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EM Office of Environmental Management
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ENHANCED CHEMICAL CLEANING CORROSION TESTING

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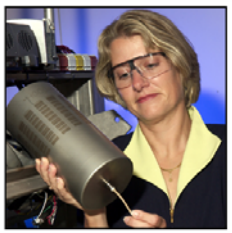
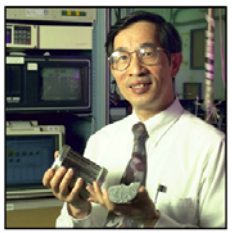
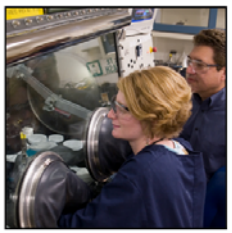
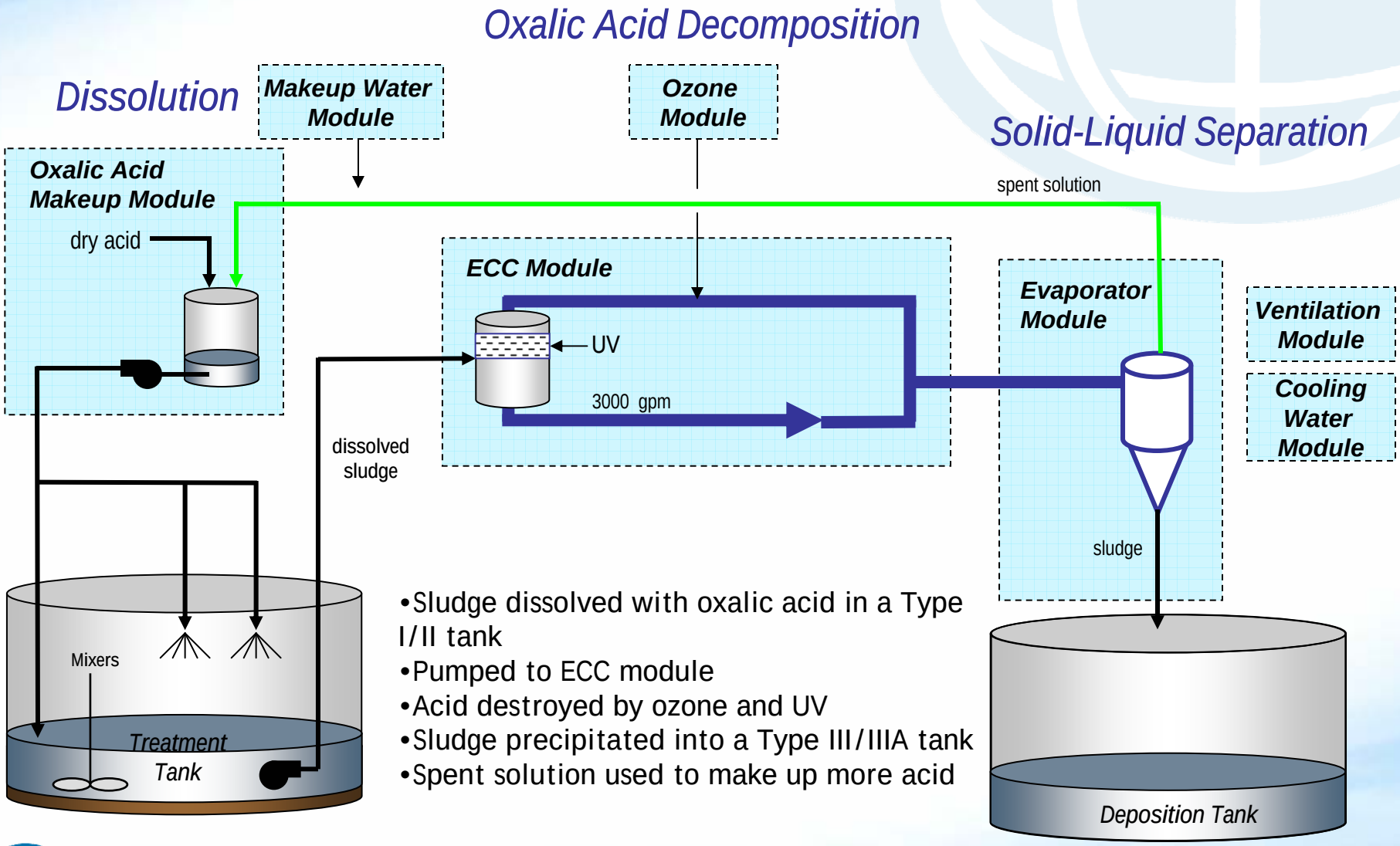
Materials Science and Technology

