

**Corrosion Susceptibility of Secondary Liner Carbon Steel of Hanford Double-Shell Tanks
Exposed to Supernatant Waste and Ground Water**

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ABSTRACT

The primary liner failure event of double-shell Tank 241-AY-102 observed in 2012 resulted in direct contact of tank waste to the inside surface of the secondary liner. The potential also exists for ground water to contact the outside surfaces of all double-shell tank secondary liners. The objective of this work was to evaluate the corrosion susceptibility of the secondary liner in contact with tank waste and ground water under double-shell tank environmental conditions. Crevice corrosion assemblies that sandwiched an A515 Grade 60 carbon steel coupon between two blocks of refractory material were used to test refractory and steel interactions when exposed to tank supernatant waste. During the year-long test in tank waste, corrosion potential and corrosion rates were monitored periodically and were compared to those obtained from a non-creviced coupon exposed to the same conditions. Crevice corrosion assemblies that sandwiched the two ends of carbon steel coupons between concrete were submerged in ground water up to 28 months to test corrosion susceptibility in contact with ground water along with coupons set above the water surface to test steel corrosion in contact with moisture. Results showed that the contact of tank waste with double-shell tank secondary liner steel creviced with refractory material over 12 months had an insignificant effect on the corrosion susceptibility of the secondary liner. However, the secondary liner material was much more susceptible to corrosion under exposure to ground water and moisture compared to the same material exposed to tank waste. The severity of corrosion under exposure to ground water, especially localized corrosion, increased with exposure time. More corrosion mechanisms, such as pitting corrosion inside the steel-concrete crevice, were evident on the 28-month exposure coupon. The alkaline condition and the presence of nitrite as a corrosion inhibitor in the tank waste may have contributed to the high corrosion resistance of the secondary liner in contact with tank waste. The absorption of carbon dioxide from the atmosphere in the ground water over extended exposure duration may have contributed to the high localized corrosion rate in the materials that were in contact with ground water.

Key words: carbon steel, secondary liner, double-shell tank, supernatant waste, ground water

INTRODUCTION

The nuclear waste at the Hanford Site is currently stored in 131 single-shell tanks and 27 double-shell tanks (DSTs). When the primary liner in Tank 241-AY-102 (AY-102) failed, the secondary liner became the principal barrier of the tank, and leaked waste interacted with the refractory foundation beneath the primary liner.¹ The high caustic concentration of the tank waste could have reacted with the tank refractory, lowering the pH and leading to increased corrosion rates of the annulus tank steel. The extent of change would depend on the waste volume to surface area ratio and other factors. In addition, the outside surface of the secondary liner of this tank, as well as all other DSTs, is subject to corrosion attack from percolating water in the vadose zone.² Current testing and discussions with the Tank Integrity Expert Panel have also brought up concerns about ground water and its impact on corrosion of the secondary liners, which is applicable to a number of DSTs. For example, recent ultrasonic examination of the annulus floor of Tank 241-AP-102 has shown excessive secondary liner thinning in some areas near or above channels in the concrete base.³ The recent events in AY-102 that resulted in direct contact of tank waste to the inside surface of the secondary liner and the prevalence of ground water contact to the outside surfaces of all DST secondary liners led to the need to test the corrosion susceptibility in these environments. To better understand these corrosion risks, work was performed at the laboratory to simulate tank steel exposed to refractory wetted with tank waste as well as to simulate tank steel exposed to ground water in the tank's concrete base and leak detection channels.

EXPERIMENTAL METHODS

Crevice Corrosion Assemblies Exposed to Sampled Supernatant Waste

An A515 Grade 60 carbon steel coupon polished up to 600 grit with sand paper was sandwiched between two blocks of refractory material as shown in Figure 1 to form the crevice corrosion assembly, which simulated the contact of the refractory to the carbon steel secondary liner exposed to large amount of tank waste.

