SRNL-STI-2009-00600, REVISION 0

Key Words:
Corrosion
Waste Tanks
Stress Corrosion Cracking

Retention: Permanent

DETERMINATION OF CORROSION INHIBITOR CRITERIA FOR TYPE III/IIIA TANKS DURING SALT DISSOLUTION OPERATIONS – SUMMARY DOCUMENT

B. L. Garcia-Diaz
J. I. Mickalonis
B. J. Wiersma

OCTOBER 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808
Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-08SR22470

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

REVIEWS AND APPROVALS

J. I. Mickalonis, Author Date
Materials Performance & Corrosion Technology
Materials Science & Technology Directorate

B. L. Garcia-Diaz, Author Date
Materials Performance & Corrosion Technology
Materials Science & Technology Directorate

B. J. Wiersma, Author Date
Materials Performance & Corrosion Technology
Materials Science & Technology Directorate

R. L. Sindelar, Technical Reviewer Date
Materials Science & Technology Directorate

K. E. Zeigler, Manager Date
Materials Performance & Corrosion Technology
Materials Science & Technology Directorate

N. C. Iyer, Manager, Date
Materials Science & Technology Directorate

M. E. Maryak, Date
Engineering Programs
SRR Programs Engineering

TABLE OF CONTENTS

LIST OF FIGURES....................iv
LIST OF TABLES....................iv
LIST OF ACRONYMS....................v

1.0 EXECUTIVE SUMMARY....................1

2.0 INTRODUCTION....................2

3.0 EXPERIMENTAL PROCEDURE....................2
  3.1 Long-Term Non-Polarized U-Bend Coupon Test....................2
  3.2 Polarized U-Bend Coupon Test....................4
  3.3 Electrochemical Testing....................5
    3.3.1 Testing with Mill Scale Coupons....................5
    3.3.2 Testing with Weld Metal Coupons....................6
  3.4 Slow Strain Rate Testing....................7

4.0 RESULTS....................8
  4.1 Long-Term Non-Polarized U-Bend Coupon Test....................9
  4.2 Polarized U-Bend Coupon Test....................11
  4.3 Electrochemical Testing....................14
    4.3.1 Testing with Mill Scale Coupons....................14
    4.3.2 Testing with Weld Metal Coupons....................16
  4.4 Slow Strain Rate Testing....................18

5.0 DISCUSSION....................21
  5.1 Pitting....................21
  5.2 Stress Corrosion Cracking....................21

6.0 CONCLUSIONS AND RECOMMENDATIONS....................22

7.0 ACKNOWLEDGEMENTS....................23

8.0 REFERENCES....................24

LIST OF FIGURES

3-1 Position of U-bend Coupons in Test Vessel for Long-Term Non-Polarized Tests 4
3-2 Test set up of slow strain rate test for exposure to oil 7
3-3 Cup-cone failure morphology of A537 pulled in oil 8
4-1 Corrosion on as-received U-bend coupons exposed during long-term non-polarized testing at 50 C in 8.5M $NaNO_3$, and 0.1 M each NaOH and $NaNO_2$ for 18 months ... 10
4-2 Long-term polarization of U-bend coupons at 50 °C in 5.5M $NaNO_3$, and 0.01 M each NaOH and $NaNO_2$ 11
4-3 Long-term polarization of U-bend coupons at 50 °C in 7.0M $NaNO_3$, and 0.01 M each NaOH and $NaNO_2$ 12
4-4 Long-term polarization of U-bend coupons at 50 °C in 7.0M $NaNO_3$, and 0.1 M each NaOH and $NaNO_2$ 13
4-5 Photographs of polarized U-bend coupons after 150 days at 50 °C 13
4-6 Polarization results for mill scale coupon exposed at 50 °C in 5.5M $NaNO_3$, and 0.6 M NaOH and 0.2M $NaNO_2$ 14
4-7 Polarization scans for ground weld coupons at 50 °C in 5.5M $NaNO_3$, and different inhibitor concentrations 17
4-8 Load-time plots from SSRT for A537 tensile bars in solutions containing 7.0 M $NaNO_3$, 0.01M NaOH, 0.01M $NaNO_2$ at 50 °C and in oil 19
4-9 SEM micrograph of cracks in gage length of A537 tensile sample exposed to solution containing 7.0 M $NaNO_3$, 0.01M NaOH, 0.01M $NaNO_2$ at 50 °C 19
4-10 Load-time plots from SSRT for A537 tensile bars in solutions containing 7.0 M $NaNO_3$ and various inhibitor level 20
4-11 SSRT samples after testing at 50 °C in: (A) 7.0 M $NaNO_3$, 0.3M NaOH, 0.1M $NaNO_2$ and (B) 7.0 M $NaNO_3$, 0.3M NaOH, 0.1M $NaNO_2$ 20

LIST OF TABLES

3-1 Long-Term Non-Polarized U-Bend Test Matrix 3
3-2 Concentration of Added Chemical Species in Test Solutions 3
3-3 Polarized U-Bend Coupon Test Matrix 5
3-4 Electrochemical Test Matrix For Mill Scale Coupon 6
3-5 Electrochemical Test Matrix For Weld Metal Coupons 6
3-6 Slow Strain Rate Test Matrix 8
4-1 Visual Evaluation of Long-Term Non-Polarized U-Bend Coupons 9
4-2 OCP of Long-Term Non-Polarized U-bend Coupons at LAI 10
4-3 Polarization Parameters from CPP Tests for Mill Scale Coupons Exposed to 5.5M $NaNO_3$ 15
4-4 Polarization Parameters from CPP Tests for Weld Coupons Exposed to 5.5M $NaNO_3$17
4-5 Slow Strain Rate Test Conditions in 7M $NaNO_3$ at 50 °C and Measured Mechanical Parameters 18

LIST OF ACRONYMS

A537	A537 Carbon Steel, Grade 1
AR	As-Received
BP	Breakdown Potential
C	Cracked
CI	Crack Indication
CP	Corrosion Potential
CPP	Cyclic Potentiodynamic Polarization
GW	Ground Weld
HT	Heat Treated
I	Indented
IP	Passive Current
LAI	Liquid Air Interface
MS	Mill Scale
OCP	Open-Circuit Potential
P	Polished
PW	Polished Weld
SCC	Stress Corrosion Cracking
SCE	Saturated Calomel Electrode
SSRT	Slow Strain Rate Test
VS	Vapor Space

1.0 EXECUTIVE SUMMARY

Dissolution of salt from Type III/IIIA waste tanks at the Savannah River Site may create solutions with inhibitor concentrations below those currently required (0.6M OH^- and 1.1M OH^- + NO_2^-) per the Corrosion Control Program for high nitrate salt solutions (5.5 to 8.5M NO_3^-). An experimental program was conducted to evaluate the corrosion susceptibility of grade A537 carbon steel for waste simulants containing 4.5-8.5M $NaNO_3$ with maximum inhibitor concentrations of 0.6M NaOH and 0.2M $NaNO_2$. These maximum inhibitor concentrations used in this program are at a reduced level from those currently required. Current requirements were initially established for the Types I, II and IV tanks made of A285 carbon steel.

The experimental program involved corrosion testing to evaluate the pitting and stress corrosion stress corrosion cracking (SCC) susceptibility of the Type III/IIIA waste tank materials. The program was conducted in two phases; the results of the first phase were reported previously (WSRC-STI-2006-00029). In this second phase, the corrosion specimens were modified to represent the "as-fabricated" condition of the tank wall, and included specimens with mill scale, ground welds and stress-relief heat treatments. The complete description of the corrosion testing and the results are reported herein.

The collective corrosion test results for A537 carbon steel in high nitrate waste simulants (4.5 - 8.5M) with the maximum inhibitor concentrations of 0.6M NaOH and 0.2M $NaNO_2$ were as follows:

- In long-term non-polarized U-bend testing, heat treatment, similar to the waste tank stress relief regime, reduced the incidence of cracking over the 18-month test period. Vapor space SCC was found to initiate on non-heat treated U-bend coupons.
- In polarized U-bend testing, cracking occurred on U-bend coupons that had welds prepared similar to those in the waste tanks, i.e. ground and heat treated.
- In electrochemical testing, pitting occurred on all coupons independent of heat treatment, inhibitor concentration, temperature, surface preparation, or welding.
- In slow strain rate testing, cracking occurred on samples tested in solutions containing up to the maximum inhibitor concentration.

The primary conclusion derived from this experimental program is that A537 carbon steel exposed to high nitrate (> 5.5M) solutions at inhibitor levels below the current specifications (0.6M OH^- and 1.1M OH^- + NO_2^-) are susceptible to localized corrosion in the form of pitting and stress corrosion cracking. Long-term storage (e.g., greater than 100 days) of dissolved salt solutions not meeting the current inhibitor specifications for high nitrate salt chemistries in Type III waste tanks shall be avoided. Short term storage (e.g., less than 100 days) at low temperatures (e.g., less than 50 °C) in these tanks is permissible for waste removal purposes. The stress relief process reduces the risk of SCC in the Type III waste tanks. On the other hand, the current inhibitor specifications should be strictly followed for the Type I, II and IV waste chemistry to prevent initiation of localized corrosion mechanisms. These tanks were not stress relieved and are more susceptible to SCC.

