Contract No:

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Evolution of Corrosion Potential of Carbon Steel Storage Tanks Containing High-Level Nuclear Waste

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Outline

- Background
- Objective and technical approach
- Experiments
- Data and Results
- Conclusions
- Acknowledgements

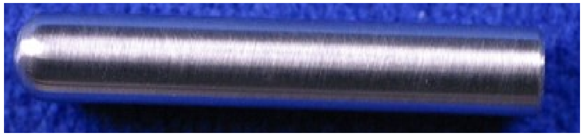
Background

- High-level radioactive waste is stored in underground carbon-steel storage tanks at the Hanford site
- Waste chemistries are alkaline with pH between 10 and 14; carbon steel is expected to undergo passive dissolution
- Corrosive species in waste chemistries could cause pitting and stress corrosion cracking; assumption is that the risk increases with drift in open circuit potential (OCP) in anodic direction
  - Pitting corrosion is likely when corrosion potential exceeds repassivation potential
  - Cyclic potentiodynamic polarization (CPP) experiments are conducted to identify risk of pitting corrosion and stress corrosion cracking
  - OCP evolves over couple of months whereas CPPs are initiated 2 hours after setup; potential gap between CPP data and OCP evolution resulting in under-assessment of the risk

Background

- **Factors affecting OCP evolution**
  - Chemistry of the waste
  - Temperature
  - Surface conditions; focus was to study effects of surface conditions and chemistry on OCP evolution

- **CPP tests are conducted using bullet coupons**
  - 600 grit polished surface



- **Field conditions**
  - Tank construction process involved large carbon steel sheets welded together
  - Sheets would have contained mill-scale plus atmospheric corrosion products
  - Construction related activities would have disturbed the as-received carbon steel sheet conditions, but not to the extent of being a polished surface
  - 600 grit polished surface represents one extreme
  - Mill-scale plus corrosion product represents another extreme
  - Actual condition is expected to be somewhere in-between

Technical Approach

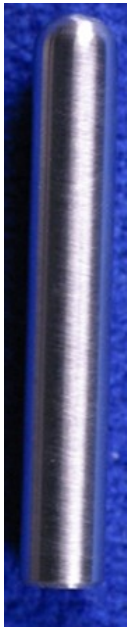
- Technical approach:
  - several separate experiments, temperature 35 °C, different chemistry for each experiment, three surface conditions: (i) polished to mirror surface, (ii) mill-scale plus corrosion products, and (iii) partly polished surface of a mill-scale coupon, i.e., combination of (i) and (ii)
  - Three/two coupon electrodes per experiment, surface conditions of the electrodes differed
    - *Bullet coupon (600 grit polished surface)*
    - *Mill-scale plus corrosion product coupon (mill-scale)*
    - *Partly polished surface of a mill-scale coupon (partial mill-scale)*
  - OCP monitoring for four months, followed by electrochemical impedance spectroscopy and CPP measurements

Experiments

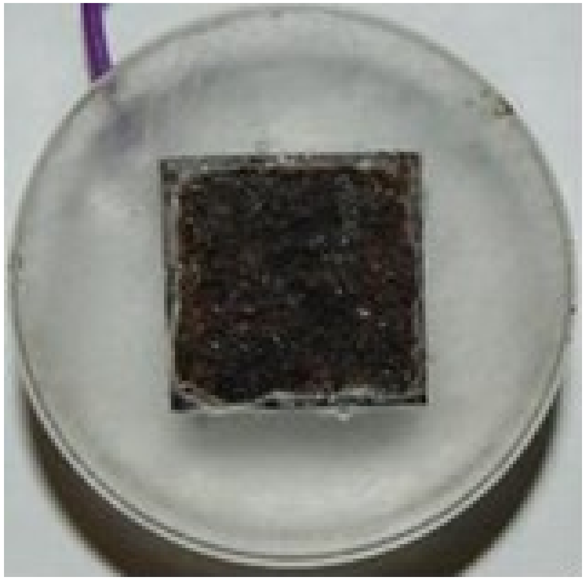
- **Material**

Chemical Composition of AAR TC 128 Steel (wt.%)						
	C	**Mn**	**P**	**S**	**Si**	**Fe**
Specification	0.24 (max.)	0.9 (max.)	0.035 (max.)	0.04 (max.)	0.13- 0.33	Balance
Measured	0.212	1.029	0.012	0.013	0.061	Balance

- **Coupons**



Bullet



Mill-scale

Partial mill-scale

Experiments

- **Coupons**

Coupon Resistance Data	
Coupon	**Resistance (Ω) using a multimeter**
Bullet (no mill scale)	< 0.1 Ω
Mill-scale coupon 1	20.7 MΩ, 2.1 kΩ, 22,6 MΩ, 21.5 MΩ, and 22.8 MΩ
Mill-scale coupon 2	7.4 kΩ
Mill-scale coupon 3	280 Ω, 194 Ω, 160 kΩ, 0.7 MΩ

Experiments: Chemistry

Chemical Composition of the Simulants Used to Study Evolution of Open Circuit Potential