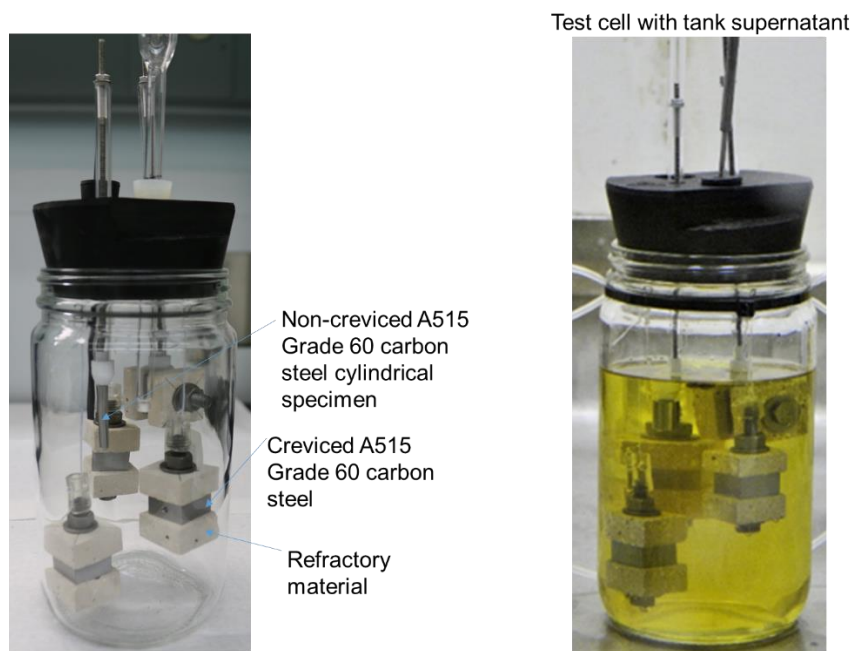


Figure 1: Crevice corrosion assemblies used to test refractory and steel interactions under exposure to tank supernatant waste

The refractory material mainly contained aluminum silicate, calcium carbonate, perlite, crystalline silica, and aluminum oxide. The crevice assemblies were constructed by first wrapping the bolt with polytetrafluoroethylene tape to ensure there was no metal contact to the steel coupon. The bolt was then inserted into a stack created with a washer, refractory block, the steel coupon, a second refractory block, and another washer; a nut was then used to secure the stack to finger tight. In total, four crevice assemblies were made. Three assemblies were suspended in a glass jar using polytetrafluoroethylene tubing, and the fourth assembly was attached to a glass electrode holder to make the electrical connection for electrochemical measurement. A cylindrical electrode made from A515 Grade 60 carbon steel without any crevice former was also incorporated into the jar using a second glass electrode holder for comparison.

Tank supernatant waste was added to the glass jar with the four crevice assemblies and the non-creviced carbon steel electrode. Selected chemical analysis results, showing several constituents in the tank waste known to affect corrosion, are provided in Table 1. The pH of this liquid waste was about 13.8 calculated from the concentration of hydroxide. The glass jar was capped with a large rubber stopper, and a long glass reflux tube was inserted into a hole in the stopper to allow ambient air to interact with the waste during the testing. Because the tank waste was radioactive mainly from alpha and beta emitters, the test was conducted in a hot cell. The actual dose rate on the coupon surface was not measured. It is uncertain if radiolysis products could form on coupon surface. The jar was left in the hot cell at ambient temperature ($\sim 28^\circ\text{C}$) for 1 yr. Corrosion potential and linear polarization resistance (LPR) measurements were conducted periodically throughout the 1-yr experiment. The LPR analysis was performed by scanning through the open circuit potential (OCP) within a 50-mV range (± 25 mV) with a scanning rate of 0.167 mV/S. These LPR runs were used to obtain the corrosion rate averaged over the entire surface area after a 1-hr time delay. A crevice assembly was removed from the solution after 2, 4, 6, and 12 months. The exposed coupons were cleaned and analyzed by optical and scanning electron microscopy (SEM). The cleaning consisted of rubbing with a damp paper tissue to remove loose residue, followed by wiping with isopropyl alcohol.

Table 1
Concentration of Corrosion-Relevant Species in Tank Supernatant Waste

Analyte	Cl^-	NO_2^-	NO_3^-	OH^-	F^-	Na^+	Aluminate	Total inorganic carbon	Total organic carbon
Concentration, M	0.026	0.82	0.74	0.68	0.072	4.2	0.18	8,720 mg/L	868 mg/L

Ground Water Exposure Testing

To represent the secondary liner resting on top of the concrete base of a tank, an archived concrete tank wall core sample previously drilled from a tank at Hanford was used. The concrete sample was cut into small rectangular pieces using a low-speed diamond saw. These concrete pieces were then stacked with A515 Grade 60 carbon steel flat bar coupons, arranged so that half of the coupons were submerged in ground water, and the remaining coupons were positioned a few millimeters above the water surface as shown in Figure 2. The dimensions of the coupons were about 7.6 cm $\times$ 1.3 cm $\times$ 0.16 cm with a 0.48-cm diameter hole at one end of the coupon. The surface area of the coupon was about 22 cm². Archived ground water collected in the leak detection pit of Tank AY-102 was used to fill the test cell. Table 2 shows the concentration of detectable chemical species in the two water samples used to composite the ground water for the exposure testing. The test cell was left at ambient temperature, and the ground water was exposed to room air with a long glass reflux tube.

