**CORROSION STUDY FOR WASTE TANKS EXPOSED TO HIGH
TEMPERATURE AND SALT CONCENTRATION CONDITIONS (U)**

By

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Corrosion Study For Waste Tanks Exposed To High Temperature And Salt Concentration Conditions (U)

Summary

During salt dissolution, waste compositions may reach temperature and nitrate concentrations not covered by the present technical standards. Stress corrosion cracking (SCC) is a possible degradation mechanism of waste tank steels. Accelerated electrochemical tests were performed to identify potential ranges where SCC could occur for ASTM A537 and A285 plain carbon steels. The results showed that the only probable potential range for SCC would be that for the normal oxide state (-0.200 to -0.400 V). Possible oxide instability was also identified for the range of 0.000 to 0.200 V. These ranges will be used for the planned slow strain rate test to determine SCC susceptibility.

Introduction

Potentiodynamic polarization test were performed to determine electrochemical potential ranges where plain carbon steels could be susceptible to stress corrosion cracking (SCC). These tests are part of the task related to TTR-HLE-94090, entitled "Temperature Effects During Salt Dissolution" [1]. The primary objective of this task is to determine the corrosion inhibitor and temperature requirements during salt dissolution [2]. High temperatures ($>70^{\circ}\text{C}$) and high nitrate concentrations ($>8.0\text{ M}$), which have occurred during dissolution, may cause SCC of the waste tank. SCC is known to occur within certain potential ranges, which change with the material of construction and waste composition [3]. Potentiodynamic polarization testing was used to determine possible potential ranges which would be used in the slow strain rate test (SSRT) matrix.

Experimental Procedure

Potentiodynamic polarization testing (PPT) consists of applying a sequentially changing potential to a sample that is exposed to the solution of interest. The responding current is measured to establish a current-potential relationship. The data, which are normally displayed as potential-log current graphs, are analyzed to determine the probable corrosion mechanisms. Various relationships are characteristic of certain corrosion mechanisms. SCC has been found to be prevalent at potentials where the responding current has a large change. This change was associated with a transformation in the passivity of the material.

The PPT was performed with disc-shaped samples of both ASTM Types A285 and A537 plain carbon steels, which are the materials of construction for Type II and some Type III waste tanks, respectively. The tests were limited to these alloys since ASTM Types A516 and A106 plain carbon steels have chemistries that are similar to A537 and A285. A516 and A285 are the materials of construction for some Type III waste tanks and the cooling

coils. The test samples were obtained from Metals Sample (Munsford, AL) and their compositions are given in Table 1. The surface was prepared with a 600-grit finish just prior to a test. The surface area that was exposed to the test solution was 1 cm^2 .

Test solutions were simulated waste compositions in which the sodium nitrate, hydroxide, and nitrite concentrations were varied. The compositions were chosen based on previous salt dissolutions and the maximum nitrate concentration that could be experimentally obtained [4]. Solutions at high and low values for both the nitrate concentration and temperature were tested to determine a range of results. The compositions and test temperatures for the solutions are given in Table 2. Fixed concentrations of other salts were also added to all the solutions. These additional components were: 0.1 M sodium carbonate, 0.1 M sodium sulfate, 0.05 M sodium chloride, 0.05 M sodium hypophosphate, and 0.005 M sodium chromate.

A schematic diagram of the test cell is shown in Figure 1. The cell, which was a standard electrochemical cell, consisted of a Pyrex glass container with graphite counter electrodes and a Ag/AgCl reference electrode. A temperature controller was used with a thermometer to maintain a temperature of either 75 or 95 °C. The solutions were not stirred or purged with a gas. The test samples were placed in the solution and allowed to reach an equilibrium steady state potential prior to starting the test.

The test procedure was similar to that given in ASTM G5-87, "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements" [5]. After a sample stabilized in the solution, a potential of -0.800 V versus the open-circuit potential was applied and held for five minutes. This polarization reduces surface oxides on the sample. Following this step, the sample potential was ramped to 0.800 V at a scan rate of 16.7 mV/sec (fast scan). The sample was allowed to stabilize after this test for 30 minutes. The procedure was repeated on the same sample, except the scanning rate was changed to 0.33 mV/sec (slow scan). Duplicate tests were run for each solution.

