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Revision 0

Report on Electrochemical Corrosion Testing of 241-SY-102 Grab Samples from the 2012 Grab Sampling Campaign

R. B. Wyrwas
M. E. Lamothe
Washington River Protection Solutions LLC

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Acronyms and Abbreviations

CPP	cyclic potentiodynamic polarization
E_{corr}	corrosion potential
I_{corr}	corrosion current
LPR	linear polarization resistance testing
MPY	calculated corrosion rate
OCP	open circuit potential
R_p	polarization resistance
SY-102	tank 241-SY-102

Units

°C	degrees Centigrade
cm	centimeter
hr	hour
mL	milliliter
mV	millivolts
mA	milliamperes
mil	0.001 inches
mpy	mils per year
min	minute
M	moles per liter
nA	nanoamperes
sec	second

1 INTRODUCTION

This report describes the results of the electrochemical testing performed on tank 241-SY-102 (SY-102) grab samples that were collected in support of corrosion mitigation under RPP-PLAN-51499, *Tank 241-SY-102 Grab Sampling and Analysis Plan for Waste Chemistry Control.* The objective of the work presented here was to determine corrosion resistance of tank SY-102 to the grab samples collected using electrochemical methods up to 50 °C as well as to satisfy the data quality objectives in RPP-8532, *Double-Shell Tanks Chemistry Control Data Quality Objectives.*

Grab samples were collected at multiple elevations from Riser 003. The sample location and chemistry data relevant to corrosion control are given in Table 1. Grab samples 2SY-12-01, 2SY-12-03, and 2SY-12-04 are not within the operating specifications laid out in OSD-T-151-00007, *Operating Specifications for the Double-Shell Storage Tanks.* The minimum concentration value for the sum of the hydroxide and nitrite inhibitors in each of the grab samples 2SY-12-01, 2SY-12-03, and 2SY-12-04 needs to be greater than 0.4 M; they do not meet this requirement. There was not adequate sample volume to perform corrosion potential testing on all three of these samples. A composite was constructed from the remaining 2SY-12-03 and 2SY-12-03DUP.

Table 1. Sample Location and Chemical Data from 2SY-12 Grab Samples and Composite Samples.

Grab Sample	Sample Location[a]	NO_2^-, M[b]	NO_3^-, M[b]	OH^-, M (pH)[b]	$OH^- + NO_2^-$, M
2SY-12-01	0.25" below liquid surface	0.22	1.00	0.16 (12.7)	0.38
2SY -12-02	0.25" above liquid surface and collect until full	0.23	1.01	0.17 (12.8)	0.40
2SY -12-03	14" below liquid surface	0.22	1.00	0.17 (12.7)	0.39
2SY -12-04	50" below liquid surface	0.22	0.99	0.17 (12.7)	0.39
2SY -12-05	100" below liquid surface	0.32	1.59	0.57 (13.0)	0.89
2SY-12-06	10" above solids	0.37	1.76	0.66 (13.1)	1.03

[a] As described in inches; see Table 3-1 in RPP-PLAN-51499 for additional details.
[b] From RPP-RPT-54004, *Final Report for Tank 241-SY-102 Samples in Support of the Waste Chemistry Control, Strategic Planning, and Waste Compatibility Programs*, given in moles per liter (M).

The electrochemical corrosion testing was planned to consist of linear polarization resistance testing (LPR) and cyclic potentiodynamic polarization (CPP) testing at 50 °C. The temperature would be lowered to 40 °C and the test repeated if the CPP curve indicated pitting corrosion at 50 °C. If no pitting was indicated by the CPP curve, then a duplicate scan would be repeated at 50 °C to confirm the first result. The testing would be complete if the

duplicate CPP scan was consistent with the first. This report contains the CPP results of the testing of grab sample 2SY-12-03 and 2SY-12-03DUP composite sample tested under these conditions. There was no indication of pitting at 50 °C, and the duplicate scan was in agreement with the first scan. Since no further testing was required, a third scan with a shorter rest time was performed and is present in this report.