2.0 INTRODUCTION

Dissolution of salt from Type III/IIIA waste tanks at the Savannah River Site (SRS) may create solutions with inhibitor concentrations below those required currently for high nitrate salt solutions [1]. At these high nitrate solutions (>5.5 M $NaNO_3$), nitrate stress corrosion cracking (SCC) is the primary concern and inhibitor requirements are in place to preclude SCC [1]. An experimental program was established to evaluate operating conditions for the Type III/IIIA waste tanks at inhibitor concentrations below those currently used, which were established for A285 carbon steel [2]. The results from the first phase of testing were reported previously [3]. This report is the final document of this program, which summarizes the latest experimental results and provides guidance to the corrosion inhibitor criteria. The experimental results in this report include those from the following tests:

1. long-term, non-polarized U-bend coupon tests to determine if SCC occurs in the vapor space (VS) or at the liquid-air interface (LAI),
2. polarized U-bend coupon testing to determine if weld surface preparation similar to the as-fabricated condition of the tank wall affects SCC initiation,
3. electrochemical testing on mill scale and weld metal coupons to evaluate the effect of as-fabricated waste tank material condition (mill scale and heat treated surfaces, ground welds) on localized corrosion susceptibility,
4. and slow strain rate testing in which samples are tested to failure for a range of solutions below current inhibitor requirements

The test conditions and results are fully discussed in this report. Recommendations for the inhibitor controls for salt dissolution operations based on these results are provided.

3.0 EXPERIMENTAL PROCEDURE

The experimental testing in this phase of the task consisted of four testing regimes: long-term, non-polarized U-bend testing; polarized U-bend testing; electrochemical testing of weld metal and heat-treated A537 carbon steel with the mill scale still in tact; and slow strain rate testing.

3.1 LONG-TERM NON-POLARIZED U-BEND TESTING

The long-term, non-polarized U-bend testing was conducted to assess the susceptibility of A537 carbon steel (A537) to SCC in VS and LAI exposures. A second objective was to determine if the waste tank heat treatment affected this susceptibility. The solutions chosen (5.5 and 8.5M $NaNO_3$, 0.01M NaOH and 0.01M $NaNO_2$) were those that have shown SCC for polarized U-bends [3]. Indents through the mill scale and oxides on the U-bends surface were also used to assess the effect of oxide-free areas on the corrosion process.

The U-bend coupons were made from the same heat of material as those used in the previous testing [3]. These U-bend coupons had the mill scale oxide still intact and were made with a weld that was along the long axis of the U-bend coupons (See Figure 3-1). Eight pairs of A537 U-bend coupons with mill scale on the surface were exposed to three different salt solution chemistries. One U-bend coupon in each pair was exposed completely in the VS and the other was exposed partially-immersed with a LAI. Four pairs were heat-treated to simulate the stress relief given to the Type III/IIIA waste tanks. The test matrix is shown in Table 3-1 below. The inhibitor concentrations for this testing were chosen to cover a range below the current requirements. The test temperature was 50 °C.

Table 3-1 Long-Term Non-Polarized U-Bend Test Matrix

Solution Chemistry (M)			Exposure*	Temperature (°C)	Surface Prep*
$NaNO_3$	NaOH	$NaNO_2$			
8.5	0.01	0.01	LAI, VS LAI, VS	50	AR+I HT+I
8.5	0.01	0.01	LAI, VS LAI, VS	50	AR HT
8.5	0.1	0.1	LAI, VS LAI, VS	50	AR+I HT+I
5.5	0.01	0.01	LAI, VS LAI, VS	50	AR+I HT+I

* VS – vapor space, LAI – liquid-air interface, AR – as-received, HT – heat treated, I – indented

Besides the principal species of nitrate, hydroxide and nitrite, the test solutions contained additional chemical species that were common to all test solutions. The concentrations of these species are shown in Table 3-2 below. pH measurements were not made since standard laboratory pH meters do give accurate measurements at these high pH values. Instead, the measured weight of the sodium hydroxide salt was varied as meeting the desired value for the given molar concentration.

Table 3-2 Concentration of Added Chemical Species in Test Solutions

Chemical	Concentration (M)
$NaAlO_2$	0.5
Na_2CO_3	0.1
Na_2SO_4	0.1
$Na_2HPO_4 \cdot 7H_2O$	0.05
NaCl	0.1

The heat treat cycle was conducted in a furnace with an air atmosphere in sequence as follows: from ambient to 1100 °F at a heating rate of 90 °F/hour, held at 1100 °F for 60 minutes, from 1100 °F to ambient at a cooling rate of 115 °F/hr [3]. Indents were placed in the samples using a Rockwell hardness tester and penetrated through the mill scale and oxide into the base metal. The U-bend coupons with a LAI were instrumented to continuously monitor the open-circuit potential (OCP) over the course of the exposure period. A computer-controlled Gamry PC4-750 potentiostat with a multiplexer was used and the potentials measured against a Ag/AgCl reference electrode. The U-bend coupons were immersed in the test solution for one hour. After removal, they were allowed to dry so that salt crystals formed. Figure 3-1 is a picture of the coupons in their respective positions in the test vessel.

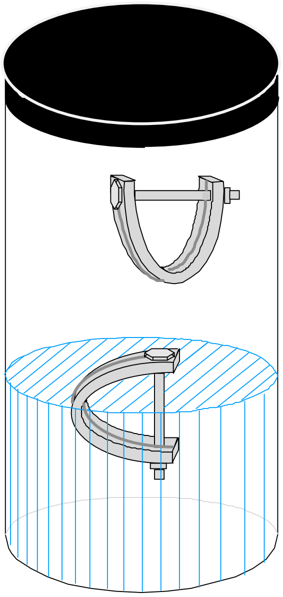

Figure 3-1 Positions of U-bend Coupons in Test Vessel for Long-Term Non-Polarized Tests

Tests were conducted for approximately 18 months. After testing the samples were cleaned in an inhibited acid solution to remove the corrosion products, but not attack metal. After cleaning, the samples were visually examined with a low-power microscope (up to 10X) and photographed.

3.2 POLARIZED U-BEND TESTING

The polarized U-bend testing was conducted to evaluate if the waste tank surface preparation, i.e., ground welds and heat treated surfaces, affected the susceptibility to SCC or pitting. The weld bead on the U-bend coupon was located above the metal surface, which was similar to welds during waste tank fabrication. These welds were ground flat, followed by the stress relieving heat-treatment (described in Section 3.1). The samples were also polarized in a manner similar to the previous testing on the as-received U-bend coupons [3].

These U-bend coupons were instrumented with a computer-controlled Gamry PC4-750 potentiostat with a multiplexer. The samples were polarized to 0.0 V vs. Ag/AgCl similar to the previous experiments on the as-received U-bend coupons. The current response was recorded throughout the experiment.

Three U-bend coupons were exposed to different solution chemistries known to cause SCC in as-received samples. All U-bend coupons came from the same heat of material as coupons used in previous work [3]. The U-bend coupons were pre-treated prior to immersion by dipping in the test solution and drying, which allowed salts to form on the surface. The test matrix is shown in Table 3-3. All solutions also contained the additional chemical species listed in Table 3-2. Testing was conducted at 50 °C.

Tests were run for approximately four months. After testing the samples were cleaned in an inhibited acid solution to remove the corrosion products, but not attack metal. After cleaning, the samples were visually examined with a low-power microscope (up to 10X) and photographed.

Table 3-3 Polarized U-Bend Coupon Test Matrix

Solution Chemistry (M)			Exposure	Temperature (°C)	Surface Prep*
$NaNO_3$	NaOH	$NaNO_2$			
7.0	0.01	0.01	Immersed and polarized	50	GW+HT
7.0	0.1	0.1	Immersed and polarized	50	GW+HT
5.5	0.01	0.01	Immersed and polarized	50	GW+HT

* GW – ground weld, HT – heat treated

3.3 ELECTROCHEMICAL TESTING

The electrochemical testing was performed using two types of sample, base metal with the mill scale and the weld. Previous electrochemical testing had characterized the corrosion behavior of A537 in the polished, non-heat treated condition only [3]. This testing evaluated the effects of mill scale and the tank surface preparation for welds on the corrosion behavior of A537.

The electrochemical testing used in this phase was only cyclic potentiodynamic polarization (CPP) measurements. Samples once immersed were allowed to reach a steady state OCP for approximately 1-2 hours. CPP measurements are performed by applying a cyclic potential ramp (0.2 mV/sec) up to vertex potential (1V anodic from OCP) and back to the OCP. A computer-controlled Princeton Applied Research Model 273A potentiostat was used. Test solutions, when heated, used a standard laboratory hot plate.

