The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

Corrosion in amine pilot plants

4th Post Combustion Capture Conference

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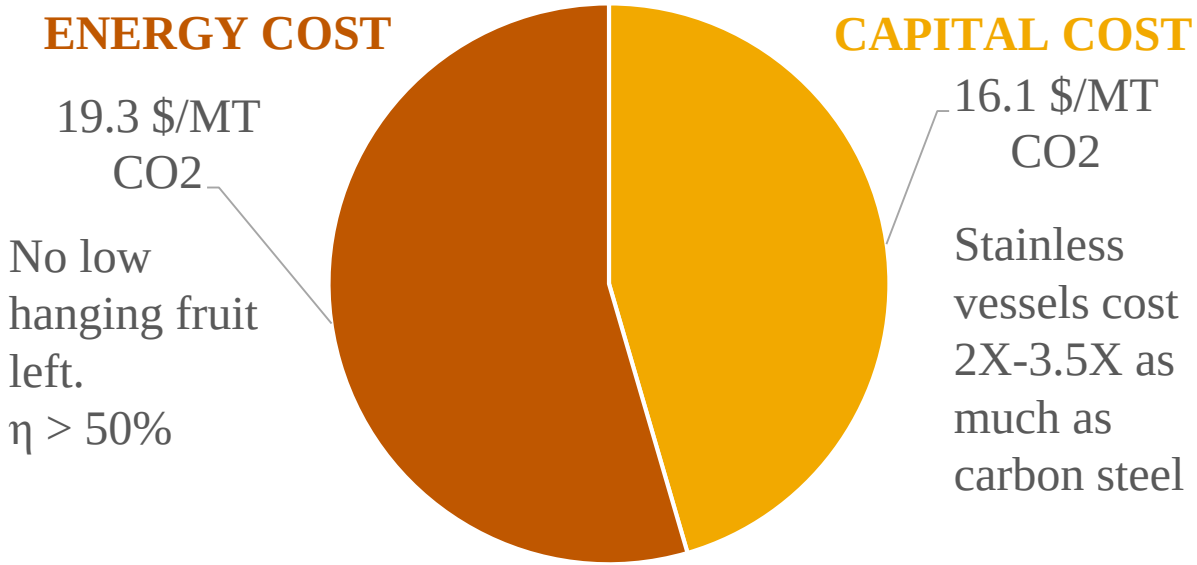
SS construction means CAPEX is high



At less than 100% operating time, capital cost is even more important!

Frailie, 2014

Outline

- SRP 2017 piperazine pilot plant ER probe results
- Pilot vs. bench scale ER probe comparison
- SRP coupon analysis
- NCCC 2017 ethanolamine ER probe results

Electrical resistance corrosion probe

- Sacrificial wire in amine solution corrodes

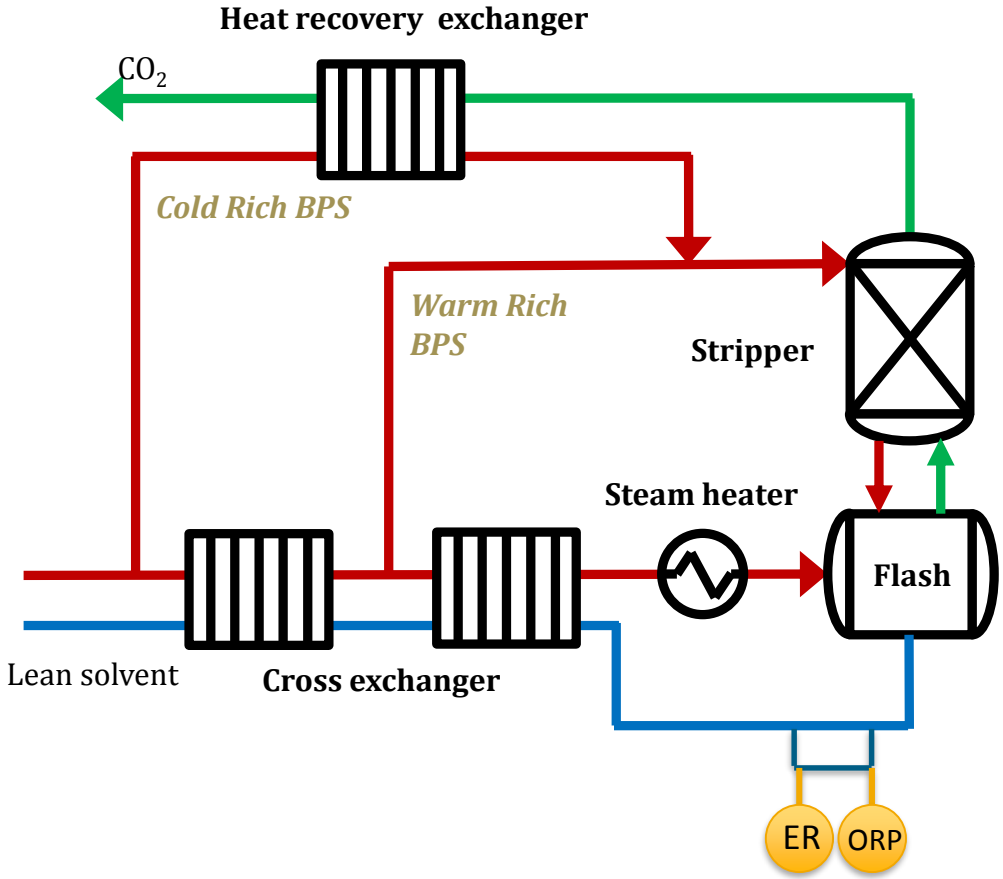
$$R \propto \frac{1}{A}$$

  - R = resistance (Ω)
  - A = wire cross sec. area
- Resistance ↑, current ↓, measure current and convert to corr. rate