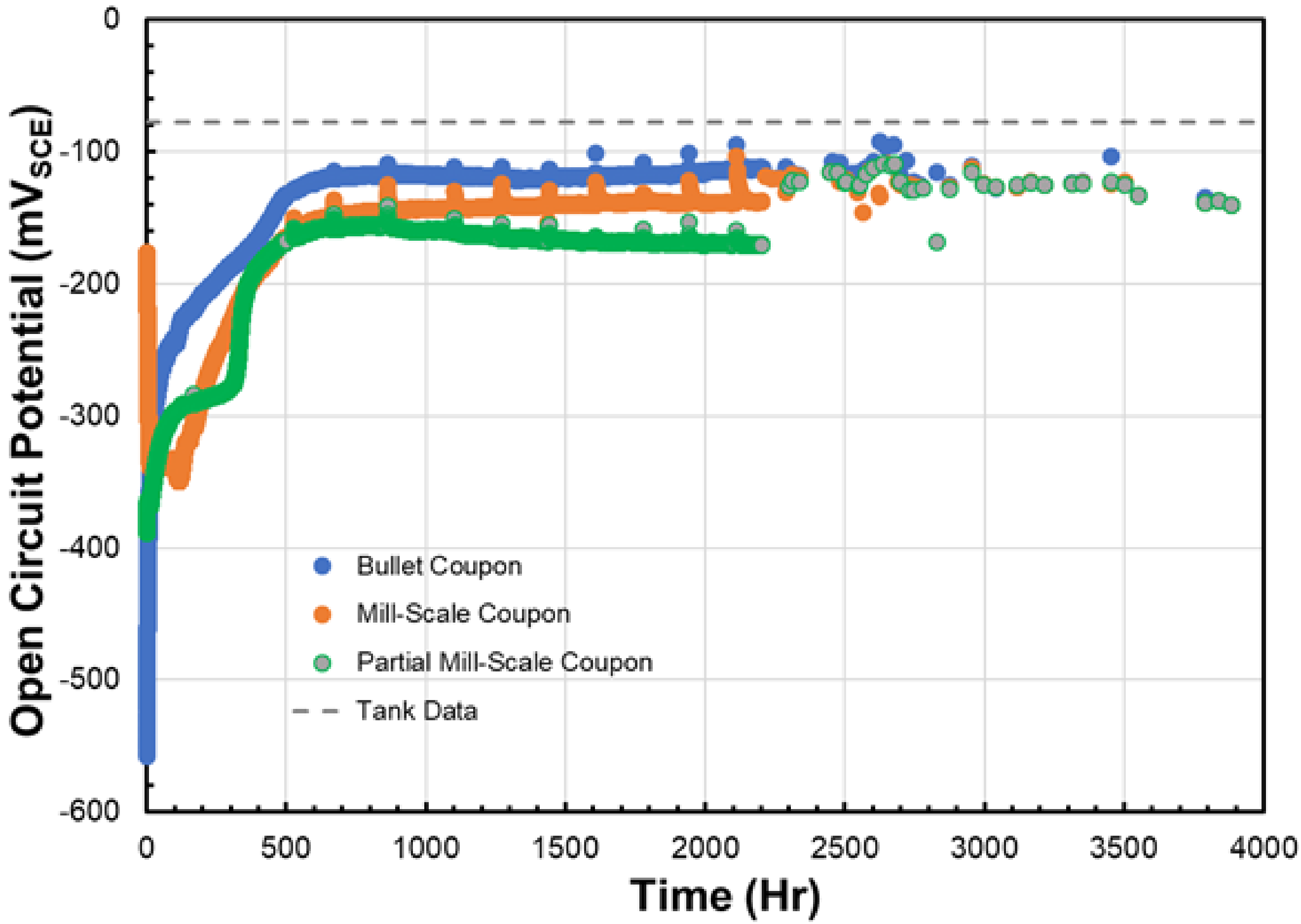
Chemical	Concentration (M)		
	AY-101	AW-105 with small organic acids (i.e., formate, acetate, glycolate)	SY-101
Sodium hydroxide	0.688	1.735	0.600
Sodium nitrite	1.251	1.000	0.259
Sodium nitrate	1.911	1.101	1.032
Sodium chloride	0.070	0.046	0.027
Sodium fluoride	0.025	0.108	0.021
Sodium sulfate	0.056	0.021	0.020
Trisodium phosphate, 12-hydrate	0.036	0.012	0.083
Sodium carbonate	0.743	0.751	0.206
Sodium bicarbonate	0.000		0.001
Sodium formate	0.026	0.008	0.010
Sodium acetate, 3-hydrate	0.012	0.012	0.003
Sodium glycolate	0.0029		0.003
Sodium oxalate	0.0062	0.004	0.022
Ammonium bicarbonate	0.0013	0.00866	0.006
Sodium aluminate	0.261	0.324	0.131
Potassium nitrate	0.089	0.719	0.008
Solution pH at 21 °C	14	14	14

Experiments: Chemistry

Chemical Composition of AW-105 with Organics

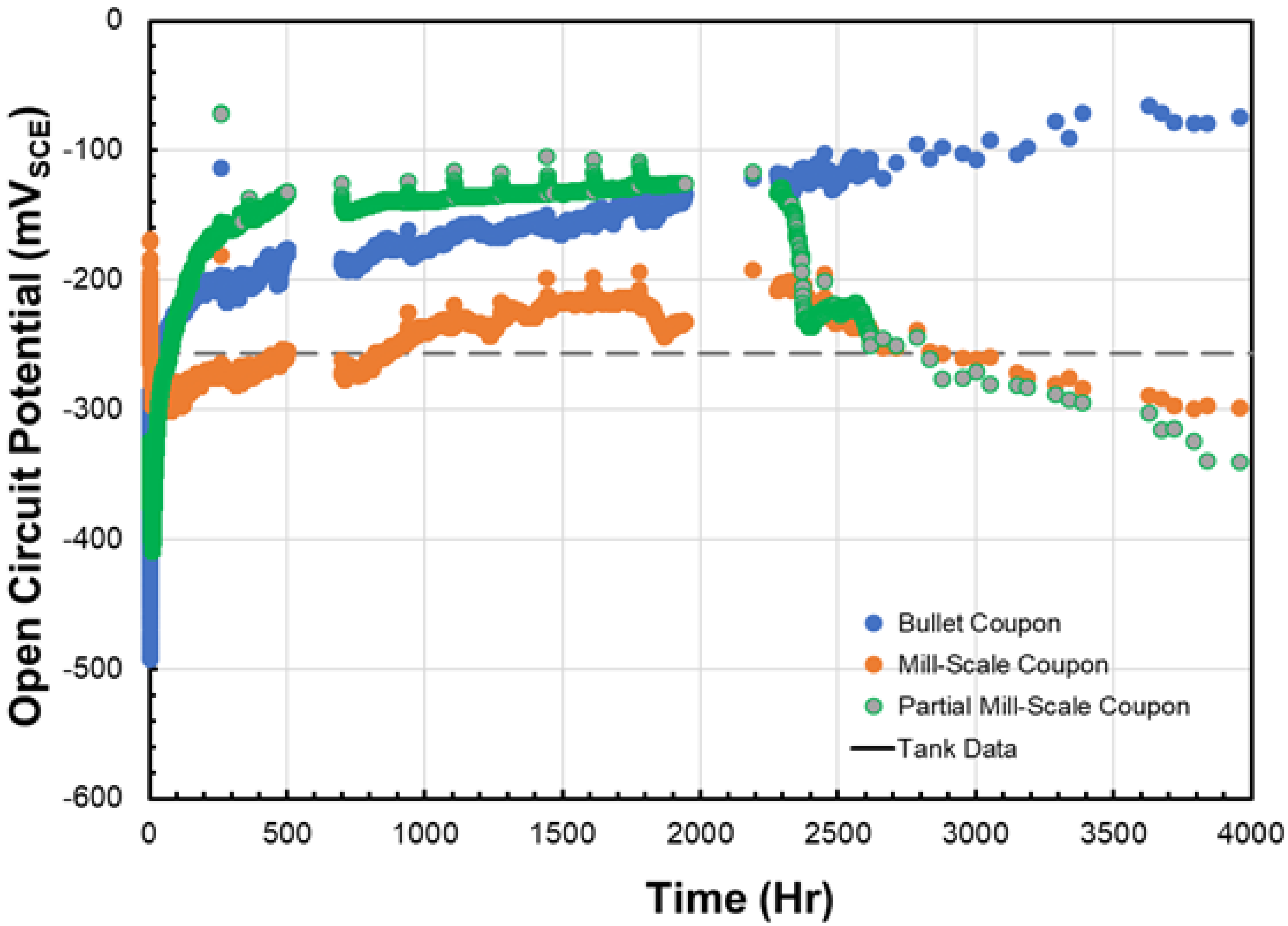
Chemical	Concentration (M)	
	AW-105 with small organic acids, tributylphosphate family, normal paraffin hydrocarbon	AW-105 with small organic acids, spiked tributylphosphate family, normal paraffin hydrocarbon
Propionic acid	0.0000703	0.0000703
Sodium acetate, 3 hydrate	0.012	0.12
Sodium glycolate	0.0029	0.029
Sodium butyrate	0.000149	0.000149
Tributyl phosphate	0.0000412	0.0000412
1-Butanol	0.000177	0.000177
n-butyl phosphate: mixture of mono-n-butyl and di-n-butyl	0.0034	0.034
Bis(2-ethylhexyl)phtalate	2.80E-06	2.80E-06
2-methyl-2-nitrobutane (tert-nitrobutane)	0.000719	0.000719
tetradecanoate (myristic acid)	1.00E-05	1.00E-05
Butanone-2 (ethyl methyl ketone)	0.00001	0.00001
Methylbutanone-2 (3-hydroxy-3-methyl-2-butanone)	0.00001	0.00001
Undecane	1.00E-08	1.00E-08
Dodecane	1.00E-08	1.00E-08
Tridecane	1.00E-08	1.00E-08
Tetradecane	1.00E-08	1.00E-08
1-Octanol	1.00E-06	1.00E-06
2-Octanone	1.00E-06	1.00E-06
Octanoate (ethyl octanoate)	1.00E-05	1.00E-05
1-Tetradecanol (myristil alcohol)	1.00E-06	1.00E-06
2-Tetradecanone	1.00E-06	1.00E-06

