Hanford Double-Shell Tank Testing Program - 15341

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ABSTRACT

The corrosion testing program and Hanford regularly tests waste chemistries to analyze threats and develop new corrosion chemistry guidelines. Over the past few years, the focus of testing has been on the threat of leaked wastes in Tank 241-AY-102 (AY-102). From the tests conducted to date, it appears that the potential waste compositions in the annulus of tank AY-102 do not show a propensity for localized corrosion or stress corrosion cracking. The threat of exterior corrosion from the liquid and moisture in the leak detection pit (LDP) is a potential concern that will continue to be evaluated in the coming year.

INTRODUCTION

With guidance from an independent panel of nationally recognized experts in waste chemistry and corrosion, the Hanford site maintains a corrosion testing program to protect double-shell tanks (DSTs) from the threats of corrosion and better understand how changes in waste chemistry impact corrosion mechanisms. Additional testing can develop new chemistry control limits that, while still acceptable, would require lower levels of caustic addition and thus minimize the total volume of waste that must be treated by the Waste Treatment and Immobilization Plant.

While past corrosion testing has focused on a general approach to improving our chemistry control limits, the detection of a primary liner leak in AY-102 in 2012 has impacted the prioritization of corrosion testing for the past few years. The focus of corrosion testing for 2014 and 2015 lies in two major areas:

1. Integrity testing of the AY-102 liner to determine if a threat exists from leaked waste
2. Integrity testing of exterior of the AY-102 liner due to LDP water intrusion that continually allows moisture to contact the external surface of the liner

The integrity of Tank AY-102 secondary liner is of great importance and was a top priority for testing in 2014 because of concerns of a breach in the secondary liner. The concerns with the liner focus on pitting corrosion and stress corrosion cracking from the waste and the waste reacted with refractory. Corrosion is possible on the internal surface of the secondary liner that is exposed to leaked waste, but there is also concern for corrosion on the external surface of the secondary liner that may be exposed to moisture from outside sources. With these concerns in mind, a full testing matrix was developed to address all potential waste chemistries on the secondary liner floor. These chemistries could vary depending on potential reactions of the leaked waste.

Historically, corrosion testing techniques for the Hanford site have focused primarily on cyclic-potentiodynamic polarization (CPP) measurements, slow strain rate (SSR) tests, and long-term (LT) tests to understand the effect of waste composition on corrosion. Improvements have been made in the past two years to add new testing protocols to improve the testing. The Tsujikawa-Hisamatsu Electrochemical (THE) method (ASTM G192) tests are being used to confirm CPP results and understand when pitting repassivates and whether pitting is a true threat to the liner. Also, a new wet simulant type, called a poultice, is being used to better represent Tank AY-102 annulus waste contact conditions. Changes have been made to the coupon samples as well. The steel is treated to represent the welding and flame straightening that occurred on the Tank AY-102 liner during construction. These additions and changes are improving the representativeness of the corrosion testing program.

TESTING TECHNIQUES

A variety of testing techniques were used during corrosion chemistry testing. CPP, THE, SSR, crack growth rate, LT, and LDP corrosion tests were conducted. A brief overview of the techniques are included below.

Cyclic Potentiodynamic Polarization

CPP testing is used to identify electrochemical parameters and the propensity for pitting to occur. CPP testing was performed in accordance with ASTM G61-86, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*. Prior to CPP testing, the open circuit potential (OCP) was monitored for 2 hours. Then the potential scan was started at -100 mV vs. OCP and a scan rate of 0.167 mV/s was used. The scan reversed at 1 V vs. saturated calomel electrode (SCE) or when the current reached a current density of 1 mA/cm^2. After completion of the test, the specimen was removed and analyzed for evidence of corrosion attack.

Tsujikawa Hisamatsu Electrochemical Test

THE test was conducted in accordance with ASTM G192-08, *Standard Test Method for Determining the Crevice Repassivation Potential of Corrosion-Resistant Alloys Using a Potentiodynamic-Galvanostatic-Potentiostatic Technique.* These tests were performed to determine the potential necessary to repassivate a growing pit. This test involves three main steps.

1. The sample is polarized starting at -100 mV vs. OCP and with a scan rate of 0.167 mV/s. The potential is increased until a preset current density is reached (typically 50 uA/cm^2).
2. The sample is held at the present current density for 4 hours to allow for pits to grow. During this step, the potential output is monitored.
3. The potential is controlled in a stepwise manner while the current output is monitored. In the stepwise manner, the potential is reduced by 10 mV and held for two hours, and then the potential is reduced again and held for two more hours, etc. The

protection potential is determined by located the highest potential at which the current does not increase during the two hour hold.

