Contract No:

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Performance of Vapor Corrosion Inhibitors for Localized Corrosion Mitigation of Double Shell Storage Tanks at Hanford

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CORROSION 2021

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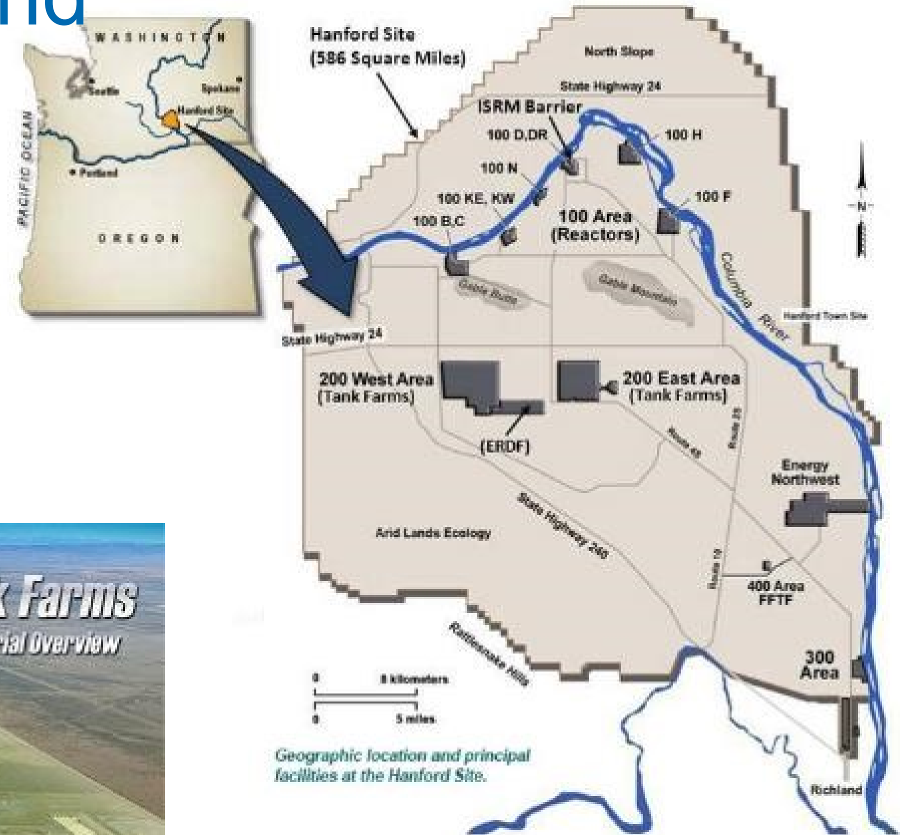
Outline

- Background
  - Hanford Site
  - Waste Tanks and Secondary Liner
  - Ultrasonic Testing and Motivation
  - Previous Work
- Experimental
  - Corrosion Inhibition
- Results and Discussion
- Summary

Hanford Site Background

- Hanford site located in Washington State and established in 1943: 1460 km^2
- Since 1988 the site has been engaged in a comprehensive environmental clean-up effort.



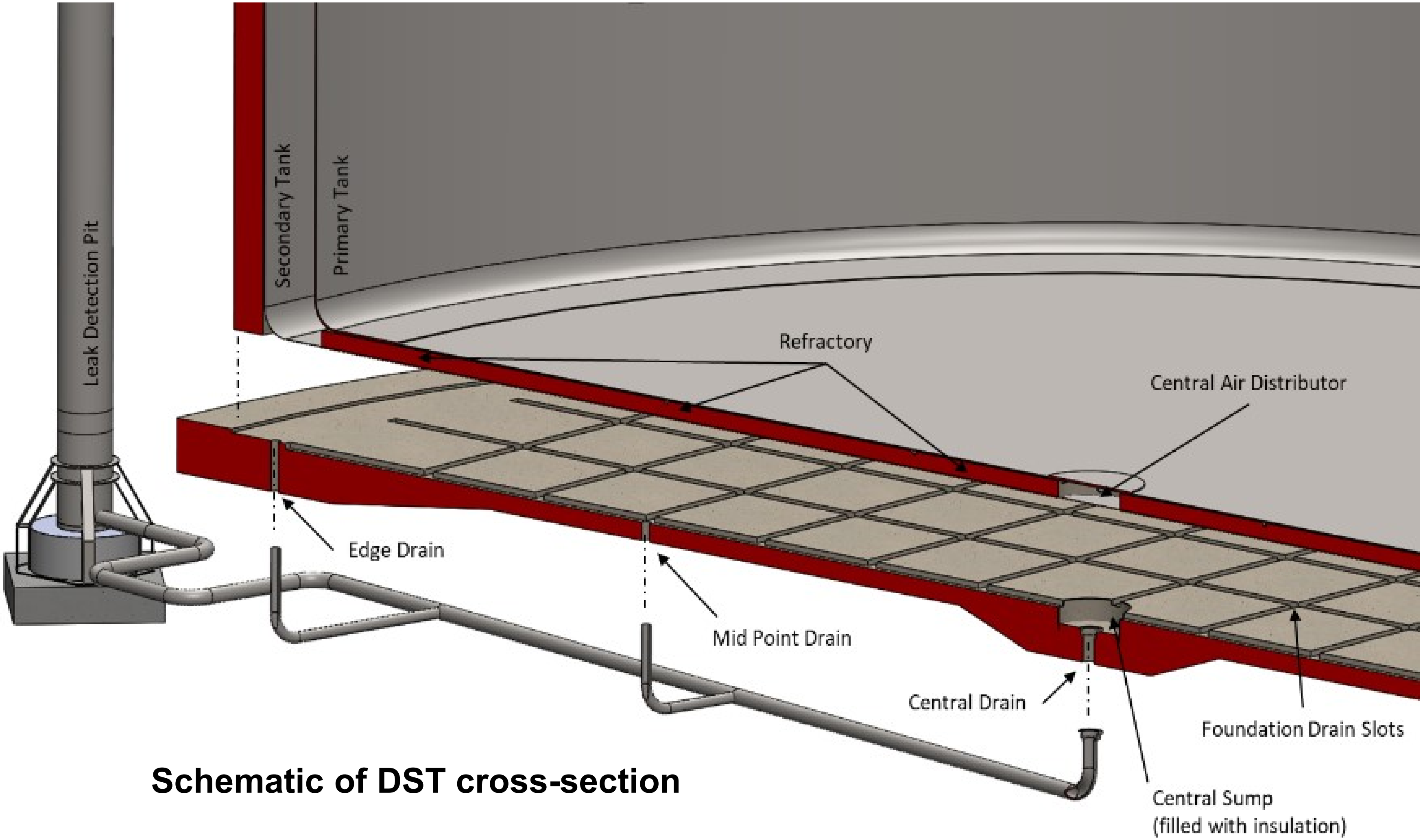
Geographic location and principal facilities at the Hanford Site.

