Corrosion Testing in Simulated Tank Solutions

E.N Hoffman[1], P.E. Zapp[1], B.J. Wiersma[1], A. Felmy[2], O. Qafoku[2]
(SRNL[1], PNNL[2])

Introduction

Vapor space localized corrosion in the form of pitting in the vapor space of tank walls is a potential challenge to overcome in maintaining the structural integrity of the liquid waste tanks at the Savannah River Site and Hanford Site.

Liquid waste condensate chemistry influences the amount of corrosion that occurs along the walls of the storage tanks.

To minimize pitting corrosion, an effort is underway to gain an understanding of the pitting response in various simulated waste solutions.

Experimental Method

Electrochemical testing has been used as an accelerated tool in the investigation of pitting corrosion.

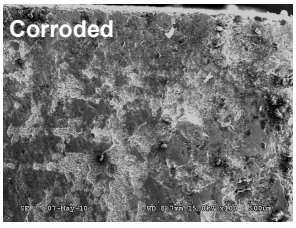
Prior to electrochemical testing, samples were characterized using X-ray diffraction and SEM/EDS with particular focus on the corrosion-scale and mill-scale.

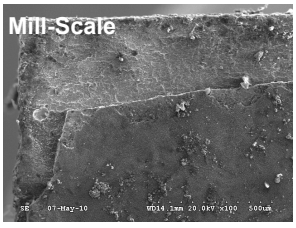
RDE-2 instrument used to reduced solution volume.

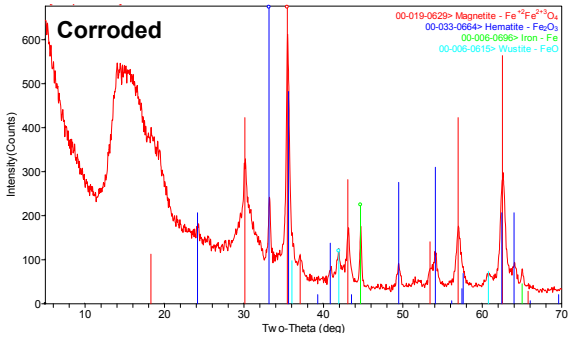
Material of Interest: ASTM A537 Carbon Steel

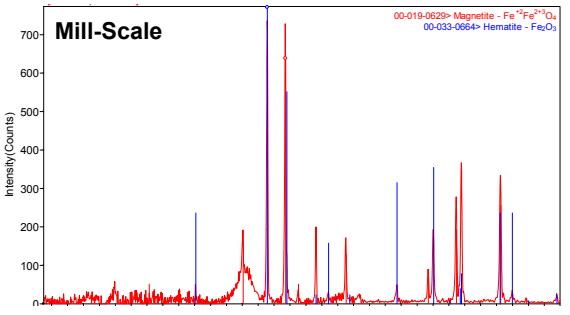
To evaluate the actual tank steel surface, a variety of surfaces were used:

- Polished
- Mill-scale
- Corroded scale
- Polished with pre-existing salt deposit









Testing Solutions

Solutions were formulated at PNNL to replicate tank conditions, and in the case of SY-102, exceed Cl^- and NO_3^- conditions, respectively, to provide a contrast between in and out of specification limits.

The ratio of NO_2/NO_3 for the SY-102 (high nitrate) solution is 0.026 versus 100 and 0.431 for the AY-102 and AN-107, respectively.

AY-102 is not a nitrate-ion waste, but a carbonate-ion waste, which yields a significantly higher NO_2/NO_3 ratio compared to AN-107 and SY-102 (high nitrate).

Solution #1: SY-102

	Molarity	Salt compound	Molarity	MW (g)	Mass (g) for 1L
Na^{+1}	4.641		4.641		
Al^{+3}	0.069	$NaAlO_2$	0.069	81.97	5.659
K^{+1}	0.001	$KHCO_3$	0.001	100.114	0.056
Br^{-1}	0.074	NaBr	0.074	102.89	7.581
Cl^{-1}	0.013	NaCl	0.013	58.44	0.747
CrO_4^{-2}	0.011	$Na_2CrO_4\ 4H_2O$	0.011	161.97	1.833
F^{-1}	0.003	NaF	0.003	41.99	0.137
NO_3^{-1}	4.215	$NaNO_3$	4.215	84.99	358.255
NO_2^{-1}	0.112	$NaNO_2$	0.112	69.00	7.722
PO_4^{-3}	0.028	Na_3PO_4 x $12H_2O$	0.028	380.10	10.519
SO_4^{-2}	0.054	Na_2SO_4	0.054	142.05	7.681
Inorganic C	0.198	Na_2CO_3	0.200	105.99	21.198
		$NaHCO_3$	0.190	84.006	15.96