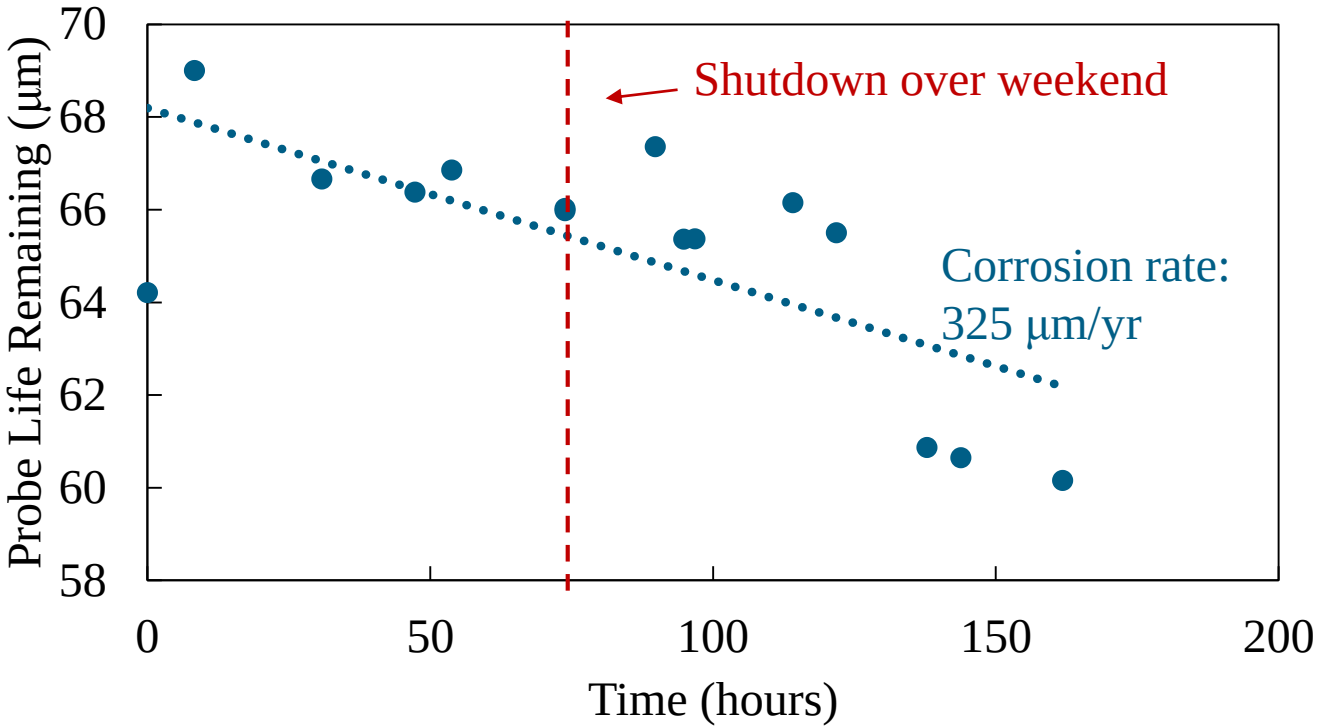
Corrosion (µm/yr)	
Good	100 - 500
Poor	1000 - 5000
Unacceptable	5000+

SRP pilot plant corrosion 2017

- April-May 2017
- Two ER corrosion probes in hot, lean stream leaving stripper
  - 316L SS
  - 1010 CS
- One ORP Probe
- In addition, one ER probe in absorber sump

