LIQUID AIR INTERFACE CORROSION TESTING FOR FY 2010

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December, 2010

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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Prepared for
U.S. Department of Energy

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EXECUTIVE SUMMARY

An experimental study was undertaken to investigate the corrosivity to carbon steel of the liquid-air interface of dilute simulated radioactive waste solutions. Open-circuit potentials were measured on ASTM A537 carbon steel specimens located slightly above, at, and below the liquid-air interface of simulated waste solutions. The 0.12-inch-diameter specimens used in the study were sized to respond to the assumed distinctive chemical environment of the liquid-air interface, where localized corrosion in poorly inhibited solutions may frequently be observed. The practical inhibition of such localized corrosion in liquid radioactive waste storage tanks is based on empirical testing and a model of a liquid-air interface environment that is made more corrosive than the underlying bulk liquid due to chemical changes brought about by absorbed atmospheric carbon dioxide. The chemical changes were assumed to create a more corrosive open-circuit potential in carbon in contact with the liquid-air interface.

Arrays of 4 small specimens spaced about 0.3 in. apart were partially immersed so that one specimen contacted the top of the meniscus of the test solution. Two specimens contacted the bulk liquid below the meniscus and one specimen was positioned in the vapor space above the meniscus. Measurements were carried out for up to 16 hours to ensure steady-state had been obtained. The results showed that there was no significant difference in open-circuit potentials between the meniscus-contact specimens and the bulk-liquid-contact specimens. With the measurement technique employed, no difference was detected between the electrochemical conditions of the meniscus versus the bulk liquid.

Stable open-circuit potentials were measured on the specimen located in the vapor space above the meniscus, showing that there existed an electrochemical connection through a thin film of solution extending up from the meniscus. This observation supports the Hobbs-Wallace model of the development of the pitting susceptibility of carbon steel in alkaline solutions.

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1.0 Introduction

Carbon steel will undergo general or uniform corrosion at a very slow rate of less than a few thousandths of an inch per year when in contact with very alkaline (pH > 12) aqueous salt solutions. The low corrosion rate derives from the protective passive film on the steel surface that the hydroxide ion makes possible. Where the pH of the salt solution falls to 10 or less, the passive film becomes less stable and prone to local breakdown induced by aggressive solution anions such as chloride, nitrate, and sulfate. This breakdown and local oxidation or dissolution of iron atoms constitutes the corrosion process known as pitting. The steel surface in this situation remains largely passive and protected, but at essentially random locations on the surface, pitting corrosion can proceed rapidly and deeply compared with the relatively slower uniform corrosion.

The nitrate anion (NO_3^-) is the principal corrosive anion in liquid radioactive waste, so that from a corrosion point of view, it is useful to classify waste in terms of its nitrate concentration. At the Savannah River Site pitting in carbon steel tanks that store and process liquid radioactive waste is of concern where the tanks contain dilute waste compositions, that is, those wastes with a nitrate concentration < 1 M. Pitting has not been observed in concentrated wastes (> 1 M nitrate). The corrosion mode of concern in the high-nitrate, concentrated wastes is stress corrosion cracking (SCC). SCC is prevented in part through the application of the requirements of the waste tank corrosion control program, among which are minimum concentrations of hydroxide and the sum of hydroxide and nitrite and maximum waste temperatures.[1] These minimum concentrations of the corrosion-inhibiting species hydroxide and nitrite are evidently sufficient to prevent pitting of waste tank steel as well as SCC. However, service experience does show that the dilution of waste from higher nitrate concentrations to less than 1 M (as for waste processing for subsequent vitrification) renders waste tank steel susceptible to pitting.[2] The concentrations of hydroxide and nitrite that protected the steel from SCC in concentrated waste may be insufficient, when diluted, to protect the steel from pitting despite the simultaneously diluted nitrate concentration. Additional inhibitor requirements in the corrosion control program specify the minimum hydroxide and nitrite concentrations to prevent pitting in the dilute wastes.

