Electrochemical Corrosion Studies for Tank 241-AN-107, Core 309 Segments 21R1 and 21R2

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Abstract: Liquid waste in tank 241-AN-107 is below Technical Safety Requirements Administrative Control 5.16 (AC 5.16) limits. Electrochemical corrosion testing was performed on Core 309, Segments 21R1 and 21R2, to provide information on the conductivity and corrosive tendencies of the tank saltcake and interstitial liquid. This report describes data obtained under the execution of RPP-PLAN-29001, "Electrochemical Corrosion Studies for Tank 241-AN-107 Core 309, Segments 21R1 and 21R2." Analytical results are presented that show supernatant was within the limits while the interstitial liquid remained below the limits for the analytical cores. Applicable AC 5.16 chemistry control limits for AN-107 are presented.

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Revision 1

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TABLE OF CONTENTS

List of Figures

List of Tables

List of Terms

Abbreviations

AC	Administrative Control
AN-107	tank 241-AN-107
ASTM	American Society for Testing and Materials
CPP	cyclic potentiodynamic polarization
OCP	open circuit potential
TGA	thermogravimetric analysis

Units

°C	degrees Centigrade
kgal	kilogallon
µA	microampere

µg/mL	micrograms per milliliter
<u>M</u>	molar or moles per liter
mL	milliliter
mpy	mils per year
mV	millivolt
wt	wt%

1. INTRODUCTION

Revision 1 of this test report incorporates the addition of a cyclic potentiodynamic polarization (CPP) scan for tank 241-AN-107 (AN-107) supernatant as well as Tafel scans (Appendix A). These scans were carried out under test plan RPP-PLAN-34379, *Electrochemical Corrosion Test Plan for Tanks 241-AW-103, 241-AZ-102, 241-AN-106, 241-AN-107, 241-AY-101, and 241-AY-102*. The results of the Tafel scans are reported in RPP-RPT-34697, *Electrochemical Corrosion Report for Tanks 241-AW-103, 241-AZ-102, 241-AN-106, 241-AN-107, 241-AY-101, and 241-AY-102.*

The liquid waste in AN-107 has been below the HNF-SD-WM-TSR-006, *Tank Farms Technical Safety Requirements*, Administrative Controls (AC) 5.16, "Corrosion Mitigation Controls," since before November 1984 (internal memorandum 7C240-92-072, "Action Plan for Adding Caustic to Tank 241-AN-107"). The supernatant was mitigated in February 2002 with a 42-kgal addition of 50-wt% sodium hydroxide (caustic). This initial caustic addition volume was less than required to mitigate the bulk tank waste. Concerns with solids precipitation existed at the time and prevented one large addition. A second caustic addition, 23.6 kgal of 50-wt% caustic, was made to the tank in April 2003 to return the calculated bulk waste within the AC 5.16 limits.

The tank was core sampled, Core 309, between June and August 2003 following the second caustic addition. Analytical results from the sampling event are presented in Table 1. The supernatant was within the limits while the interstitial liquid remained below the limits for the analytical cores.

Table 1. Tank 241-AN-107 Core 309 Analytical Results.

Segment Number	OH^- (µg/mL)	NO_2^- (µg/mL)	NO_3^- (µg/mL)
1	2.38E+04	5.66E+04	2.13E+05
9	2.24E+04	5.70E+04	2.16E+05
16	2.36E+04	5.89E+04	2.25E+05
Segment Number	**pH**	**NO_2^- (µg/mL)**	**NO_3^- (µg/mL)**
18R1UH	11.6	6.86E+04	1.93E+05
18R1LH	11.2	6.99E+04	1.95E+05
19	11.1	6.88E+04	1.90E+05
20	11.0	5.84E+04	1.82E+05
21	11.6	6.78E+04	1.86E+05

Note: Data from interoffice memo 7S120-HLB-03-001, "Update Tank 241-AN-107 Fiscal Year 2003 Core Sample Analytical Results for the Final Report."

Table 2 presents the applicable AN-107 AC 5.16 chemistry limits. The nitrate (NO_3^-) concentration in AN-107 is greater than 3.0 M (1.86E+05 µg/mL). The 0.3 M hydroxide (OH^-) concentration lower limit is equivalent to 5.10E+03 µg/mL or approximately pH 13.48. The lowest nitrite (NO_2^-) concentration in the tank waste (5.66E+04 µg/mL) is approximately equivalent to 1.23 M, which already meets the sum of the hydroxide and nitrite limit.

Table 2. Applicable AC 5.16 Chemistry Control Limits.

Constituent	Limit
$[OH^-]$	0.3 $\underline{M} \leq [OH^-] < 10\ \underline{M}$
$[OH^-]+[NO_2^-]$	$\geq 1.2\ \underline{M}$
$[NO_3^-]$	$\leq 5.5\ \underline{M}$

During the Core 309 sampling event, two Segment 21 retakes (309-21R1 and 309-21R2) were obtained for electrochemical corrosion testing. These retake segments are representative of the out-of-specification waste at the bottom of the tank surrounding the knuckle region. Electrochemical corrosion testing is required on these two segments to provide information on the conductivity and corrosive tendencies of the AN-107 saltcake and interstitial liquid. Results of this testing will provide actual values for parameters important to establishing proposed revised chemistry control specifications based on laboratory work using AN-107 simulant waste.