2 TESTING PROTOCOL

2.1 MATERIALS

The coupons used in this study were obtained from Metal Samples®[1] and were A537 Class 1 EL410 (right cylinder configuration) with a surface area of 5.31 cm^2. All coupons were prepared by a surface treatment of sonication in acetone for 2 min, followed by a rinse with hexane. The coupon was then fixed to a type 316 stainless steel electrode rod with a Teflon®[2] gasket and glass tube. A new sample coupon was used for each CPP scan. A coupon made of 430 stainless steel was used for the Quality Assurance test described in Section 2.2.1.

2.2 METHODS

2.2.1 Quality Assurance

As an instrument check, a scan using the ASTM®[3] G5-94, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*, was carried out in a 500-mL I-CHEM®[4] jar used as the electrochemical cell before and after the corrosion potential scans.

The data collected in this report was managed under ATS-MP-1032, *222-S Laboratory Quality Assurance Project Plan.*

2.2.2 Electrochemical Methods

The electrochemical techniques, such as open circuit potential (OCP), LPR, and CPP, are described in detail in ATS-LT-512-101, "222-S Laboratory Electrochemical Corrosion Measurements." For each test performed, the OCP of an A537 carbon steel coupon that is similar to the tank steel was measured with respect to a saturated calomel reference electrode during the rest period of at least 12 hr before polarization experiments were conducted. After the initial rest period, an LPR was performed, scanning from 25 mV below the OCP to 25 mV above the measured OCP at 0.166 mV/sec (or 10 mV/min). Following this measurement the coupon

[1] Metal Samples® is a division of Alabama Specialty Products, Inc., Munford, Alabama.
[2] Teflon® is a registered trademark of I. E. du Pont de Nemours and Company, Wilmington, Delaware.
[3] ASTM is a registered trademark of the American Society for Testing and Materials, West Conshohocken, PA.
[4] I-CHEM® is a subsidiary and registered trademark of Nalge Nunc International Corporation, Rochester, New York.

was allowed to re-equilibrate at OPC for 1 hr. The OCP was measured during this rest period; at the end of the 1-hr rest period, a CPP scan was performed. The CPP scan ranged from -200 mV below the OCP and reversed at 2.5 mA/cm^2 at a scan rate of 0.166 mV/sec (or 10 mV/min.), unless otherwise specified. Temperature controllers and regulating blocks were implemented for these experiments. The regulating system allowed for the temperature to be raised or lowered and provided a more stable temperature for the duration of the experiment. All experiments were performed on the sample as received and open to the air. The electrochemical cell was fitted with a reflux tube to allow for the expansion of the headspace during temperature adjustments and to restrict liquid loss.

2.3 TERMINOLOGY

Corrosion Potential (E_{corr}): the potential at which all of the oxidation and reduction reactions are at equilibrium. The values reported here were determined using the Tafel slope calculation and polarization resistance calculation discussed in ATS-LT-512-101.

Corrosion Current (I_{corr}): a measurement of the corrosion rate expressed in term of nanoAmperes (10^{-9} Amperes). This is determined from the Tafel slope calculation or polarization resistance measurements discussed in ATS-LT-512-101.

Polarization Resistance (R_p): the slope linear portion of the voltage vs. current measurement resulting from the LPR measurement at or around the corrosion potential.

3 RESULTS AND DISCUSSION

The CPP scans for the 2SY-12-03 Composite grab sample at 50 °C are plotted in Figures 1 and 2. The CPP curves show a negative hysteresis indicated by the reverse scan (red) returning at a lower current density than the forward scan (black). This means there is no susceptibility of pitting based on the samples tested. Table 2 gives the measured and calculated values for the corrosion potential (E_{corr}), corrosion current (I_{corr}), polarization resistance (R_p), and calculated corrosion rate (MPY) in mils per year (mpy). Appendix A contains all the corrosion calculation data from the calculations.

Figure 1. Primary Cyclic Potentiodynamic Polarization Scan for 2SY-12-03 Composite at 50 ℃.