3.3.1 Testing With Mill Scale Coupons

The electrochemical testing on mill scale coupons consisted of CPP measurements on 0.75" diameter disk samples of A537 carbon steel. In the previous experiments, disks from the plate were placed in a metallurgical mount and ground to a 600-grit surface finish prior to performing electrochemical measurements [3]. The samples for the current work were cut from the same plate and mounted, but were not polished so that the layer of mill-scale oxide present on the plate remained on the test sample. This mill scale oxide would be more representative of the inside surface of the waste tanks than a 600-grit ground surface.

Since the Type III/IIIA waste tanks were stress relieved, some mill scale coupons were heat treated using a procedure described in Section 3.1. After the CPP measurements, samples were ground to a 600-grit surface and the testing repeated to corroborate results obtained in previous testing [3]. Again, half the coupons were heat treated. The coupons came from the same heat of material as used in the previous work [3].

The samples were exposed to 5.5M sodium nitrate solutions with two inhibitor levels. Testing was performed at 25 and 50 °C. The test matrix is given in Table 3-4. Each test in the matrix was run in duplicate. The test solutions also contained the additional chemical species given in Table 3-2.

Table 3-4 Electrochemical Test Matrix For Mill Scale Coupons

Solution Chemistry (M)			Exposure	Temperature (°C)	Surface Prep*
$NaNO_3$	NaOH	$NaNO_2$			
5.5	0.01	0.01	Immersed and polarized	25, 50	MS MS+HT P P+HT
5.5	0.6	0.2	Immersed and polarized	25, 50	MS MS+HT P P+HT

* MS – mill scale in place, HT – heat treated, P – polished

3.3.2 Testing With Weld Metal Coupons

The CPP measurements were performed on weld areas sectioned from U-bend coupons, which were from the same material heat as those used in the previous testing [3]. To prepare the CPP coupons, U-bend specimens first had the weld areas ground flat. A macro-etch of the U-bend was performed to define the weld area on the coupon. The CPP coupons were then cut out of the arms of the unstressed U-bend coupons by electrical discharge machining. Only weld metal made up the test coupon. The size of the coupons varied depending on the actual weld. Half of the coupons were heat treated and then mounted, with no polish of the surface. The remaining coupons were not heat treated and were ground to a 600-grit surface finish after mounting.

The samples were exposed to 5.5M sodium nitrate solutions with two inhibitor levels. Testing was performed at 25 and 50°C. The test matrix for these electrochemical tests is given in Table 3-4. Each test in the matrix was run in duplicate. The test solutions also contained the additional chemical species given in Table 3-2.

Table 3-5 Electrochemical Test Matrix For Weld Metal Coupons

Solution Chemistry (M)			Exposure	Temperature (°C)	Surface Prep*
$NaNO_3$	NaOH	$NaNO_2$			
5.5	0.01	0.01	Immersed and polarized	25, 50	PW PW+HT
5.5	0.6	0.2	Immersed and polarized	25, 50	PW PW+HT

* PW –polished weld, HT – heat treated,

3.4 SLOW STRAIN RATE TESTING

The slow strain rate test is an accelerated corrosion test for detecting susceptibility of A537 to SCC. Unlike the U-bend testing, a SSRT results in sample failure. The SSRT is a tensile test at a very low crosshead speed while the sample is exposed to a corrosive solution. Figure 3-2 shows the test set up used for this testing with a sample exposed to oil. Testing conducted in mineral oil at the desired test temperature provides a baseline load-time curve for comparison of results obtained for corrosive solutions. If SCC occurs, then changes are observed in this load-time curve and the strength and ductility parameters for the material are affected.

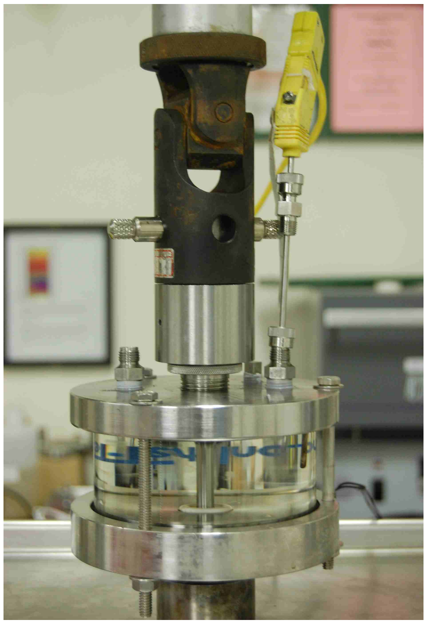

Figure 3-2 Test set up of slow strain rate test for exposure to oil

The tests were conducted both at the OCP and at polarized potentials anodic (more positive) to the OCP. Polarization is used to bring the sample into potential regimes where SCC may occur. These potentials were identified through the electrochemical test results. Testing was conducted at 50 °C and some samples were also tested in heat-treated condition. The test matrix is given in Table 3-6.

The polarization was conducted using a computer-controlled Gamry PC4-750 potentiostat with a Ag/AgCl reference electrode and a 304L stainless steel mesh cylinder as a counter electrode. The cylindrical diameter was that of the inner diameter of the test cell wall. The test cell, as shown in Figure 3-2, had a borosilicate glass wall with a top and bottom plate made of Hastelloy C276. Heating was through the bottom platen with rod heaters controlled by a rheostat. A thermocouple was used to measure the temperature.

The polarization was conducted using a computer-controlled Gamry PC4-750 potentiostat with a Ag/AgCl reference electrode and a 304L stainless steel mesh cylinder as a counter electrode. The cylindrical diameter was that of the inner diameter of the test cell wall. The test cell, as shown in Figure 3-2, had a borosilicate glass wall with a top and bottom plate made of Hastelloy

C276. Heating of the test solution was done through the bottom platen with rod heaters controlled by a rheostat. A thermocouple was used to measure the temperature.

Table 3-6 Slow Strain Rate Test Matrix

Solution Chemistry (M)			Exposure	Temperature (°C)	Surface Prep*
$NaNO_3$	NaOH	$NaNO_2$			
7.0	0.01	0.01	OCP Polarized	50	AR AR
7.0	0.1	0.1	OCP Polarized	50	AR, HT AR
7.0	0.3	0.1	Polarized	50	AR
7.0	0.6	0.2	Polarized	50	AR
Mineral Oil			OCP	50	AR, HT

* AR –as-received, HT – heat treated

After each test, samples were visually examined by low power microscopy to identify secondary cracking along the gage length of the sample and changes in the failure surface from that observed in oil. A cup and cone type of failure was observed in the specimens tested in oil, indicating a ductile failure as shown in Figure 3-3.

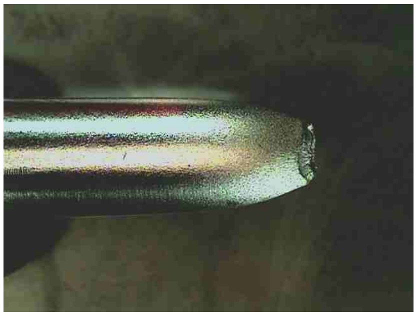

Figure 3-3 Cup-cone failure morphology of A537 pulled in oil

4.0 RESULTS

The results from this phase of testing build on those obtained in the first phase [3] and will be compared to those results as appropriate. High nitrate solutions that do not meet the current inhibitor specifications are potent cracking environments for A537. Stress corrosion cracking requires not only a susceptible material and a corrosive environment but a sufficient tensile stress. The stress relief operation for Type III/IIIA waste tanks was found to be beneficial towards reducing SCC. High nitrate solutions also result in pitting of A537 at inhibitor concentrations below the current inhibitor specifications.

4.1 LONG-TERM NON-POLARIZED U-BEND TESTING

After eighteen months, all U-bend coupons in both the VS and LAI were pitted and many had experienced SCC. Figure 4-1 has photographs of the coupons exposed to the 8.5M $NaNO_3$ solution with 0.1 M each of NaOH and $NaNO_2$. The results of the visual evaluation are given in Table 4-1. Only the modes of corrosion are given since they were not quantitatively evaluated, i.e. pit depths or number of cracks, etc. The corrosion was prevalent on both the sides and the top surface of the U-bend coupons. Inside surfaces of the U-bend coupons, which were corroded, were not closely examined.

These observations differed significantly from those at 100 days where the U-bend coupons were generally in good condition with some corrosion products and no observed cracks [4]. The immersed section of the LAI U-bend coupons had either a few or no corrosion products. VS U-bend coupons generally had a uniform layer of corrosion products. Corrosion products were not removed so as to maintain the chemistry at the surface.