Pitting has been particularly associated in laboratory testing with steel in contact with the interface between the liquid waste and the atmosphere or vapor immediately above the liquid. It has been theorized that this particular susceptibility to corrosion is due the depletion of the hydroxide ion concentration 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 liquid waste, resulting in orders of magnitude decrease in the hydroxide concentration.[3] Over time, the hydroxide concentration (that is, the pH) of the entire liquid phase may decline below a protective value, as shown in measurements of the pH of small test volumes of actual sludge waste.[4] Minimum nitrite concentrations that maintain immunity to pitting under the conditions of depleted hydroxide have been measured in the laboratory and are incorporated into the waste tank corrosion control program.[1]

Basic questions remain unanswered about the pitting corrosion of steel in contact with the interface between an aqueous electrolyte and the atmosphere above that electrolyte and the vapor space well above the interface (referred to as liquid/air interface corrosion [LAIC]). These questions include the electrochemistry of corroding steel at the interface, the role of oxygen as the primary species in the reduction reaction that supports the metal-oxidizing anodic reaction, the contribution of other cathodic reactions based on nitrite, and the composition and pH of the interfacial solution (as compared to the bulk electrolyte). LAIC in steel in contact with simulated radioactive waste solutions (that is, mainly sodium salt solutions with no radioactive species) differs from classical waterline corrosion of steel in that the metal oxidation can occur above the interface, whereas classical waterline corrosion occurs within the meniscus.[5]

Previous work on LAIC examined the phenomenon as a galvanic couple between steel in contact with relatively high-pH bulk liquid and relatively low-pH interface or meniscus liquid, according to the model that the meniscus hydroxide concentration is depleted by absorbed CO_2.[6] The objective of part of that work was to measure a galvanic current between two ASTM A537 class 1 carbon steel specimens immersed in separate high- and low-pH solutions. The galvanic current measurement approach was based on the expectation that different stable open-circuit potentials would be established for the two specimens, so that the low-pH specimen would corrode and the high-pH specimen would be immune. (The open-circuit potential is the voltage that arises between a metal specimen immersed in a particular electrolyte and some high-impedance reference electrode immersed in the electrolyte. Its relative value can indicate the thermodynamic tendency of a metal to corrode.) However, although stable open-circuit potentials could be measured for any given specimen-solution combination, it was found that repeated measurements of the same freshly polished specimen in identical fresh test solutions yield widely varying stable open-circuit potentials. Thus the direction of galvanic current between the two specimens was not consistent, so that it could not be shown that a meniscus (low-pH) specimen always corroded at the expense of an immune bulk liquid (high-pH) specimen.

As a result of the inconclusiveness of the galvanic current LAIC testing, experiments have been undertaken to measure the open-circuit potentials of small carbon steel specimens above, in, and below the meniscus of alkaline salt solutions that simulate bulk liquid waste. The goal of the experiments was to determine whether the open-circuit potential of small steel specimens varied with position relative to the meniscus of a salt solution, and to evaluate the effect of environmental and solution variables on the measured potential. Many physical and chemical variables may affect the open-circuit potential. Four variables were investigated in these scoping tests: solution concentration, pH, temperature, and aeration. This report discusses the development of the experimental specimen and the results of the potential measurements.

2.0 Experimental Procedure

2.0.1 Specimen Preparation

The specimens used in the LAIC testing program were small right cylinders of ASTM A537 Class 1 carbon steel of dimensions 0.12 in. in diameter by 0.14 in. in height (Figure 1). The specimen diameter was chosen to approximate the thickness of the meniscus liquid and to allow

convenient handling. They were cut at SRNL by electro-discharge machining from flat coupons of that steel supplied by Metal Samples, Inc. (Munford, AL). Four specimens were mounted together so that individual specimens could be exposed to conditions above, at and below the meniscus of the test solution. A multiple-step procedure was devised to fix the specimens in a metallurgical mounting compound and electrically connect the specimens in a linear array suitable for the testing. To make the electrical connections, an approximately 1-in. length of nickel wire was spot welded to one end of each specimen. Sets of four specimens were then fixed in position in a Buehler Inc. plastic metallurgical mount using double-sided adhesive tape (Tombo Monoadhesive® 62114). Neighboring specimens were spaced about 0.2 in. apart. A layer approximately 0.2 in. thick of Buehler Varidur® two-part room-temperature-curing mounting compound was poured over the specimens. This shallow layer of cured mounting compound held the specimens in position so that ~15-in. lengths of polytetrafluoroethylene-insulated multi-strand wires could be soldered to the nickel wires. A second pour of Varidur® compound covered the solder joints and insulated the electrical connection from contact with the test solution. A completed specimen array is shown in Figure 2. Specimen arrays were usually machine-polished to a 600 grit finish. In testing, the array was place in a glass holder with specimens oriented in vertically. Figure 3 shows the array in a glass holder and the position labels for each specimen in the array, which are 'L', '1', '2', and 'H' in ascending order from the lowest specimen to the highest specimen.