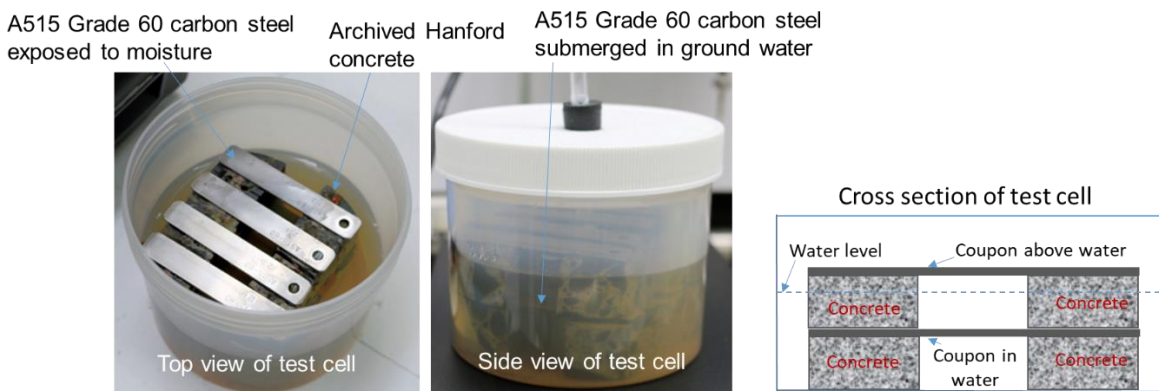


Figure 2: Carbon steel coupons in contact with concrete exposed to ground water

Table 2
Chemical Composition of Ground Water Sampled from Tank AY-102 Leak Detection Pit

Analyte	Sample 2AY-LDP-13-01DUP	Sample 2AY-LDP-13-02
Cl ⁻ , M	4.63×10 ⁻⁶	5.67×10 ⁻⁶
SO ₄ ²⁻ , M	2.49×10 ⁻⁶	2.61×10 ⁻⁶
NO ₃ ⁻ , M	3.73×10 ⁻⁵	3.89×10 ⁻⁵
Ca ²⁺ , M	1.64×10 ⁻⁴	1.66×10 ⁻⁴
Mg ²⁺ , M	2.37×10 ⁻⁵	2.38×10 ⁻⁵
K ⁺ , M	2.79×10 ⁻⁵	2.74×10 ⁻⁵
Na ⁺ , M	3.30×10 ⁻⁴	3.29×10 ⁻⁴
Silicon, mg/L	3.45	3.04
Strontium, mg/L	9.97×10 ⁻²	1.02×10 ⁻¹
U-235, mg/L	7.01×10 ⁻⁷	3.85×10 ⁻⁶
U-238, mg/L	9.6×10 ⁻⁵	5.23×10 ⁻⁴
Cs-137, mCi/L	2.77×10 ⁻⁵	2.59×10 ⁻⁵
Pu-239/240, mCi/L	2.94×10 ⁻⁸	Below detection limit
Sr-89/90, mCi/L	4.28×10 ⁻³	4.24×10 ⁻³
Other ions	Balance	Balance
pH	8.34	8.19

Coupons were removed from the solution in pairs (one submerged and one above water) at 2-, 4-, 6-, and 28-month intervals. The coupons were analyzed by optical microscopy before and after corrosion product removal using ammonium citrate solution at approximately 80 °C. Weight loss was also used to calculate general corrosion rates.