This report describes data obtained under the execution of RPP-PLAN-29001, *Electrochemical Corrosion Studies for Tank 241-AN-107 Core 309, Segments 21R1 and 21R2.*

This work was carried out under ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory*, and HNF-SD-CP-QAPP-016, *222-S Laboratory Quality Assurance Plan.*

2. MATERIALS AND METHODS

The coupons used in this study were obtained from Metal Samples®[1] and were A537 Class 1 EL410 (right cylinder configuration). All coupons were prepared by washing with hexane to remove the oxygen barrier film after fixing the coupon to the electrode rod.

As an instrument check, a scan using the ASTM G5-94, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*, was carried out in the 125-mL cell and the 500-mL cell.

Segment 21R1 horizontally extruded 17 inches of solids. The solids were light brown in color. The bottom lower half resembled a sludge slurry (D2), gradually becoming a wet slurry (D3) in the upper half (Figure 1). The CPP scans were run as the sample was received.

The solids were transferred to centrifuge cones and centrifuged using a table-top swinging bucket centrifuge for 24 hours. Approximately 60 mL of interstitial liquid was retrieved. Approximately 5 mL of the liquid was submitted for analyses (Table 3). The interstitial liquid was transferred to an [2] I-CHEM™125-mL glass jar which served as the test cell. Segment 21R2 (approximately 300 mL) was vertically extruded anaerobically under argon into a 500-mL I-CHEM™ jar that served as the test cell. Since 21R2 was extruded vertically, the discrete visualization of the segment was not possible as in a horizontal extrusion. Table 4 shows chemical analyses of the extruded saltcake.

[1] Metal Samples® is a division of Alabama Specialty Products, Inc., Munford, Alabama.
[2] I-CHEM™ is a subsidiary of Nalge Nunc International Corporation, Rochester, New York.

Figure 1. Horizontal Extrusion of Core 309, Segment 21R1.

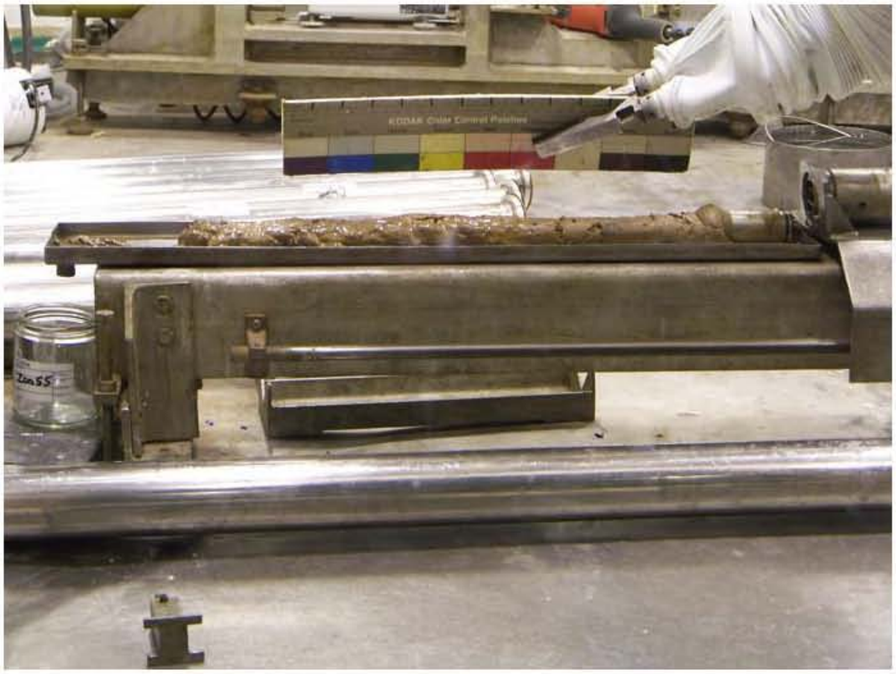


Table 3. Analytical Results, Sample number SO6T000252, Core 309, Segment 21R1 Interstitial Liquid.

Analyte	Unit	Average
pH direct	pH	11.2
% water by TGA	%	49.7
Fluoride-IC-Dionex 500 col	µg/mL	106
Glycolate-IC-Dionex 500 ORGACD	µg/mL	1.35E+04
Acetate by IC-Dionex 500 col	µg/mL	<488
Formate by IC-Dionex 500 col	µg/mL	8.98E+03
Chloride-IC-Dionex 500 col	µg/mL	1.57E+03
Nitrite-IC - Dionex 500 col	µg/mL	6.47E+04
Sulfate-IC-Dionex 500 col	µg/mL	7.77E+03
Oxalate-IC-Dionex 500 col	µg/mL	662[a]
Bromide-IC-Dionex 500 col	µg/mL	<2.96E+03
Nitrate-IC-Dionex 500 col	µg/mL	1.82E+05
Phosphate-IC-Dionex 500 col	µg/mL	2.41E+03

[a] Sample was <573, duplicate was 662.

TGA= thermogravimetric analysis

Table 4. Analytical Results Core 309, Segment 21R2 Saltcake.

Analyte	Unit	Average
Nitrate-IC Dionex 500 col	µg/g	1.05E+05
Nitrite-IC Dionex 500 col	µg/g	3.66E+04
pH	pH	11.5
% water by TGA	%	43.9

TGA= thermogravimetric analysis

3. RESULTS

All scans presented in this report used a saturated calomel electrode as the reference electrode. The results of the ASTM scans are presented in Figures 2 and 3.