Figure 1. Starting ASTM A537 Class 1 carbon steel
coupon and electrodischarge-machined specimens.

Figure 2. Array of four specimens mounted in metallurgical mounting compound.

Specimen Labeling

H

2

1

Figure 3. Specimen array placed in glass holder and specimen labeling.

2.0.2 Open-Circuit Potential Measurements

Open-circuit potentials (OCPs) were measured with a Gamry Instruments (Warminster, PA) Reference 600™ Potentiostat/Galvanostat/ZRA and ECM8™ Electrochemical Multiplexor. The Multiplexor permitted the sequential measurement of 8 specimens, so that two arrays of specimens could be tested simultaneously with one Reference 600™. Gamry Framework™ version 5.50 software controlled the operation of the potentiostat and Multiplexor. The reference electrodes were saturated calomel electrodes that were connected to the test solutions through a salt-solution bridge (Luggin capillary) filled with 0.1 M sodium nitrate solution. A glass holder with specimen array was inserted into approximately 400 mL of test solution contained in modified 1-L glass cells equipped with gas-sparging tubes and cooled reflux condensers. The cells were placed on temperature-controlled hotplates. (Figure 4).   The specimen array was normally inserted so that the solution level lay at the lower edge of the position 2 specimen as shown in Figure 5. With this configuration the position H specimen was about 0.3 in. above the

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liquid level and thus permitted verifying the existence of the electrochemically conductive liquid film extending that height above the liquid level. The position 1 and position L specimens were fully immersed.

Figure 4. Experimental apparatus for open-circuit potential measurements.
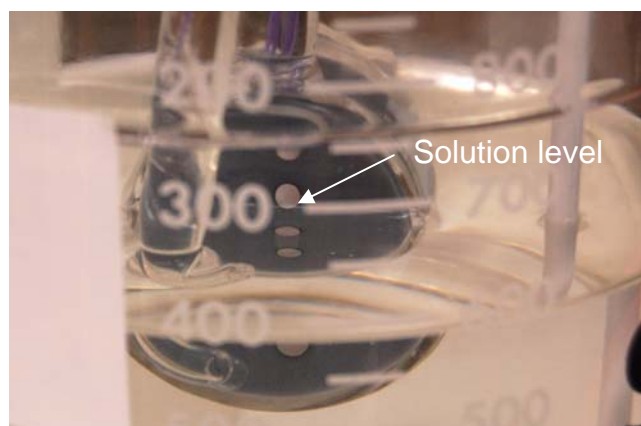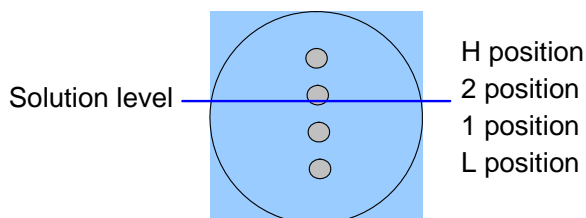

Figure 5. Diagram and photograph indicating location of solution level at lower edge of the position 2 specimen.

As soon as a specimen array was immersed to the desired depth in the test cell, the sequence of open-circuit potential measurements versus time was started. The open-circuit potentials were measured for up to 16 hours to ensure that steady-state potentials were obtained.   The Framework™ software recorded serially the potential of each of the eight individual small specimens in the two arrays under test. A single data point was the average potential from 10 samplings over approximately 1 second.