Slow Strain Rate Testing

The SSR tests were performed in accordance with ASTM G129-00, *Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking*. These tests were performed to evaluate the propensity for stress corrosion cracking in a given waste environment. The specimens were subjected to elongation at a constant extension rate of 2.54×10^{-6} cm/s (10^{-6} in./s). The specimen was loaded into the test cell, and the test simulant was added at the desired temperature. Tests were conducted at an applied potential and pulled to failure. After failure, the specimens were examined visually and by scanning electron microscopy.

Crack Growth Rate Testing

The crack growth rate tests are conducted by putting a specimen in an environment known to cause SCC (nitrate solution) to initiate crack growth and then introduce the simulant to be tested and see if the crack arrests or continues. For this testing, compact tension specimens were used and fatigue pre-cracked. The specimens were in a nitrate only solution at 50°C and cyclically loaded at 1 mHz, a K_{max} of 35.4 MPa-m$^{0.5}$ (35 ksi-in$^{0.5}$), and an R ratio of 0.8. After the crack is established in the nitrate solution, the test environment is introduced. The results are then compared to air fatigue crack growth rate curves to determine if the simulant showed a propensity to cause cracking.

Long-Term Testing

The LT tests are relatively simple experiments that expose a series of test specimens to an environment (like a waste simulant). The specimens were withdrawn at periodic intervals (weeks) and analyzed for weight loss and visual indications of corrosion.

Leak Detection Pit Testing

Vapor space, liquid-air interface (LAI), and immersion tests were conducted to determine susceptibility of tank steel to corrode in simulants representing LDP and ground water (GW). For the partial immersion (LAI) and full immersion tests, rectangular specimens were immersed at approximately 50% into solutions or fully immersed in the solutions. The specimens were analyzed visually and for weight loss after exposure to the simulants for every month or every two months. For the vapor space testing, three different vapor space levels were represented. Level 1 contained specimens that were hung about 2.54 cm (1 in.) above the liquid simulant level and dipped in the simulant once every two weeks. Level 2 contained specimens that were dipped in waste at the start of the test and then hung approximately 0.457 m (18 in.) above the liquid simulant for the duration. Level 3 contained specimens that were suspended approximately 0.914 m (36 in.) above the liquid waste simulant.

TEST SPECIMENS AND SIMULANTS

Test specimens for tank AY-102 were fabricated from Association of American Railroads Tank Car (TC) 128 Grade B steel, which is the best representative steel for ASTM A515, Grade 60 steel of which tank AY-102 was constructed. Figure 1 shows the microstructure of one of the TC 128 samples used for testing tank AY-102. In contrast, a micrograph of ASTM A537 is shown in Figure 2. This was the steel used in DST corrosion testing prior to 2006. The most significant difference between the two steels is the presence of the banded microstructure with pearlite in the TC 128 steel. The differences in microstructure can impact corrosion testing results, so using the TC 128 steel improves the representativeness of the corrosion testing.

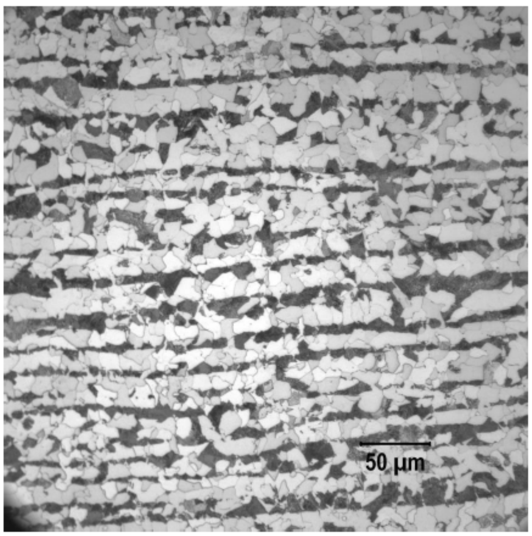

Fig. 1. Micrograph of TC 128 Grade B Steel Microstructure.

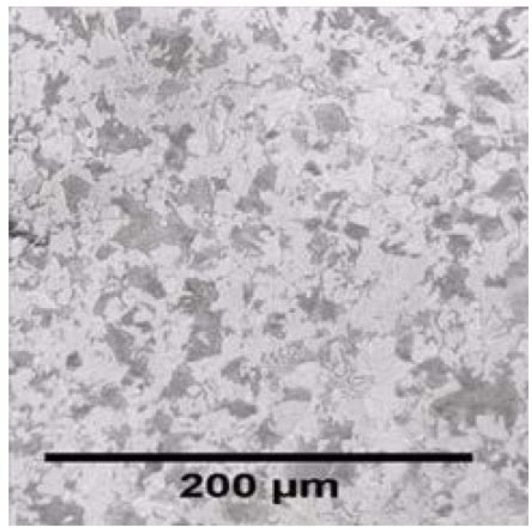

Fig. 2. Micrograph of ASTM A537 Class 2 Steel Microstructure [1].

The steel specimens for testing were used as-received, and some of the steel was welded to mimic the tank AY-102 field welds.