Results And Discussion

The data analysis entailed identifying the potentials at which the measured currents for the fast and slow scan had a ratio greater than a thousand. The technique is based on the hypothesis that SCC occurs by crack tip dissolution [6]. The dissolution reactions at the crack tip occur at a faster rate than those either along the crack sides or at the outer surface. These surfaces have a passive oxide layer which slows any dissolution reactions. The crack sides must go through an active to passive transition since at one stage the side locations were at the tip. This PPT technique identifies the potentials at which this active to passive transition occurs.

The potential and current data displayed three relationships. These relationships, which were similar, are shown in Figure 2 on a potential-log current density graph. Scans A, B, and C were obtained from three different solutions at the fast scan rate. The scans for the

slow rate are not shown for clarity. The arrows on the curves indicate the direction of scan. The first relationship as shown by Scan A had a current that steadily increased with the potential, indicating active dissolution or general corrosion. The amount of current that passes through the sample is related to the overall corrosion rate.

Scan B shows a small peak in the current which occurred at a specific potential, referred to as the peak potential. The peak potential for Scan B occurred at 0.050 V. A change in the surface characteristics was a probable cause. The third relationship as shown by Scan C also had a current increase at a specific potential, referred to as the step potential. The step potential for scan C occurred at 0.100 V. The average peak and step potentials are given in Table 3. The difference between the second and third relationship may be attributable to the surface oxide. Samples as characterized by Scan C could have a stable oxide so that the current prior to the step was constant with potential. A less stable or penetrable oxide would have increasing currents with potential as shown by Scan B. A larger current change, therefore, would occur at a transition potential for a stable oxide.

The potential-current relationships had a dependence on the nitrate and inhibitor concentrations. The results in Scans A and B were generally observed for the low nitrate solutions (5.5 and 8.0 M). The high nitrate solutions (8.7 and 9.7 M) more typically had results like Scans A and C. Solution A1, which had low inhibitor and nitrate concentrations, had results similar to the higher nitrate solutions. The more aggressive solutions with low inhibitor or high nitrate concentrations, therefore, tended to show more instability in the oxide. This instability may be an indicator of SCC susceptibility.

The results were also affected by the scan rate. The slow scans, which were not shown in Figure 2, were shifted to lower current densities than those measured for the fast scans. These lower current densities showed that the extended time needed to perform the scan allowed a more stable surface oxide to form on the sample. As explained above, the results from the slower scan apply to the corrosion processes along the crack sides and the outer surface; those from the fast scan apply to the crack tip.

The potentials that were determined from these results included the steady state potential prior to performing the test (E_{ss}), the corrosion potential (E_{corr}), the transition potential, and the specific potential. Table 3 shows the average values for each material and scan rate in the tested solutions. E_{corr} is the potential during a scan when the net current changes from cathodic to anodic. E_{ss} and E_{corr} should be similar if the polarization does not affect the sample. A large difference (> 0.100 V) was observed for the fast scan in these tests since the samples were polarized to -0.800 V to remove the surface oxide.

The transition potential was chosen as that in which the current density ratio between the fast and slow scan was greater than 1000. The only potentials at which this ratio occurred was at E_{corr} for the slow scan. These E_{corr} values were similar to the E_{ss} values and were in the range of -0.200 to -0.400 V. The specific potential, the peak and step potential discussed above, was where the oxide appeared to become less stable. These potentials fell in the range of 0.000 to 0.200 V. The current density ratios at these potentials, however,

were on the order of 10, which was not indicative of SCC susceptibility. The ranges for both the transition and specific potentials fell within the range noted for nitrate SCC (-0.300 to 0.800 V) [3].

The use of applied potentials during the Slow Strain Rate Test (SSRT), therefore, does not appear necessary. The similarity of the transition potentials to the potentials prior to testing showed that the normal state of the oxide on these steels is the most susceptible for SCC. However, since the specific potentials indicated some oxide instability several SSRT will be run under applied potential conditions. These steps would confirm the lack of SCC susceptibility at these potentials.

Pitting corrosion, which is generally associated with low nitrate waste compositions, was not found to occur in these tests. Pitting will be monitored during the wedge-opening loaded test that are planned to confirm this finding. These tests are long-term coupon tests and will be initiated after the SSRT.