2.0.3 Experimental Variables

The salt solutions in this work were simple non-radioactive simulants of a dilute radioactive waste supernate made with reagent grade chemicals and distilled water.   The solution compositions were chosen to be mildly corrosive to carbon steel. Conditions that promote localized corrosion of carbon steel are (1) a high aggressive ion concentration (in this work nitrate) relative to a low protective nitrite concentration, (2) relatively high solution temperature and (3) low pH (< 12).   The solutions contained either 0.5 M sodium nitrate and 0.1 M sodium nitrite or a more dilute 0.05 M sodium nitrate and 0.01 sodium nitrite.   The pH levels were either in the 8.5 to 9 range or in the 11.5 to 12 range, obtained by selected ratios of sodium bicarbonate   and   sodium   carbonate.   The   lower   pH   range   was   obtained   with   a bicarbonate/carbonate ratio of 19, and the higher pH range with a ratio of 0.031. Testing was performed at room temperature (which varied from about 25 °C to 29 °C) and at 50 °C. The test solutions were either not aerated or sparged with air or nitrogen.

The initial test program was conceived as a two-level five-factor matrix consisting of the variables salt concentration, pH, temperature, bicarbonate/carbonate level, and aeration. This matrix was not carried out to completion, as discussed below, as the general insensitivity of the OCP value to specimen position became clear.

3.0 Results and Discussion

The focus of the experiments was the effect of specimen position with respect to the meniscus of a salt solution on the specimen's OCP.   More specifically the objective was to observe a significant difference in open-circuit potential between the meniscus-contact position 2 specimen and the bulk-liquid-contact positions 1 and L specimens. In general, the results obtained under various conditions revealed that there was no significant difference in potential. Figures 6 through 9 show potential versus time plots where the green data points and line represent the position 2 potentials and the purple and blue points and lines represent the positions 1 and L specimens. The steady-state potentials (at the end of the data collection) cluster in the rather narrow range of -170 to -220 mV with respect to the saturated calomel reference electrode. By contrast, a difference in potential of the order of 100 mV would be considered significant, and, in situations of dissimilar metal couple, sufficient to drive the galvanic corrosion of the active member of the couple.

Figure 6 shows the plots obtained at room temperature in 0.5 M nitrate and 0.1 M nitrite with a pH of 11.8 obtained with the high bicarbonate/carbonate composition. Remarkably consistent potential curves were recorded from all 4 specimen positions. It is notable in this figure that the potential curve of the position H specimen (red symbols and line) is nearly indistinguishable from that of the position 2 specimen. The stable position H curve indicates that the saturated calomel reference electrode was in electrochemical contact with the position H specimen, which as noted above is located about 0.3 in. above the test solution surface. This contact can arise only through a film of test solution extending up the specimen array from the meniscus to position H. By revealing this electrochemical connection, the results shown in Figure 6 support

the Hobbs-Wallace model of the development of pitting susceptibility through chemical changes within a thin film of solution above the meniscus.

The reproducibility of the open-circuit potential measurements is shown in Figure 7, where the potentials of the same specimens in the same test solution are plotted but with the specimen array having been repolished to expose fresh steel surfaces. The position L, 1, and 2 steady-state potentials are in the range -180 to -200 mV vs. SCE, similar to the prior measurements. The position H specimen potential is unstable, however; it appears that the reference electrode does not "see" the specimen, which suggests that there is no continuous electrolyte film extending up from the meniscus. The absence of the film may be due to particular surface condition left by the repolishing.
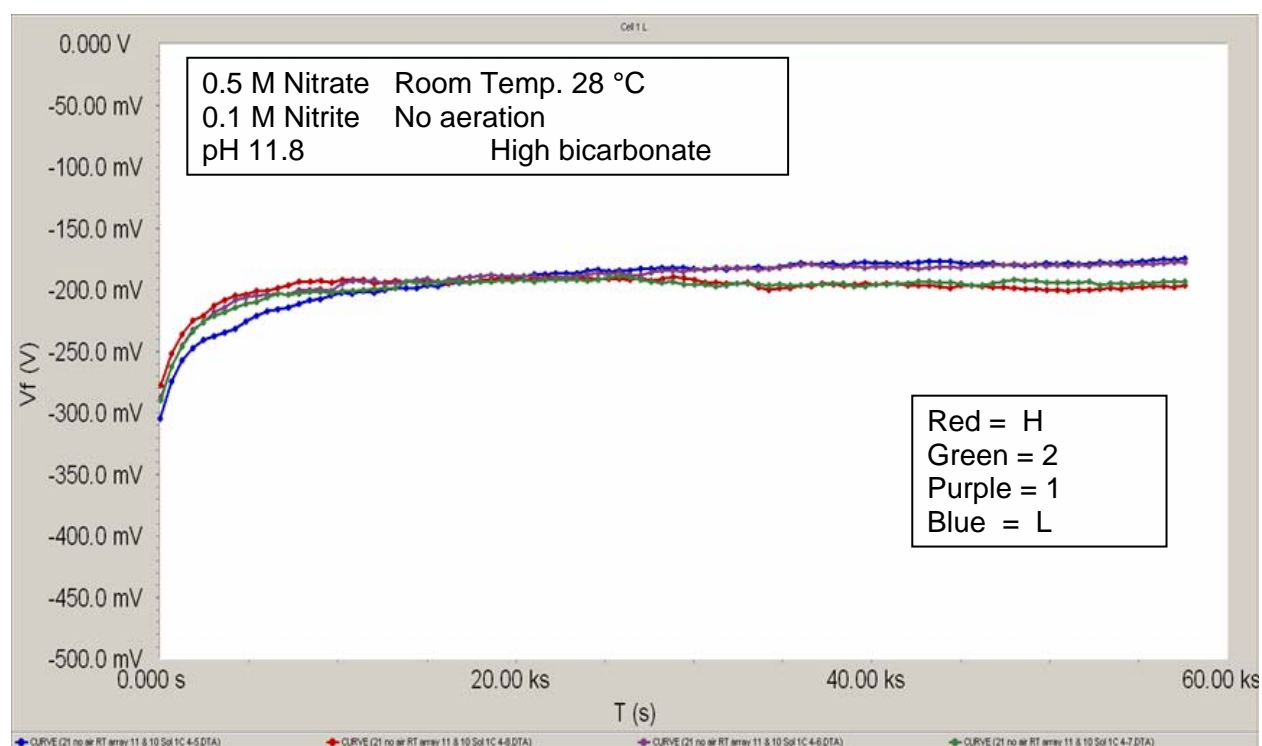