Figures 4 and 5 are CPP scans of the interstitial liquid and the saltcake carried out at ambient hot cell temperature (25 to 27 °C).

Figure 2. ASTM Scans using the 125-mL Cell.

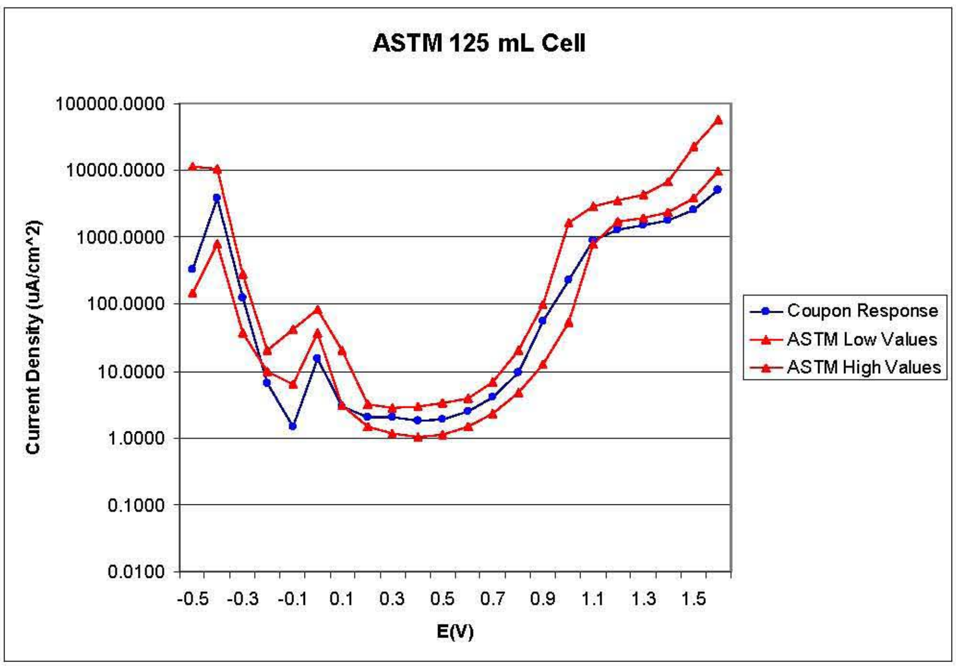


Figure 3. ASTM Scans using the 500-mL Cell.

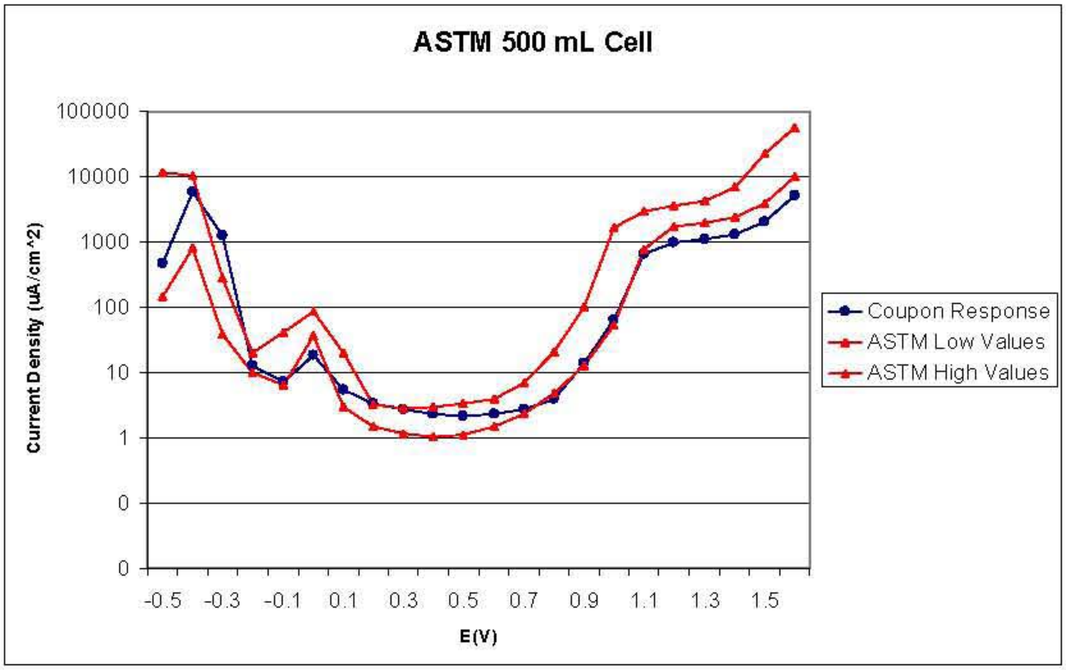


Figure 4. Cyclic Potentiodynamic Polarization of Interstitial Liquid from Core 309, Segment 21R1.