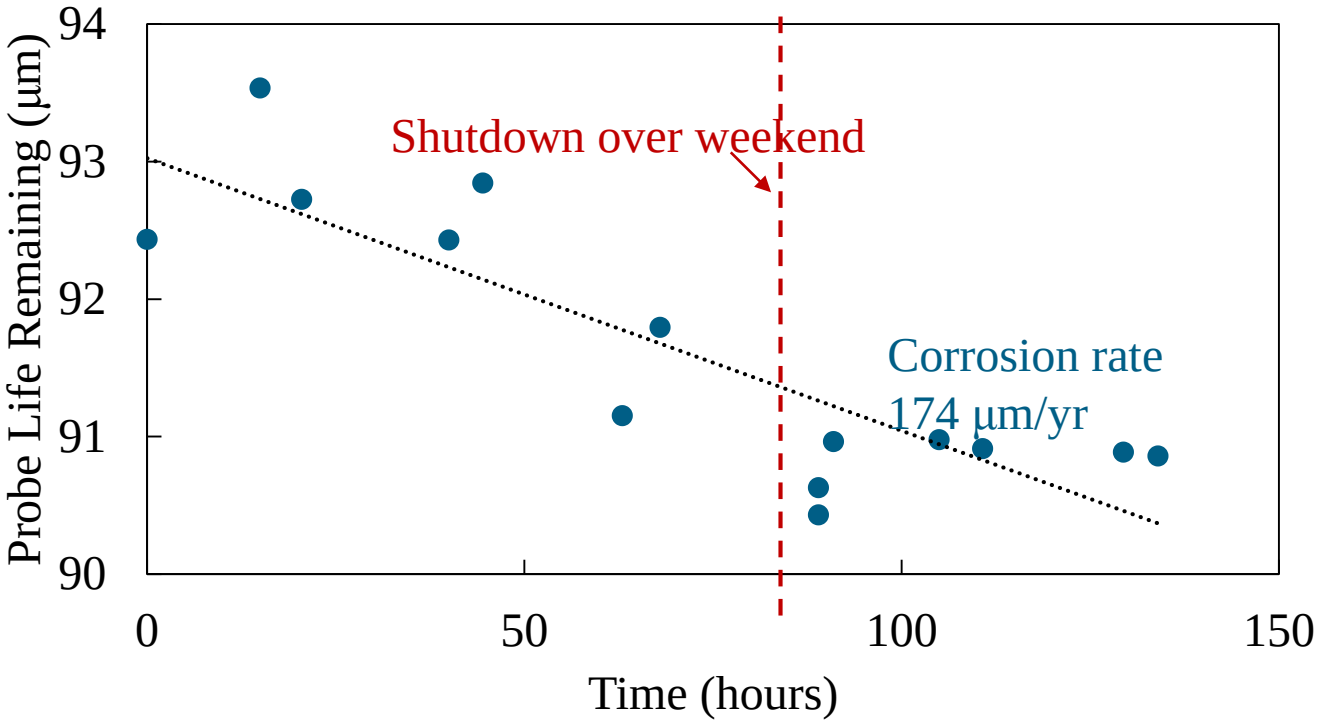


C1010 corrosion in SRP hot, lean 5 m PZ, 150°C, α = 0.21



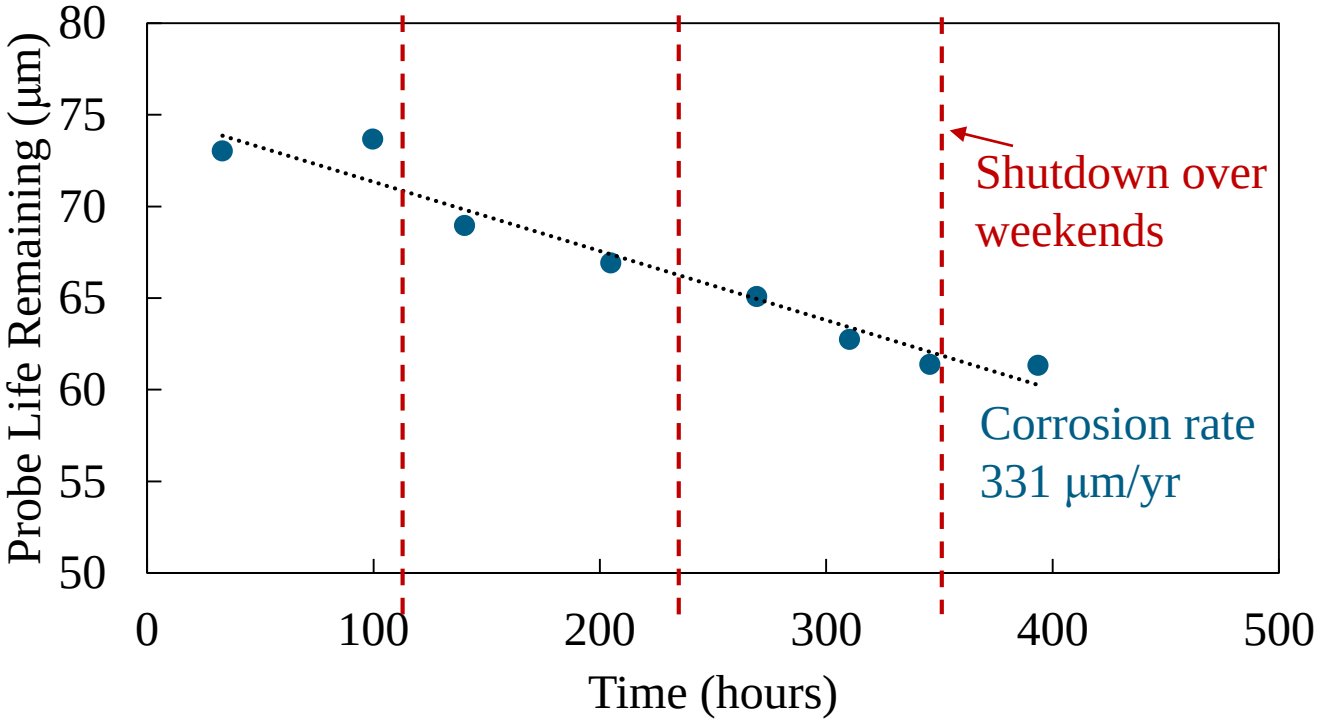
- Each point is an average reading over a steady state run