Solution #2: 241-AN-107

	Molarity	Salt compound	Molarity	MW (g)	Mass (g) for 1L
Na^{+1}	8.758		8.758		
Al^{+3}	0.043	$NaAlO_2$	0.043	81.97	3.51
K^{+1}	0.045	KOH	0.045	56.11	2.55
Br^{-1}	0.037	NaBr	0.037	102.89	3.81
Cl^{-1}	0.051	NaCl	0.051	58.44	3.00
CrO_4^{-2}	0.003	$Na_2CrO_4\ 4H_2O$	0.003	161.97	0.55
F^{-1}	0.016	NaF	0.016	41.99	0.68
NO_3^{-1}	3.469	$NaNO_3$	3.469	84.99	294.82
NO_2^{-1}	1.492	$NaNO_2$	1.492	69.00	102.93
PO_4^{-3}	0.029	Na_3PO_4 x $12H_2O$	0.029	380.10	11.02
SO_4^{-2}	0.088	Na_2SO_4	0.088	142.05	12.51
Inorganic C	1.259	Na_2CO_3	1.260	105.99	133.40
		$NaHCO_3$	0.540	84.006	45.36

Solution #3: AY-102

	Molarity	Salt compound	Molarity	MW (g)	Mass (g) for 1L
Na^{+1}	1.250		1.250		
K^{+1}	0.004	$KHCO_3$	0.004	100.114	0.37
Al^{+3}	0.021	$NaAlO_2$	0.021	81.97	1.74
Br^{-1}	0.015	NaBr	0.015	102.89	1.55
Cl^{-1}	0.001	NaCl	0.001	58.44	0.08
CrO_4^{-2}	0.000	$Na_2CrO_4\ 4H_2O$	0.000	161.97	0.01
F^{-1}	0.001	NaF	0.001	41.99	0.05
NO_3^{-1}	0.004	$NaNO_3$	0.004	84.99	0.34
NO_2^{-1}	0.296	$NaNO_2$	0.296	69.00	20.40
PO_4^{-3}	0.011	Na_3PO_4 x $12H_2O$	0.011	380.10	4.27
SO_4^{-2}	0.008	Na_2SO_4	0.008	142.05	1.07
Inorganic C	0.405	Na_2CO_3	0.370	105.99	39.22
		$NaHCO_3$	0.130	84.006	10.92