Conclusions

PPT was conducted to identify probable potential ranges for SCC susceptibility for A537 and A285 plain carbon steels during salt dissolution. Waste compositions could attain nitrate and temperature conditions that are not covered by the present technical standards. The results showed that the range of -0.200 to -0.400 V would be the most probable one for SCC, although the range of 0.000 to 0.200 V indicated some oxide instability. The solutions with a higher nitrate or lower inhibitor concentration were more aggressive. The slow strain rate tests, which are better indicators of SCC susceptibility, will be performed within these ranges.

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Table 1. Chemical Composition Of Carbon Steel Test Samples

<u>Type Steel</u>	<u>Chemical Analysis (%)</u>				
	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>
A285	0.28 max	0.90 max	0.035 max	0.045 max	---
A537	0.24 max	0.70-1.60	0.035 max	0.040 max	0.15-0.50

Table 2. Simulated Waste Compositions¹

<u>Solution Name</u>	<u>Component</u>	<u>Concentration (M)</u>	<u>Temperature (°C)</u>
Solution A	Sodium Nitrite	0.5	95
	Sodium Hydroxide	0.6	
	Sodium Nitrate	5.5	
Solution A1	Sodium Nitrite	0.3	95
	Sodium Hydroxide	0.3	
	Sodium Nitrate	5.5	
Solution B	Sodium Nitrite	0.5	95
	Sodium Hydroxide	0.6	
	Sodium Nitrate	8.0	
Solution C	Sodium Nitrite	0.5	95
	Sodium Hydroxide	1.0	
	Sodium Nitrate	8.0	
Solution D	Sodium Nitrite	0.0	95
	Sodium Hydroxide	1.0	
	Sodium Nitrate	8.0	
Solution E	Sodium Nitrite	0.0	75
	Sodium Hydroxide	1.5	
	Sodium Nitrate	8.7	
Solution F	Sodium Nitrite	0.5	75
	Sodium Hydroxide	0.6	
	Sodium Nitrate	8.7	
Solution H	Sodium Nitrite	0.0	95
	Sodium Hydroxide	1.0	
	Sodium Nitrate	9.7	

1. These components were added to all simulated wastes: 0.1 M sodium carbonate, 0.1 M sodium sulfate, 0.05 sodium chloride, 0.05 sodium hypophosphate, and 0.005 sodium chromate.

Table 3. Average Potentials From PPT Tests

Solution	Material	Steady State Potential (V)		Corrosion Potential (V)		Specific Potential (V)		Transition Potential (V)
		Fast	Slow	Fast	Slow	Peak	Step	
A	A537	-0.309	-0.239	-0.460	-0.228	0.000		-0.323
	A285	-0.351	-0.284	-0.485	-0.349	0.000		-0.447
A1	A537	-0.218	-0.174	-0.355	-0.177		0.100	-0.177
	A285*	-0.281	-0.282	-0.660	-0.386		0.1-0.2	-0.386
B	A537	-0.290	-0.275	-0.396	-0.315			-0.293
	A285	-0.286	-0.287	-0.445	-0.373			-0.373*
C	A537	-0.287	-0.285	-0.384	-0.274	0.000		-0.274
	A285	-0.459	-0.397	-0.557	-0.412	0.000		-0.412
D	A537	-0.286	-0.320	-0.384	-0.282	0.000		-0.282
	A285	-0.342	-0.313	-0.443	-0.321			-0.321
E	A537	-0.293	-0.306	-0.565	-0.399		0.15-0.31	-0.399
	A285	-0.307	-0.291	-0.557	-0.374		0.200	-0.387
F	A537	-0.371	-0.337	-0.641	-0.437		0.200	-0.437
	A285*	-0.210	-0.224	-0.464	-0.331		0.200	-0.331
H	A537*	-0.329	-0.375	-0.610	-0.496		**	-0.496
	A285*	-0.249	-0.160	-0.500	-0.210		**	-0.210

*Single result

** Over a large range of potentials

Figure 1. Schematic Diagram Of Polarization Test Cell (5)

Figure 2. Potentiodynamic Polarization Test Results For Simulated Waste Compositions

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