https://wrpstoc.com/tank-operations/the-tanks/

Waste Tanks

- 176 underground tanks storing 56 million gallons of high-level radioactive waste and chemical waste in Single Shell Tanks (SSTs) and Double Shell Tanks (DSTs)

DST Annulus



Schematic of DST cross-section

- Secondary liner rests on a concrete foundations with drain slots
- If there is a leak from the secondary liner it can be detected by the leak detection pit (LDP)

Ultrasonic Testing in Waste Tanks and Motivation

Secondary Liner Ultrasonic Inspections

Tank	Year	Max % Thinning	Area Examined
AN-105	1999	0.2%	10 ft^2
AN-107	1999	10.0%	8 ft^2
AN-105	2006	3.6%	10 ft^2
AP-106	2014	2.20%	9.8 ft^2
AP-102	2014	70.2%	52 ft^2
AN-103	2015	23.8%	65 ft^2
AN-104	2015	39.6%	69 ft^2
AW-103	2016	19.4%	66 ft^2
AN-105	2016	29.8%	62 ft^2
AN-106	2017	9.6%	60 ft^2
SY-101	2017	23%	52 ft^2
SY-102	2017	13.6%	53 ft^2
SY-103	2017	17.6%	58 ft^2

J. Johnson, "Hanford Tank Integrity Program", June 19, 2018 presentation

Reinspection of Tank AP-102

Riser	2019 Area Scanned	2019 Minimum	2014 Minimum
30	~33 ft^2	0.459" (8.2%)	0.486" (2.8%)
31	~25 ft^2	0.142" (71.6%)	0.149" (70.2%)
60	~23 ft^2	0.451" (9.8%)	N/A
61	~13 ft^2	0.415" (17%)	N/A

D. Stewart, K. Subramanian, "Hanford Double-Shell Tank-Tank Integrity Program Update", January 8, 2020 presentation

- Water can accumulate in drain slots and cause corrosion on the exterior of the secondary liner
- Ultrasonic testing showed reduction of nominal thickness
- The secondary liner needs to be protected from corrosion:
  - Preventing water intrusion and/or
  - Effective corrosion inhibitor application

The secondary liner needs to be protected in case of a leak of radioactive waste from the primary liner.

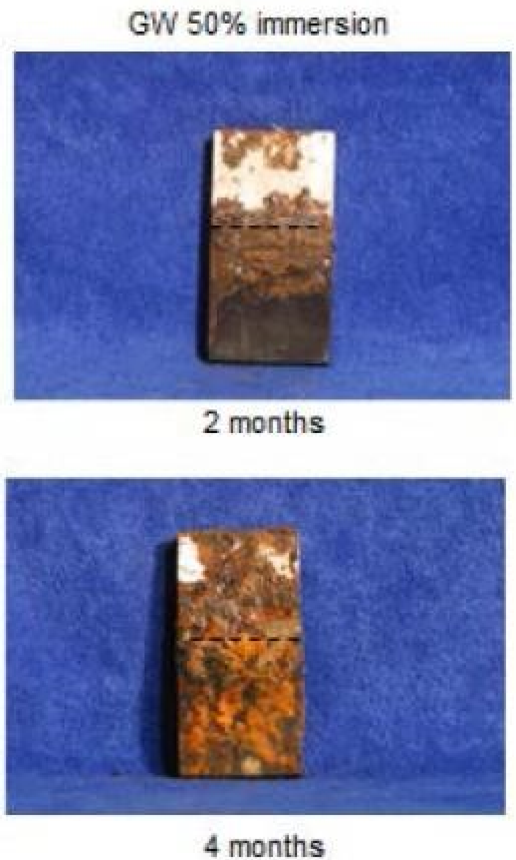
Simulants (electrolytes)

- Simulant were prepared based on analytical studies of water samples taken at leak detection pit and above zone groundwater.