Data and Results: AY-101 Simulant



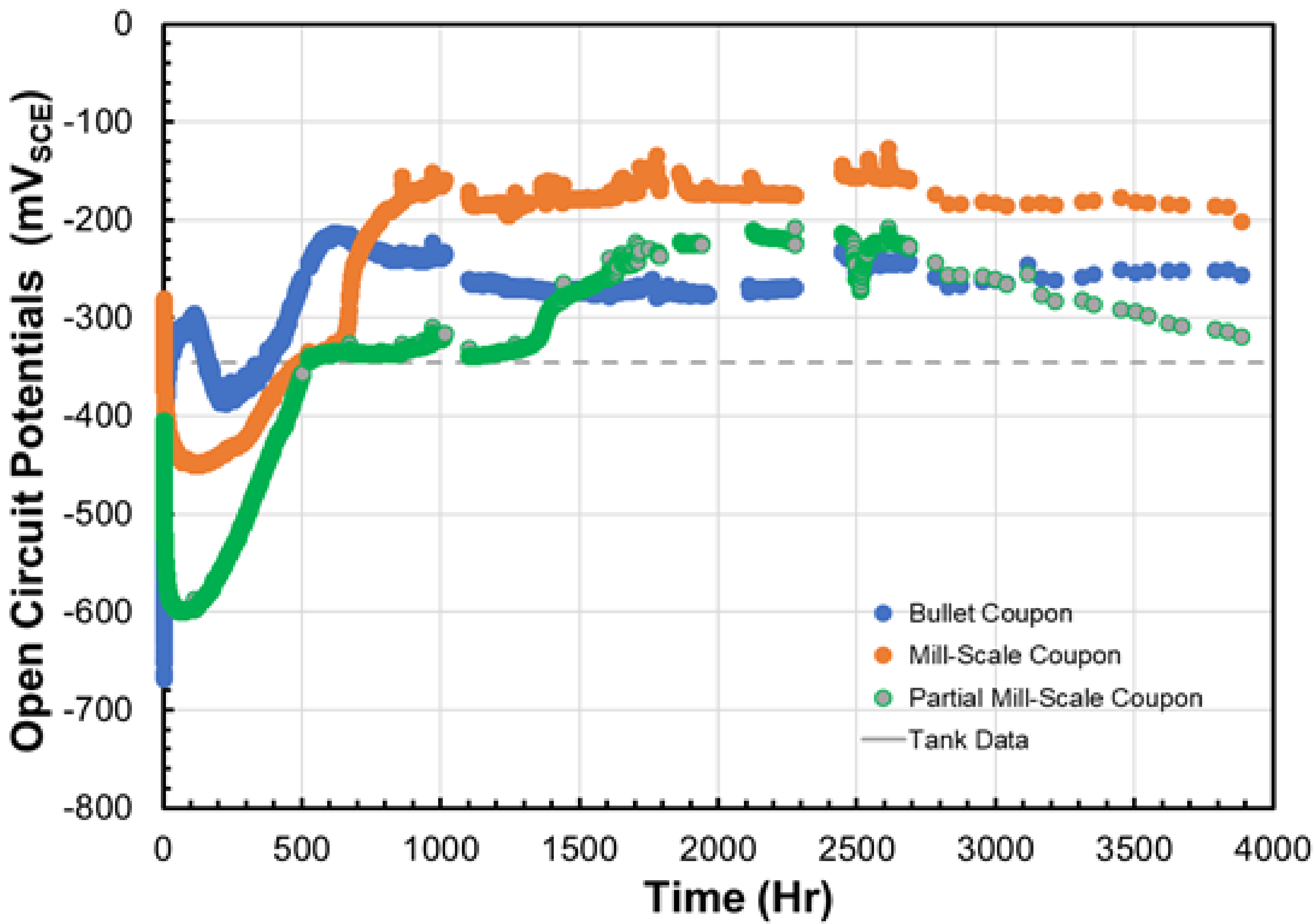
- OCP evolution is anodic for the three coupons