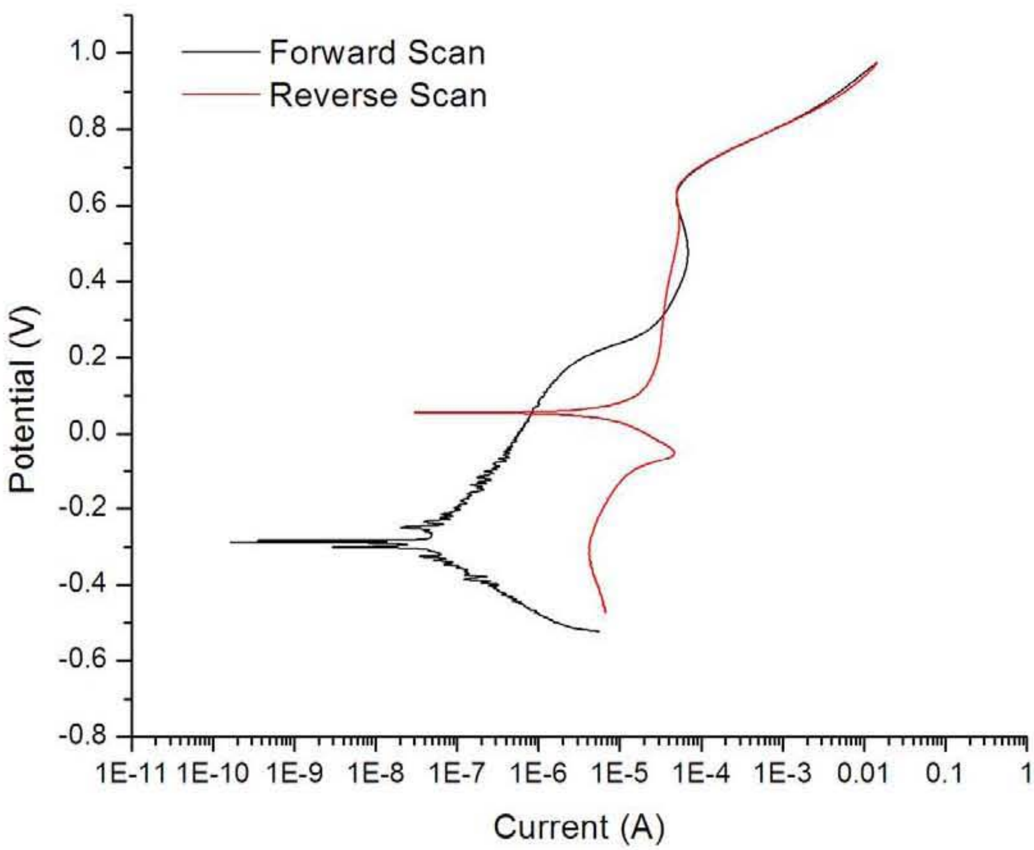


Figure 5. Cyclic Potentiodynamic Polarization of Core 309, Segment 21R2 Saltcake.

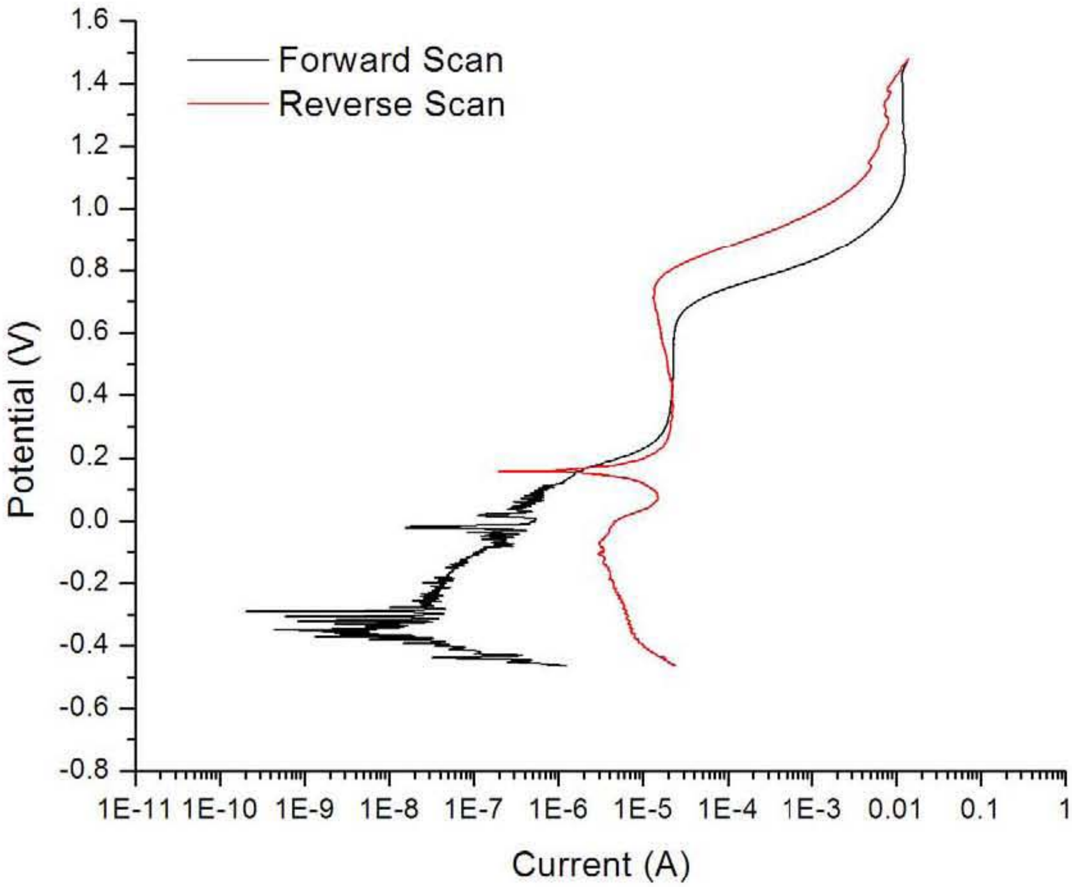


Table 5 shows scan results using PowerCORR®[3] software.