316L corrosion in SRP hot, lean
5 m PZ, 150°C, α = 0.21



- Each point is an average reading over a steady state run

C1010 corrosion in SRP absorber, 5 m PZ, 30°C, α = 0.33



- Each point is an instantaneous reading w/ handheld

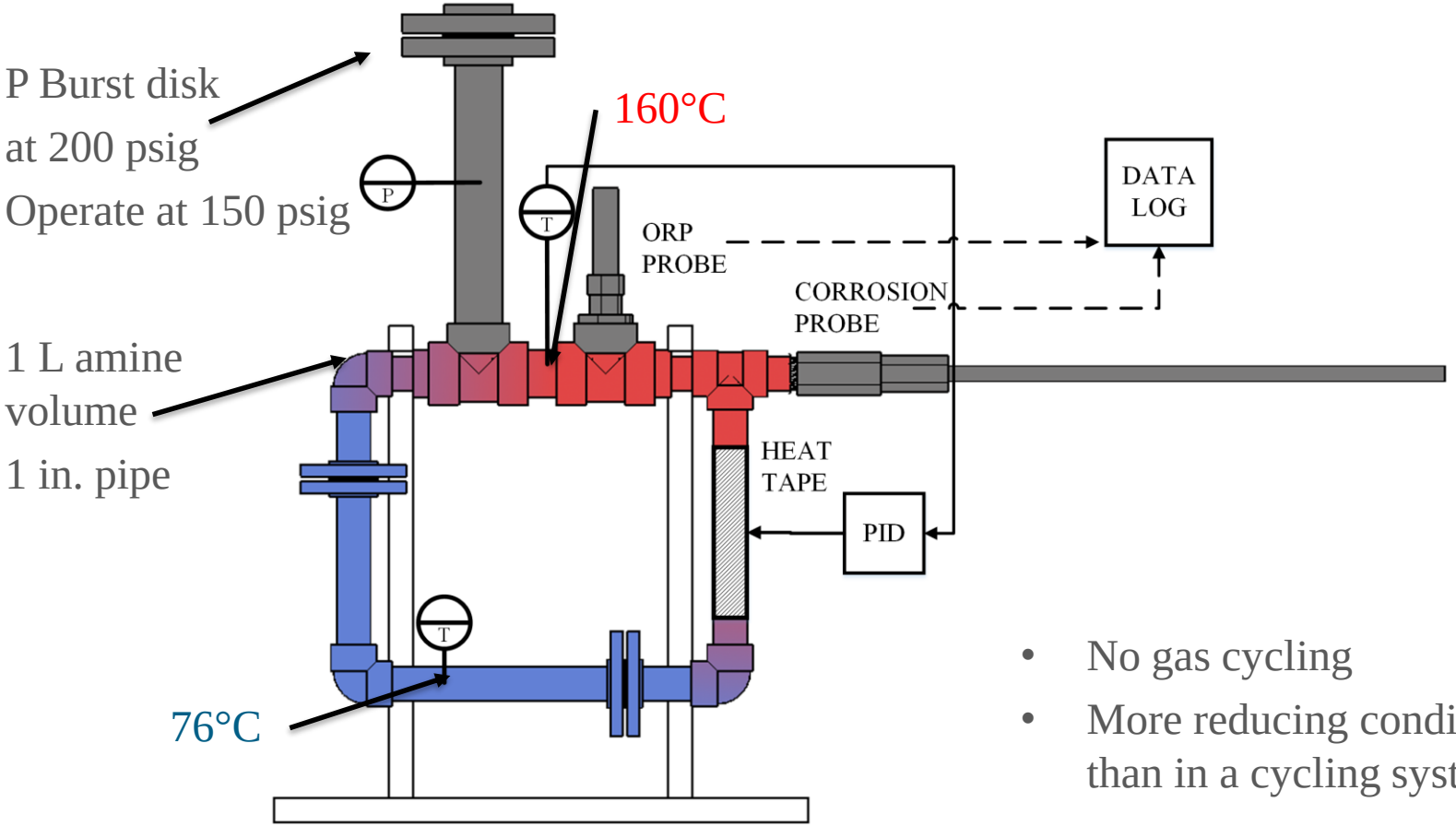
SRP pilot plant corrosion 2017

Location	**Alloy**	T (°C)	Avg. Loading (mol CO_2/mol N)	**Corrosion (µm/yr)**	Error (µm/yr)
Absorber	**C1010**	30	0.33	**331**	± 32
Hot, lean	**C1010**	150	0.21	**325**	± 92
Hot, lean	**316L**	150	0.21	**174**	± 31

- Unexpectedly high absorber corrosion!

