurements, despite the use of the same steel specimen and a volume of fresh solution from the same mixed batch. The same reference electrode was used for each solution replicate. The bulk solution open circuit potentials ranged from about -0.200 volts to -0.350 volts versus the Ag/AgCl reference, while the meniscus solution potentials ranged from approximately -0.200 volts to -0.300 volts versus Ag/AgCl. Thus, for reasons not yet known,

there is no consistent difference in these particular measurements between the set of open circuit potentials of the steel specimens exposed to the pH-9 solution and the set of those of the pH-13 solution.
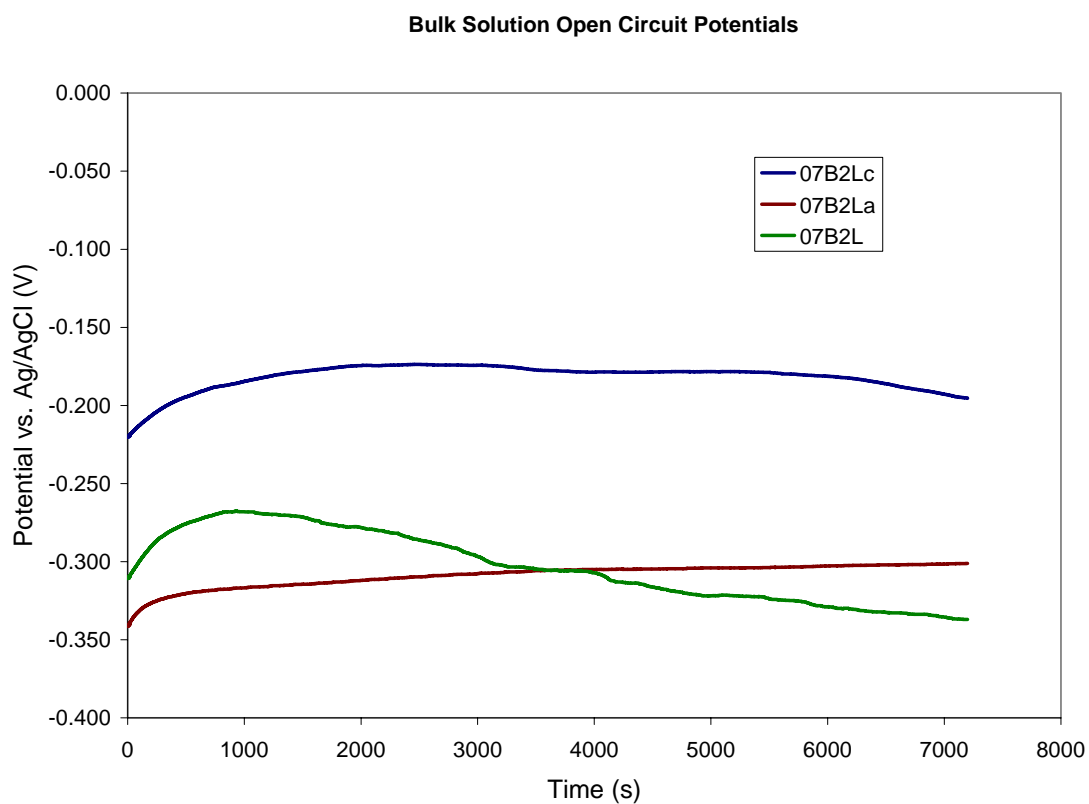
Bulk Solution Open Circuit Potentials

Figure 5. Open circuit potentials in volts versus Ag/AgCl for 3 replicates of the bulk solution.