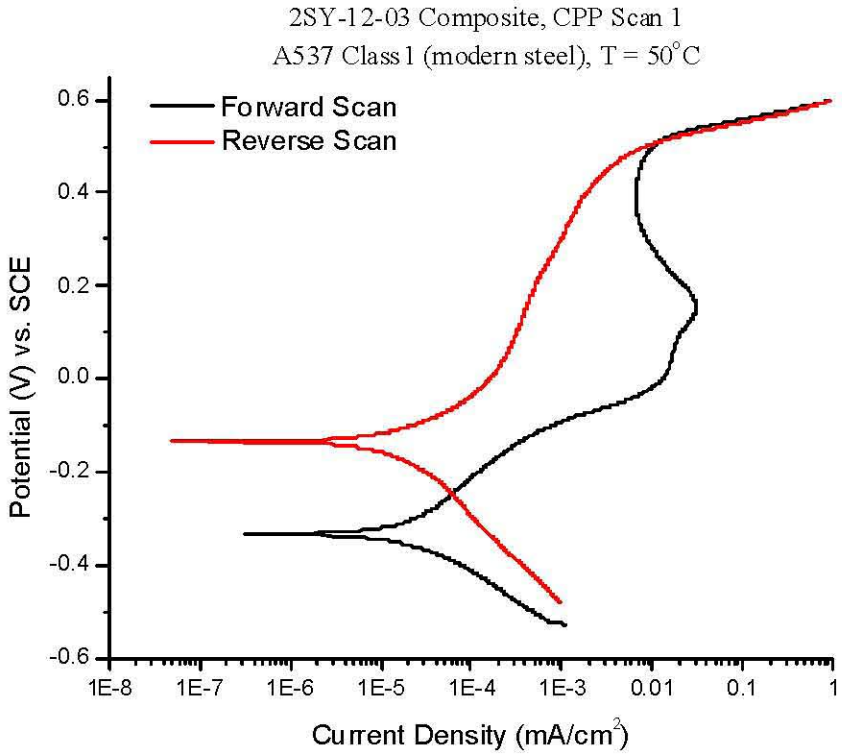


Figure 2. Duplicate Cyclic Potentiodynamic Polarization Scan for 2SY-12-03 Composite at 50 °C.