Chemical species, Temperature and pH range of maximum and minimum values

Composition of the Leak Detection Pit and Ground Water Simulants		
Source chemical	**Concentration (M)**	
	Leak Detection Pit (LDP)	**Ground Water (GW)**
Sodium bicarbonate	1.120E-03	1.750E-03
Calcium hydroxide	1.210E-04	1.500E-03
Potassium nitrate	6.750E-05	2.400E-04
Magnesium Nitrate	1.520E-05	–
Strontium Nitrate	4.040E-06	2.874E-06
Sodium sulfate	1.830E-06	–
Ferric sulfate	–	6.250E-04
Sodium Metasilicate	4.570E-05	6.000E-04
Ferric chloride	2.670E-06	7.667E-05
Manganese Chloride	–	3.100E-04
Acetic Acid	3.000E-04	3.000E-04
pH adjusted using sodium carbonate and acetic acid	7.6	7.6

Previous Work



Sample immersed in groundwater (GW) pH=7.6

- Testing using LDP and GW simulants
- Carbon steel samples sustained aggressive attacks for vapor and liquid air interface
- General corrosion rates were approximately 10 mpy, more aggressive in GW.
- The corrosion can aggravate at lower pHs.
    - Lower pHs can occur due to radiolysis of nitrogen to form nitric acid.

Before

After 4 months

Sample immersed in GW with adjusted pH=6

R. E. Fuentes. B. J. Wiersma and K. Hicks, "Hanford Double Shell Waste Tank Corrosion Studies-Final Report FY14", SRNL-STI-2014-00616, Savannah River National Laboratory, Aiken, December 2014.

R. E. Fuentes, "Hanford Double Shell Waste Tank Corrosion Studies-Final Report FY17", SRNL-STI-2018-00116, Savannah River National Laboratory, Aiken, April 2018.

Objectives and Technical Approach

- Objectives: study effects of VCIs in mitigating corrosion on weathered coupons using commercially available VCIs

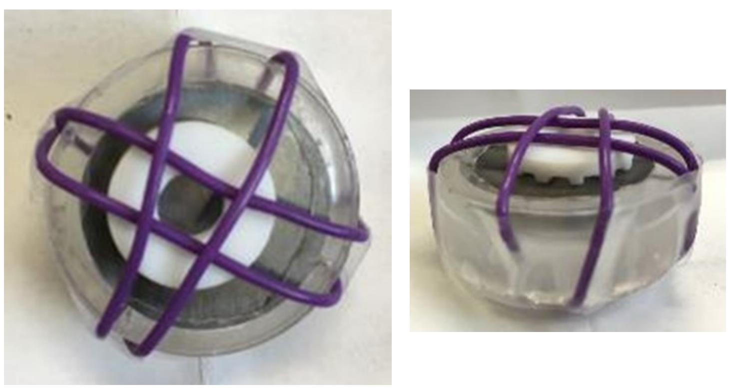
- Technical Approach
  – Disk coupons were exposed to GW electrolyte for weathering
  – Exposure time: two months
  – Two commercially available VCIs were tested: VCIs added after initial 2 months of weathering
  – 50% of coupons taken out before VCIs' addition and remaining after additional 4 months of exposure
  – Surface average and pitting corrosion rates
  – Statistical analysis of corrosion rate data

Experimental: Materials

- Carbon steel coupons from AART 128 Rail Car Steel which has approximate chemistry, microstructure and age as the steel of which the tanks were fabricated (ASTM A515 Grade 60)

Compositions (wt.%) of the Carbon Steel

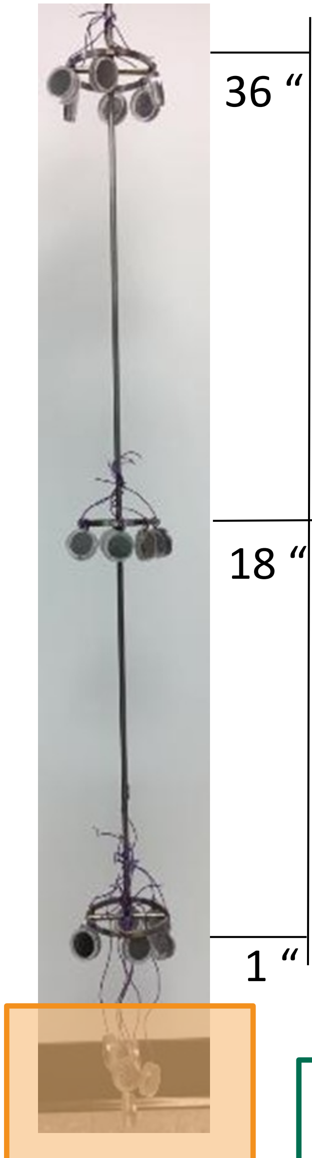
Elements	C	Mn	P	S	Si	Fe
Specification (wt%)	0.24 (max.)	0.9 (max.)	0.035 (max.)	0.04 (max.)	0.13 to 0.33	Balance
Measured (wt%)	0.212	1.029	0.012	0.013	0.061	Balance



Mounted disk coupons with polished surfaces

- Circular coupons 1” dia. from plate, 1/8” thick, crevice former
- Mount in two-part clear epoxy mixture
- Electrical Resistance (ER) probes for in-situ monitoring

Experimental: Vapor Space Corrosion Testing



Simulant

Level 3: Top level.

- Not dipped in simulant
- Representative of region only exposed to vapor and any volatile species from the solution.

Level 2: Intermediate level.

- Dipped in the simulant for five minutes prior to testing.
- No direct contact with solution after initial 5-minute exposure.

Level 1: Low level.