Table 4-1 Visual Evaluation of Long-Term Non-Polarized U-Bend Coupons

Solution Chemistry (M)			Surface Prep*	Exposure**	Visual*** Observation
$NaNO_3$	NaOH	$NaNO_2$			
5.5	0.01	0.01	AR, I	VS	P, PW, CI
				LAI	**C**, P, PW, CI
5.5	0.01	0.01	HT, I	VS	P, PW
				LAI	P, PW
8.5	0.01	0.01	AR, I	VS	**C**, P
				LAI	**C**, P
8.5	0.01	0.01	HT, I	VS	P, PW
				LAI	P, PW
8.5	0.1	0.1	AR, I	VS	P, C
				LAI	**C**, P
8.5	0.1	0.1	HT, I	VS	P, PW, CI
				LAI	P
8.5	0.01	0.01	AR	VS	**C**, P, PW, CI
				LAI	**C**, P, PW, CI
8.5	0.01	0.01	HT	VS	P
				LAI	P

* AR – as-received, HT – heat treated, I – indented
** VS – vapor space, LAI – liquid/air interface
*** C- cracking (bold – through wall), P – pitting, PW- pitting in weld, CI – crack indications

These data demonstrate that VS SCC occurs with initiation and growth of cracks. These cracks occurred primarily on the U-bend coupons which had mill scale and were not heat treated. Multiple crack indications were observed on some samples, but only one crack grew across the width of the U-bend coupon. The HT U-bend coupons had fewer pits and areas of general corrosion than AR coupons and were free of cracks. One HT coupon had crack indications, which were groove-like features in the side of the U-bend coupon. A correlation of corrosion morphology with the presence of indents could not be made, which may be due to the large amount of general corrosion that occurred. For the LAI coupons, the degree of pitting and general corrosion appeared to be more significant on the immersed portion.

The presence of VS SCC differs from results previously obtained with corrosion testing [6]. These differences may be attributed to differences in the test set up and execution. For both the previous testing regimes, the samples were exposed over a solution of hot simulated waste. The coupons themselves were not heated. In this testing, the coupons were heated to the solution temperature since the entire test cell was placed in a furnace. The test periods also differed. For the previous work on indents and VS studies the exposure periods were 60-120 days and 99 days, respectively; whereas for this testing, the test period was 18 months.

(A) (B)

Figure 4-1 Corrosion on as-received U-bend coupons exposed during long-term non-polarized testing at 50 C in 8.5M $NaNO_3$, and 0.1 M each NaOH and $NaNO_2$ for 18 months: (A) Liquid-air interface exposure; (B) Vapor space exposure

Table 4-2 OCP of Long-Term Non-Polarized U-bend Coupons at LAI

Solution Chemistry (M)			**Surface Prep***	**OCP (mV)**	
$NaNO_3$	**NaOH**	**$NaNO_2$**		**Initial**	**Final**
5.5	0.01	0.01	AR, I	-332	-210
5.5	0.01	0.01	HT, I	-304	-216
8.5	0.01	0.01	AR, I	-309	-229
8.5	0.01	0.01	HT, I	-326	-221
8.5	0.1	0.1	AR, I	-305	-98
8.5	0.1	0.1	HT, I	-283	-152
8.5	0.01	0.01	AR	-312	-151
8.5	0.01	0.01	HT	-310	-128

* AR – as-received, HT – heat treated, I – indented

Table 4-2 shows the OCP for the 8 samples at the LAI. The OCP of all the samples became more noble or less negative over the course of the test, shifting between 80 to 207 mV more positive than the OCP. The largest shifts occurred for coupons in the high inhibitor solutions (0.1M OH^- and 0.1M NO_2^-) and without the indents. These coupons also had OCP values that were more noble than coupons in the low inhibitor (0.01M OH^- and 0.01M NO_2^-) and indents.

The difference between the HT and AR was not consistent across all solution chemistries and differences were generally small (~20 mV), which differs from the observed corrosion where HT coupons did not crack. The OCP, however, is probably controlled by the general corrosion. Large amounts of corrosion products were observed on these coupons near the beginning of the test which may establish a concentration polarization dominating the OCP values [4].

4.2 POLARIZED U-BEND TESTING

The polarized U-bend testing was conducted to evaluate if the waste tank surface preparation, i.e., ground welds and heat treated surfaces, affected the susceptibility to SCC or pitting. Previous testing of U-bend coupons exposed to similar solutions but without surface modifications showed cracking within a range of 13-85 days [3]. The U-bend coupons were polarized at 0.0 V vs Ag/AgCl for segments of time up to 7 days with brief interruptions to reset the data acquisition. Figures 4-2, 4-3 and 4-4 show the current response over the course of the test period for the three different test solutions. Each data file has been plotted. A large current transient occurred when polarization was resumed at the start of each data file and is associated with a redistribution of reactants in the diffusion layer close to the coupon surface. The transient current spike lasted for up to 24 hours. Some equipment errors after two weeks of testing required a cessation of testing for approximately 40 days. The U-bend coupons remained immersed and at temperature during this time period.

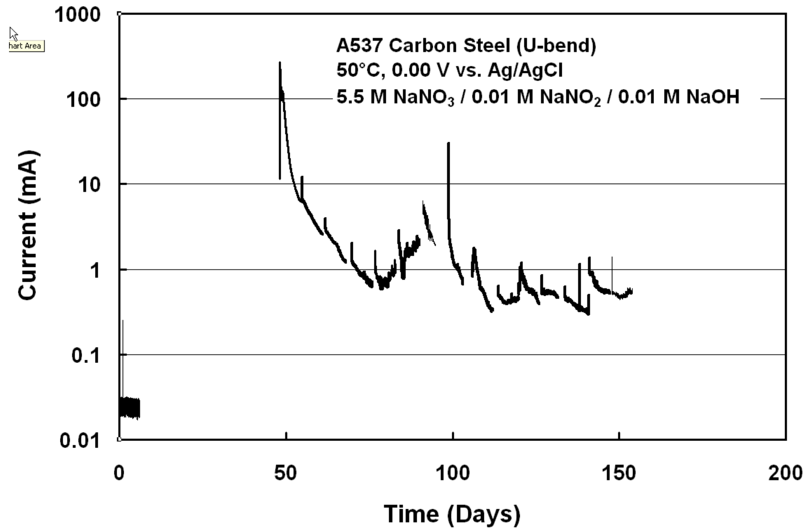

Figure 4-2 Long-term polarization of U-bend coupons at 50 °C in 5.5M $NaNO_3$, and 0.01 M each NaOH and $NaNO_2$

All of the coupons tested started with currents greater than 100 mA and the currents decreased below 1 mA within 1 month of continuous testing. The decrease in current is mostly caused by the build up of corrosion products on the coupon surface that creates a diffusion barrier for reactants in the electrolyte to reach the surface.

The results of the long-term U-bend polarization in 5.5 M nitrate with low inhibitor levels (0.01 M OH^- and 0.01M NO_2^-) in Figure 4-2 showed an increase in current from 0.6 mA to 6 mA from day 80 to day 90 of testing. This protracted increase in current may be associated with the cracking that occurred in the U-bend coupons. The current from this U-bend coupon decreased back to 0.3 mA from day 90 to day 112 days of testing. This decrease in current is attributed to the formation of a diffusion barrier inside the newly formed crack and on the U-bend exterior surface.

Figure 4-3 displays the results for the 7.0 M nitrate solution with low inhibitor levels. The current for the U-bend in this solution steadily dropped to 0.01 mA and stayed constant at that value until day 140. After day 140, the current slowly started to increase until the end of the test where the current was approximately 0.06 mA. This increase may correlate with the beginning of crack formation that was observed on the U-bend coupon. The rate of current increase in this solution was much slower than for the 5.5 M nitrate solution and the current magnitude was smaller.

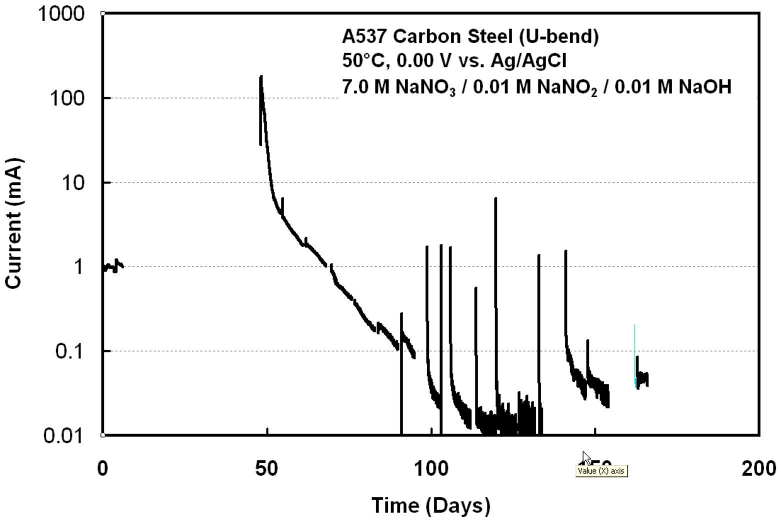

Figure 4-3 Long-term polarization of U-bend coupons at 50 °C in 7.0M $NaNO_3$, and 0.01 M each NaOH and $NaNO_2$

Figure 4-4 shows the current data for the polarized U-bend in 7.0 M nitrate solution with high inhibitor levels (0.1 M OH^- and 0.1M NO_2^-). The current for this U-bend coupon decreased to 0.045 mA by day 85 before increasing to 0.11 mA by day 110. The increase was most likely caused by the development of a small crack. The current data suggest that a second crack started near day 120 when a second increase in the current started.