Outline

- Background on Enhanced Chemical Cleaning (ECC) Process and Materials Performance Testing Objectives
- Treatment Tank Corrosion Studies (SRNL)
  - Tests with oxalic acid with sludge simulants
- Deposition Tank Corrosion Studies (SRNL/AREVA)
  - Tests with destruction loop effluents
- Summary

Background: Enhanced Chemical Cleaning Process



- Sludge dissolved with oxalic acid in a Type I/II tank
- Pumped to ECC module
- Acid destroyed by ozone and UV
- Sludge precipitated into a Type III/IIIA tank
- Spent solution used to make up more acid

Background: ECC Treatment Tank Corrosion Studies

- Changes in process variables
  - Oxalic acid concentration reduced from 8 wt.% to 1 wt.%.
  - pH of environment at ~2
  - PUREX, HM, and a blend of PUREX and HM

- Other process variables considered
  - Temperature
  - Agitation
  - Aeration

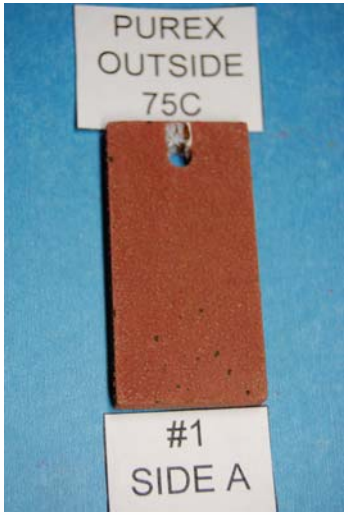
- Desired results from laboratory testing
  - General corrosion rates
  - Susceptibility to localized corrosion
  - Propensity for hydrogen generation

Treatment Tank: Immersion Testing

- ASTM A285 carbon steel coupons
- Vessel-in-Vessel design
- Simulated sludge solids in contact with 1 wt.% oxalic acid
  - ~250 ml of sludge solids
  - ~3000 ml of oxalic acid
- pH of solution ~ 2; controlled by periodic addition of 1 wt.% oxalic acid
- Temperature: 45 and 75 °C
- Agitated and stagnant
- Time: 28 days