In addition, two heat treatments were performed on the as-received and welded metal samples. The heat treatments were intended to mimic the effects of flame-straightening of the secondary liner bulges during construction and were conducted in two ways:

1. Heated at 649°C (1200°F) for 1 hour followed by a water quench
2. Heated at 871°C (1600°F) for 1 hour followed by a water quench

A variety of simulants were needed to represent the range of potential chemical and physical environments that may be present on the tank AY-102 annulus floor. They fall into two categories—liquid waste and semi-solid waste.

Liquid waste simulants, their descriptions, and their simulant identification numbers are introduced in Table I. The bullets below describe the groups of liquid simulants that were tested:

- Group 1: compositions based on 100% supernatant, 100% interstitial liquid, and 50 vol% mixture of supernatant and interstitial liquid.
- Group 2: compositions based on Group 1 simulants that have been equilibrated with CO_2 in air. Within Group 2, there are simulants that have fully (Group 2A) and partially (Group 2) equilibrated with CO_2 in air. These compositions came from thermodynamic modeling [2].
- Group 3: compositions based on Group 1 simulants that have evaporated and equilibrated with CO_2 in air. Within Group 3, there are simulants that have fully (Group 3A) and partially (Group 3) equilibrated with CO_2 in air.
- Refractory contact simulants- In addition to the annulus waste being created from variations in equilibration and evaporation, there is also the possibility for the waste to react with the refractory as it flows into the annulus. The simulant formations were created by thermodynamic modeling results for AY-102 waste reacted with refractory. After the refractory reactions, the simulants were also modeled to evaporated and react with CO_2 in air.

In addition to liquid waste simulants, a semi-solid (poultice) simulant was used for corrosion testing. The waste on the annulus floor visually appears as a semi-solid waste, so this simulant was created to represent this observation. The simulant was created using the dry sample results of the 2012 annulus sampling event. The liquid portion of the poultice was created using thermodynamic modeling. The poultices were created with varying degrees of wetness to simulant variations in the annulus waste.

Additional simulants were created to represent the ground water at the Hanford site and the LDP water. These simulants were developed from LDP sample analysis and were tested at 45 °C to represent the temperature of the secondary liner. These simulants were intended to represent the liquid or moisture in contact with the exterior of the secondary liner.

TESTING AND RESULTS

Cyclic Potentiodynamic Polarization Testing

CPP testing was performed with liquid waste simulants from all three groups and refractory contact simulants on as-received TC 128 samples at 50°C and/or 77°C. An example of CPP results for a simulant that did not exhibit corrosion is shown in Figure 2, and an example of a result exhibiting corrosion is shown in Figure 3. Some of the CPP results did not exhibit such clear distinction between pitting and non-pitting, and warranted a “mixed hysteresis” classification. An example of this result is shown in Figure 4, and shows a scan that had both a negative and then positive hysteresis. Overall, a number of simulants, particularly the aggressive Groups 3 and 3A simulants, showed a propensity for corrosion with a positive or mixed hysteresis. The complete results and descriptions of the simulants are summarized in

Table I. In order to assess the practical pitting threat of the simulants that exhibited pitting behavior in the CPP tests, further testing with THE and LT tests were conducted.

CPP tests in simulant 15 were conducted on the two heat-treated steels (649 °C and 871 °C), and indicated similar results to the non-heat-treated steels. Additional CPP tests will be tested with heat-treated samples in 2015.