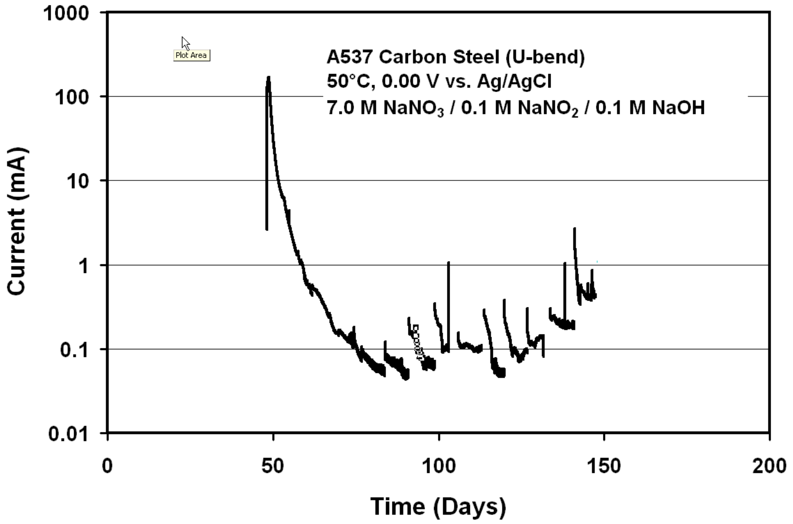

Figure 4-4 Long-term polarization of U-bend coupons at 50 °C in 7.0M $NaNO_3$, and 0.1 M each NaOH and $NaNO_2$

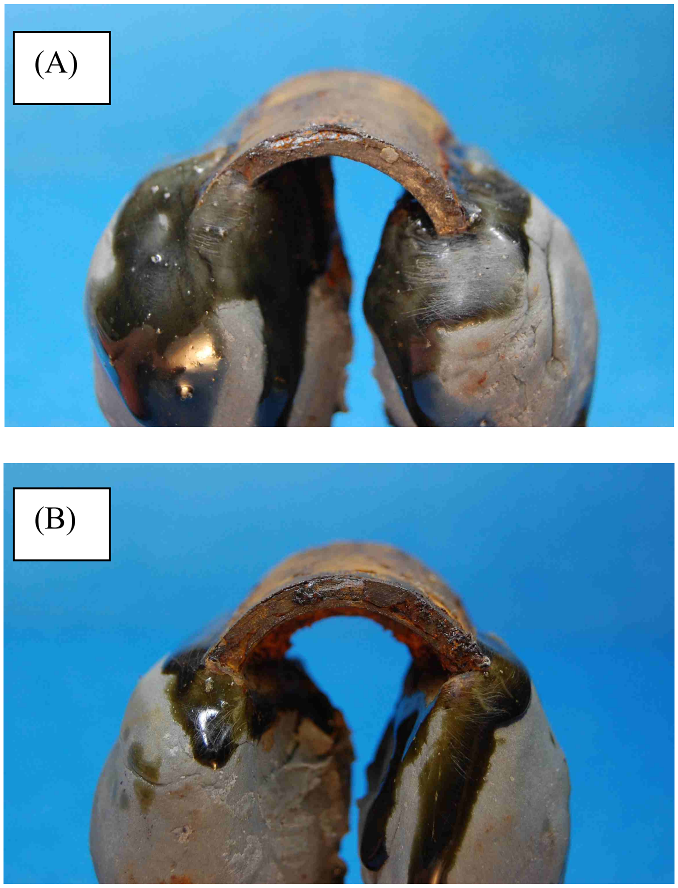

Figure 4-5 Photographs of polarized U-bend coupons after 150 days at 50 °C in: (A) 7.0M $NaNO_3$, and 0.01 M each NaOH and $NaNO_2$ and (B) 7.0M $NaNO_3$, and 0.1 M each NaOH and $NaNO_2$

All the polarized U-bend coupons had a similar corrosion morphology and showed signs of cracking, although no major through wall cracking occurred. Figure 4-5 shows photographs of the U-bend coupons after testing in the 7M $NaNO_3$ solutions. All samples showed some degree of end-grain type attack where the grain boundaries were preferentially attacked into the rolling plane of the metal. This attack appears to have produced an exfoliation of corrosion product layers as can be observed in the photographs. Small cracks running perpendicular to the coupon stress were also observed. The U-bend coupons did not show significant pitting like the non-polarized U-bend coupons, but these coupons had significant corrosion products indicative of a high corrosion rate at the polarized potential of 0.0 V.

4.3 ELECTROCHEMICAL TESTING

CPP testing was conducted to evaluate the localized corrosion susceptibility of a metal. The resulting polarization plot, which is generally potential versus the current density, has specific features if localized corrosion occurs. Features which indicate pitting and crevice corrosion include a negative hysteresis where the reverse scan has currents greater than the forward scan and a repassivation potential that is within approximately 200 mV of the corrosion potential. For this testing, coupons were visually examined after the test to confirm active corrosion mechanisms.

4.3.1 Testing with Mill Scale Coupons

The CPP testing of the mill scale coupons involved testing both with and without the mill scale and heat treating in both these conditions. The test results are summarized in Table 4-3 which include key potential values of Corrosion Potential (CP), Breakdown Potential (BP), and Repassivation Potential (RP), the passive current density (IP), and the state of the hysteresis (negative or positive). Figure 4-6 shows a representative example of pitting on the mill scale coupon tested at 50 °C in the high inhibitor (0.6M OH^- and 0.2M NO_2^-) solution. The nitrate concentration for all tests was 5.5M $NaNO_3$.

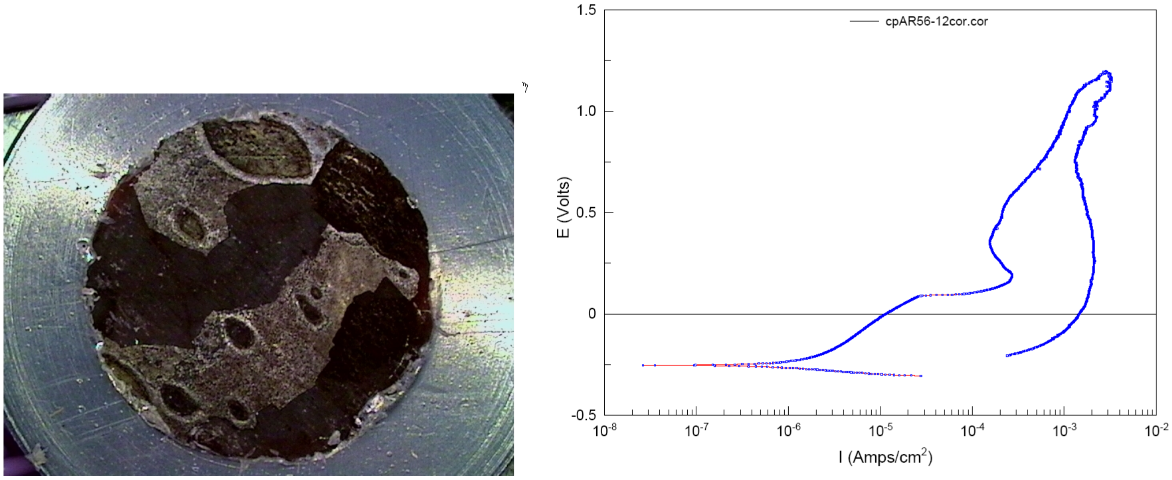

Figure 4-6 Polarization results for mill scale coupon exposed at 50 °C in 5.5M $NaNO_3$, and 0.6 M NaOH and 0.2M $NaNO_2$: (A) Post-test photograph of coupon; (B) Polarization scan showing a negative hysteresis with a high BP

Several trends are apparent in Table 4-3. As shown by the predominance of a negative hysteresis, most samples were susceptible to pitting, which was verified by the post-test visual examination of the test coupons. The hysteresis for the ground samples was larger than that for the mill scale samples indicating a greater degree of pitting.