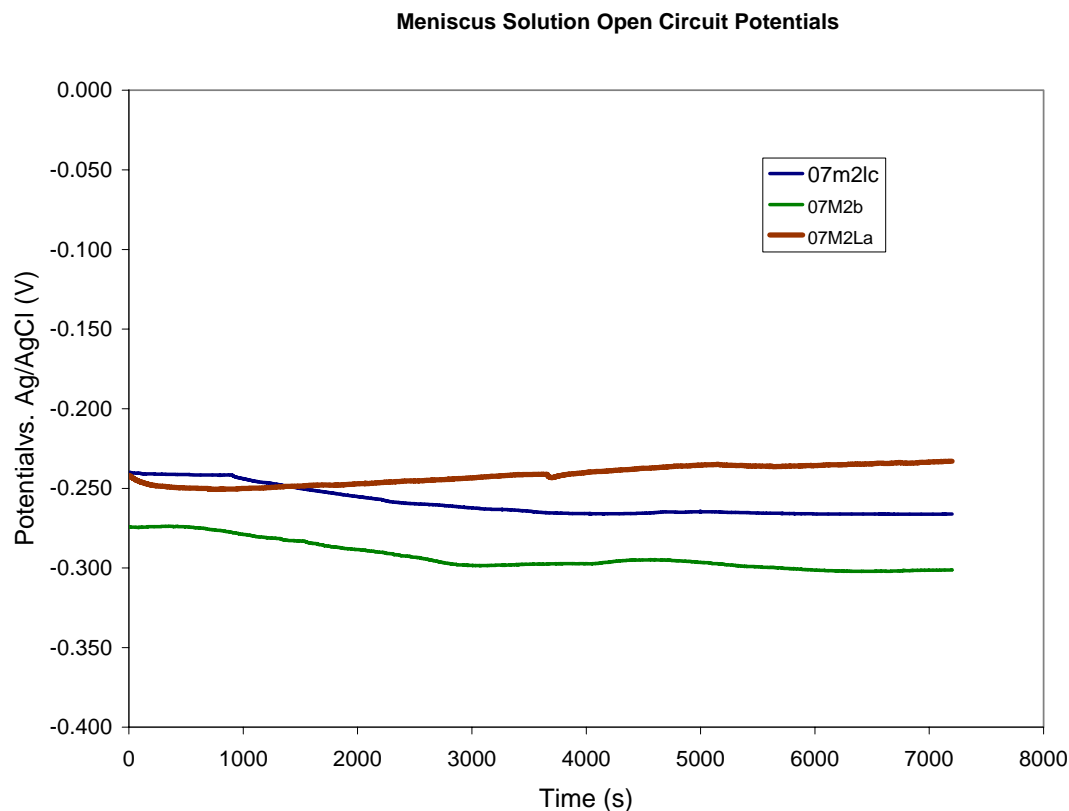**Meniscus Solution Open Circuit Potentials**

Figure 6. Open circuit potentials in volts versus Ag/AgCl for 3 replicates of the meniscus solution.

When the steel specimens in the two solutions were electrically connected through the ZRA, the specimens were forced to assume the same electrochemical potential. The current measured by the ZRA reflects the corrosion response of the two specimens to their new potential resulting from the electrical connection. The consequence of the overlap in the sets of open circuit potentials is that the current flow is not consistently of one sign; that is, either specimen may corrode at the expense of the other. This variation in sign of current flow is shown in Figure 7, where, based on the electrical connections to the ZRA, positive currents indicate oxidation (corrosion) of the meniscus specimen and negative currents indicate oxidation (corrosion) of the bulk specimen.

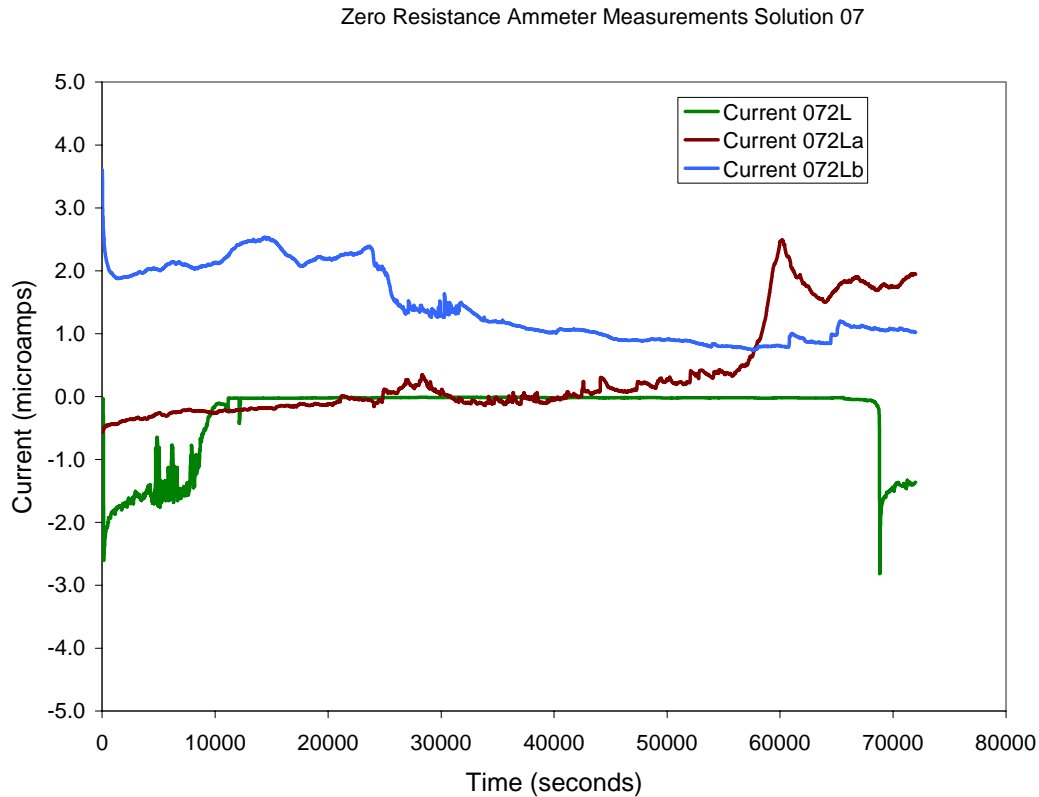Zero Resistance Ammeter Measurements Solution 07