Data and Results: SY-101 Simulant



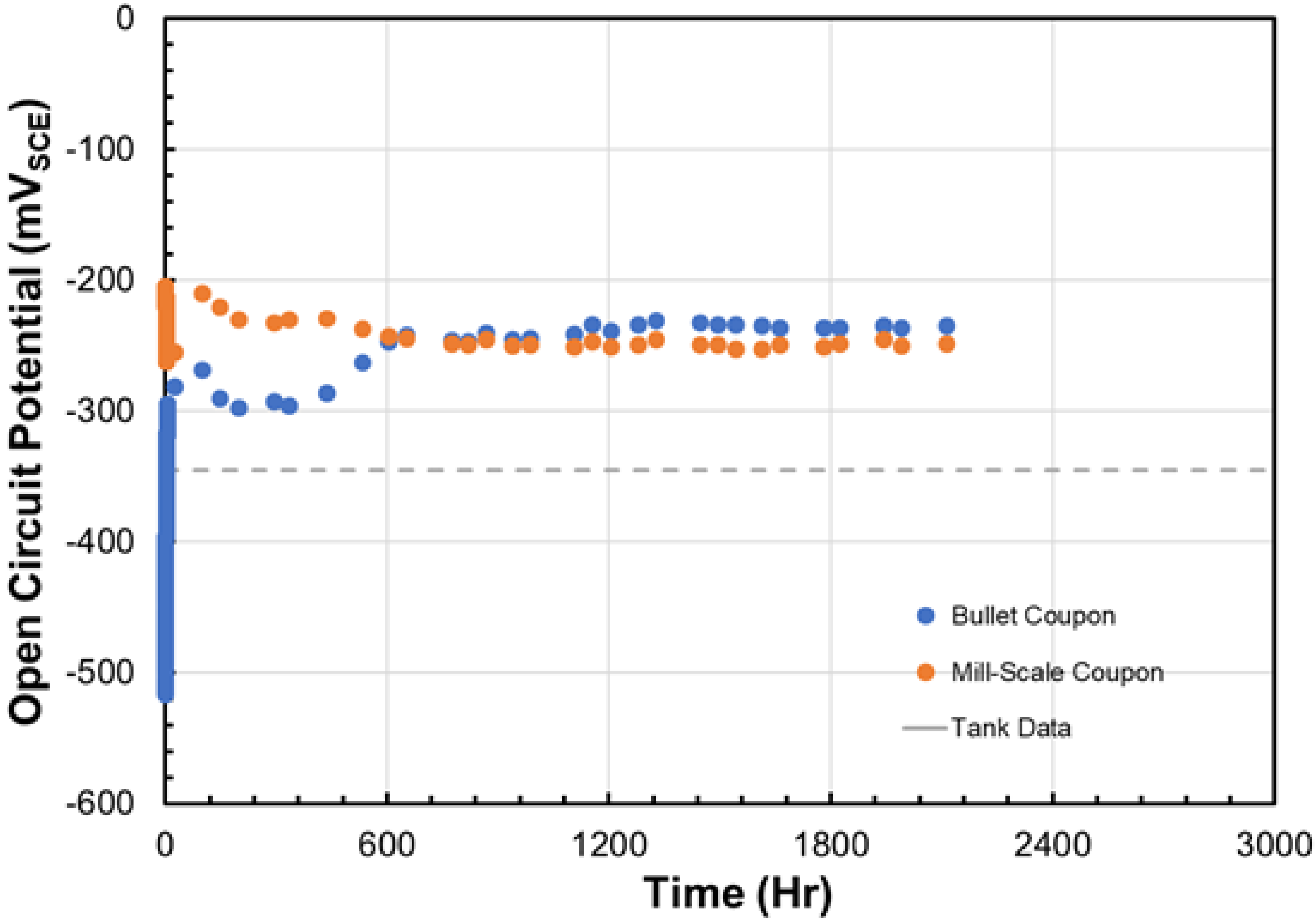
- OCP evolution is anodic for the bullet coupon, but didn't reach steady state
- OCP evolution is initially anodic for mill- and partial mill-scale coupons, but turned cathodic after 2500 hours, no steady-state

Data and Results: AW-105 with small organic acids



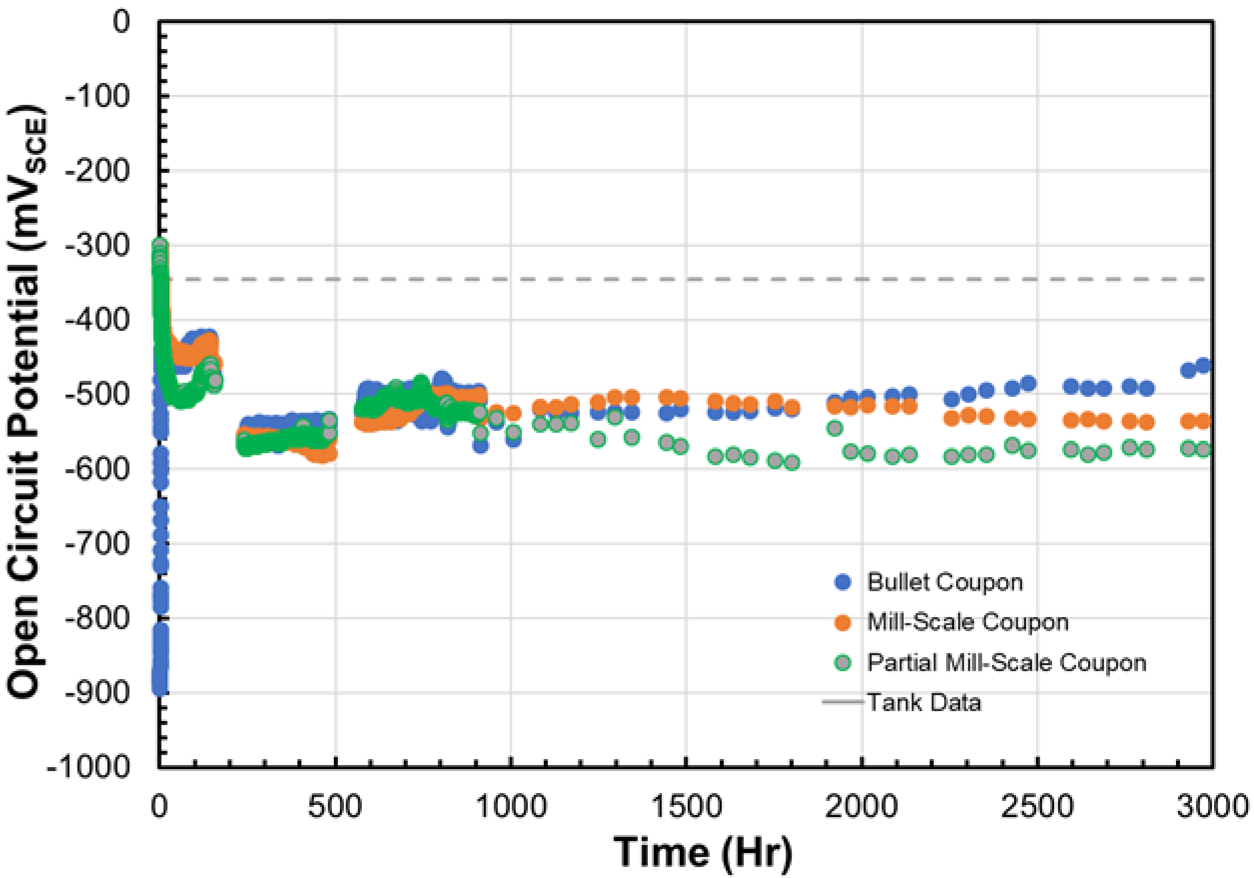
- OCP evolution is anodic for the three coupons, steady-state was not observed