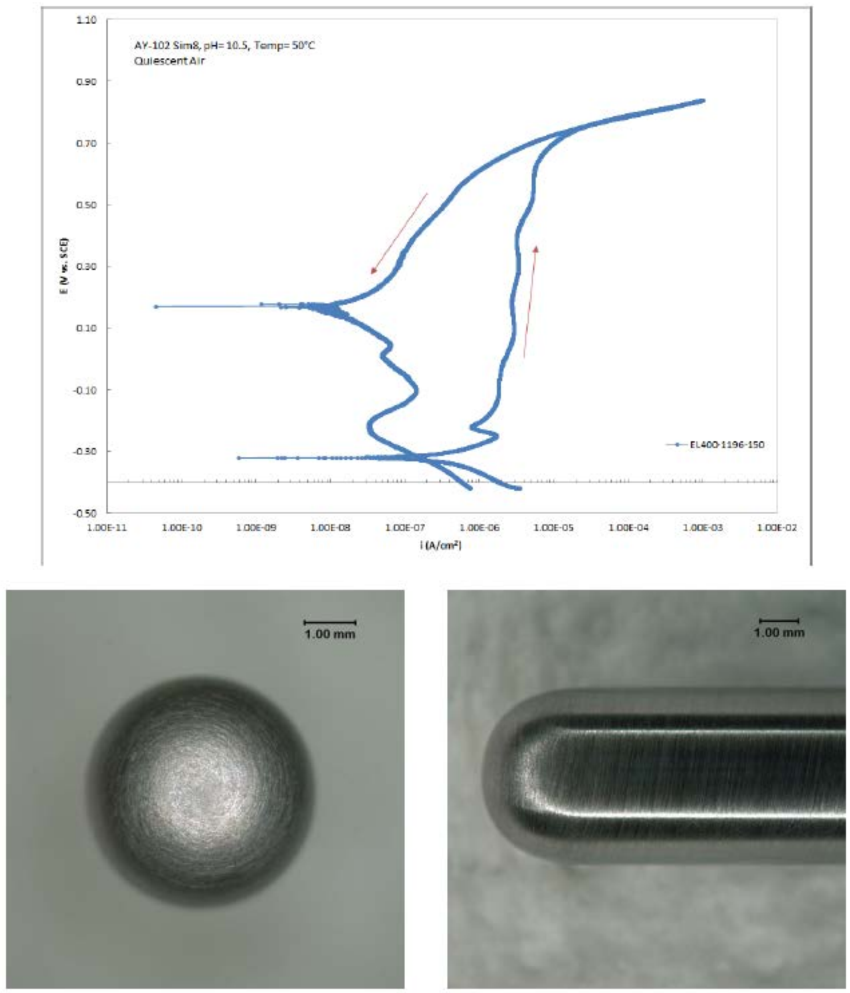

Fig. 3. CPP Results Showing Negative Hysteresis and No Pitting (Simulant 8).

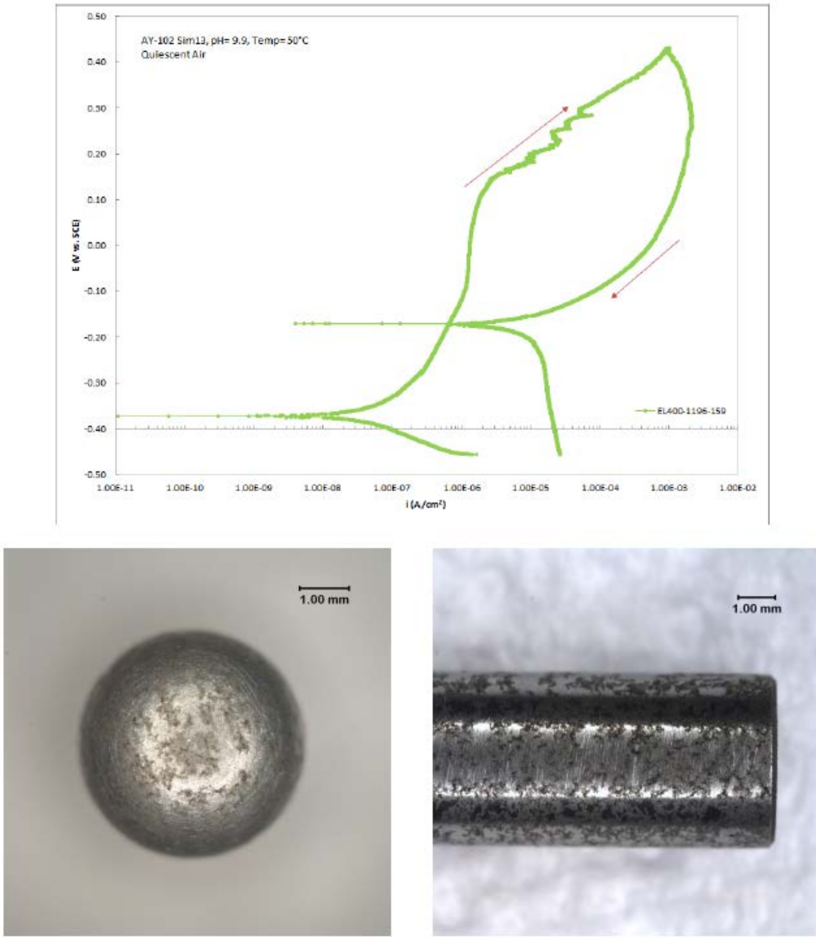

Fig. 4. CPP Results Showing Positive Hysteresis and Severe Pitting (Simulant 13).