Figure 7. ZRA current measurements from three tests in a 0.5 M nitrate, 0.1 M nitrite solution. Positive current indicates corrosion of the meniscus specimen; negative current indicates corrosion of the bulk specimen.

5.0 Conclusions

Experiments were conducted into the VSC and LAIC of carbon steel in simulated liquid waste environments. Localized forms of VSC in carbon steel, pitting or stress corrosion cracking, are expected to develop in the presence of an electrolyte that contains aggressive anions such as chloride, nitrate, or sulfate that are found in the aqueous phase of liquid waste. One hypothesis for the formation of an electrolyte on steel in contact with the waste tank vapor space is the condensation of evaporated liquid waste on the relatively cooler tank wall above that liquid waste. A condensation collection cell was devised and fabricated to test this hypothesis. Simulated, non-radioactive waste composed of sodium salts was heated to 40 °C in the cell and the condensate collected from the surface of an A285 carbon steel specimen suspended above the heated liquid. Ion chromatography of multiple condensate samples collected from an as-received steel specimen showed no measurable concentrations of the aggressive anions chloride, nitrate, and sulfate or of the corrosion-inhibiting ion nitrite. In a second test the condensate was collected from an A285 specimen that had been pre-coated with the sodium salts of these anions. Analysis of the condensate from this specimen showed that the process of evaporation and condensation eventually led to a condensate with no detectable anion concentrations. These experiments indicate that under the conditions tested, an electrolyte capable of inducing localized VSC does not form by a process of evaporation and condensation.

LAIC has been observed frequently in laboratory tests of partially immersed steel coupons. A long-standing model for the corrosive environment at the LAI of liquid waste tanks is the development of a locally corrosive electrolyte by the depletion of the protective hydroxide concentration (that is, lowering the pH) [3]. This depletion is hypothesized to result from the reaction of absorbed atmospheric carbon dioxide with soluble hydroxide ions. An experiment was conducted to explore LAIC as a form of galvanic corrosion where the steel in contact with the lower-pH meniscus liquid at the LAI assumes a more corrosive electrochemical potential than the steel in contact the high-pH bulk solution. The ZRA technique was used to measure the possible galvanic current flow between A537 carbon steel specimens immersed in non-radioactive simulants of the meniscus and bulk waste. Initial results show that steel specimens exposed to solutions with pH 9 simulating the meniscus and solutions with pH 13 simulating the bulk waste did not significantly differ in their open-circuit potentials. Repeated ZRA measurements showed inconsistent galvanic current flow.

6.0 Future Work

Recent work at SRNL has shown that localized corrosion in the form of SCC can occur in stressed coupons suspended in the vapor space above high-nitrate test solutions [12]. Future work in VSC will be focused on determining the composition of the electrolyte that caused the observed cracking. LAIC work will be focused on determining the solution and purge gas compositions that yield a sustained corrosion current of the meniscus coupon in the ZRA test.

7.0 References

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