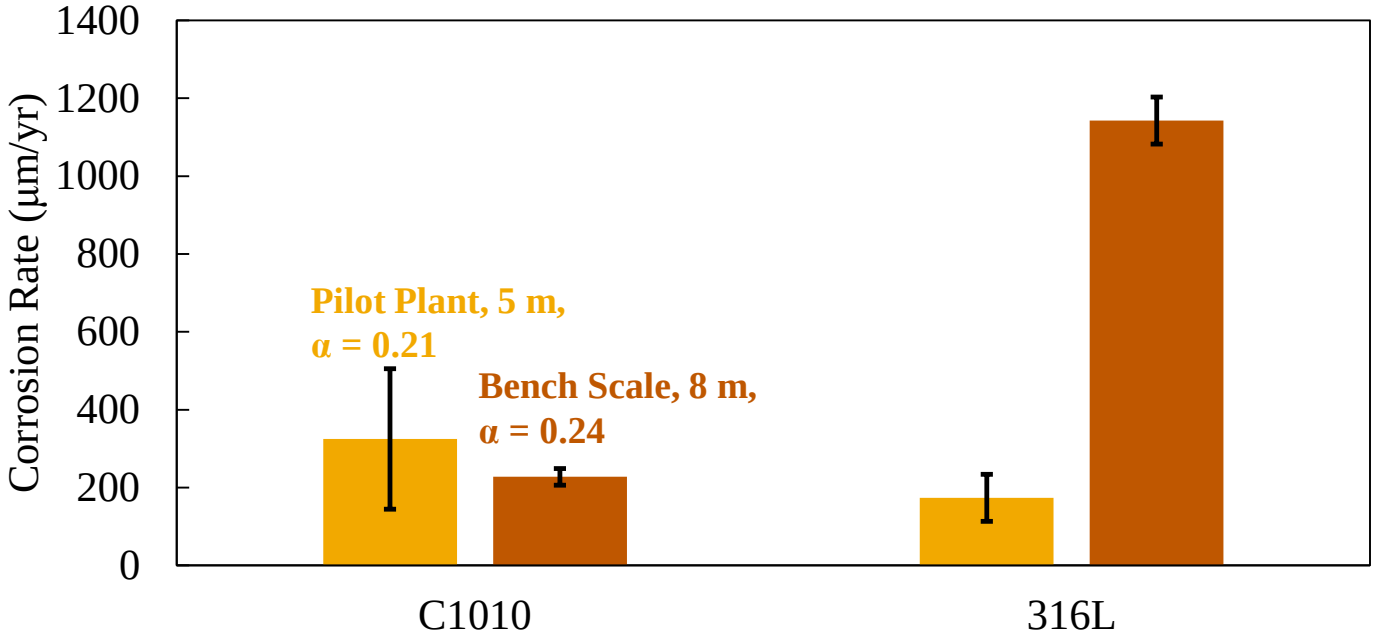
Corrosion (µm/yr)	
Good	100 - 500
Poor	1000 - 5000
Unacceptable	5000+

Corrosion loop



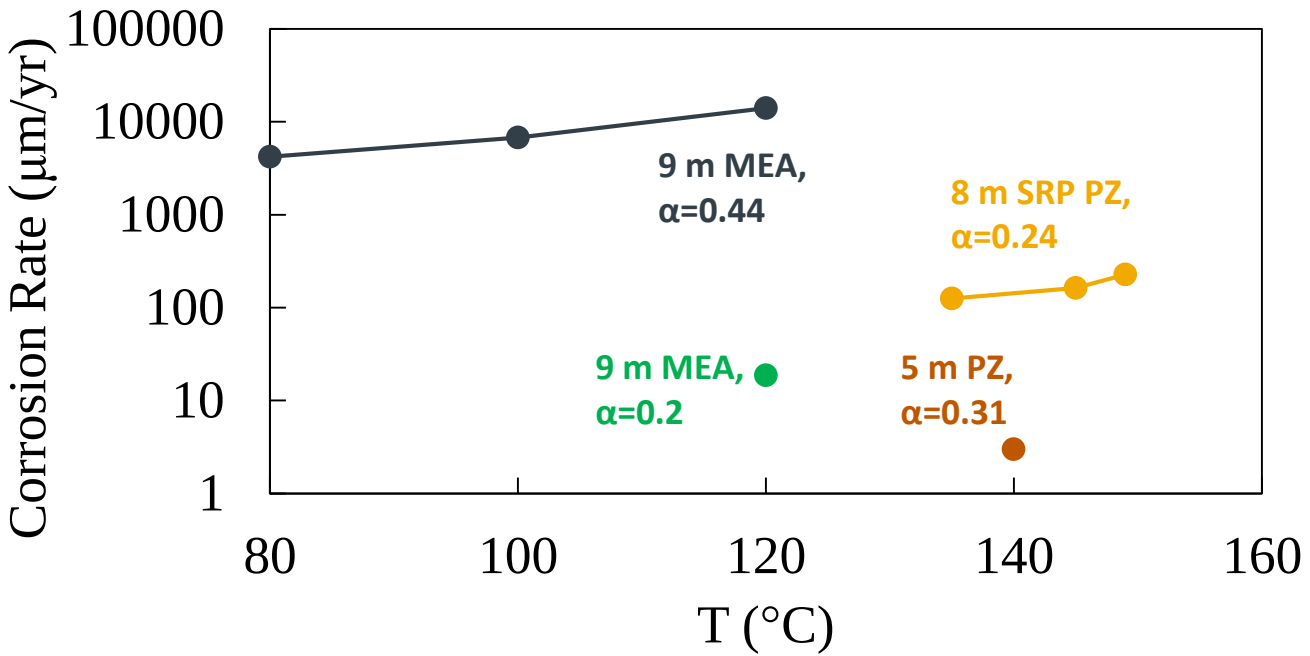
- No gas cycling
- More reducing conditions than in a cycling system

Pilot vs bench-scale SRP PZ, 150°C, 95% confidence intervals shown



- Bench scale C1010 measurements agree w/ pilot
- Bench scale 316L measurements overpredict

C1010 corrosion at bench-scale



- PZ at many degradation levels, loadings is 2 orders of magnitude less corrosive to C1010 than rich MEA