RESULTS AND DISCUSSION

Corrosion Susceptibility of Secondary Liner Carbon Steel Exposed to Tank Waste

Corrosion Potentials and General Corrosion Rates Measured from LPR

The corrosion potentials and general corrosion rates calculated from LPR for the non-creviced and creviced carbon steel electrodes exposed to tank waste measured periodically throughout the year-long

experiment are plotted in Figure 3. The two plots in Figure 3(a) indicate that it took about 3 months for the corrosion potential of the creviced electrode to begin to stabilize around -170 to -160 mV versus saturated calomel electrode (SCE), and even after a full year, it appears that some still trended to higher potentials. The non-creviced working electrode shows a similar trend, although with a slightly lower corrosion potential. The higher corrosion potential from the crevice assembly could be caused by carbon steel interaction with the refractory material in the crevice. However, the similar trend of the creviced and non-creviced electrodes suggests that the steel and refractory interaction didn't lead to active crevice corrosion conditions in the crevice. The two plots in Figure 3(b) indicate that general corrosion rates decreased significantly in the first month. Afterwards, the rates began to stabilize around 0.06 to 0.08 $\mu\text{m}/\text{yr}$ for the crevice assembly and 0.02 to 0.03 $\mu\text{m}/\text{yr}$ for the non-creviced electrode. Similar to the corrosion potential shown in Figure 3(a), even after a full year the trend to lower corrosion rates continued. The slightly higher general corrosion rates from the crevice assembly could also be caused by carbon steel interaction with the refractory material in the crevice.

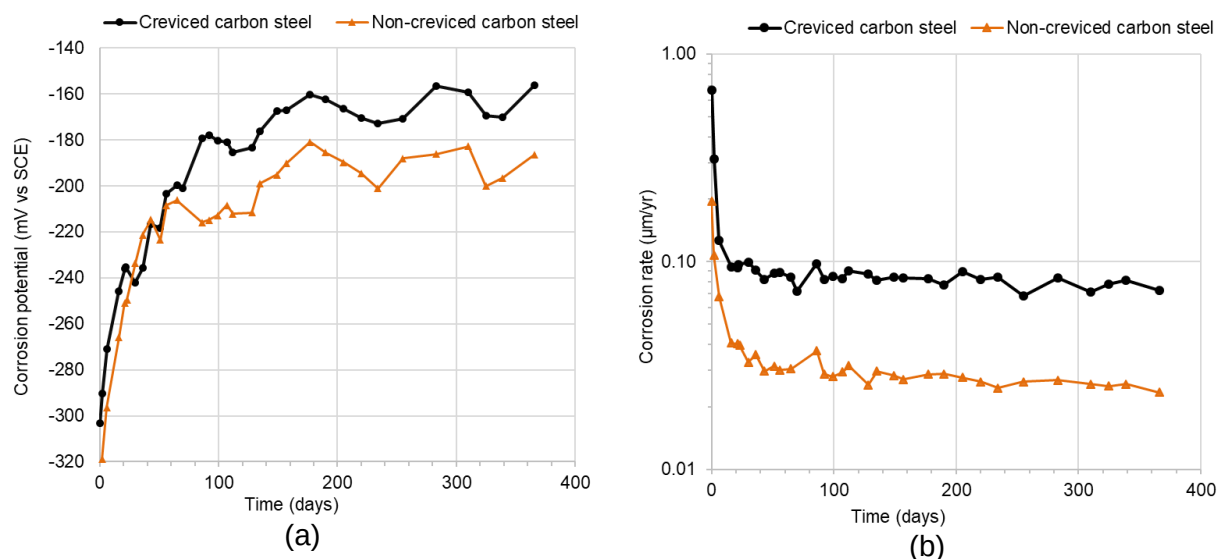


Figure 3: (a) Corrosion potential and (b) general corrosion rates measured on a crevice assembly and a non-creviced carbon steel electrode exposed to tank waste throughout the year-long experiment

2-Month Crevice Coupon Analysis

Figure 4(a) shows photographs of the front and back surfaces of the posttest carbon steel coupon (the two surfaces that were in contact with the refractory) after cleaning. Both surfaces were viewed using varying magnifications under the optical microscope and no crevice corrosion or corrosion products were observed. The coupon was imaged using SEM with energy dispersive spectrometry (EDS) to obtain higher magnification of any features and elemental analysis of materials and residues on the surface. Small pit-like features were observed scattered over both the front and back surfaces of the coupon. Figure 4(b) shows one of these with size measurements made by the SEM software. It is uncertain that these features are pitting corrosion caused by the refractory crevice. Little to no corrosion product was detected in the EDS; the low intensity oxygen peak could be solely associated with the calcium aluminum silicate residue. Comparing these pit-like features to the ones observed on the longer exposure coupons suggests that they are not active corrosion sites (see next sub-sections).