Data and Results: AW-105 with small organic acids plus tributylphosphate family plus normal paraffin hydrocarbons



- OCP evolution is anodic for the two coupons, steady-state reached after 1200 hours

Data and Results: AW-105 with small organic acids plus spiked tributylphosphate family plus normal paraffin hydrocarbons



- OCP evolution is anodic for the bullet coupon, but steady-state seemed to change after 3000 hours
- OCP evolution is cathodic for mill- and partial mill-scale coupons, reached steady-state

Data and Results: OCP Evolution Summary

Summary of Open Circuit Potential (mV_{SCE}) Data

Simulant	Bullet		Mill-Scale		Partial Mill-Scale	
	Initial	After	Initial	After	Initial	After
AY-101	-557	-140	-175	-140	-388	-140
SY-101	-492	-74	-183	-298	-324	-340
AW-105 with small organic acids (i.e., formate, acetate, glycolate)	-668	-256	-284	-186	-405	-319
AW-105 with small organic acids plus tributylphosphate family plus normal paraffin hydrocarbon	-516	-239	-205	-237	–	–
AW-105 with small organic acids plus spiked tributylphosphate family plus normal paraffin hydrocarbon	-893	-494	-300	-459	-299	-480

Data and Results: Tank Data

Open Circuit Potential (mV_{SCE}) Data of Tanks

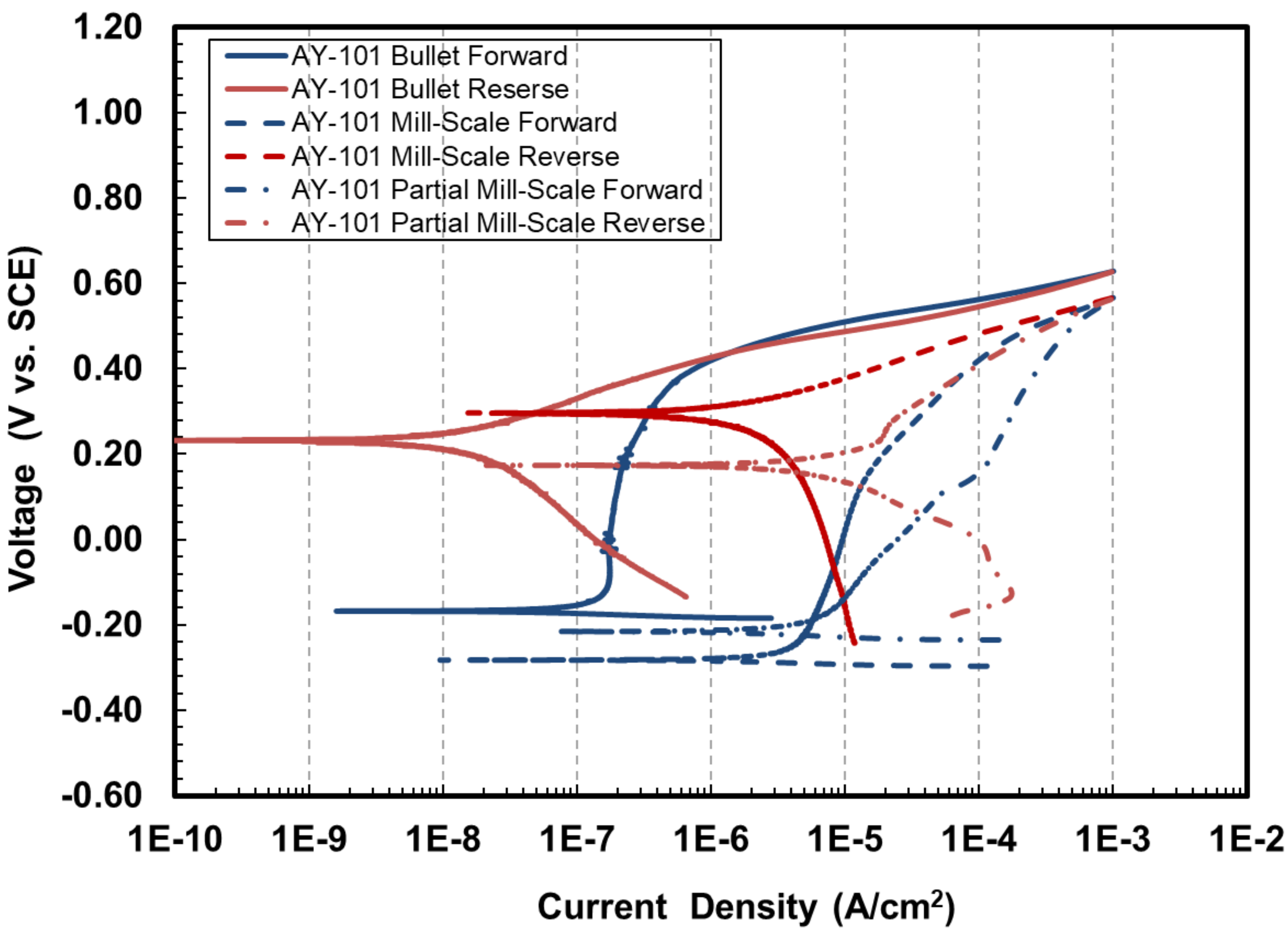
Tank	Years of Service of Reference Electrode	Initial Potential (mV_{SCE})	Final Potential (mV_{SCE})	Average Potential (mV_{SCE})	Std. Dev. (mV_{SCE})
AY-101	0.5	-80	-74	-77	NA
SY-101	5.5	-257	-279	-257	13
AW-105	6.5	-253	-394	-345	78