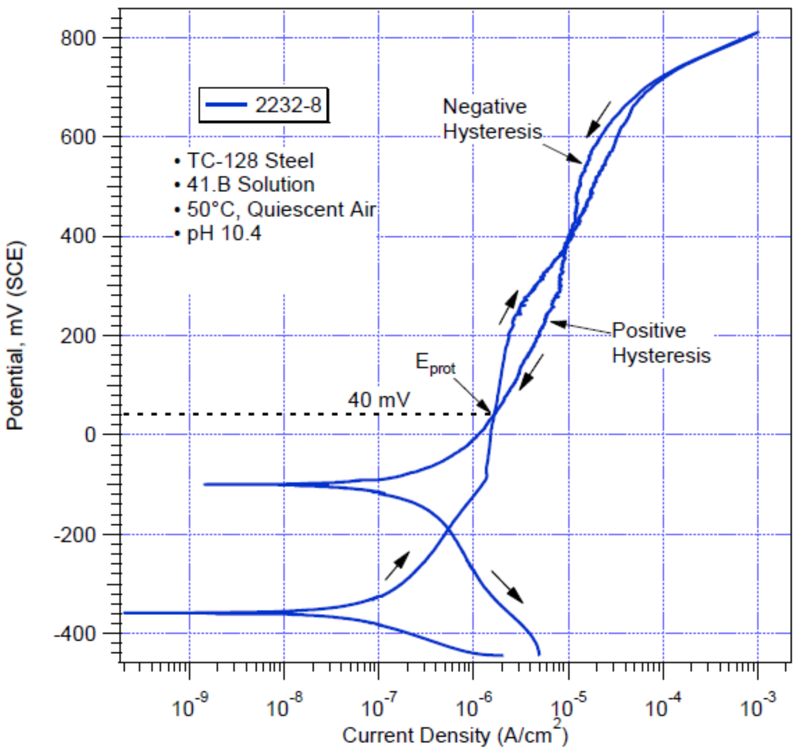

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Fig. 5. CPP Scan Showing Mixed Hysteresis (Simulant 15).

TABLE I. Results of CPP tests

Simulant Number	Group	Solution	Temperature (°C)	Visual Pitting	Hysteresis	pH	Comments
1	1	100%S, no CO_2, no evap,	50 77	No Yes	Negative Negative	14+ 14+	Slight precipitation Slight precipitation, small pits
2	1	100%IL, no CO_2, no evap	50 77	No Yes	Negative Negative	13.4 13.4	Slight precipitation Slight precipitation, small pits
3	1	50/50, no CO_2, no evap	77	No	Negative	13.9	Precipitation
4	2	100%S, partial CO_2, no evap	77	Yes	Negative	11.3	Minor pitting
5	2	100%IL, partial CO_2, no evap	77	Yes	Negative	11.5	Minor pitting
6	2	50/50, partial CO_2, no evap	77	Yes	Negative	11.3	Minor pitting

Simulant Number	Group	Solution	Temperature (°C)	Visual Pitting	Hysteresis	pH	Comments
7	2A	100%S, full CO_2, no evap	50 77	Yes Yes	Negative Positive	10.7 10.7	Precipitation, small pits Precipitation, visible pitting
8	2A	100%IL, full CO_2, no evap	50 77	No Yes	Negative Negative	10.5 10.5	 Small pits
9	2A	50/50, full CO_2, evap	77	Yes	Negative	10.3	Minor pitting
10	3	100%S, partial CO_2, evap	50	Yes	Mixed	11.1	Small pits
12	3	50/50, partial CO_2, evap	50	Yes	Mixed	11.1	Small pits, slight precipitation
13	3A	100%S, full CO_2, evap	50	Yes	Mixed	9.8	Severe pitting, precipitation
14	3A	100%IL, full CO_2, evap	50 77	No No	Negative Negative	10.1 10.1	precipitation
15	3A	50/50, full CO_2, evap	50	Yes	Mixed	10.2	Slight precipitation, small pits
R-7	NA	Refractory contacted, 100% IL, full CO_2, evap	50	Yes	Mixed	9.7	Small pits
R-9	NA	Refractory contacted, 100% IL, full CO_2, evap	50	No	Negative	9.8	Some precipitation
R-11	NA	Refractory contacted, 100% S, full CO_2, no evap	50	Yes	Mixed	9.5	Minor pitting

Where S is supernatant, IL is interstitial liquid, 50/50 is 50vol% S and 50vol% IL, and evap is evaporation

Tsujikawa Hisamatsu Electrochemical Testing

The THE tests showed that when there was a negative or mixed hysteresis during CPP, the protection potential where the steel would repassivate is very positive. An example of THE results is shown in Figure 5. It appears in this test that the pit growth was not stable and after the first reduction in potential, the current began to decrease which indicates that the pits have repassivated. The protection potential was located at around 522 mV vs. SCE. This result was similar to the other tests, and all the results are summarized in Table II.

The protection potentials determined by the THE tests are much more positive than those determined by the CPP tests, so this gives confidence that the margin of protection against pitting is much greater than suggested from the CPP results. These results will be explored further in 2015.

Additionally, THE testing using refractory simulants will be conducted in 2015.