Table 4-3 Polarization Parameters from CPP Tests for Mill Scale Coupons Exposed to 5.5M $NaNO_3$

Solution Chemistry		T (°C)	Surface Prep*	Potentials (V, SCE)			Passive Current (µA)	Hysteresis
NaOH	$NaNO_2$			CP	BP	RP		
0.01	0.01	25	MS, HT	-0.259	0.737	NA	20	Negative
0.01	0.01	25	MS, HT	-0.248	0.86	NA	2	Negative
0.01	0.01	25	MS	-0.279	-0.013	NA	20	Negative
0.01	0.01	25	MS	-0.32	1.1	-0.142	100	Negative
0.6	0.2	25	MS, HT	-0.42	0.488	-0.18	100	Negative
0.6	0.2	25	MS, HT	-0.347	0.544	NA	150	Positive
0.6	0.2	25	MS	-0.31	0.395	-0.219	3	Negative
0.6	0.2	25	MS	-0.393	0.544	0.016	350	Negative
0.01	0.01	50	MS, HT	-0.349	0.079	NA	15	Negative
0.01	0.01	50	MS, HT	-0.33	-0.127	NA	30	Negative
0.01	0.01	50	MS	-0.391	-0.112	-0.286	160	Negative
0.01	0.01	50	MS	-0.48	-0.115	-0.267	160	Negative
0.6	0.2	50	MS, HT	-0.269	0.107	-0.197	60	Negative
0.6	0.2	50	MS, HT	-0.316	0.135	NA	180	Negative
0.6	0.2	50	MS	-0.295	0.106	NA	70	Negative
0.6	0.2	50	MS	-0.254	0.088	NA	10	Negative
0.01	0.01	25	GR, HT	-0.336	0.308	NA	50	Negative
0.01	0.01	25	GR, HT	-0.339	0.502	NA	200	Negative
0.01	0.01	25	GR	-0.356	-0.098	NA	15	Negative
0.01	0.01	25	GR	-0.386	-0.106	-0.337	50	Negative
0.6	0.2	25	GR, HT	-0.269	0.1	NA	20	Negative
0.6	0.2	25	GR, HT	-0.32	0.1	-0.103	5	Negative
0.6	0.2	25	GR	-0.218	0.502	NA	5	Negative
0.6	0.2	25	GR	-0.252	0.527	NA	12	Negative
0.01	0.01	50	GR, HT	-0.311	0.133	0.092	10	Negative
0.01	0.01	50	GR, HT	-0.343	0.939	NA	8	Negative
0.01	0.01	50	GR	-0.433	-0.112	NA	20	Negative
0.01	0.01	50	GR	-0.424	-0.079	NA	20	Negative
0.6	0.2	50	GR, HT	-0.264	0.837	NA	150	Negative
0.6	0.2	50	GR, HT	-0.4	0.094	-0.265	690	Negative
0.6	0.2	50	GR	-0.335	-0.031	NA	30	Negative
0.6	0.2	50	GR	-0.334	0.331	NA	40	Negative

* MS – mill scale coupon, HT- heat treated, GR – ground coupon (mill scale removed), NA – not measureable

At higher temperature and higher inhibitor concentration, there is less of a difference in corrosion behavior as a function of heat treatment or the presence of a mill scale. CP values were generally more active with temperature, but similar with the presence of mill scale and high inhibitor levels. CP values ranged from -0.48 to -0.218 V which is typical for carbon steel in SRS simulated waste solutions. IP values tended to be lower with heat treatment at the lower temperature with more mixed results at the higher temperature. IP values fell between 2 and 690 μA, which is a large range of values. BP values fell into two ranges, either high (> 0.400 V) or low (-0.1 to 0.1V). The highest range of BP values occurred for the mill scale coupons at the lower temperature which indicates an increase corrosion resistance. Most of the conditions produced RP values that were below the CP values indicative that A537 is readily susceptible to pitting.

In the first phase of testing, the high inhibitor solution (0.6M OH^- and 0.2M NO_2^-) was found to be passive on polished samples without mill scale. In the second phase of testing, the ground samples were found to pit. IP values were slightly greater than observed previously (5-20 μA at 50 °C, 2-7 μA at 25 °C) and BP values were similar [3]. At low inhibitors ((0.01M OH^- and 0.01M NO_2^-), pitting was also observed. Differences between the two data sets may be associated with the complete removal of the mill scale from the test coupons in the present phase of testing. The ground coupons were re-used after CPP testing with the mill scale oxide. If this oxide and the corrosion film from the previous CPP testing were not fully removed, pit initiation sites could still remain.

4.3.2 Testing with Weld Coupons

The CPP measurements were performed on weld areas sectioned from U-bend coupons. Table 4-4 summarizes the results of CPP experiments for all conditions tested. For weld metal, the high inhibitor (0.6M OH^- and 0.2M NO_2^-) concentration reduced the negative hysteresis, especially at high temperature. At lower temperatures, positive hystereses were observed for the ground coupons. In some cases a mixed hysteresis was observed, which indicates the hysteresis was positive at the top of the reverse scan and became negative during the course of the scan.

In solutions with low levels of corrosion inhibitors (0.01M OH^- and 0.01M NO_2^-), coupons were susceptible to pitting independent of temperature or surface preparation. In Figure 4-7, the polarization scans are shown for both the low and high inhibitor of the ground coupon at 50 °C. The BP values were below 0.0 V indicating the easy onset of localized corrosion. The polarization scans had large negative hysteresis loops. At 50 °C only, coupons did not have a RP so CP was above the RP indicating that carbon steel readily pits in these solutions.

The effectiveness of the heat treatment at improving corrosion resistance was mixed. An indication of improved corrosion resistance is the difference between CP and BP. The larger this difference the more difficult for localized corrosion to be initiated. At 25°C, this difference was approximately 500 mV for HT coupons and 100-200 mV for polished coupons. The heat treatment was not effective at 50°C where the difference for HT coupons was less than that for ground coupons. HT coupons also had large current densities in the passive region at both temperatures. The polished coupons had IP values less than 20 μA while the HT coupons had passive currents greater than 50 μA. This higher IP for HT coupons may be associated with initial rough, non-ground surface prior to heat treatment, resulting in a non-uniform oxide.

Table 4-4 Polarization Parameters from CPP Tests for Weld Coupons Exposed to 5.5M $NaNO_3$

Solution Chemistry		T (°C)	Surface Prep*	Potentials (V, SCE)			Passive Current (µA)	Hysteresis
NaOH	$NaNO_2$			CP	BP	RP		
0.01	0.01	25	HT	-0.492	-0.031	-0.458	90	Negative
0.01	0.01	25	HT	-0.485	-0.031	-0.452	60	Negative
0.01	0.01	25	P	-0.286	-0.186	NA	1	Negative
0.01	0.01	25	P	-0.379	-0.172	-0.343	3	Negative
0.6	0.2	25	HT	-0.314	0.507	0.44	50	Negative
0.6	0.2	25	HT	-0.313	0.506	0.48	150	Mixed
0.6	0.2	25	P	-0.345	0.502	0.63	3	Positive
0.6	0.2	25	P	-0.339	0.497	0.63	3	Positive
0.01	0.01	50	HT	-0.351	-0.213	NA	160	Negative
0.01	0.01	50	P	-0.337	-0.147	NA	2	Negative
0.01	0.01	50	P	-0.393	-0.144	NA	70	Negative
0.6	0.2	50	HT	-0.254	0.486	0.406	60	Negative
0.6	0.2	50	HT	-0.293	0.49	0.448	150	Mixed
0.6	0.2	50	P	-0.393	0.489	0.475	20	Negative
0.6	0.2	50	P	-0.357	0.485	0.399	20	Negative

* HT- heat treated, P – polished, NA – not measureable, ND – no data

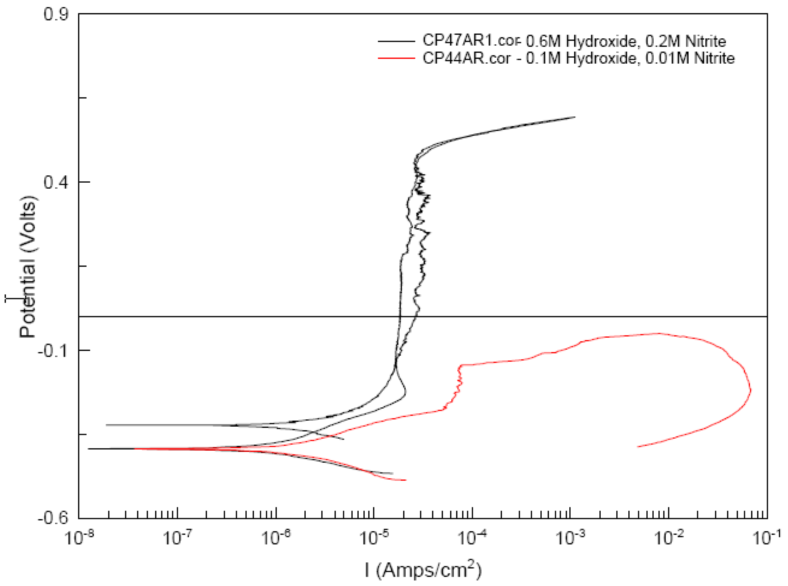

Figure 4-7 Polarization scans for ground weld coupons at 50 °C in 5.5M $NaNO_3$, and different inhibitor concentrations

4.4 SLOW STRAIN RATE TESTING

The SSRT results showed that at all inhibitor concentrations tested that SCC was a concern. The data results are summarized in Table 4-5.

All solutions contained 7.0M $NaNO_3$. Parameters that were used to evaluate SCC susceptibility included the maximum load, the reduction in area, and time to failure. Percent elongation is another common parameter but was not used since measuring the final length of a failed sample had greater errors than the other parameters.