Table 5. Scan Results using PowerCORR Software.

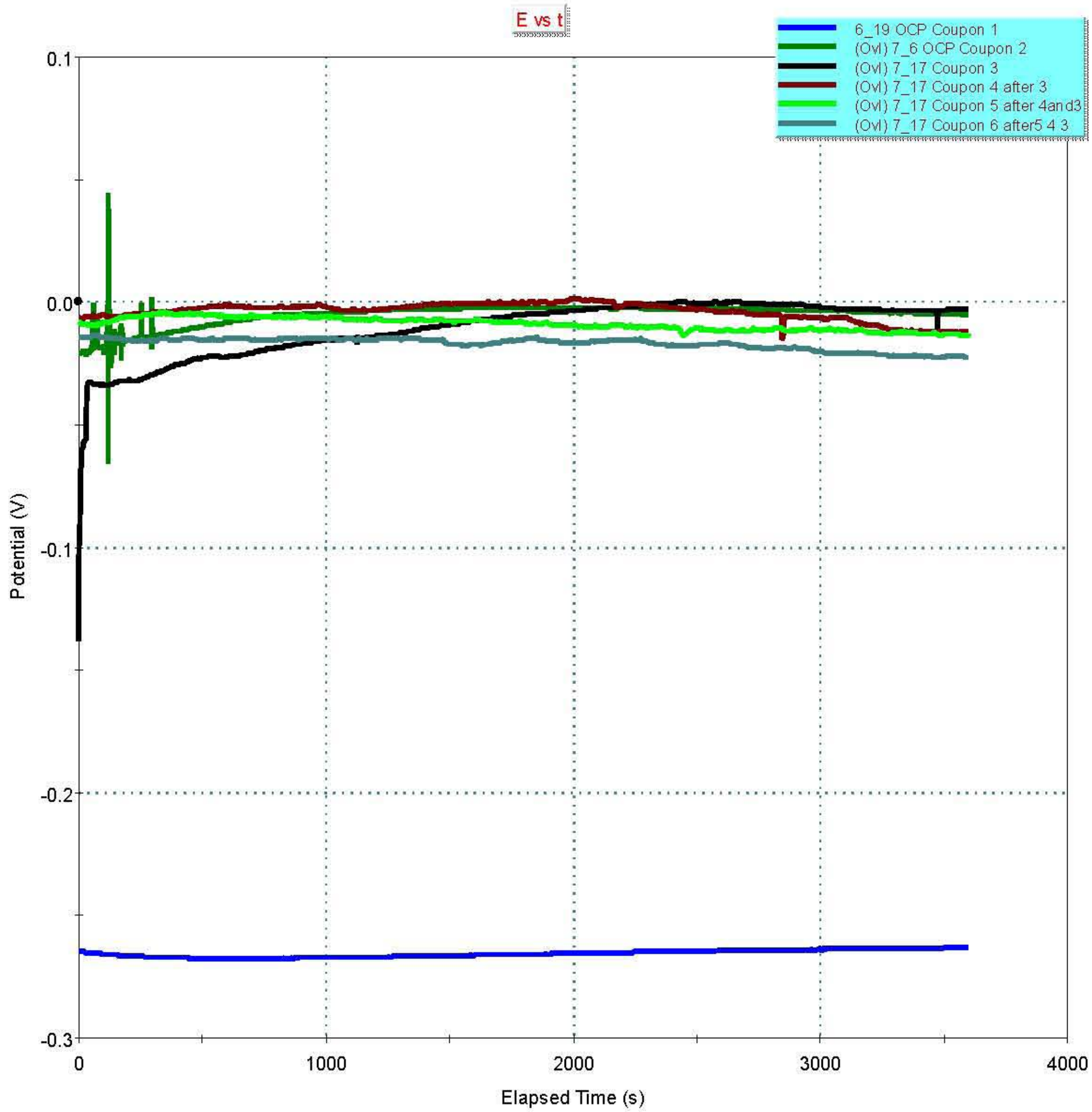
Parameter	Interstitial Liquid	Saltcake
Open circuit potential	-293.3	-347.9
Icorr (µA)	4.7E-02	1.7E-02
Ca Beta (mV)	142.4	110.3
An Beta (mV)	261.5	380.2
Co. Rate (mpy)	3.6E-03	1.3E-03
Chi-square	54.6	65.2

A long-term open circuit potential (OCP) was performed on six coupons placed in saltcake. The first OCP was run after 10 days residence time. The second OCP was run after 27 days residence time. During the execution of the second OCP, it was noticed that the electrochemical cell had a fracture line towards the bottom of the cell. From outside the hot cell, it appeared as if no liquid material had escaped. The cell was observed over the next several days and at day 38 residence

[3] PowerCORR® is a registered trademark of Princeton Applied Research®, a business unit of Advanced Measurement Technology, Inc., a division of AMETEK, Inc., Oak Ridge, Tennessee.

time, it was noticed that the cell had begun leaking. At day 38 residence time, coupon 3 was scanned, followed by coupons 4, 5, and 6. Figure 6 shows the OCP scan results.