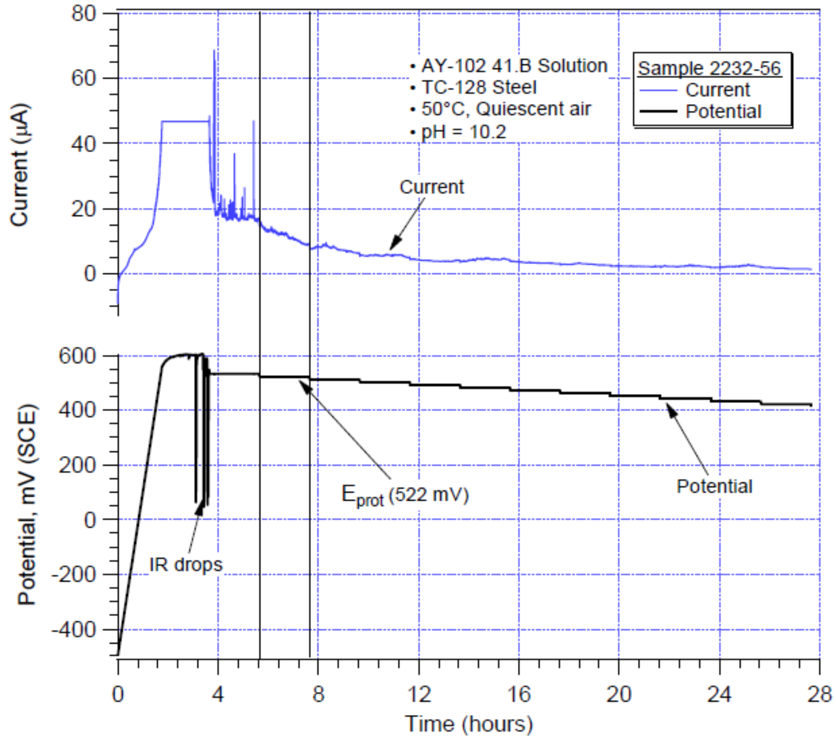

Fig. 6. THE Test for Simulant 15.

TABLE II. Results of THE tests in comparison to CPP results

Simulant Number	Temperature (°C)	Hysteresis Type	E_{prot} (mV vs. SCE)	
			CPP	THE
1	77	Negative	Undefined	340*
2	77	Negative	Undefined	≥530
4	77	Negative	Undefined	≥568
5	77	Negative	Undefined	≥585
7	77	Positive	-81	520
8	77	Negative	Undefined	≥680
9	77	Negative	Undefined	665
10	50	Mixed	250	633
13	50	Mixed	26	≥733
15	50	Mixed	40	522

*Uncertain if pitting occurred.

Long-Term Testing

Tank AY-102 LT tests are currently being conducted with both liquid simulants and semi-solid poultice. Liquid simulant tests were performed on TC 128 steel specimens. The parameters being monitored for liquid simulant testing, in addition to weight loss, are shown below in Table III.

TABLE III. Long-term immersion tests in AY-102 liquid simulants

LT Set No.	Potential	Immersion	Monitored Parameters	Temperature (°C)	Simulants
1	Potentiostatic control	Partial	Current	77	1,2,8,9
2	Open circuit	Partial	OCP	77	1,2,8,9
3	Open circuit	Full	OCP, Polarization Resistance	77	1,2,8,9
4	Open circuit	Full	OCP	77 50	3,4,5,6,7 7,10,12,13,15

The semi-solid poultice tests used adjusted simulant compositions. Poultice testing is underway, and multiple simulants were used to evaluate the effects of varying pH, composition, and amount of liquid. The tests were conducted at 50 °C with TC 128 steel specimens. Preliminary results indicate that the specimens show minimal weight loss and no evidence of pitting. Testing will continue in 2015.

Slow Strain Rate Testing

SSR tests were performed for all of the AY-102 liquid simulants and the poultice simulants discussed in the LT tests. These tests were done at 50 °C and/or 70 °C with as-recieved TC 128 steel. All of the tests resulted in ductile fracture except one. A simplified simulant 15 showed secondary cracking on the specimen with grain facets consistent with intergranular cracking. This sample is shown in Figure 6.

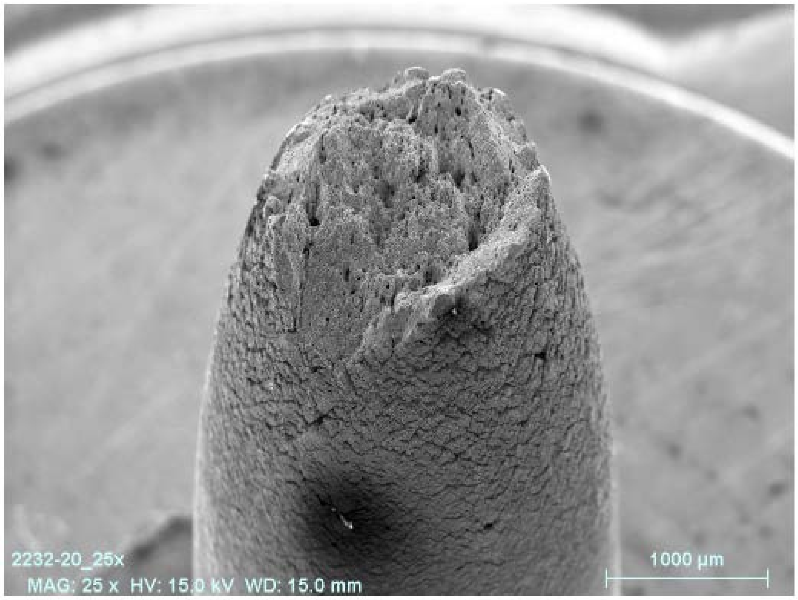

Fig. 7. Image of SSR Specimen from Test in Simplified Simulant 15.