Corrosion slowed by passive film formation

- **Passivation of C1010 by $FeCO_3$**

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+$$

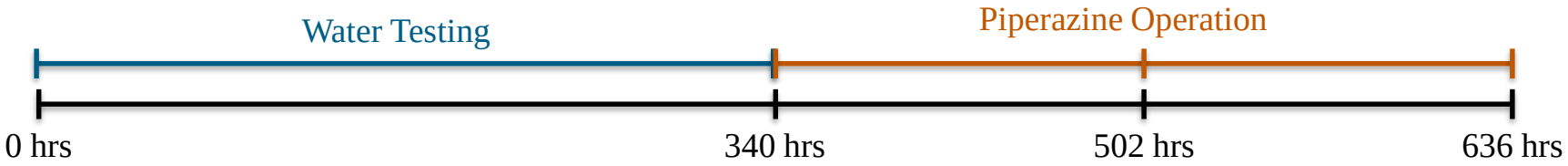
  - Sensitive to loading, Fe^{2+} solubility

- **Passivation of 316L by Cr_2O_3**

$$2Cr + 3H_2O \rightarrow Cr_2O_3 + 6H^+ + 6e^-$$

  - Sensitive to reducing conditions, O_2 depletion
  - Bench-scale apparatus depassivated 316L

SRP coupon removal timeline



Hot lean coupons (Set #1)
340 hrs H_2O Testing, 162 hrs PZ operation

Hot lean coupons (Set #2)
134 hrs PZ operation

Absorber Coupons
340 hrs H2O Testing, 392 hrs PZ operation

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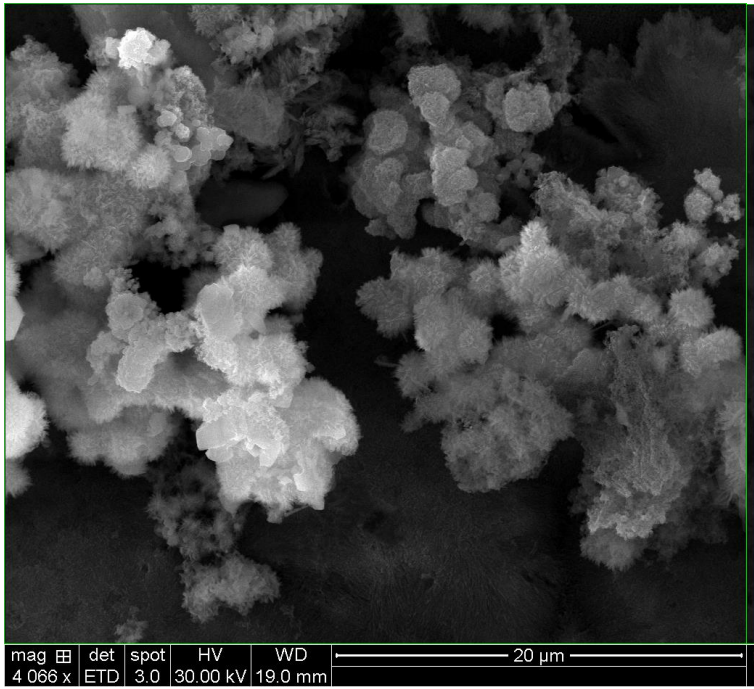
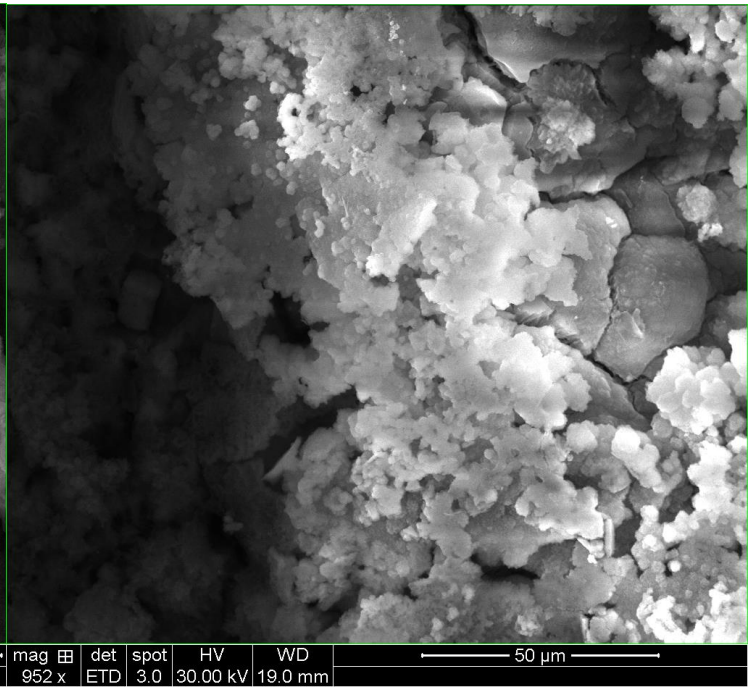
SRP hot lean coupons. 340 hours H_2O testing, 162 hours of operation w/ 5 m PZ, 150°C, α = 0.21





Red Product:
FeO(OH)

Black Product:
Fe_3O_4 (Magnetite)