Treatment Tank: Immersion Testing

Oxalic Acid



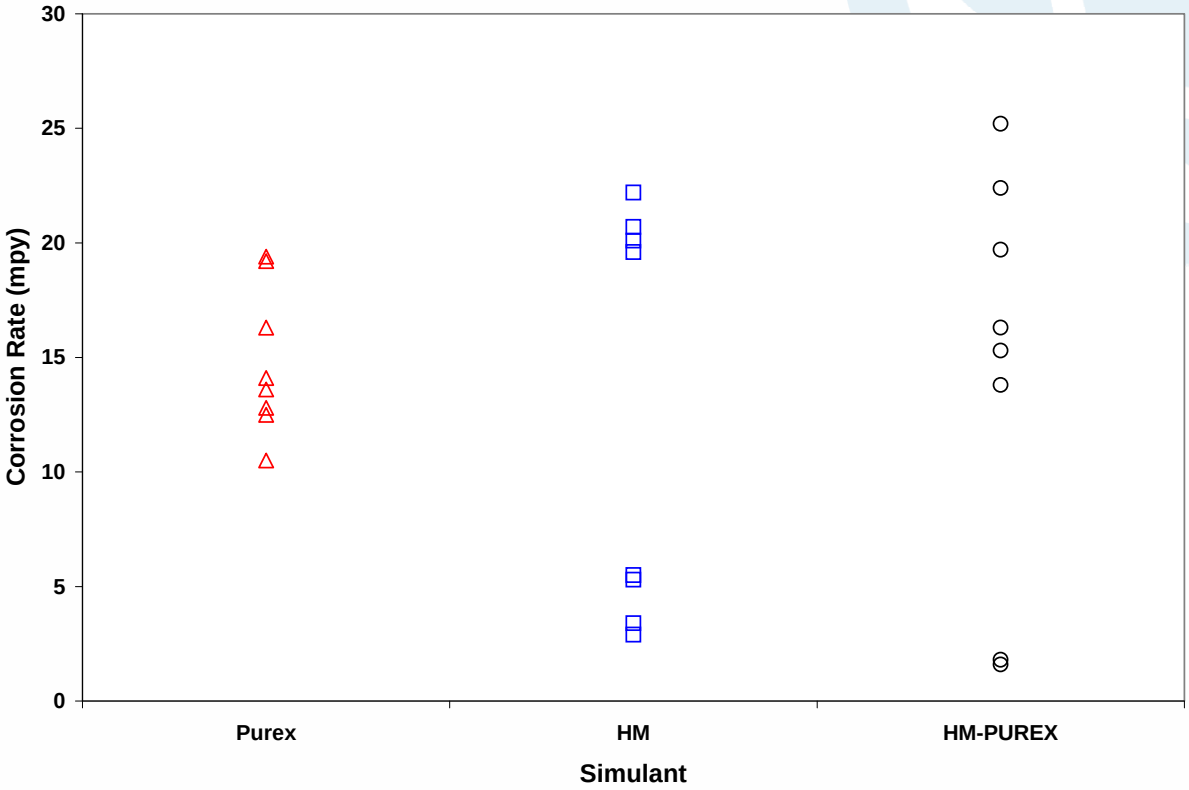
PUREX + Oxalic Acid

HM + Oxalic Acid

HM-PUREX + Oxalic Acid

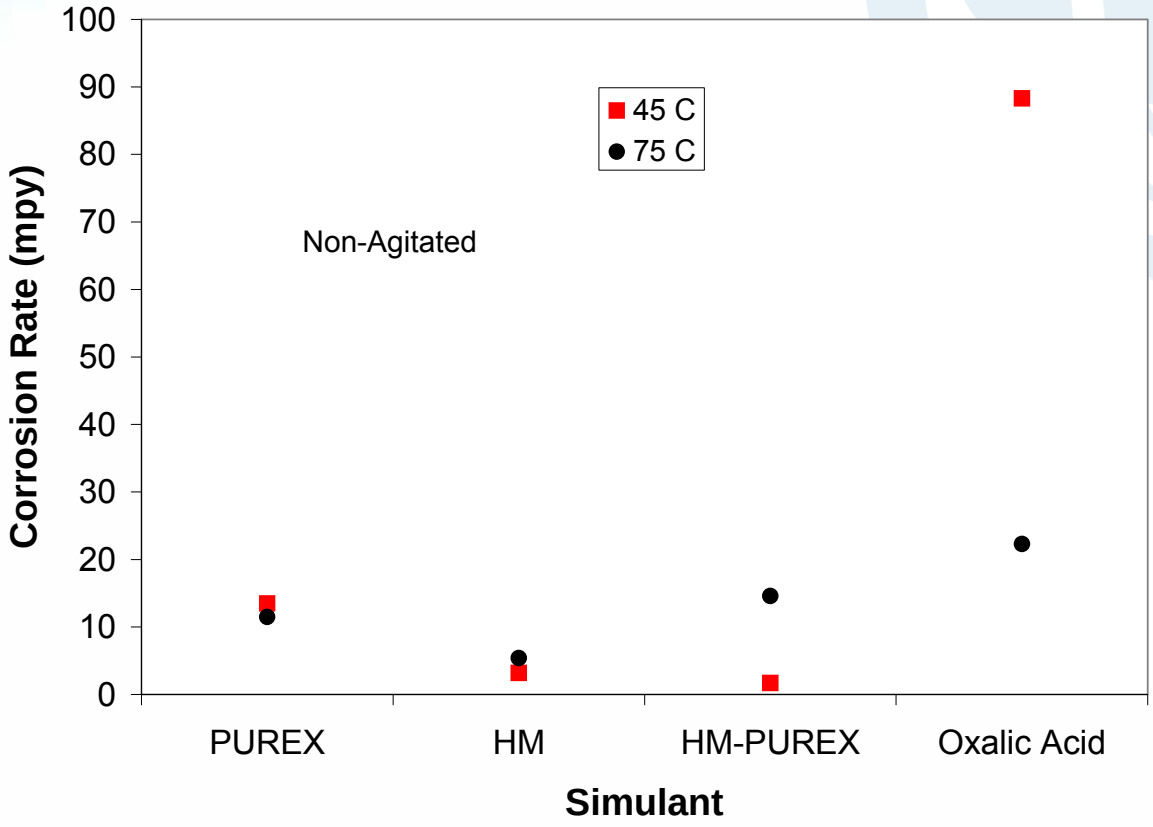
- Temperature 75 °C; Agitated Solutions
- Sludge particles appear to be embedded in matrix of ferrous oxalate on the metal surface.
- PUREX: Ferrous oxalate, Hematite, Goethite, Akaganeite
- HM: Ferrous oxalate, Corrundum, Hematite
- HM-PUREX: Ferrous oxalate, Hematite, Goethite

Treatment Tank: Immersion Test Results