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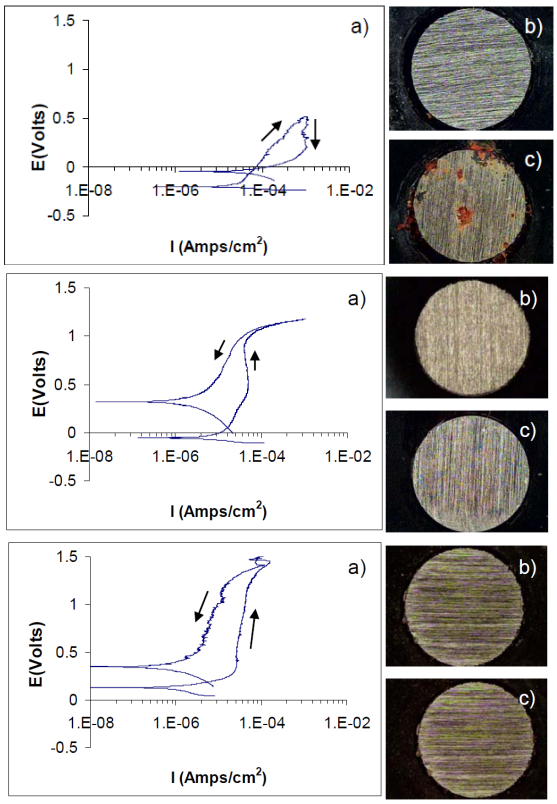
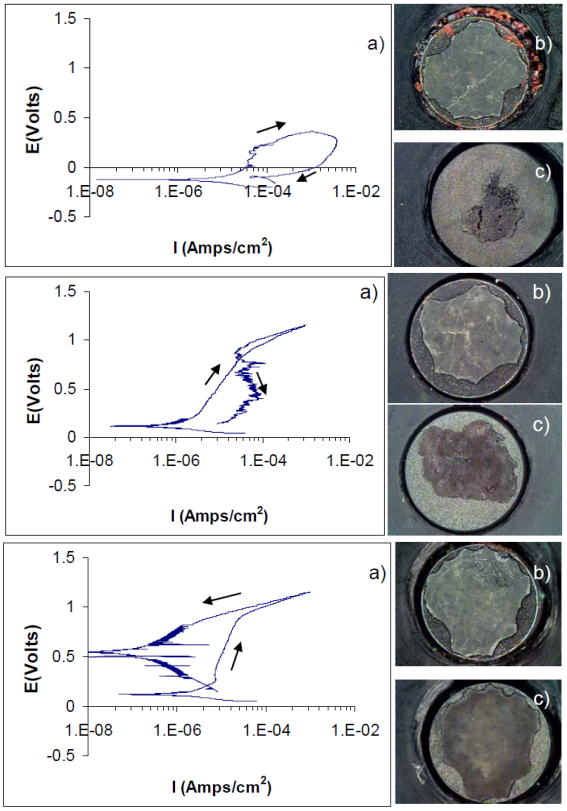
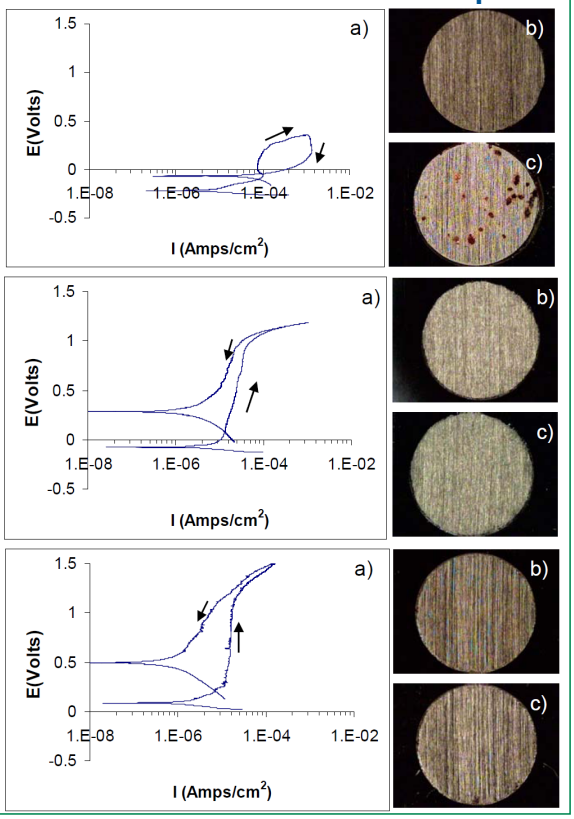
Electrochemical Results: Polished