Table 4-5 Slow Strain Rate Test Conditions in 7M $NaNO_3$ at 50 °C and Measured Mechanical Parameters

Solution Chemistry		**Surface Prep***	**Polarized Potential (V)**	**SSRT Parameters**			**Initial OCP (V)**	**Cracks**
NaOH	**$NaNO_2$**			**Max Load (lb)**	**RIA (%)**	**Time (hr)**		
Oil		HT	NA	3486	53	99.5	ND	No
Oil		AR	NA	3502	50	98	ND	No
0.01	0.01	AR	NA	3490	50	97	-0.375	No
0.01	0.01	AR	-0.25	3442	37	74	-0.355	Yes
0.1	0.1	HT	NA	3489	53	89	-0.255	No
0.1	0.1	HT	0.0	ND	ND	ND	-0.370	ND
0.1	0.1	AR	NA	3490	51	98	-0.300	No
0.1	0.1	AR	0.1	2347	ND	44	-0.300	Yes
0.1	0.1	AR	0	2486	ND	52	-0.305	Yes
0.1	0.1	AR	-0.2	2878	16	53	-0.425	Yes
0.3	0.1	AR	-0.2	3197	24	58	-0.361	Yes
0.6	0.2	AR	-0.1	3020	ND	ND	-0.257	Yes

* HT- heat treated, P – polished, ND – not applicable, ND – no data, RIA- reduction in area

Initial testing was performed in oil at temperature to determine the baseline for comparison with the other data. The sample failure was ductile with a standard cup –cone morphology as shown previously in Figure 3-3. In the low inhibitor solutions ((0.01M OH^- and 0.01M NO_2^-), only AR samples were used since U-bend coupons had failed in these solutions previously. The load-time plots for the low inhibitor solutions are shown in Figure 4-8 along with the baseline oil plot. As can be seen in the figure and Table 4-5, the maximum load and time to failure for the polarized sample are reduced from those values in oil and at the OCP. The polarized sample had an RIA that dropped to 37% from the approximately 50% for oil and non-polarized samples. Figure 4-9 shows a scanning electron micrograph (SEM) of the cracks along the gage length below the failure point of the polarized sample. Note the intergranular nature of the attack, which is typical for nitrate SCC. The samples also experienced general corrosion, although pitting was not observed.

Several SSRT were performed at different polarizations in the solution containing 7.0 M $NaNO_3$, 0.1M NaOH, and 0.1M $NaNO_2$ at 50 °C. As can be seen from the data, all the polarized samples had greatly reduced failure times and maximum loads with values decreasing with increasing polarization potentials. The RIA value could not be calculated for the 0.0 and 0.1 V polarizations because the samples had significant general corrosion and the diameter at the end of the test could not be adequately measured. The sample tested at OCP showed no detrimental effects although general corrosion products were prevalent.

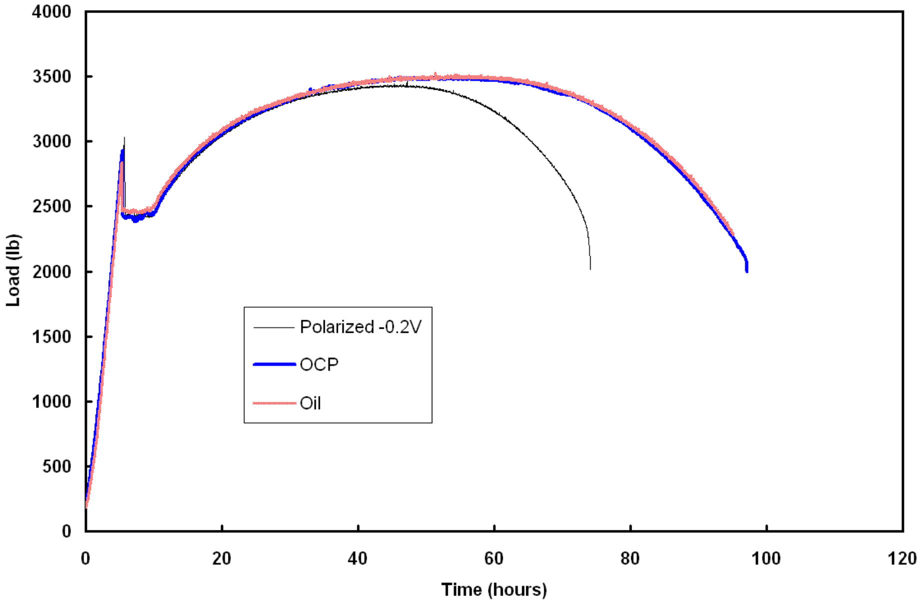

Figure 4-8 Load-time plots from SSRT for A537 tensile bars in solutions containing 7.0 M $NaNO_3$, 0.01M NaOH, 0.01M $NaNO_2$ at 50 °C and in oil

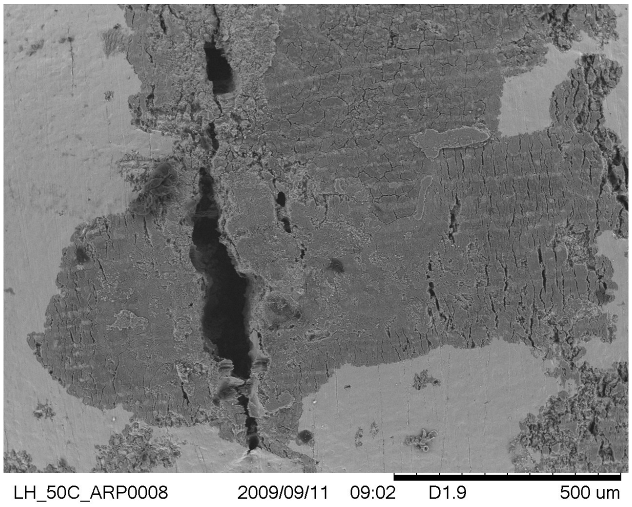

Figure 4-9 SEM micrograph of cracks in gage length of A537 tensile sample exposed to solution containing 7.0 M $NaNO_3$, 0.01M NaOH, 0.01M $NaNO_2$ at 50 °C

Since SCC had occurred at the inhibitor level of 0.1M OH$^-$ and 0.1M NO$_2^-$, higher inhibitor levels were tested. The sample tested in 7.0 M NaNO$_3$, 0.3M NaOH, 0.1M NaNO$_2$ at 50 °C had reduced SSRT parameters as shown in Table 4-5 and cracks were observed in the gage length.

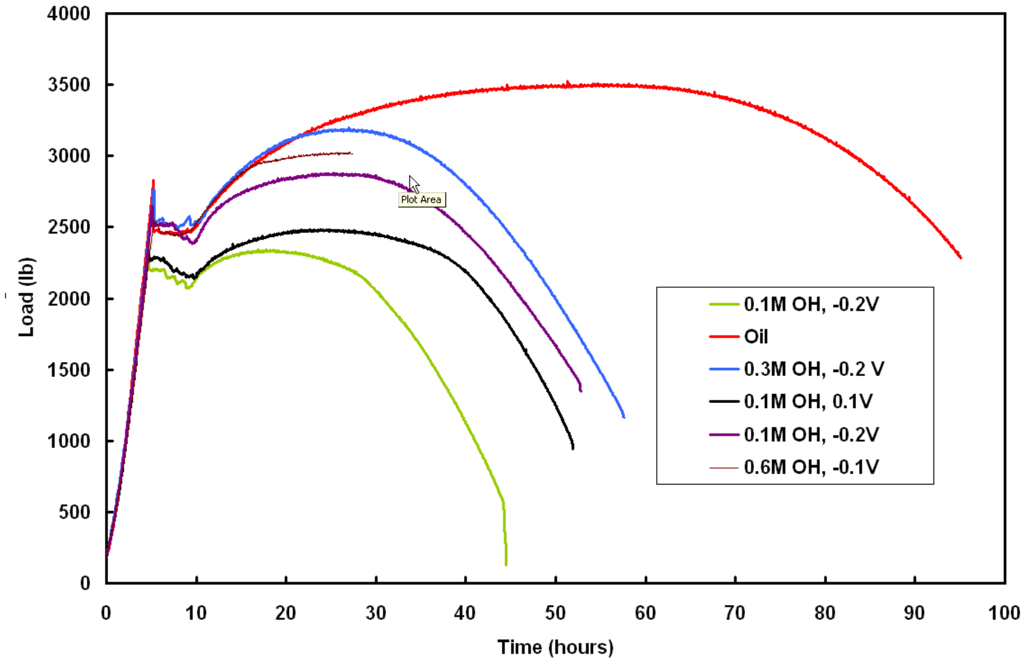

Figure 4-10 Load-time plots from SSRT for A537 tensile bars in solutions containing 7.0 M NaNO$_3$ and various inhibitor levels

(A) (B)

Figure 4-11 SSRT samples after testing at 50 °C in: (A) 7.0 M NaNO$_3$, 0.3M NaOH, 0.1M NaNO$_2$ and (B) 7.0 M NaNO$_3$, 0.3M NaOH, 0.1M NaNO$_2$ (arrows indicate corroded cracks)

The sample tested in 7.0 M NaNO$_3$, 0.6M NaOH, 0.2M NaNO$_2$ was stopped during testing since the load-time plot indicated that reduced loads were being sustained by the sample. The samples were examined and found to have cracks indicating the start of the SCC. The load-time plots for these samples along with those tested with inhibitor level of 0.1M NaOH and 0.1M $NaNO_2$ are shown in Figure 4-10. Figure 4-11 shows photographs of the failed tensile bars for both the 0.1M and 0.3M OH^- inhibitor levels polarized at -0.2V. Note the corroded cracks near the tip of each sample.