- All corrosion rates for carbon steel exposed to oxalic acid with sludge present were less than 25 mils/yr.
- Variability observed due to process variables (e.g., agitation)

Treatment Tank: Immersion Test Results



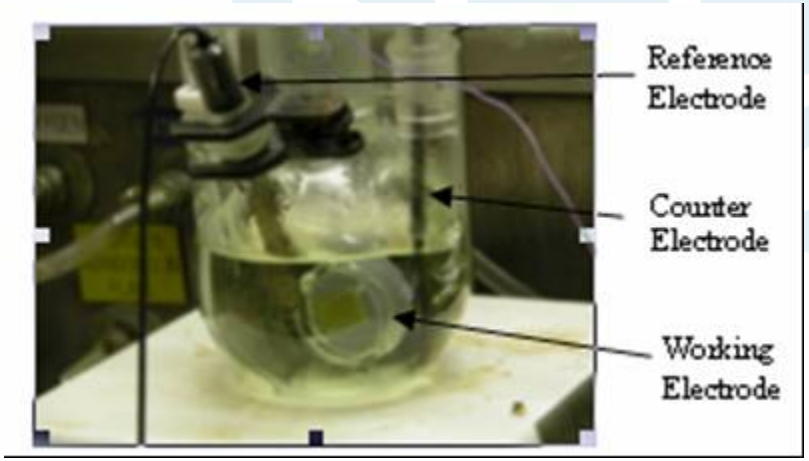
- Temperature effect is less noticeable in the presence of oxalic acid with sludge solids.
- Corrosion rate of carbon steel is lower in the presence of oxalic acid with sludge solids than it is with oxalic acid alone.