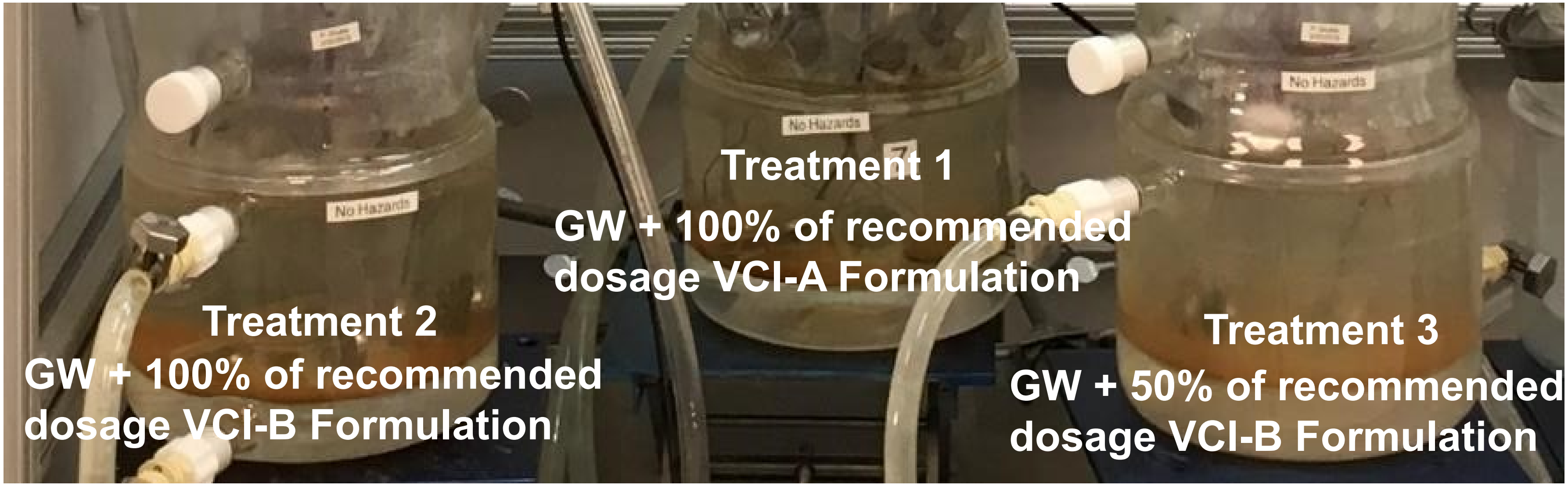
- Dipped in the simulant prior to testing and every two weeks
- Representative of the situation when secondary liner bottom plate experienced periodic wetting/drying.

Temperature: 45 ºC (GW simulant)
Duration of testing: 6 months

Setup Image

Experimental: Vapor Corrosion Inhibitors (VCI) Corrosion Strategy

- Initial two-month exposure with GW, and then GW+VCI thereafter
  - **VCI-A**
    - VpCI-337® mixed at 10% v/v in GW simulant
  - **VCI-B**
    - VpCI-609® (10 wt.%) and VpCI-649MF® (0.75% v/v) in GW simulant



- Half of the coupons were taken out before VCIs' addition

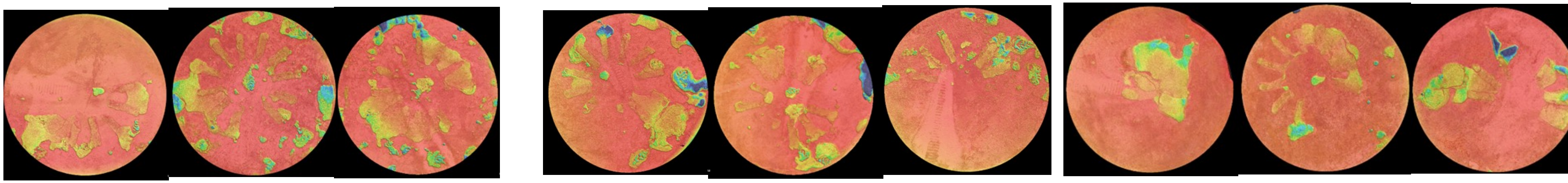
Results: VCI Treatment Summary

Solution	Treatment Vessel	Notes
Initially GW simulant, and then 100% of the recommended dosage of VCI-A after 2 months	Vessel 1	• 6 coupons each in immersed, Level 1, Level 2, and Level 3 positions, total 24 coupons. • ER probes at each level. Cylindrical element probes at immersed, Levels 1 and 2, and wire element probe at Level 3.
Initially GW simulant, and then 100% of the recommended dosage of VCI-B after 2 months	Vessel 2	• 6 coupons each in immersed, Level 1, Level 2, and Level 3 positions, total 24 coupons. • ER probes at each level. Cylindrical element probes at immersed, Levels 1 and 2, and wire element probe at Level 3
Initially GW simulant, and then 50% of the recommended dosage of VCI-B after 2 months	Vessel 3	• 6 coupons each in immersed, Level 1, Level 2, and Level 3 positions, total 24 coupons. • Cylindrical element probe at Level 2 and wire element probe at Level 3