5.0 DISCUSSION

In the first phase of this work, electrochemical and U-bend coupon testing was conducted in a wide range of nitrate concentrations (4.5-8.5M $NaNO_3$) and inhibitor concentrations (0.01-0.6M NaOH, 0.01-0.3M $NaNO_2$) [3,4]. The results indicated that at inhibitor concentrations up to the maximum test values of 0.6M OH^- and 0.2M NO_2^- general corrosion rates remained low (<1 mpy). In testing on polarized (0.0-0.2 V) U-bend coupons, cracking was not observed within 3.5 months for 7.0M $NaNO_3$ solutions with inhibitor concentrations greater than 0.01M OH^- and 0.01M NO_2^- and up to 0.3M NaOH and 0.3M $NaNO_2$. These polarized U-bend tests were in good agreement with the electrochemical tests in which cracking was not expected at potentials below 0.2 V. Heat treatment was effective in preventing SCC at the lowest inhibitor level tested (0.01 M OH^- and 0.01 M NO_2^-) for an eighteen-week accelerated exposure period. These tests, however, did not clarify the effect of waste tank construction procedures on the corrosion susceptibility and did not determine if VS or LAI SCC would occur.

In this second phase of the work, the data from electrochemical, U-bend and slow strain rate testing has shown that up to maximum inhibitor levels of 0.6M hydroxide and 0.2M nitrite pitting and SCC occur in simulate waste solutions containing 5.5 to 8.5M nitrate, but that time to significant corrosion is greater than 100 days.

5.1 PITTING

Based on the electrochemical data, the susceptibility to pitting was improved with heat treatment and the presence of mill scale but only at the lower temperature of 25 °C. Differences in susceptibility as a function of heat treatment or the presence of a mill scale were smaller in solutions with the maximum inhibitor concentration although pitting was observed in all tests at the base metal. Some resistance to pitting was observed in the electrochemical testing on weld metal (Table 4-4) where passivity was noted in solutions with maximum inhibitor concentrations at 25 °C. The reason for this difference is unknown but may be associated with microstructural differences [3]. Any differences between the weld and base metal appear to diminish with time since pitting was observed in both the weld and base metal in the long-term non-polarized U-bend testing which had a maximum inhibitor concentration of 0.1M OH^- and 0.1 M NO_2^-. These tests were also at a higher nitrate concentration of 8.5M and a temperature of 50 °C. After 100 days, these U-bend coupons were found to have minimal corrosion with no significant pitting especially on immersed sections of the coupons.

5.2 STRESS CORROSION CRACKING

In both the U-bend coupon (Table 4-1) and SSRT testing (Table 4-5), SCC was observed at inhibitor concentrations up to 0.6M hydroxide and 0.2M nitrite. The HT U-bend coupons in the long-term non-polarized test showed resistance to cracking since only AR U-bends had cracks. The crack indications observed on the one heat-treated U-bend coupon was a groove-like feature. In the SSRT, cracking was observed only on polarized samples but with applied potentials as small as approximately 100 mV from the OCP. This small polarization could easily occur during exposure of the carbon steel to these solutions as noted by the OCP data for the long-term U-bend coupons that were exposed at the LAI (Table 4-3) where potential shifts of 80-207 mV were noted.

In the first phase of testing, cracking was not observed on polarized U-bend coupons that were not heat treated for higher inhibitor concentrations (>0.1M), whereas in this phase of testing cracking was observed on heat treated U-bend coupons. The attack on these samples also appeared to be end-grain attack in nature, which was not observed previously. Heat treatment may sufficiently change the nature of grain boundaries for this type of attack to occur. Further investigation of this phenomenon would be needed.

Similar types of SSRT results were obtained by Ondrejcin although his test technique differed slightly [7]. Ondrejcin's results were used to establish the current inhibitor requirements.

An important finding of this work is the initiation of cracks in the VS. Previous experimental efforts were unsuccessful since these tests were performed for much shorter times (approximately 3 months versus 18 months for the current tests). The initiation of VS cracks therefore may take extended periods of time at conditions below the current inhibitor requirements. The length of these cracks has not been measured at this time. The re-exposure of these samples would be useful to determine if arrested cracks that experience some degree of general corrosion can re-initiate crack growth, like the growth of cracks observed in Tank 15 [8]. Additional testing may also include the effect of inhibitor concentration change (inside requirements to outside requirements) on this initiation.

A537 carbon steel exposed to high nitrate (> 5.5M) solutions at inhibitor levels below the current specifications (0.6M OH^- and 1.1M $OH^- + NO_2^-$) is susceptible to pitting and SCC. Salt dissolution processing should maintain current inhibitor requirements for high nitrate salt chemistries to prevent initiation of these localized corrosion mechanisms.

6.0 CONCLUSIONS AND RECOMMENDATIONS

This experimental program was conducted to evaluate the pitting and SCC susceptibility of the Type III/IIIA waste tank materials in high nitrate waste simulants (4.5 -8.5M) with the maximum inhibitor concentrations of 0.6M NaOH and 0.2M $NaNO_2$. The program was conducted in two phases; the results of the first phase were reported previously (WSRC-STI-2006-00029). In this second phase, corrosion testing using several test methods (U-bend, CPP, and SSRT) was performed on A537 carbon steel specimens that were modified to represent the "as-fabricated" condition of the tank wall, including specimens with mill scale, ground welds and stress-relief heat treatments. The key corrosion test results are the following:

- In long-term, non-polarized U-bend testing, heat treatment, similar to the waste tank stress relief regime, reduced the incidence of cracking over the 18-month test period. Vapor space SCC was found to initiate.

- In polarized U-bend testing, cracking occurred on U-bend coupons that had welds prepared similar to those of the waste tanks, i.e. ground and heat treated.

- In electrochemical testing, pitting occurred on all coupons independent of heat treatment, inhibitor concentration, temperature, surface preparation, or welding.

- In slow strain rate testing, cracking occurred on samples tested in solutions containing up to the maximum inhibitor concentration.

The primary conclusion derived from this experimental program is that A537 carbon steel exposed to high nitrate (> 5.5M) solutions at inhibitor levels below the current specifications (0.6M OH^- and 1.1M $OH^- + NO_2^-$) are susceptible to localized corrosion in the form of pitting and stress corrosion cracking. Long-term storage (e.g., greater than 100 days) of dissolved salt solutions not meeting the current inhibitor specifications for high nitrate salt chemistries in Type III waste tanks shall be avoided. Short term storage (e.g., less than 100 days) at low temperatures (e.g., less than 50 °C) in these tanks is permissible for waste removal purposes. The stress relief process reduces the risk of SCC in the Type III waste tanks. On the other hand, the current inhibitor specifications should be strictly followed for the Type I, II and IV waste chemistry to prevent initiation of localized corrosion mechanisms. These tanks were not stress relieved and are more susceptible to SCC.

Further investigation of the VS SCC is recommended to increase the understanding of conditions that lead to its initiation and propagation.

7.0 ACKNOWLEDGEMENTS

The authors would like to acknowledge the following people for their dedicated assistance and experimental contributions to this work: K. M. Counts, T. H. Murphy, K. R. Hicks, D. L. Williams, and M. J. Williamson.

8.0 REFERENCES

1. “CSTF Corrosion Control Program: Program Description Document,” WSRC-TR-2002-00327, Rev. 3, November 1974

2. B. J. Wiersma, “Task Plan for the Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations,” SRNL-MST-2005-50019, August 2005

3. B. J. Wiersma, J. I. Mickalonis, “Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations,” WSRC-STI-2006-00029, November, 2006

4. K. M. Counts et al, “Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations – Interim Report,” WSRC-STI-2007-00552, December, 2007

5. K. M. Counts et al, “Task Plan for the Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations – Additional Testing,” SRNL-MST-2007-00097, May 2007

6. K. Subramanian et al, “Vapor Space Stress Corrosion Cracking of Radioactive High Level Waste Tanks,” Corrosion2009, #09436, NACE International, Houston TX, 2009

7. R. S. Ondrejcin, “Prevention of Stress Corrosion Cracking in Nuclear Waste Storage Tanks,” DP-MS-83-79, April 1984

8. P. E. Zapp and L. S. Lam, “Preliminary Evaluation of Tank 15 Vapor Space Cracking,” WSRC-TR-2000-00187, June 2000

DISTRIBUTION

Liquid Waste
C. M. Cole
M. E. Maryak
A. W. Wiggins

Savannah River National Laboratory
B. L. Garcia-Diaz
N. C. Iyer
J. I. Mickalonis
R. L. Sindelar
B. J. Wiersma
K. E. Zeigler