Treatment Tank: Electrochemical Testing

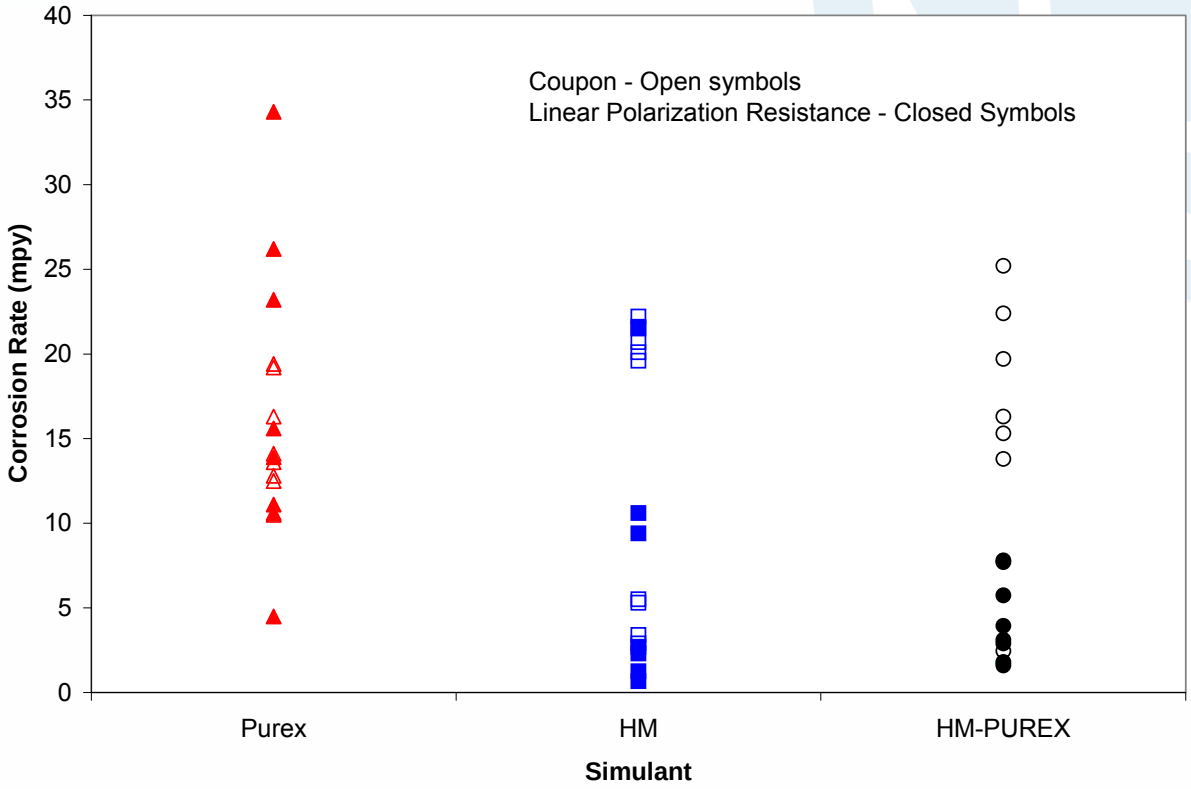
Technique	Information
• Linear Polarization Resistance	• General corrosion rate
• Cyclic Potentiodynamic Polarization	• Localized corrosion susceptibility
• Open Circuit Potential Monitoring	• Propensity for hydrogen generation • Stability of the passive film
• Cathodic Potentiodynamic Polarization	• Propensity for hydrogen generation • General corrosion rate

Treatment Tank: Electrochemical Test Set-up

- Three electrode system for measuring electrochemical parameters:
  - Working Electrode: ASTM A285 Carbon steel
  - Counter Electrode: Graphite rod
  - Reference Electrode: Ag/AgCl
- Gamry™ 600 Potentiostat
- Solutions: 1 wt.% oxalic acid with and without sludge simulant solids at pH ~ 2
  - Sludge Simulants: HM, PUREX, HM-PUREX blend
- Temperature: 45 and 75 °C
- Agitated and Stagnant
- Aerated and De-aerated