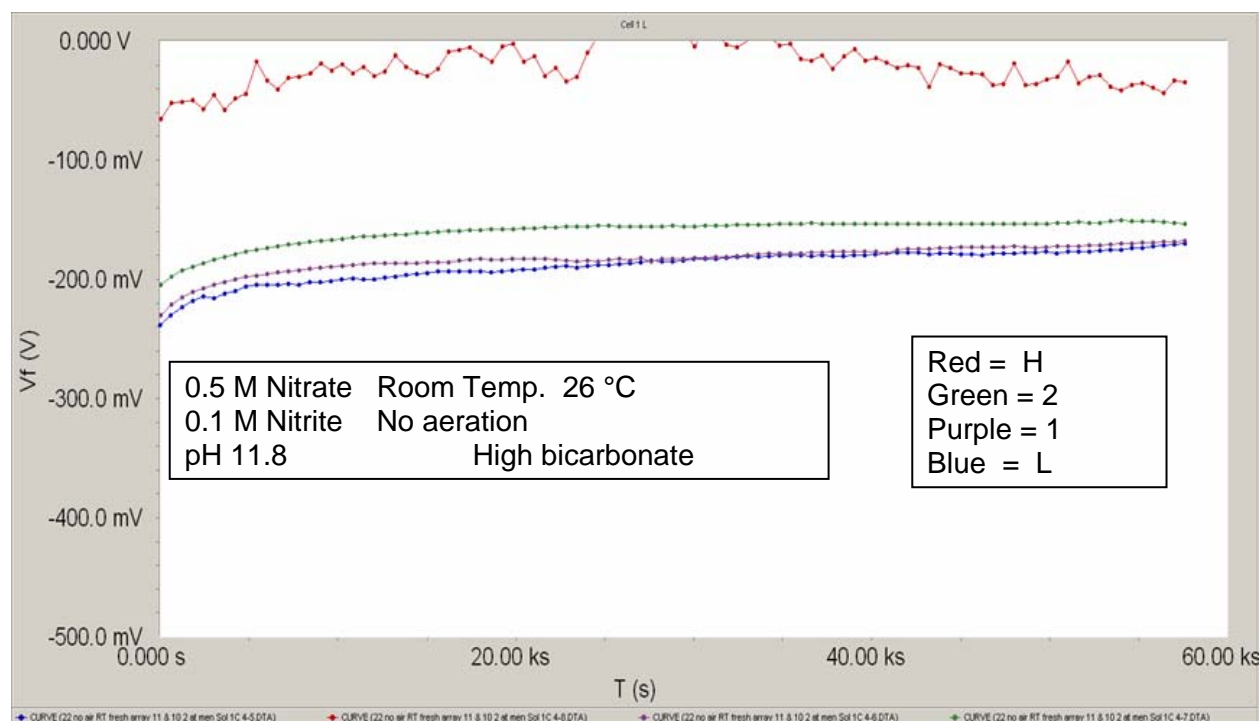Figure 6. Open-circuit potentials versus time at the noted test conditions.