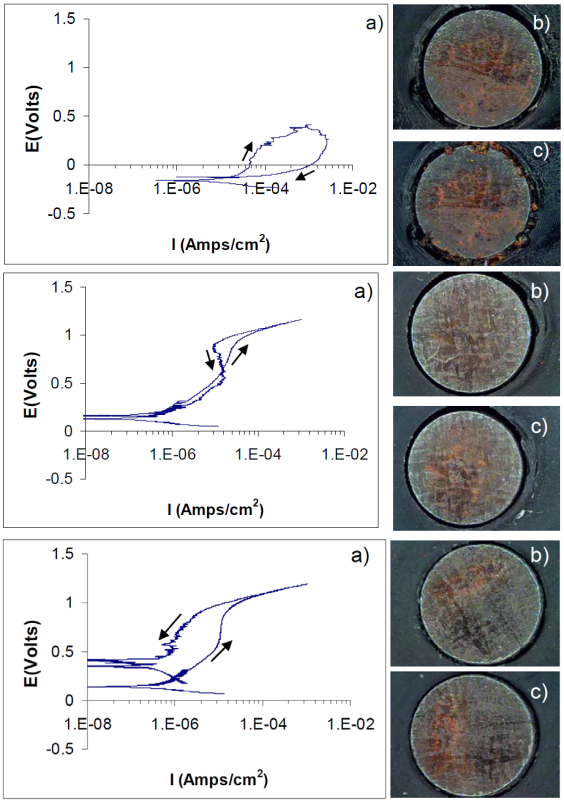
Electrochemical Results: Mill-Scale



Electrochemical Result: Pre-Salt Deposit



Electrochemical Results: Corroded-Scale



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Summary of Results

Solution SY-102 (high nitrate) was the only solution that resulted in repassivation during the reverse scan.

Of the SY-102 (high nitrate) solutions, only the mill-scale condition did not result in a repassivation potential, E_{rp}.

Values for E_{rp} ranged from -0.028 to -0.129 V for the polished and corroded surfaces, respectively.

The transpassive potential, E_{trans}, was within 300 mV of 1.0 V for solutions AN-107 and AY-102.

Solution	Sample Surface	E_{corr} (V)	E_{pit} or E_{trans} (V)	E_{rp} (V)
AN-107	Corroded	0.126	0.961	--
AN-107	Polished	-0.053	0.990	--
AN-107	Polished with Pre-salt	-0.074	1.005	--
AN-107	Mill-scale	0.125	0.920	--
AY-102	Corroded	0.152	0.935	--
AY-102	Polished	0.127	1.287	--
AY-102	Polished with Pre-salt	0.089	1.169	--
AY-102	Mill-scale	0.119	0.925	--
SY-102 (high nitrate)	Corroded	-0.161	0.280	-0.129
SY-102 (high nitrate)	Polished	-0.205	0.449	-0.028
SY-102 (high nitrate)	Polished with Pre-salt	-0.222	0.272	-0.047
SY-102 (high nitrate)	Mill-scale	-0.123	0.304	--

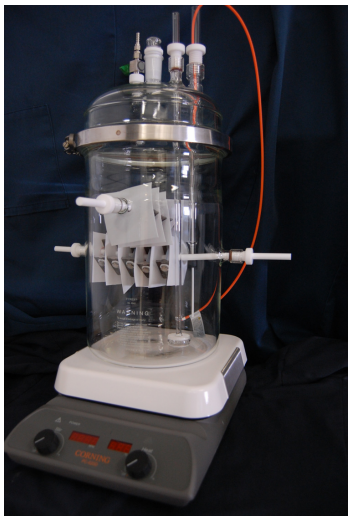
Radiation Vessel

Nitric acid forms as a result of the irradiation of moist air.

The formation of a nitric acid vapor, followed by deposition onto the tank wall will accelerate corrosion in the vapor space region.

The objective was to design a vessel to provide a simulated radiation environment resulting in the formation of a nitric acid condensate depositing onto metallic coupons representing the tank wall.

Additionally, the effects of carbon dioxide and ammonia in the vapor space gas will be evaluated.



A glass vessel capable of holding 3 liters of solution has been designed and fabricated.

The vessel has the flexibility to also provide a nitric acid and ammonia vapor environment via a connection to a gas mixture of 20 ppm NO_2 and 50 ppm NH_3.

A salt solution will be added to the vessel to control the relative humidity based on ASTM E104-02.

Corrosion samples can be suspended from two different rods at two different levels within the vapor space.

Conclusions

Out of three solutions tested, both optical and electrochemical results show that carbon steel corroded much faster in SY-102 (high nitrate) compared to the other two solutions, AN-107 and AY-102, with lower ratios of nitrate to nitrite.

The effect of the surface preparation was not as strong as the effect of solution chemistry.

In areas with pristine mill-scale surface, no corrosion occurred even in the SY-102 (high nitrate) solution.

Corrosion occurred in the areas where the mill-scale was damaged or flaked off due to machining.

The loss of mill-scale on the samples is most likely due to a corrosive attack occurring at the edge of the mill-scale, then spreading to under the mill-scale.

This reaction could have resulted in the breakdown of the mill-scale adhesion to the sample surface.

While mill-scale itself is protective against corrosion, when exposed to a corrosive solution, the scale can be compromised through crevice attack.

Acknowledgements

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Radiation vessel constructed by D. Fisher, G. Creech, and G. Dobos.

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