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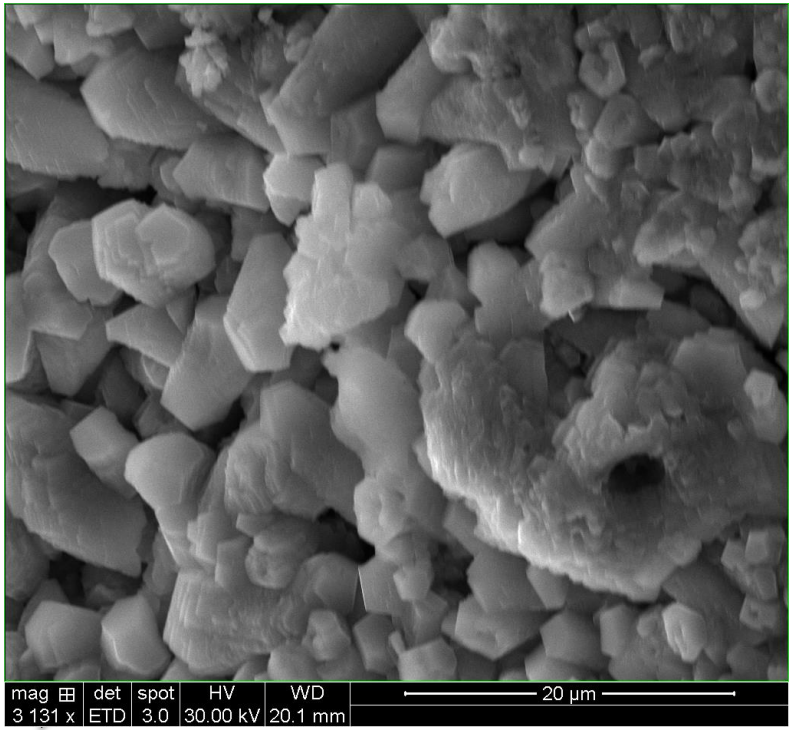
SRP hot lean coupons. 134 hours operating operation w/ 5 m PZ, 150°C, α = 0.21



Black Product: $FeCO_3$ (Siderite)

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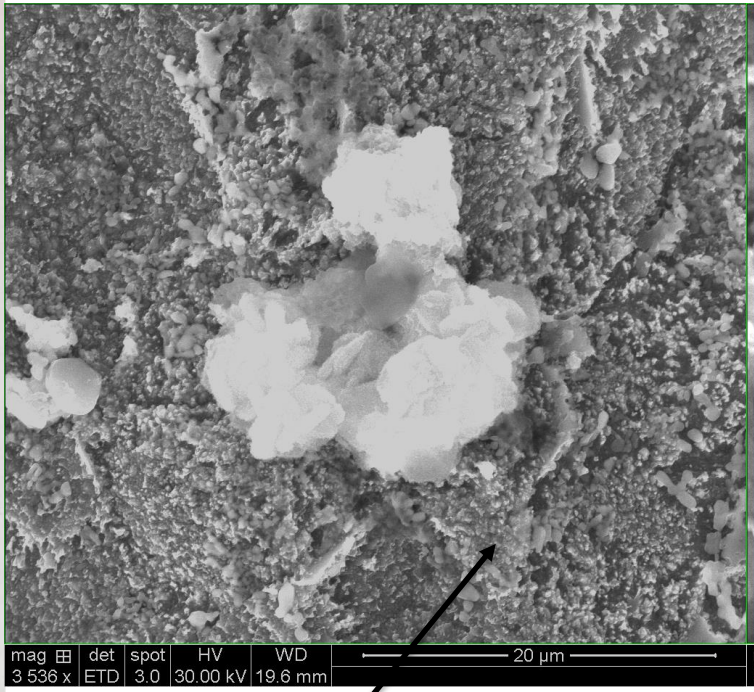
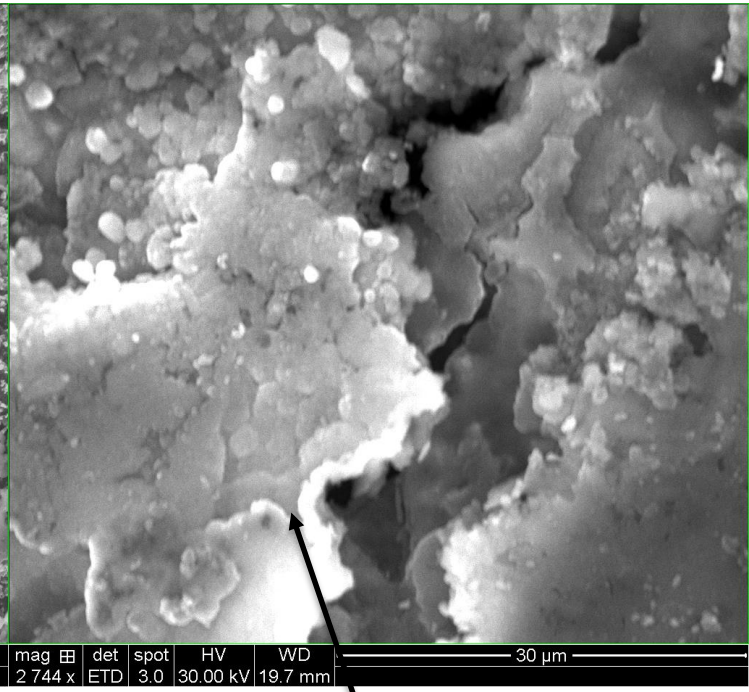
SRP absorber. 340 hrs H2O testing. 392 hrs operating w/ 5 m PZ, 30°C, α = 0.33