Data and Results: Comparison

Comparison of Tank Wall and Simulant Open Circuit Potential Data

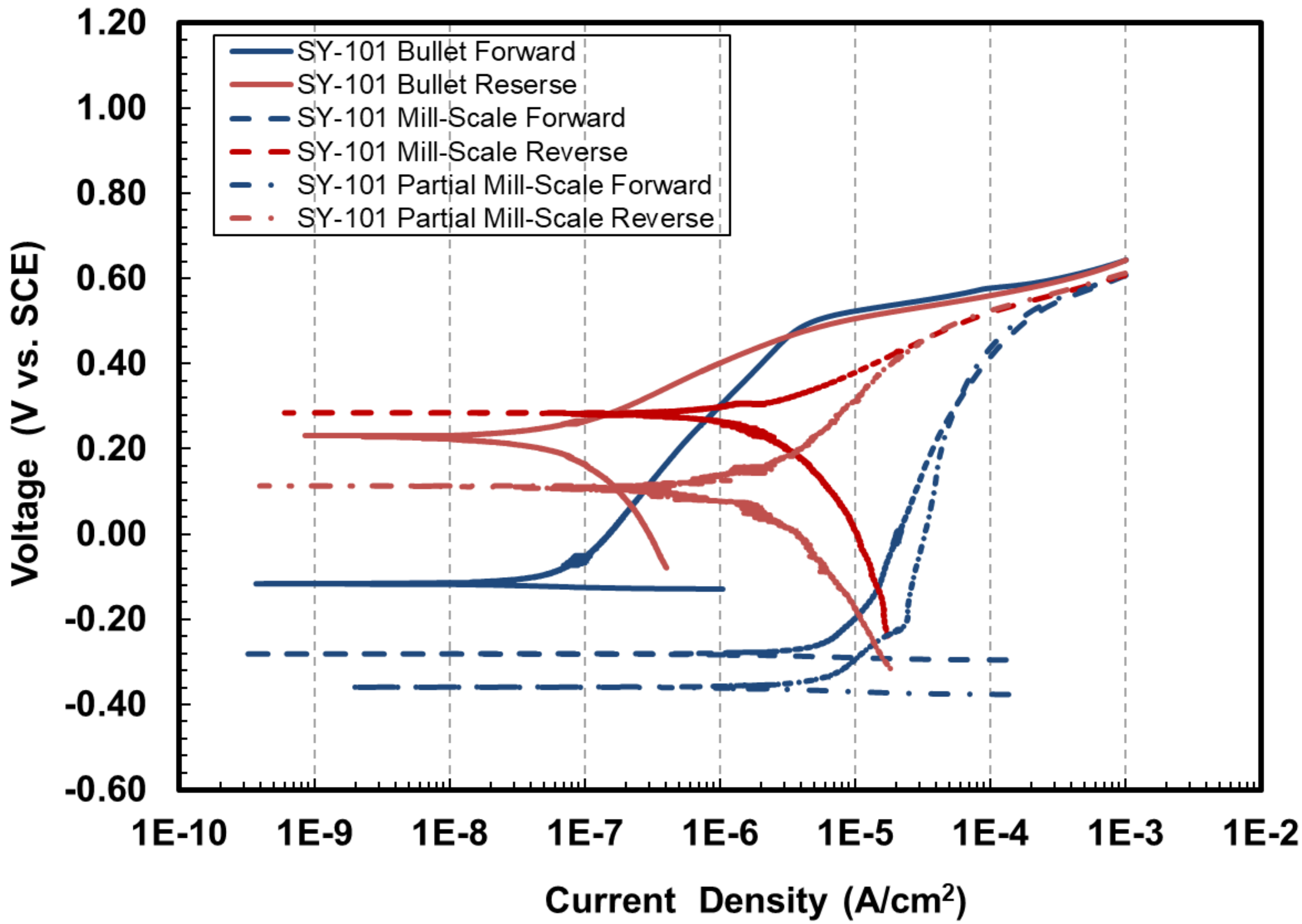
Tank	Tank-Wall Open Circuit Potential	Simulant Open Circuit Potential Data and Notes
AY-101	-77 mV_{SCE}	• -140 mV_{SCE} for all three coupons; simulant OCPs are -63 mV more cathodic than the tank-wall OCP
SY-101	-257 ± 13 mV_{SCE} (-244 to -270 mV_{SCE})	• Mill-scale coupon's OCP are closest to the tank-wall data
AW-105	-345 ± 78 mV_{SCE} (-267 to -423 mV_{SCE})	AW-105 with small organic acids • Partial mill-scale coupon's OCP is within the tank-wall OCP range • Mill-scale and bullet coupons' OCPs are close to the tank data
		AW-105 with small organic acids plus tributylphosphate family plus normal paraffin hydrocarbon • Both bullet and mill-scale coupons' OCPs are near the range, within 30 mV of the tank data
		AW-105 with small organic acids plus spiked tributylphosphate family plus normal paraffin hydrocarbon • Coupons' OCPs are outside the range