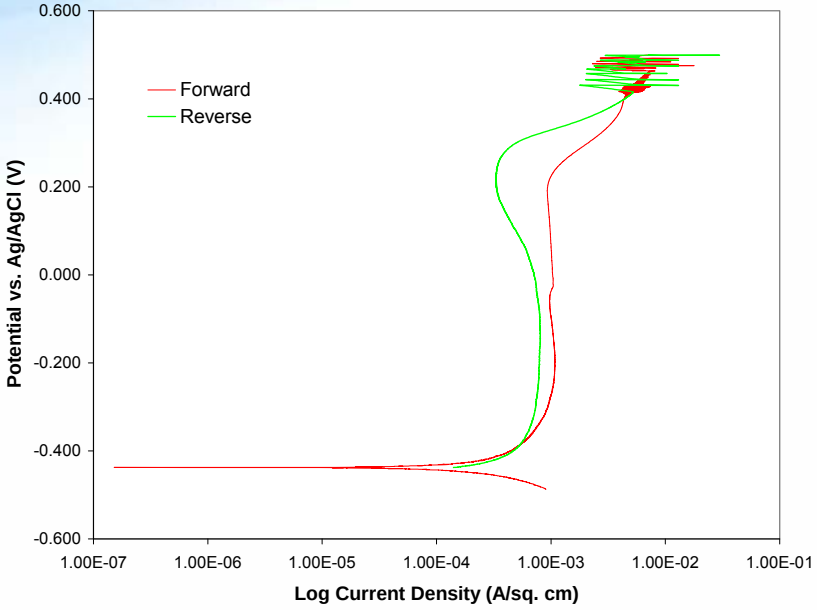


Treatment Tank: Linear Polarization Test Results



- All corrosion rates for carbon steel exposed to oxalic acid with sludge present were less than 25 mils/yr.
- Generally good agreement with coupon immersion tests; trends with respect to process variables were the same.