Additional SSR tests were conducted with heat-treated TC 128 steel (649 °C and 871 °C) in simulant 15 at 77 °C, and showed ductile fracture and no sign of SCC.

SSR test results from the refractory contacted simulants were not available at the time of this draft. Further SSR testing on refractory contacted simulants using notched welded and heat-treated samples are planned for 2015.

Crack Growth Rate Testing

Because the simplified simulant 15 showed potential for cracking during SSR testing, additional testing was conducted with a crack growth rate test at 50 °C, R-ratio of 0.8, simulant 15, and as-received and both heat-treated steels (649 °C and 871 °C). The results showed that the heat-treated steels were not more susceptible to SCC than the as-received steels. A sample of the crack length vs. cycles plot of the 649 °C heat-treated steel in Simulant 15 is shown below in Figure 7. The orange line is the nitrate solution to initiate crack growth, and the blue line is the tested simulant. By looking at the blue line, the crack did not grow significantly in the simulant. Additional testing was conducted at an R-ratio of 0.9, which was expected to increase crack growth, and showed almost no variation in crack growth.

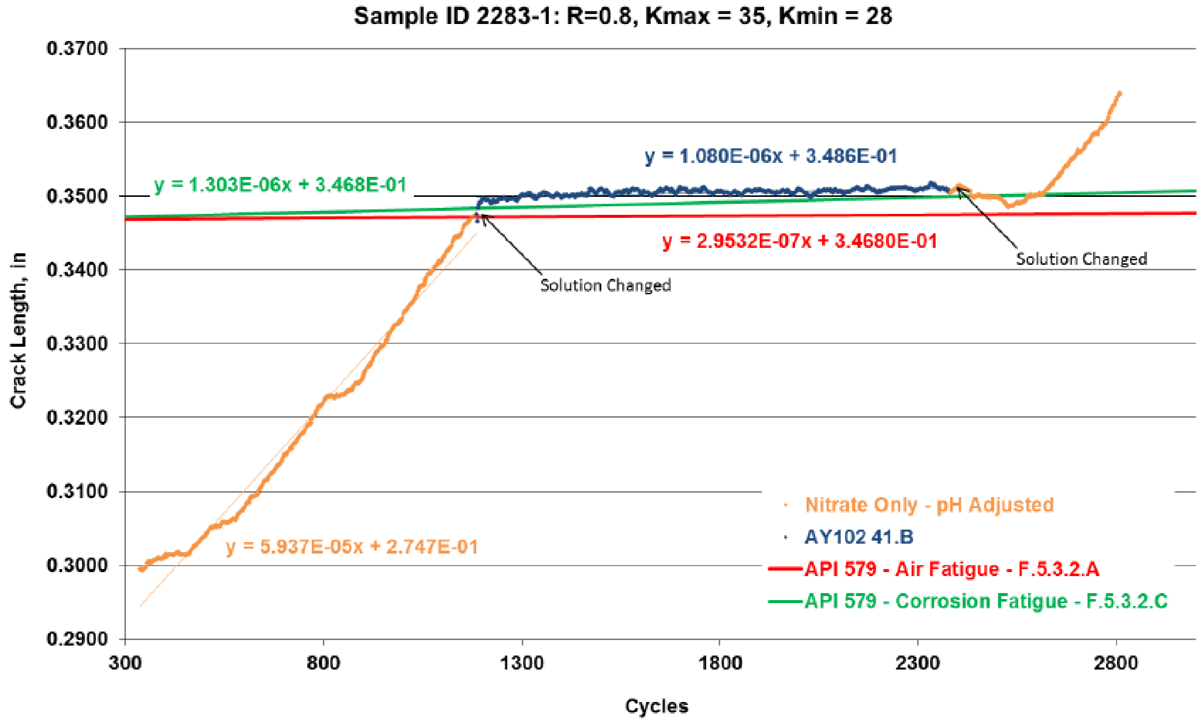

Fig. 8. Crack length vs. cycles for simulant 15 and heat-treated steel.

The method of crack growth rate testing will be explored further in 2015 with known aggressive solutions to show that the method will detect cracking. Additional crack testing is planned on welded and heat-treated steels.