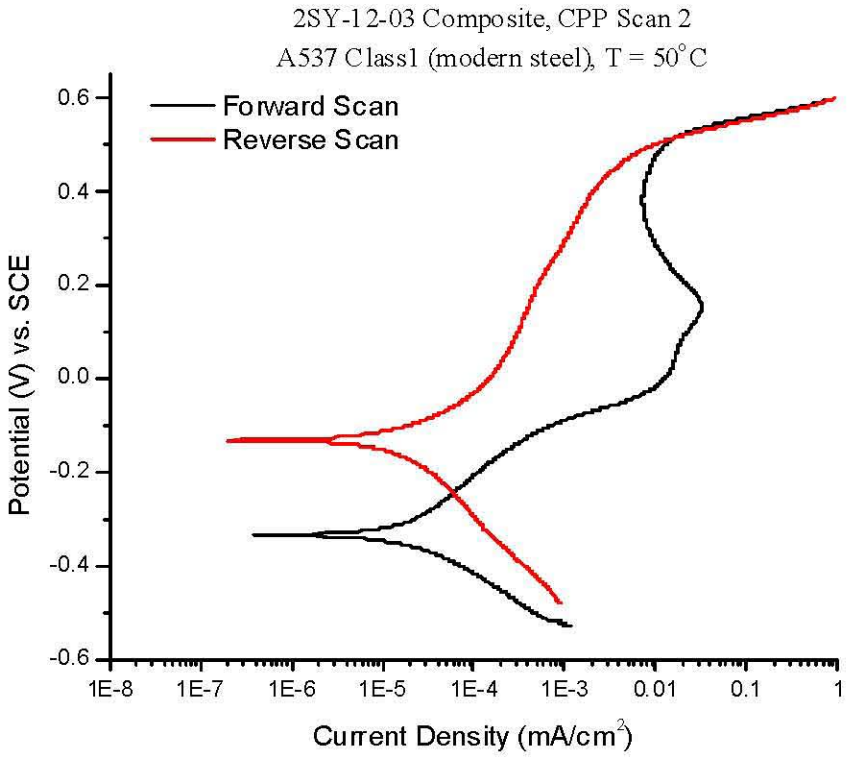


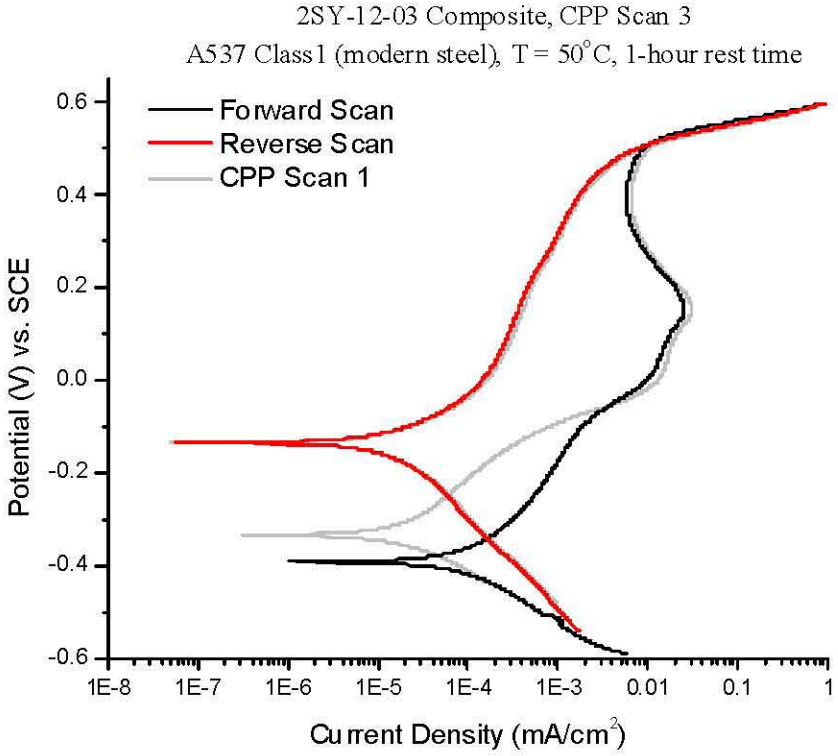
Table 2. Values from Corrosion Potential Measurements from Cyclic Potentiodynamic Polarization Tests and Linear Polarization Resistance Tests.

	E_{corr} (mV)	I_{corr} (nA)	R_p (ohms)	MPY
Scan 1 CPP	-331	157	-	0.014
LPR	-334	164	2.16 E+5	0.014
Scan 2 CPP	-331	139	-	0.012
LPR	-333	145	2.36 E+5	0.013
Scan 3 CPP	-390	836	-	0.072

The data presented in Figure 3 represents the CPP curve collected after a 1-hr rest period (Scan 3) as opposed to the 12-hr rest period used in Scans 1 and 2. An overlay of Scan 1 is included to demonstrate the difference in the two scans. The shorter rest period yielded slightly more aggressive results indicated by a lower corrosion potential and higher corrosion current.

The Tafel calculations provided in Table 2 also confirm a more aggressive corrosion rate from the short 1-hr rest period.

Figure 3. Cyclic Potentiodynamic Polarization Scan for 2SY-12-03 Composite at 50 °C with a Shortened 1-Hour Rest Period.



4 CONCLUSIONS

Grabs samples 2SY-12-03 and 2SY-12-03DUP were composited and corrosion potential measurements were conducted by electrochemical methods at 50 °C. The test results indicated that there is no propensity for pitting. The calculations conducted on the CPP and LPR data indicate low corrosion rates under these conditions. A third test was performed with a short 1-hr rest period in comparison to the long 12-hr rest period. The shorter rest period resulted in a more aggressive result, but still indicated no propensity for pitting.

5 REFERENCES

ASTM G5-94, 2004, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (Reapproved 2004),* ASTM International, West Conshohocken, Pennsylvania.

ATS-LT-512-101, "222-S Laboratory Electrochemical Corrosion Measurements," as revised, Washington River Protection Solutions LLC, Richland, Washington.

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OSD-T-151-00007, 2012, *Operating Specifications for the Double-Shell Storage Tanks,* Rev. 11, Washington River Protection Solutions LLC, Richland, Washington.

RPP-8532, 2012, *Double-Shell Tanks Chemistry Control Data Quality Objective*, Rev. 13, Washington River Protection Solutions LLC, Richland, Washington.