Figure 7. Open-circuit potentials measured on the same specimen array and solution as in Figure 6, but with freshly repolished specimens.

The potentials in Figure 8 were recorded immediately after raising to 50 °C the specimens and solution used in Figure 7. The steady-state potential values for the position L, 1, and 2 specimens are little changed from those measured at 26 °C, which indicates the stability of the surface films on these specimens. Notably the potentiostat no longer recorded a potential (it was off-scale, high) for the position H specimen at the 50 °C temperature. The film that was apparently unstable at 26 °C became discontinuous due to evaporation.

A 50 °C test temperature does not preclude the existence of a conductive film to a specimen in position H, as can be seen in Figure 9, where potentials are plotted specimens contacted with a low-bicarbonate/carbonate version of the same solution as used in Figures 6, 7, and 8. The position H curve is stable with a steady-state value of about -150 mV vs. SCE, slightly positive with respect to the again consistent position L, 1, and 2 specimen values lying in the -200 to -250 mV vs. SCE range. The low-bicarbonate/carbonate solution had the same bicarbonate to carbonate ratio as the previous solutions but was only one-fifth as concentrated. The ratio yielded nearly the same pH (11.5). The lower concentration was tested to explore the impact of the lower concentration on the OCP. The results indicate no significant impact.
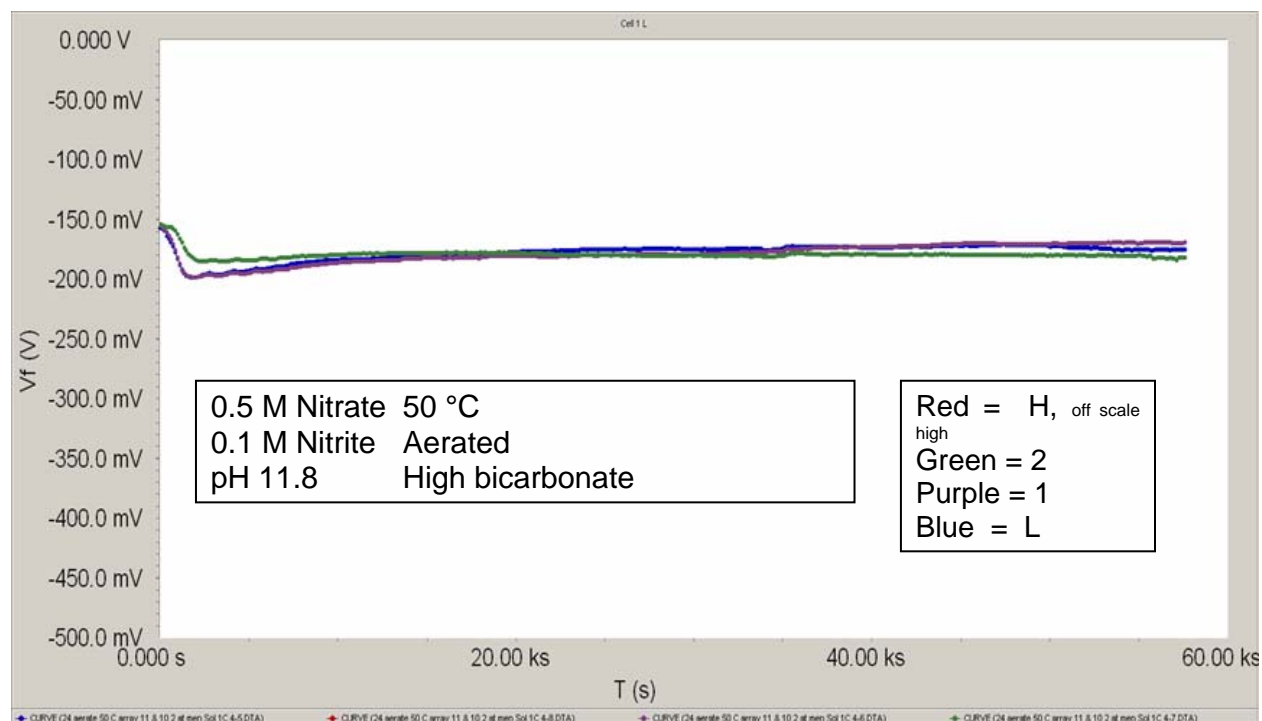
Figure 8. Open-circuit potentials measured on the same specimen array and solution as in Figure 7, with solution temperature raised to 50 °C.
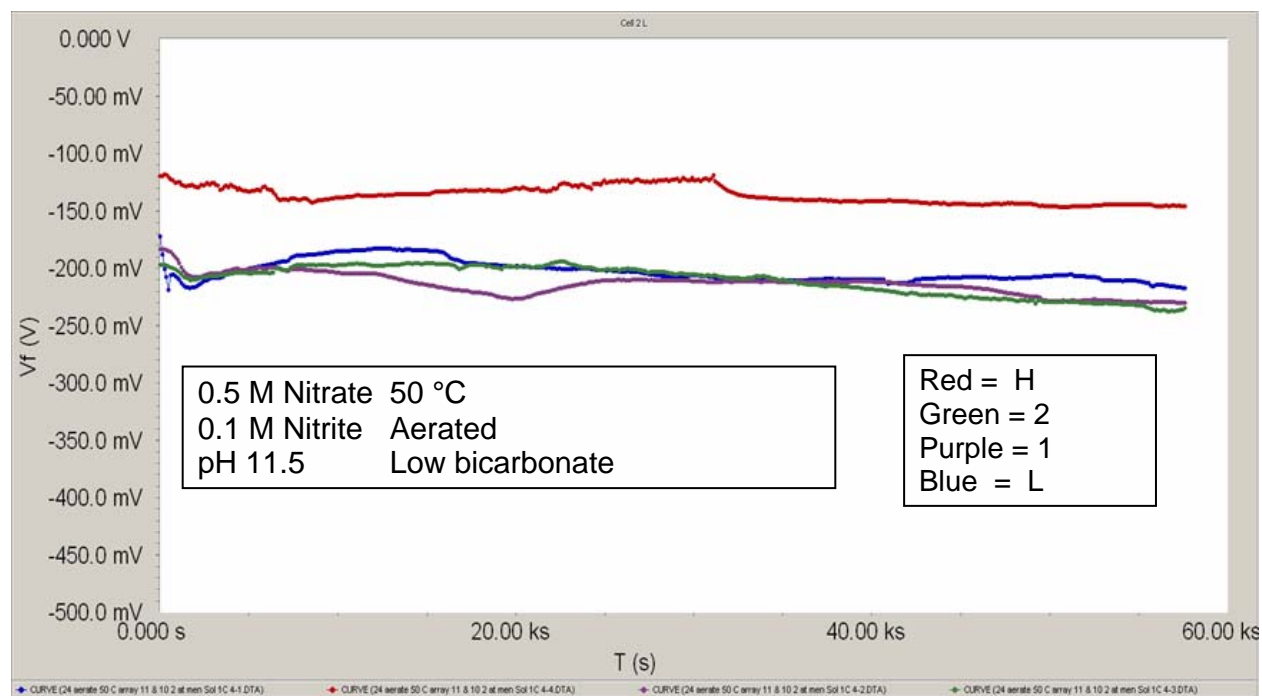

Figure 9. Open-circuit potentials measured at 50 °C in a low-bicarbonate/carbonate version of the solution in Figure 8.