Figure 6. Long-Term Open Circuit Potential Scan Results.



4. DISCUSSION

As indicated by the CPP scans in Figures 4 and 5, there was no evidence of pitting propensity. Figure 7 and 8 are scanning electron micrographs of a control (nonexposed) coupon and the coupon used in the saltcake scan. As evidenced from the micrographs, there is no significant difference in the surfaces of the two coupons.

Figure 7. Scanning Electron Micrograph of Control Coupon.

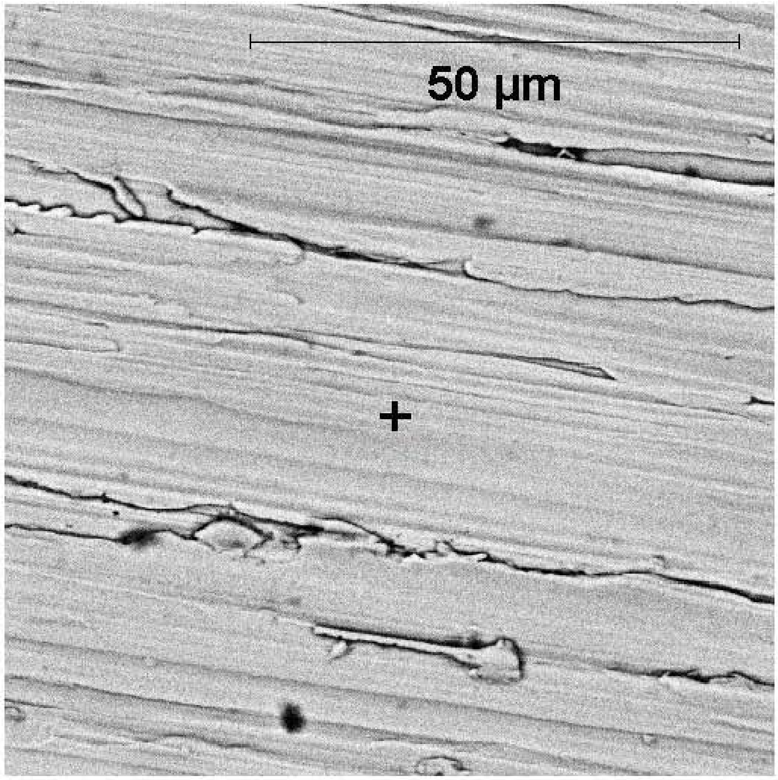
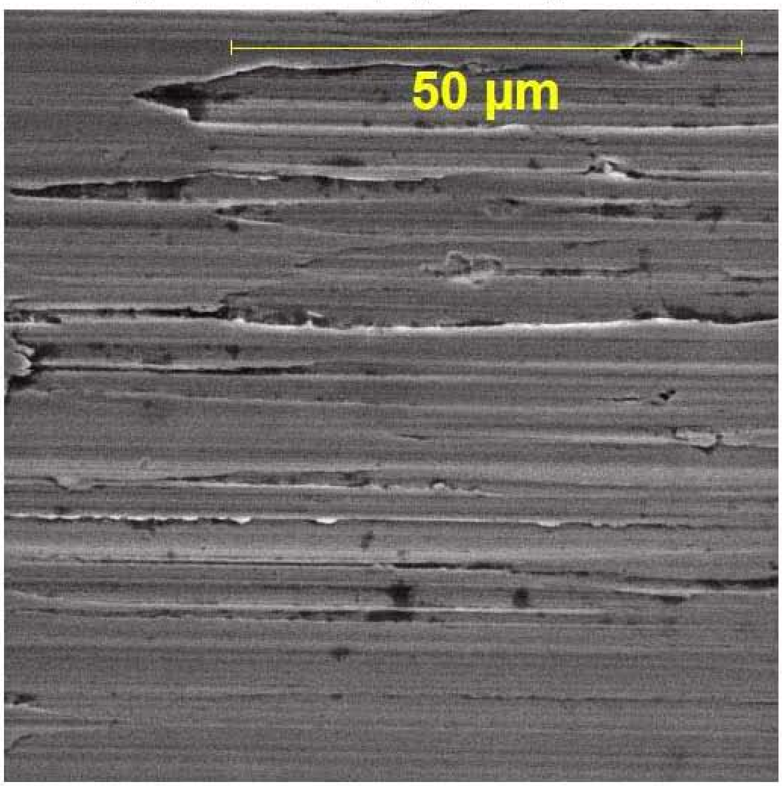


Figure 8. Scanning Electron Micrograph of Coupon Scanned in Saltcake.



The OCP graph indicates that the longer exposure to the saltcake, the more positive the OCP becomes. The OCP of the coupons placed in the interstitial liquid and the saltcake measured 293.3 and -347.9, respectively.

Due to the sample material being both radioactive and aggressive chemistry, it was not possible to track OCP as a continuous function. However, it can be safely assumed that the OCP did, in most probability, maintain a positive slope from an initial point. Evans et al., "Long Term Corrosion Potential and Corrosion Rate of Creviced Alloy 22 in Chloride Plus Nitrate Brines," showed that a long-term OCP test (using different steel) did attain a positive slope.