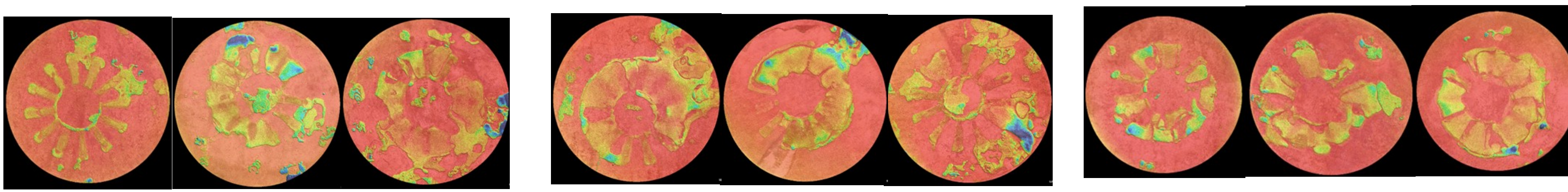
Results: VCI Corrosion Inhibition Strategy

Profiled images of coupons after 2 months

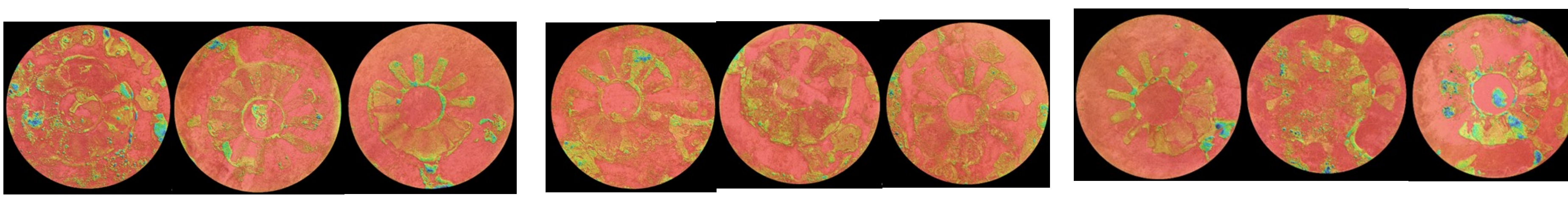
GW simulant (no 100 % VCI-A) | **GW simulant (no 100 % VCI-B)** | **GW simulant (no 50% VCI-B)**