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The internal consistency of OCP measurements from the various specimen positions was also seen in a test solution with a lower pH of 9.0 and lower nitrate/nitrite concentrations. Figure 10 shows room-temperature potential plots in a solution with 0.05 M nitrate and 0.01 M nitrite. The steady-state potentials are about 100 mV positive to those measured in the higher pH and more concentrated nitrate/nitrite solutions. As pH decreases, the potential shifts toward more positive values. They are closely grouped and again there is no significant difference between the meniscus position 2 specimen and the fully immersed position L and 1 specimens. The overall higher potentials are consistent with the expectation that the more dilute less alkaline solution should be more corrosive to carbon steel.
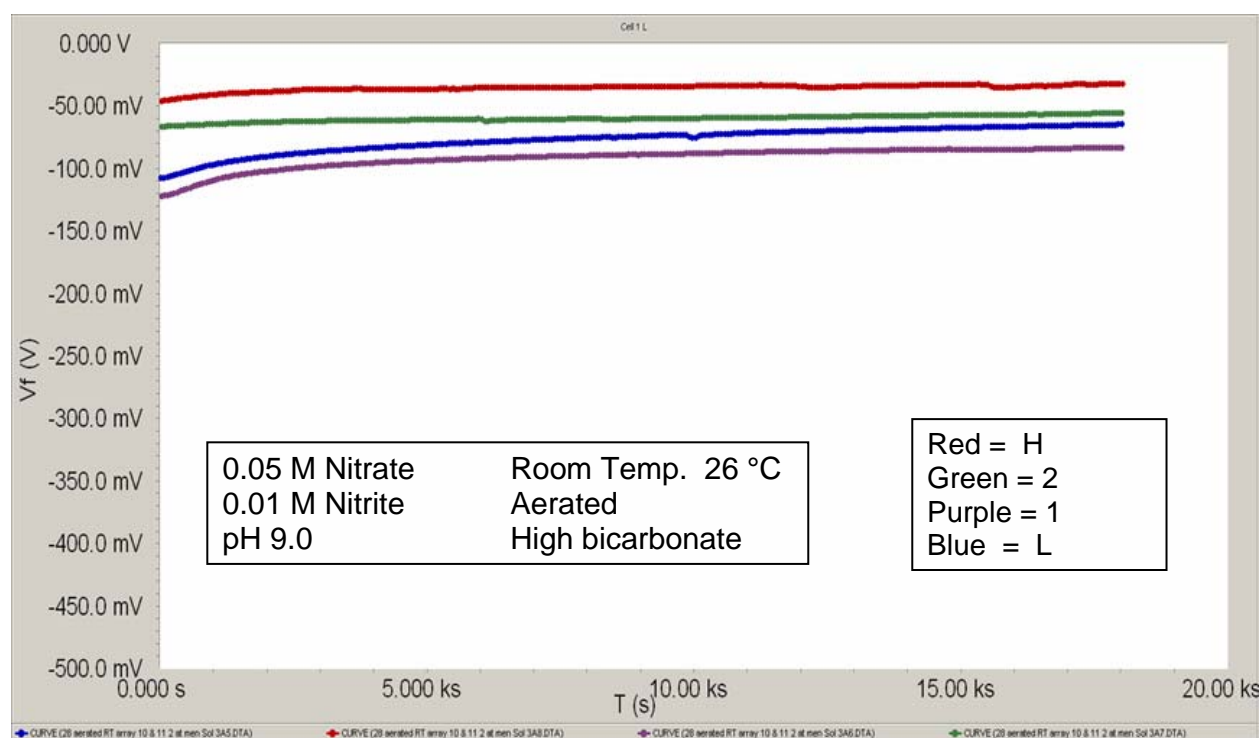

Figure 10. OCP measurements in the dilute nitrate/nitrite, low-pH solution at room temperature.

4.0 Conclusions

An experimental study was undertaken to investigate the corrosivity to carbon steel of the liquid-air interface of dilute simulated radioactive waste solutions. Open-circuit potentials were measured on ASTM A537 carbon steel specimens located slightly above, at, and below the liquid-air interface of simulated waste solutions. Arrays of 4 small (0.12-in.-diameter) specimens spaced about 0.3 in. apart were partially immersed so that one specimen touched the top of the meniscus of the test solution. Two specimens contacted the bulk liquid below the meniscus and one specimen was positioned in the vapor space above the meniscus. Measurements were carried out for up to 16 hours to ensure steady-state had been obtained. The results showed that there was no significant difference in open-circuit potentials between the meniscus-contact specimens and the bulk-liquid-contact specimens. With the measurement

technique employed, no difference was detected between the electrochemical conditions of the meniscus versus the bulk liquid. Consistent open-circuit potentials were measured on some of the vapor contact specimens, confirming the existence of a thin, conductive aqueous film extending above the meniscus.

5.0 References

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