Data and Results: CPP Curves in AY-101 Simulant



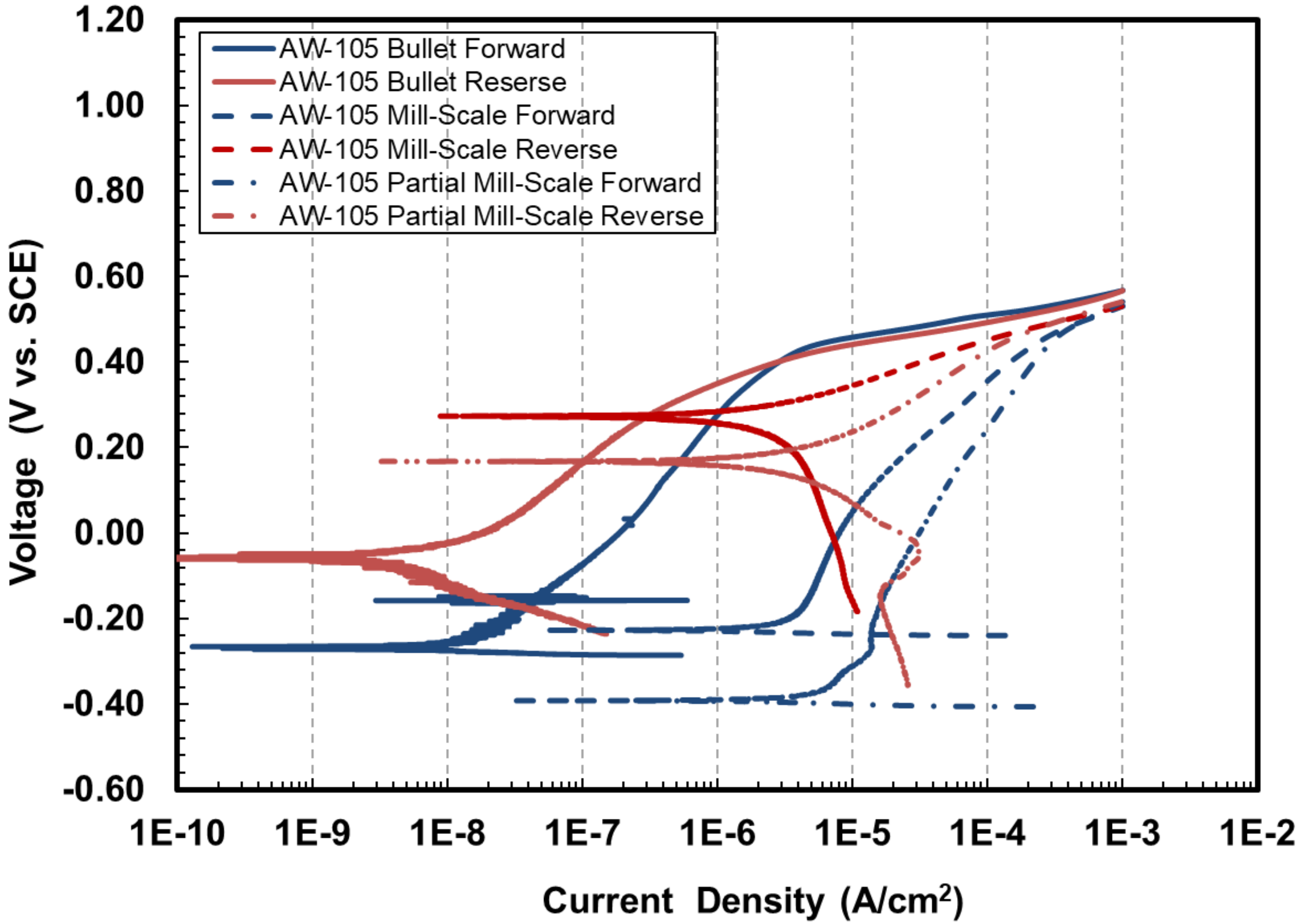
- Forward scans by blue curves, and reverse scans by red curves
- Category 1 response for all three coupons
- Mill-scale and partial mill-scale coupons' forward scan current density is higher than the bullet's

Data and Results: CPP Curves in SY-101 Simulant



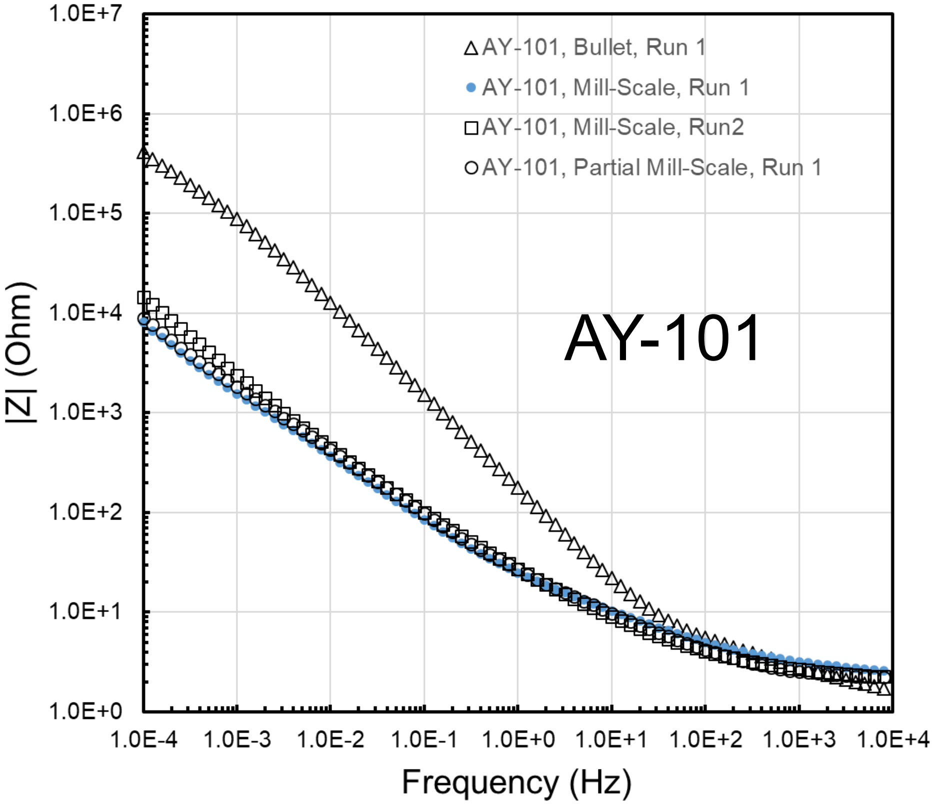
- Forward scans by blue curves, and reverse scans by red curves
- Category 1 response for all three coupons
- Mill-scale and partial mill-scale coupons' forward scan current density is higher than the bullet's