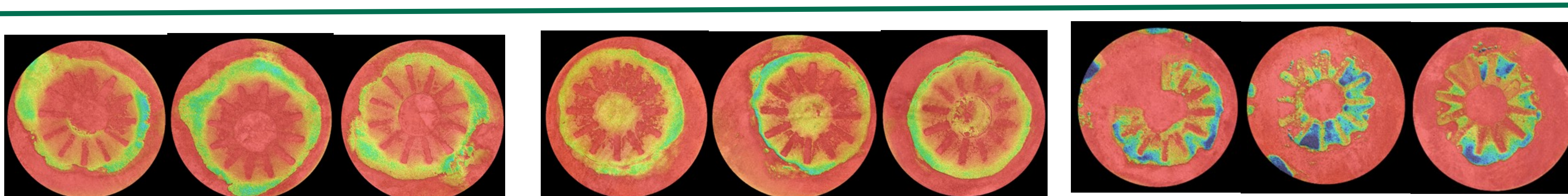
Level 3



Level 2



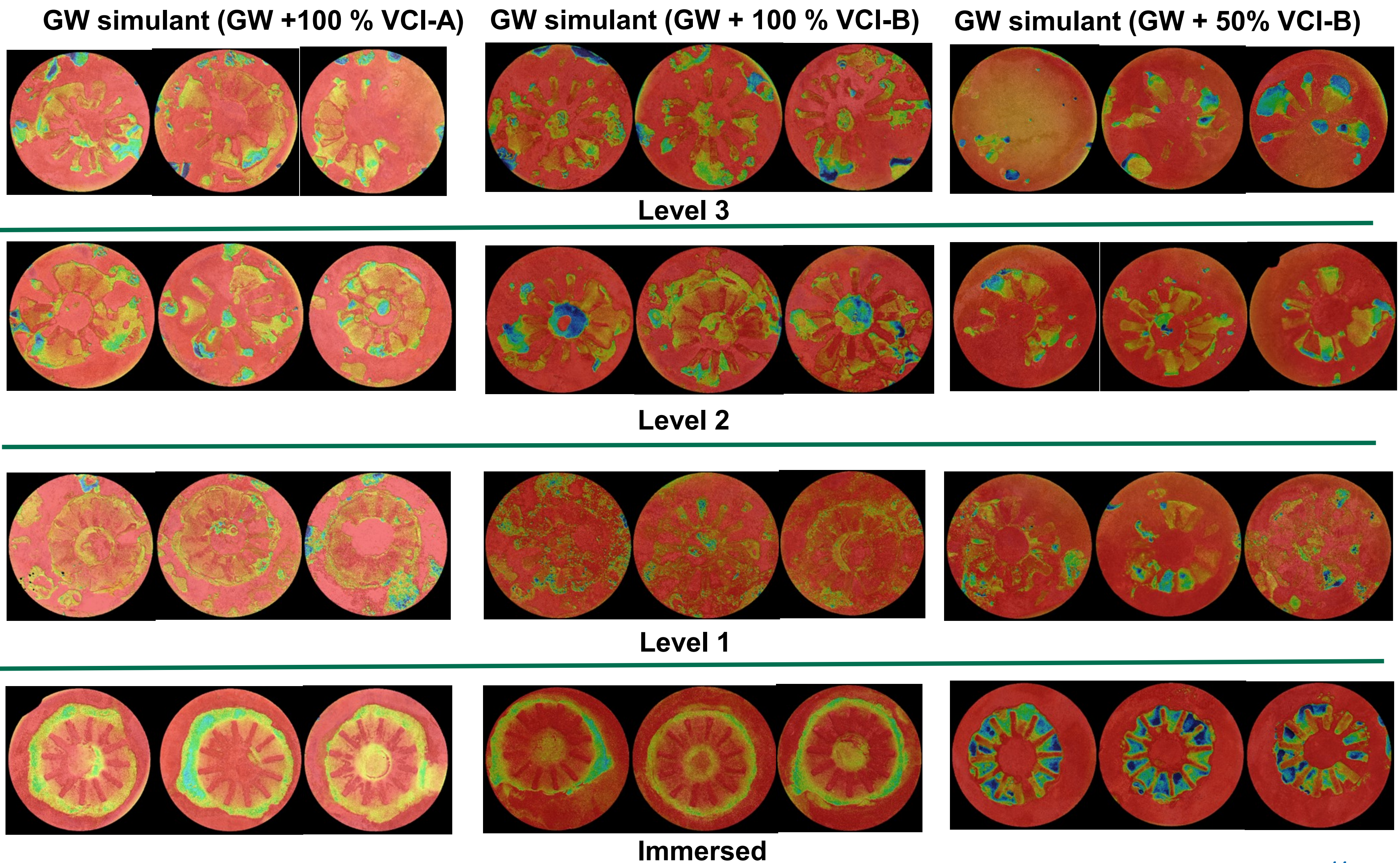
Level 1



Immersed

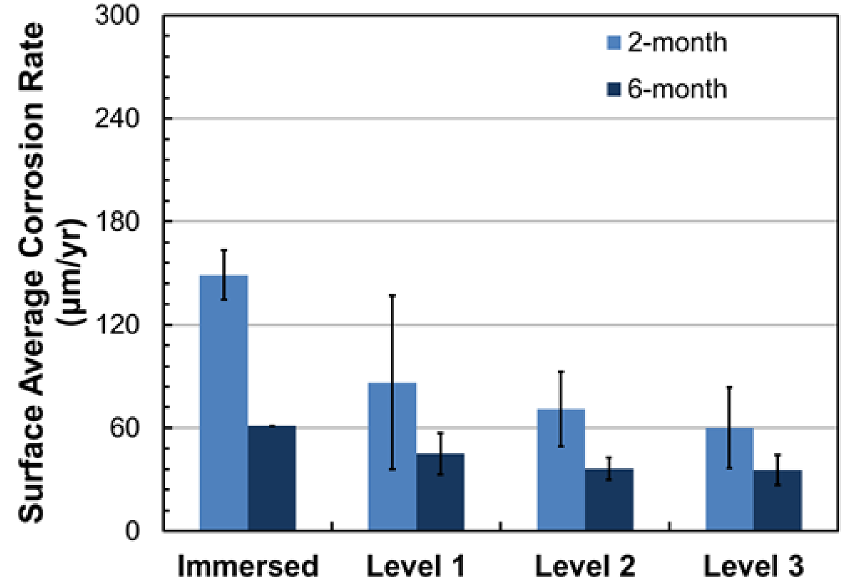
Results: VCI Corrosion Inhibition Strategy

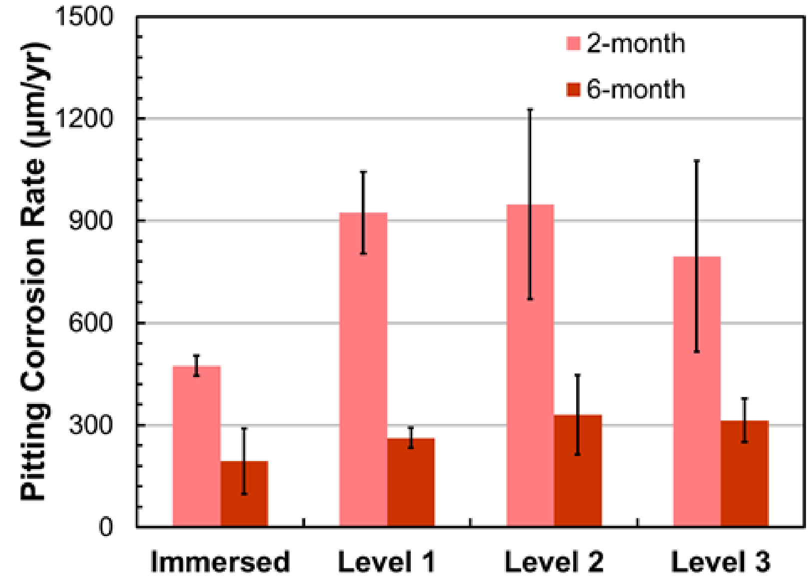
Profiled images of coupons after 2+4 months



Results: GW and GW + 100% VCI-A

GW for 2 months, GW + 100% VCI-A thereafter			
Coupon Position	**MONTH**	**Surface Average Corrosion Rate ± std* (µm/yr)**	**Pitting Corrosion Rate ± std* (µm/yr)**
Immersed	**2**	149 ± 14.4	474 ±29
	6	61 ± 0	195 ± 96
Level 1	**2**	86.4 ± 50.6	923 ± 120
	6	44.9 ± 12	263 ± 29
Level 2	**2**	71.1 ± 21.7	948 ± 279
	6	36.4 ± 6.4	330 ± 116
Level 3	**2**	60.1 ± 23.5	796 ± 281
	6	35.6 ± 8.8	313 ± 64