Treatment Tank: Cyclic Potentiodynamic Polarization Results



1 wt.% oxalic acid

75 °C

Agitated

No localized attack

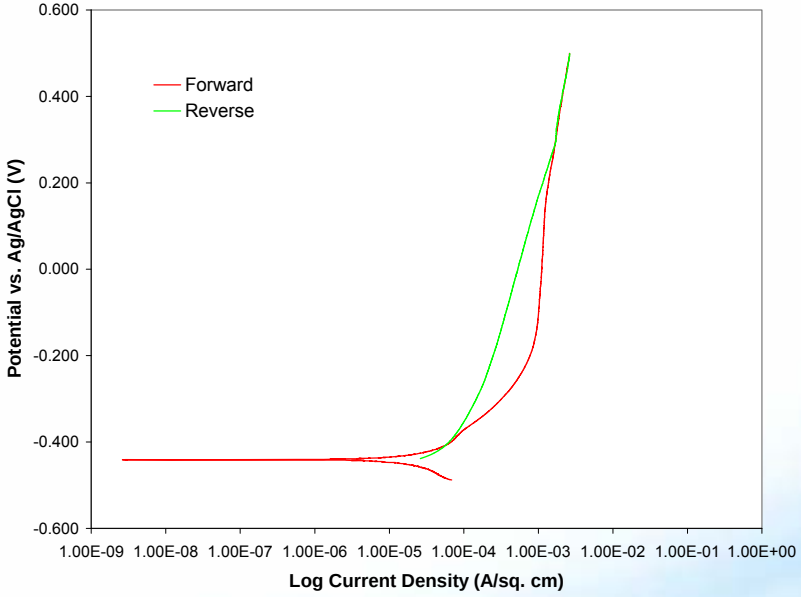
PUREX

1 wt.% oxalic acid

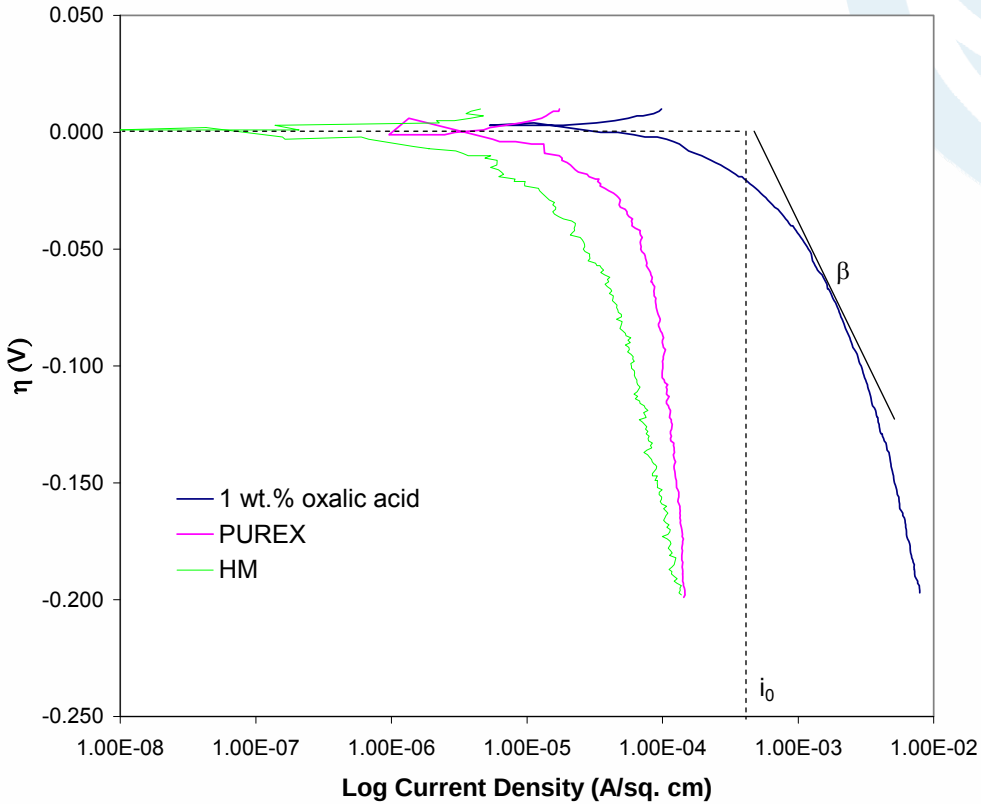
75 °C

Agitated

No localized attack



Treatment Tank: Cathodic Polarization Test Results



- Cathodic behavior in the presence of oxalic acid and sludge is significantly different
- Concentration polarization occurring in the presence of sludge.

Treatment Tank: Cathodic Polarization Test Results

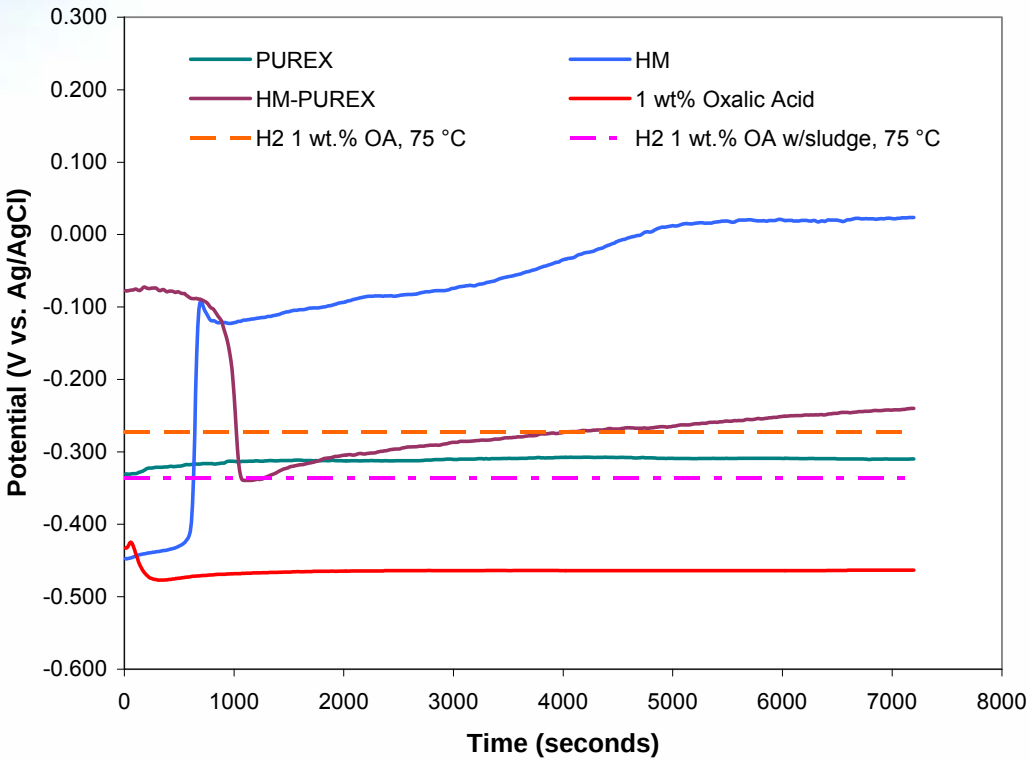
- For hydrogen evolution on an iron surface the transfer coefficient, α, is typically between 0.4 and 0.6.