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Appendix A

Tafel and Cyclic Potentiodynamic Polarization Curves

Figure A-1. Core 309, Segment 1, Coupon A, Supernatant Cyclic Potentiodynamic Polarization Scan, Potential versus Saturated Calomel Electrode.

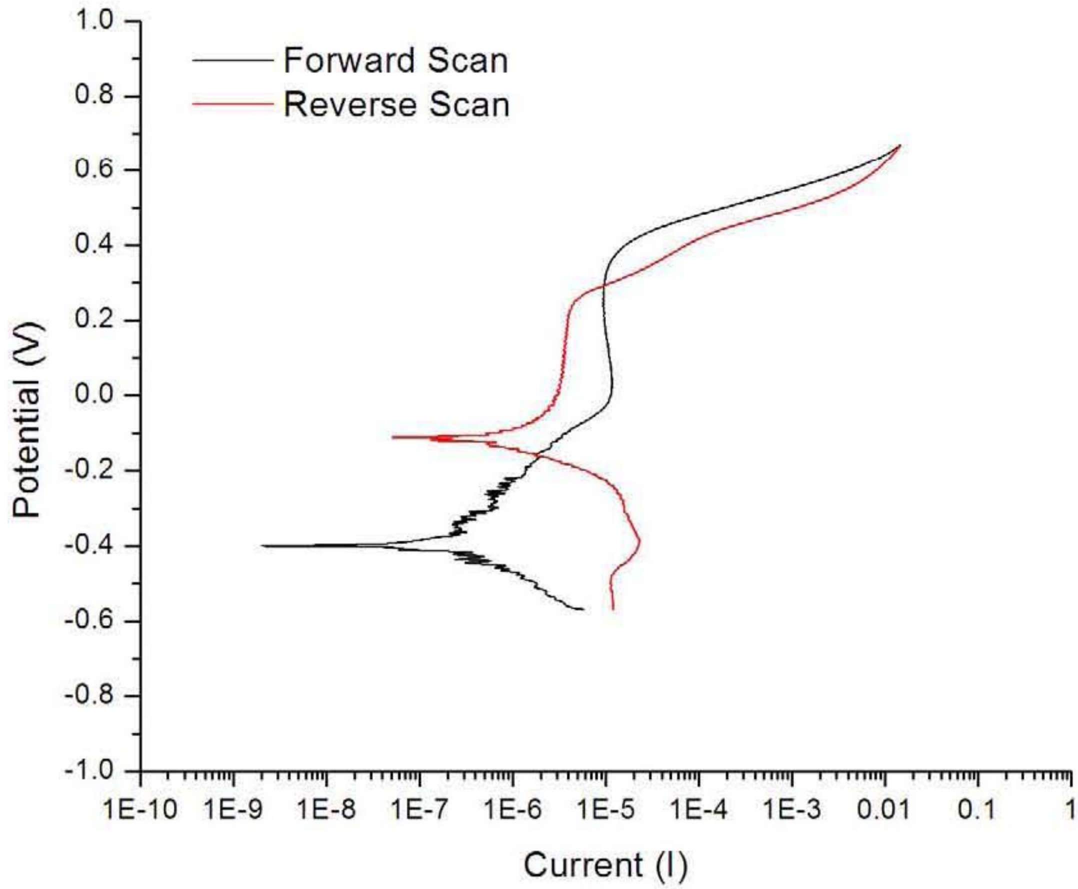

Figure A-2. Tafel Scan for Tank 241-AN-107 Supernatant, Coupon 1, Potential versus Saturated Calomel Electrode.