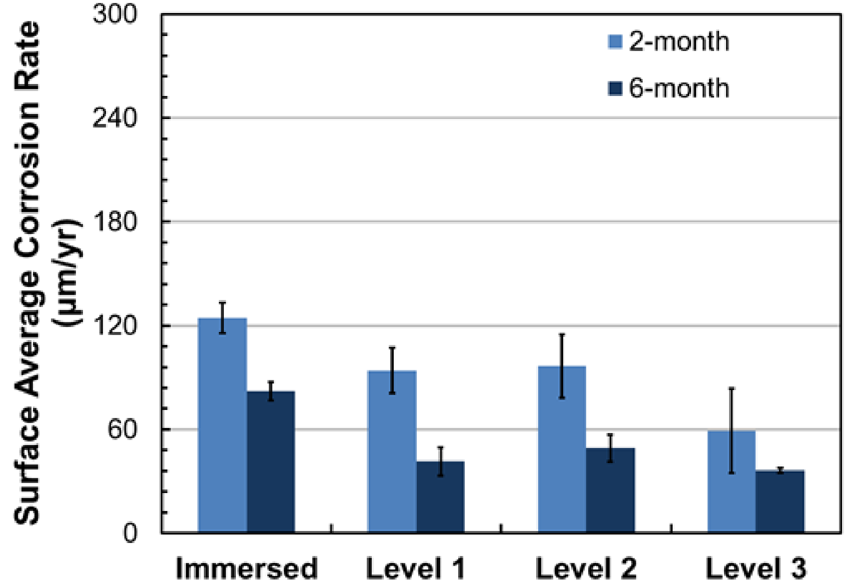


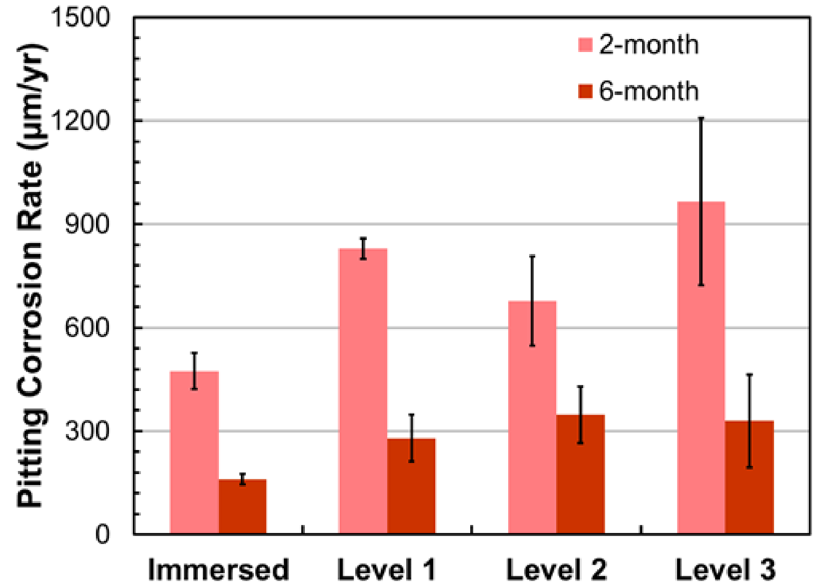


***Each data point is average of 3 coupons**
2 months: GW
6 months: GW for first 2, and then GW + VCI for additional four months

Results: GW and GW + 100% VCI-B

GW for 2 months, GW + 100% VCI-B thereafter			
Coupon Position	MONTH	Surface Average Corrosion Rate ± std* (µm/yr)	Pitting Corrosion Rate ± std* (µm/yr)
Immersed	2	125 ± 9	474 ±53
	4	82 ± 5	161 ±15
Level 1	2	94 ± 13	830 ± 29
	4	42 ± 8	279 ± 67
Level 2	2	97 ± 18	677 ± 130
	4	49 ± 8	347 ± 82
Level 3	2	59 ± 24	965 ± 242
	4	36 ± 2	330 ± 134