RPP-PLAN-51499, 2013, *Tank 241-SY-102 Grab Sampling and Analysis Plan for Waste Chemistry Control,* Rev. 1, Washington River Protection Solutions LLC, Richland, Washington.

RPP-RPT-54004, 2012, *Final Report for Tank 241-SY-102 Samples in Support of the Waste Chemistry Control, Strategic Planning, and Waste Compatibility Programs*, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

Appendix A

ELECTROCHEMICAL CALCULATION DATA

2SY-12-Composite 50 ℃

Scan 1

=== Tafel Fit (04/16/13 14:52) ===
results:
Ecorr = -334.111 mV vs. Ref
Icorr = 0.157 µA
beta c = 132.3 mV
beta a = 216.5 mV
Chi² = 0.478 906
Chi / sqrt(N) = 0.039 368 2
equivalent weight = 28.000 g/eq.
density = 7.870 g/cm3
surface area = 5.310 cm²
corrosion rate = 0.013 548 9 mpy

=== Rp Fit (04/16/13 14:56) ===
selection:
  trace: <I> vs. Ewe
  from point: 21614
    X : -0.355 1 V
    Y : -0.107 6e-3 mA
  to point: 21759
    X : -0.310 5 V
    Y : 0.106 3e-3 mA
  total points = 146
parameters:
  beta c = 132.3 mV
  beta a = 216.5 mV
  range = +/- 25.0 mV
results:
  Rp = 216 480 Ohm
  Ecorr = -334.867 mV vs. Ref
  correlation = 0.997 5
  Icorr = 0.164 929 µA
Corrosion rate = 0.014 mpy

Scan 2

=== Tafel Fit (04/16/13 14:35) ===
results:
Ecorr = -334.801 mV vs. Ref
Icorr = 0.139 µA
beta c = 126.2 mV
beta a = 208.4 mV
Chi² = 0.430 086
Chi / sqrt(N) = 0.038 118 2
equivalent weight = 28.000 g/eq.
density = 7.870 g/cm3
surface area = 5.310 cm²
corrosion rate = 0.011 995 5 mpy

=== Rp Fit (04/16/13 14:38) ===
selection:
  trace: <I> vs. Ewe
  from point: 21627
    X : -0.349 8 V
    Y : -73.49e-6 mA
  to point: 21757
    X : -0.309 7 V
    Y : 99.52e-6 mA
  total points = 131
parameters:
  beta c = 126.2 mV
  beta a = 208.4 mV
  range = +/- 25.0 mV
results:
  Rp = 235 741 Ohm
  Ecorr = -334.319 mV vs. Ref
  correlation = 0.998 5
  Icorr = 0.144 967 µA
Corrosion rate = 0.013 mpy

Scan 3

=== Tafel Fit (04/16/13 14:58) ===
results:
Ecorr = -392.399 mV vs. Ref
Icorr = 0.836 µA
beta c = 165.2 mV
beta a = 247.0 mV
Chi² = 0.056 257 3
Chi / sqrt(N) = 0.013 342 8
equivalent weight = 28.000 g/eq.
density = 7.870 g/cm3
surface area = 5.310 cm²
corrosion rate = 0.072 145 8 mpy

Electronically Approved by:

UserName: Wyrwas, Richard (h3390899)
Title: APD Chemist
Date: Wednesday, 08 May 2013, 01:47 PM Pacific Time
Meaning: Approved by the author or delegate

UserName: Page, Jason (h2841343)
Title:
Date: Wednesday, 08 May 2013, 02:07 PM Pacific Time
Meaning: Additional approval obtained

UserName: Seidel, Cary (h0009079)
Title: APD Manager
Date: Monday, 13 May 2013, 06:10 AM Pacific Time
Meaning: Approved by the customer or delegate

UserName: Elkins, Robert (h3882872)
Title:
Date: Wednesday, 15 May 2013, 09:12 AM Pacific Time
Meaning: Approved by Quality Assurance or delegate

UserName: Seidel, Cary (h0009079)
Title: APD Manager
Date: Tuesday, 21 May 2013, 07:58 AM Pacific Time
Meaning: Approved by the Group Manager or delegate

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