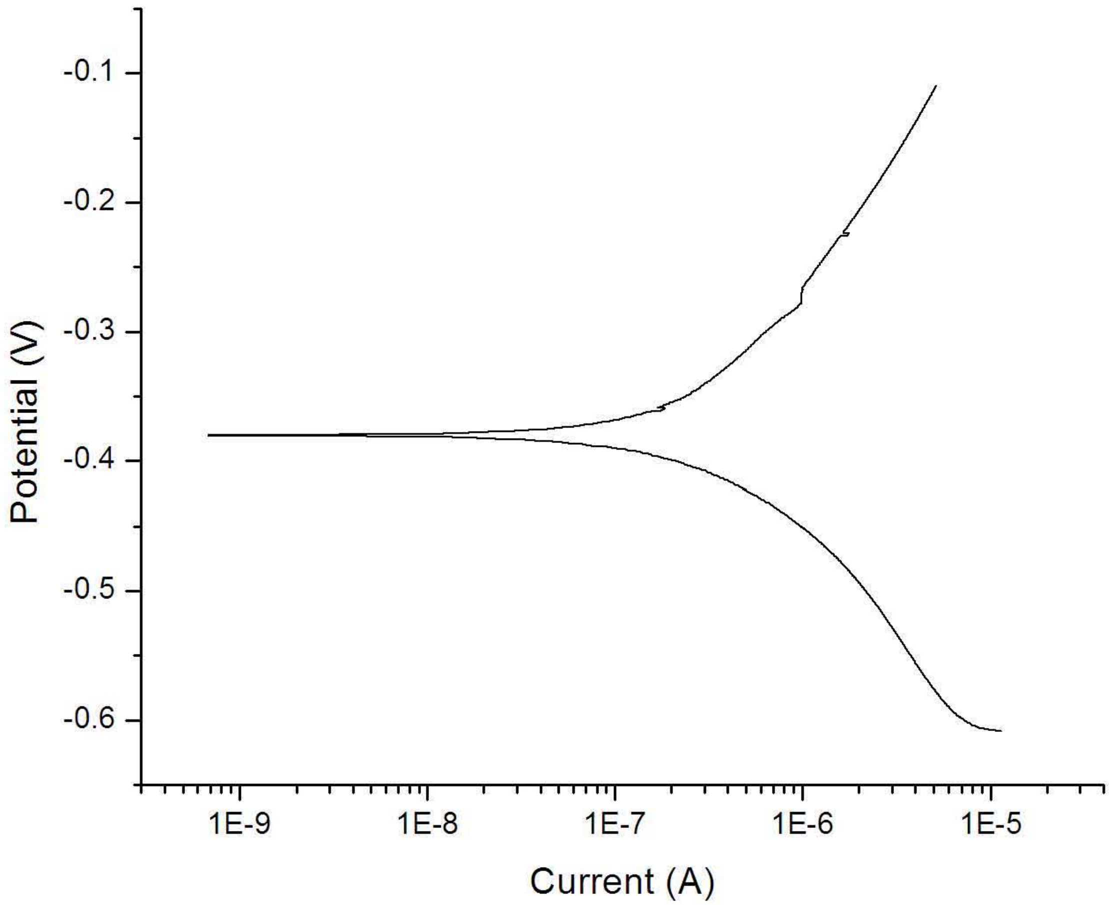

Figure A-3. Tafel Scan for Tank 241-AN-107 Supernatant, Coupon 2, Potential versus Saturated Calomel Electrode.

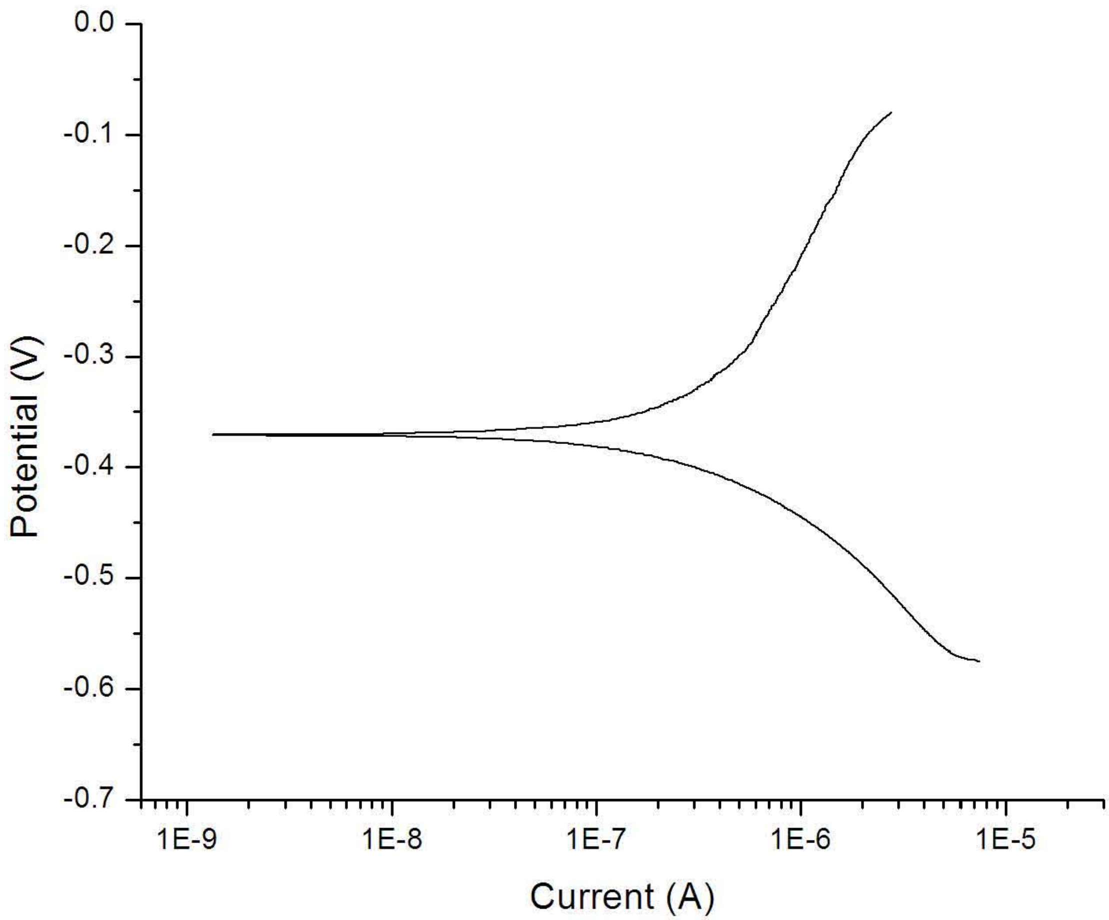

Table A-1. Corrosion Rates for Cyclic Potentiodynamic Polarization and Tafel Scans.

Coupon	OCP (mV)	i_{CORR} (μA)	Corrosion Rate (mpy)	χ^2
1	-379.8	2.76E-01	2.16E-02	1.68
2	-370.7	4.75E-01	3.72E-02	0.55
A	-398.4	4.00E-01	3.14E-02	76.1