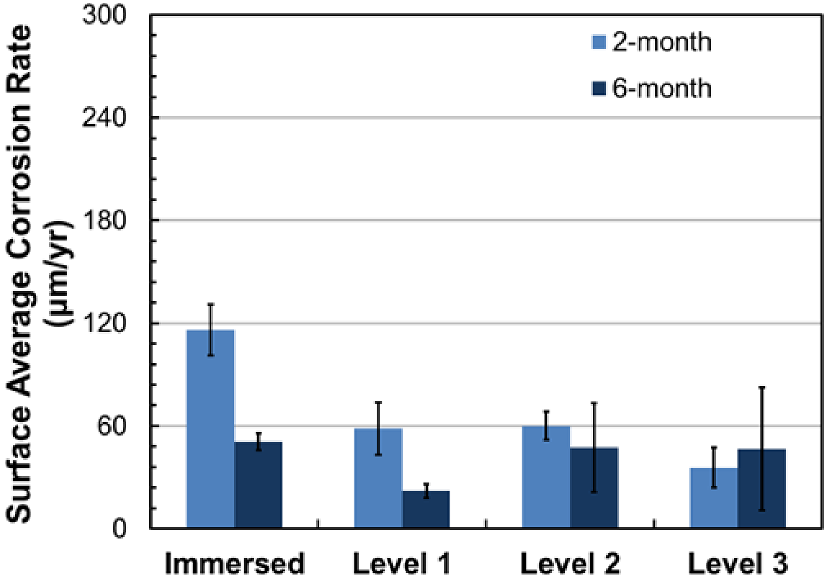


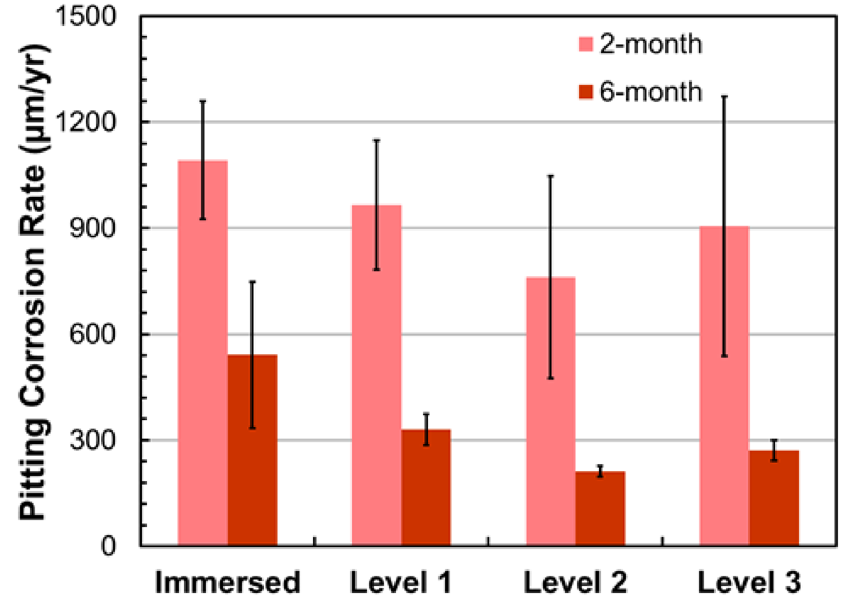


***Each data point is average of 3 coupons**
2 months: GW
4 months: GW for first 2, and then GW + VCI for additional four months

Results: GW and GW + 50% VCI-B

Coupon Position	MONTH	Surface Average Corrosion Rate ± std* (µm/yr)	Pitting Corrosion Rate ± std* (µm/yr)
GW for 2 months, GW + 50% VCI-B thereafter			
Immersed	2	116 ± 15	1092 ± 167
	6	51 ± 5	542 ± 207
Level 1	2	58 ± 15	965 ± 183
	6	22 ± 4	330 ± 44
Level 2	2	60 ± 8	762 ± 286
	6	47 ± 26	212 ± 15
Level 3	2	36 ± 12	906 ± 368
	6	47 ± 36	271 ± 29





***Each data point is average of 3 coupons**
2 months: GW
4 months: GW for first 2, and then GW + VCI for additional four months

Statistical Analysis

- Student's t-Test was applied, if P-values ≤ 0.05, statistically significant difference
  - Surface average + Pitting corrosion: all three VCI treatment show effectiveness
  - GW + 100% VCI-A: effective in mitigating pitting corrosion (slightly marginal at Level 3)

Student's t-Test P-values* for comparison between coupons before and after VCI treatment								
Corrosion Cell	**Corrosion Type**							
	Surface Average Corrosion				**Pitting Corrosion**			
	Immersed	**Level 1**	**Level 2**	**Level 3**	**Immersed**	**Level 1**	**Level 2**	**Level 3**
GW + 100% VCI-A	0.01	0.29	0.10	0.20	0.03	0.01	0.05	0.09
GW + 100% VCI-B	0.00	0.01	0.03	0.25	0.01	0.00	0.03	0.03
GW + 10% VCI-B	0.01	0.05	0.49	0.66	0.02	0.02	0.08	0.09

*P-value of 0.05 or less indicate statistically significant difference with 95% confidence

Statistical Analysis

- Student’s t-Test was applied, if P-values ≤ 0.05, statistically significant difference
  - GW + 100% VCI-B: effective in mitigating pitting corrosion; also surface average except at Level 3
  - GW + 50% VCI-B: effective in mitigating pitting and surface average corrosion in immersed and Level 1; marginally effective in mitigating pitting corrosion at Levels 2 and 3

Student’s t-Test P-values* for comparison between coupons before and after VCI treatment

Corrosion Cell	Corrosion Type							
	Surface Average Corrosion				Pitting Corrosion			
	Immersed	Level 1	Level 2	Level 3	Immersed	Level 1	Level 2	Level 3
GW + 100% VCI-A	0.01	0.29	0.10	0.20	0.03	0.01	0.05	0.09
GW + 100% VCI-B	0.00	0.01	0.03	0.25	0.01	0.00	0.03	0.03
GW + 10% VCI-B	0.01	0.05	0.49	0.66	0.02	0.02	0.08	0.09

*P-value of 0.05 or less indicate statistically significant difference with 95% confidence

Conclusions

- Vapor space and Immersion studies using GW simulants were conducted to study the effect of two VCIs (VCI-A and VCI-B) in mitigating corrosion on bottom side of the secondary liner of DSTs

- VCI-A and VCI-B
  - Both VCIs were effective in mitigating the pitting corrosion rate in immersed, Levels 1 and 2 coupons at the 100% recommended dosages. VCI-B was effective in mitigating the corrosion rate even at Level 3
  - 50% VCI-B was also effective in mitigating the pitting corrosion rate in immersed and Level 1 coupons with 95% confidence. The pitting corrosion rate was also mitigated at Levels 2 and 3 coupons, but with approximately 90% confidence
  - 100% VCI-B was also effective in mitigating the surface average corrosion rate in the immersed, Level 1, and Level 2 coupons with 95% confidence, VCI-A was only in immersed conditions

Acknowledgements

- United States Department of Energy
- Hanford Tank Integrity Expert Panel - Corrosion Subgroup