Leak Detection Pit Testing

The LDP and GW testing was conducted at 45 °C with as-received TC 128 steel. During the LDP and GW partial and total immersion tests, aggressive corrosion behavior was observed on the specimens. Table IV summarizes the results, and Figure 8 shows an example of the corrosion due to LDP water when 50% submerged for 2 months.

TABLE IV. Partial and full immersion test results with leak detection pit simulants

Simulants	Months Exposure					
	Two months			Four months		
	weight loss (g)	Corrosion rate (mpy)	Pitting	weight loss (g)	Corrosion rate (mpy)	Pitting
Solution 12 LDP simulant 50% immersion	0.5797	5.34	Depths 0.1-3.1 mils, large pits around waterline	2.2387	10.3	Depths 1.1-5.0 mils, large pits on around waterline
Solution 13 LDP simulant 100% immersion	0.9999	9.2	Depths 0.6-2.6 mils, broad pits	2.3817	10.96	Depths 0.9-8.6 mils, larges pits on all of sample
Solution 14 GW simulant 50% immersion	1.0397	9.57	Depths 0.6-3.6 mils, strong corrosion by waterline	2.3651	10.88	Depths 0.5-7.8 mils, large pits around waterline
Solution 15 GW simulant 100% immersion	1.0780	9.92	Depths 1.1-1.8 mils, broad pits	2.5246	11.62	Depths 0.6-6.0 mils, broad pits

Fig. 9. Steel Specimen after Two Months 50% Submerged in Leak Detection Pit Water.

LDP and GW vapor space corrosion testing was conducted for 4 months as well, and the samples were pulled every month. Vapor space corrosion above the LAI was highest for the coupons above GW simulant. Specifically, those coupons that were located right next to the simulant solutions and experienced wet and dry cycles had the highest rates of corrosion. The 4 month specimens will be examined in the future. A summary of the results is shown in Table V. [2]

TABLE V. Vapor space weight loss coupons and different levels

Level in vessel	Time exposure (month)	Weight loss (g)	
		LDP	GW
High (Level 3)	1	0.0174	0.0155
High (Level 3)	2	0.0111	0.0147
High (Level 3)	3	0.0110	0.0439
High (Level 3)	4	NA	NA
Middle (Level 2)	1	0.0109	0.0311
Middle (Level 2)	2	0.0062	0.0147
Middle (Level 2)	3	0.0061	0.0137
Middle (Level 2)	4	NA	NA
Low (Level 1)	1	0.0341	0.0101
Low (Level 1)	2	0.0477	0.0121
Low (Level 1)	3	0.0045	0.0065
Low (Level 1)	4	NA	NA

CONCLUSIONS

The testing for AY-102 was conducted to evaluate the risk of two threats to the secondary liner. The first threat is the leaked waste on the annulus floor. The chemical composition of the tank waste could be altered by evaporation, reaction with CO_2 in air, and reaction with the refractory. The CPP testing showed that there was a propensity for pitting in those aggressive simulants that included equilibration with CO_2 in air and evaporation; however, the THE testing showed that the repassivation potential in these situations is much more positive than the corrosion potential, indicating that tested AY-102 leaked waste compositions are not likely to cause localized corrosion. Heat treatment of the steel did not alter the CPP behavior significantly. Crack testing to date also indicated that the possible AY-102 leaked wastes are not likely to cause SCC. Heat treatment of the steel did not alter the susceptibility to cracking.

The second threat is the liquid in the LDP and the consequent moisture in contact with the external surface of the secondary liner. Testing to date indicates that there is a propensity for corrosion in the liquid and vapor spaces of LDP and GW simulants. Additional testing is underway.

Testing will continue in 2015 to evaluate the LDP moisture threat and the threat of leaked waste reacted with refractory. Specimens will include welded and heat-treated samples, and testing will involve CPP, THE, LT, SSR, and crack growth. Simulants will focus on refractory-contact simulants and actual waste samples from the LDP.

The results of corrosion testing reinforce the importance of continued diligence in understanding how the waste chemistries affect the integrity of the steel tank liners. When new chemistries or environments arise, it is important to test and understand the impacts of these new environments because a breach of the primary or secondary containment could have long-term consequences for the public and environment. The waste tanks at the Hanford site need to remain in sound condition until the WTP can process all of the waste, so maintaining tank integrity is imperative to the Hanford site mission.

REFERENCES

1. K. D. BOOMER, RPP-RPT-56141, “FY2013 DNV DST and SST Corrosion and Stress Corrosion Cracking Testing Report,” Revision 0, Washington River Protection Solutions, LLC, Richland, Washington (2013).
2. B. J. WIERSMA, K, HICKS, and R. FUENTES, SRNL-STI-2014-00616, “Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2014,” Revision 0, Savannah River National Laboratory, Aiken, South Carolina (2014).