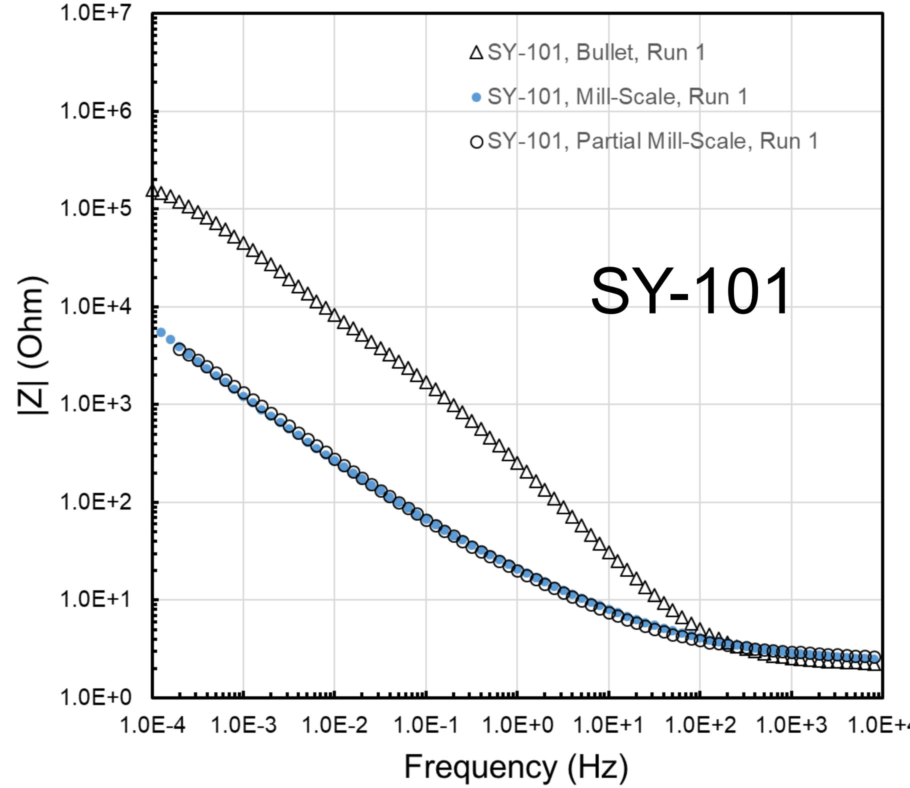
Data and Results: CPP Curves in AW-105 Simulant with Small Organic Acids



- Forward scans by blue curves, and reverse scans by red curves
- Category 1 response for all three coupons
- Mill-scale and partial mill-scale coupons' forward scan current density is higher than the bullet's

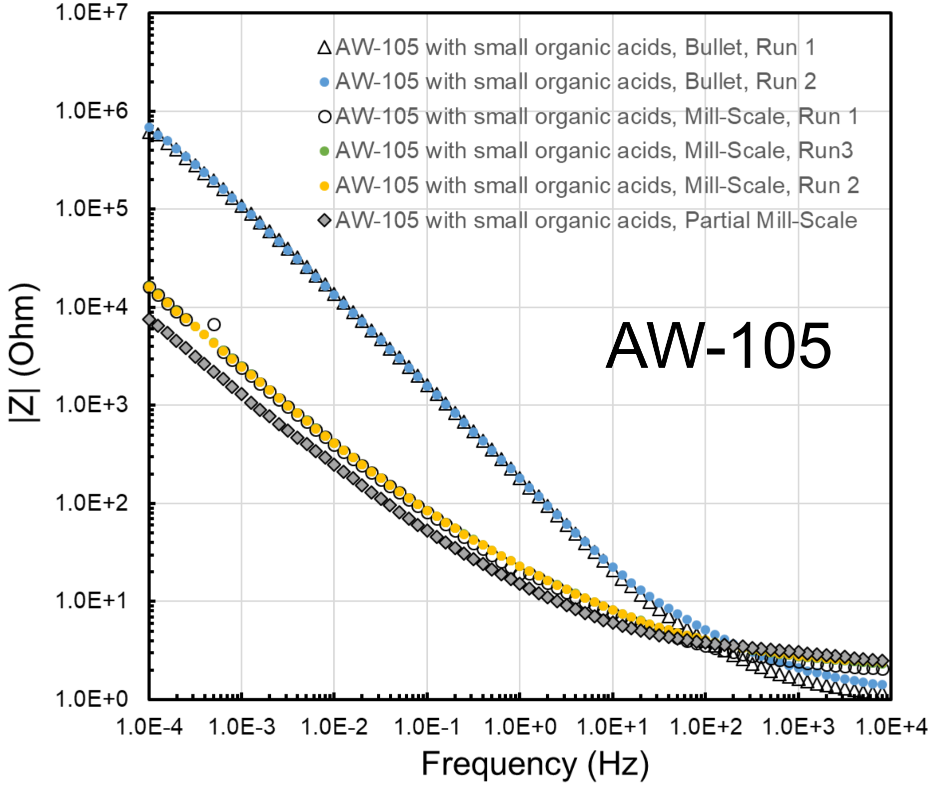
Data and Results: EIS Data for AY-101 and SY-101





- Bullet coupons' lower-frequency impedances are higher than the mill-scale and partial mill-scale coupons
- One time constant in the impedance spectra

Data and Results: EIS Data for AW-105 Simulant with Small Organic Acids



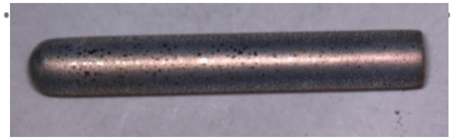
- Bullet coupons’ impedances are higher than the mill-scale and partial mill-scale coupons
- One time constant in the impedance spectra

Data and Results: Coupons Images

(a) AY-101 bullet

(b) AY-101 mill-scale

(c) AY-101 partial mill-scale



(d) SY-101 bullet

(e) SY-101 mill-scale

(f) SY-101 partial mill-scale

(g) Bullet in AW-105 with small organic acids bulle

(h) Mill-scale in AW-105 with small organic acids bullet

(i) Partial mill-scale in AW-105 with small organic acids

Conclusions

- Coupons with differing surface conditions
  - Polished
  - Mill-scale plus corrosion products
  - Partly polished of mill-scale plus corrosion products

- OCP evolution summary
  - AY-101: three coupons evolved to same steady state
  - SY-101: coupons' corrosion potentials differed as much as by 250 mV, and continued to evolve even after 4000 hours
  - AW-105 with small organic acids: corrosion potentials were in the range of -200 to -300 mV_{SCE} after 4000 hours of exposure
  - AW-105 with small organic acids and other organics (TBP+NPH): corrosion potentials were in the range of -200 to -300 mV_{SCE} after 2100 hours of exposure, steady-state
  - AW-105 with small organic acids and spiked organics (TBP+NPH): corrosion potentials were in the range of -400 to -600 mV_{SCE} after 4000 hours of exposure, steady-state

Conclusions

- CPP response
  - Category 1 response of all three coupon types, i.e., pitting corrosion is unlikely,
  - Passive current density part of the CPP forward scans are dependent on the surface conditions, 1-2 order magnitude higher passive current density for the mill-scale and partial mill-scale coupons compared to polished bullet coupons

- Impedance responses
  - One time-constant type impedance spectra
  - Low frequency impedance of the bullet coupons are higher compared to mill-scale and partial mill-scale coupons
  - Consistent with CPP data

Acknowledgements

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