$$\alpha = 2.3\ R\ T/(\beta\ F)$$

- Hydrogen likely to evolve with carbon steel in oxalic acid
- Unlikely to evolve in the presence of sludge.

Simulant	Temperature (°C)	α
1 wt.% oxalic acid	45	0.454
1 wt.% oxalic acid	75	0.473
HM/oxalic acid	45	0.247
HM/oxalic acid	75	0.284
PUREX/oxalic acid	75	0.117

Treatment Tank: Open Circuit Potential Monitoring Test Results



Agitated

75 °C

$$E = E° - 2.303 \frac{RT}{F} * pH$$

Hydrogen evolution unlikely in the presence of sludge solids

Background: ECC Deposition Tank Corrosion Studies

- Ozonation destroys the organic compounds such as oxalate by creating hydroxyl radicals and secondary oxidizers. The radicals and oxidizers may impact the corrosion that occurs in the deposition tank.
- Corrosion tests being performed in conjunction with Hazardous Simulant Tests at AREVA.
- Tests on the effluents from the destruction loop:
  - PUREX and HM sludge simulants
  - Three different UV lamp conditions
  - Multiple treatment tank strikes
- Tests on final deposition tank solutions:
  - Evaporator
  - Hydroxide Adjustment
  - Supernate level and composition
- Tests on oxalic acid that returns to the dissolution tank, but is saturated with ozone.

Deposition Tank Corrosion Testing

- Initial tests performed on the solution exiting the destruction loop.
- Immersion - A537 carbon and 304L stainless steel; Electrochemical - A537 carbon steel.
- Corrosion testing included open-circuit monitoring, linear polarization resistance (LPR) and cyclic polarization (CP).
- 18 hour tests for each acid strike; 14 hours with multiple LPR measurements followed by CP.
- Three acid strikes were performed.

Deposition Tank: Preliminary Results from PUREX Simulant Tests

- Test temperature was 50 °C
- pH of solution ranged between 7 and 9 during the tests.
- Oxidation-reduction potentials ranged between 200-400 mV vs. NHE during the tests
- Open-circuit potentials and corrosion rates similar for carbon steel in waste processed with the three light conditions
- Carbon steel corrosion rates varied between 2-10 mpy
- Corrosion behavior changes slightly during subsequent strikes from anodic dissolution or slight pitting to pitting without repassivation

Summary

- Treatment tank corrosion tests
  - Low general corrosion rates (< 25 mpy)
  - No susceptibility to localized attack
  - Low propensity for hydrogen evolution
- Deposition tank corrosion tests
  - Performed in conjunction with hazardous simulant tests at AREVA
  - Initial results indicate that solutions exiting the destruction loop
    - Low general corrosion rates
    - Slight propensity for localized attack
  - Testing will continue on into FY11

Acknowledgements

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Questions?