Black Product: Fe

Red Product: FeO(OH)

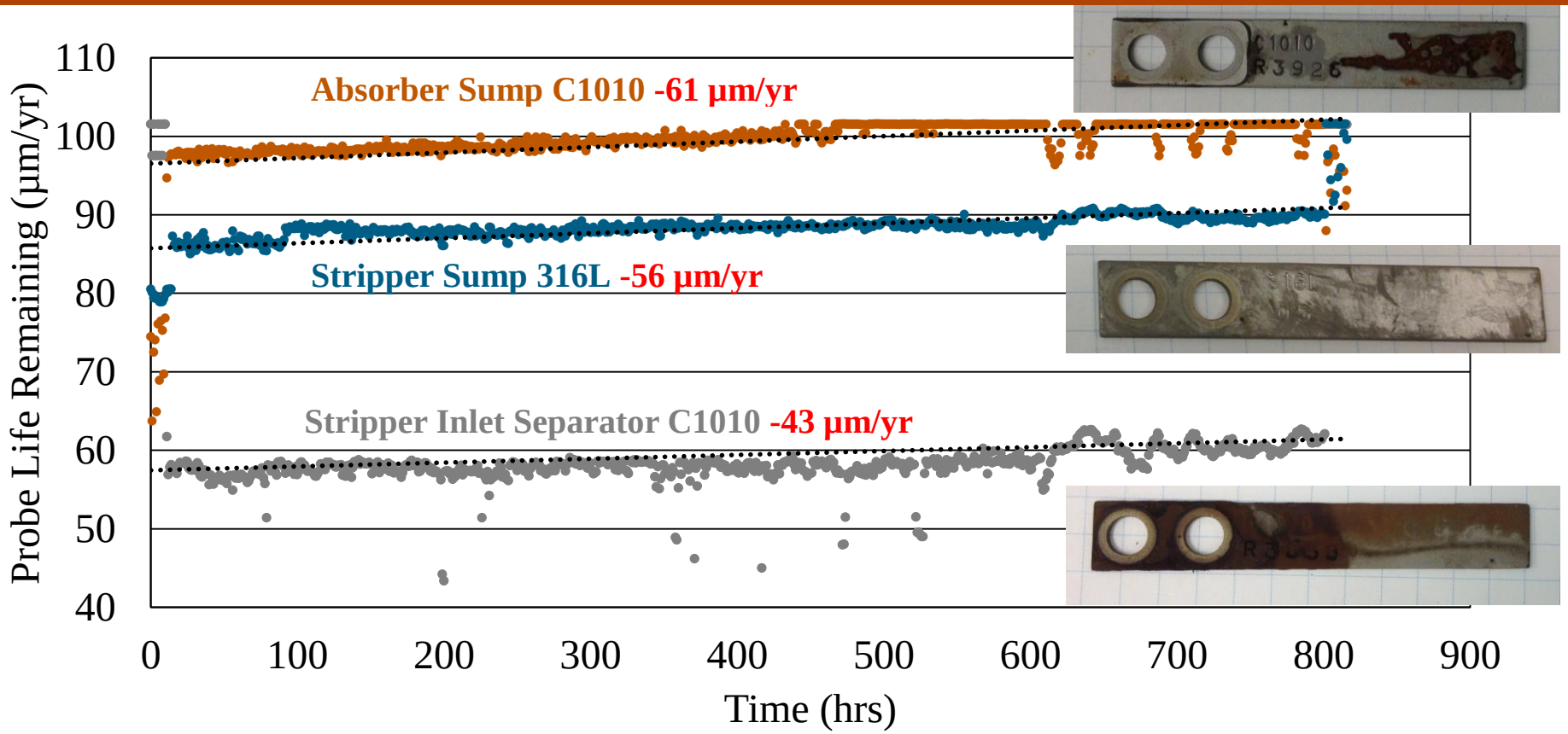
Conclusions from SRP

- Higher than expected C1010 corrosion in absorber
- 316L performance in hot, lean better than expected
- C1010 in hot, lean 5 m PZ
  - Sometimes forms tight, crystalline layer of $FeCO_3$
  - Sometimes forms flakey layer of FeO(OH) and Fe_3O_4, may have been caused by extended H_2O testing.
- C1010 in cold, rich 5 m PZ
  - Formed patchy, flakey layer of Fe and FeO(OH)
- Can we modify conditions so that we always form $FeCO_3$ protective layer?

MEA Corrosion at NCCC

- 3 ER probes
  - Absorber Sump
  - Stripper Sump, Stripper Inlet Separator
- 6 coupons near each ER probe location
- June 14, 2017 – July 17, 2017
- Coupons not yet analyzed

MEA Corrosion at NCCC



Conclusions from NCCC

- ER probes are sometimes unreliable.
- Should always check ER probe results against coupons.
- Low corrosion rates could be genuine. Will double check ER corrosion rates versus coupon corrosion rates.
- Currently working on SEM/XRD characterization.
- White film in stripper sump could be contamination from a previous NCCC run.

Questions?

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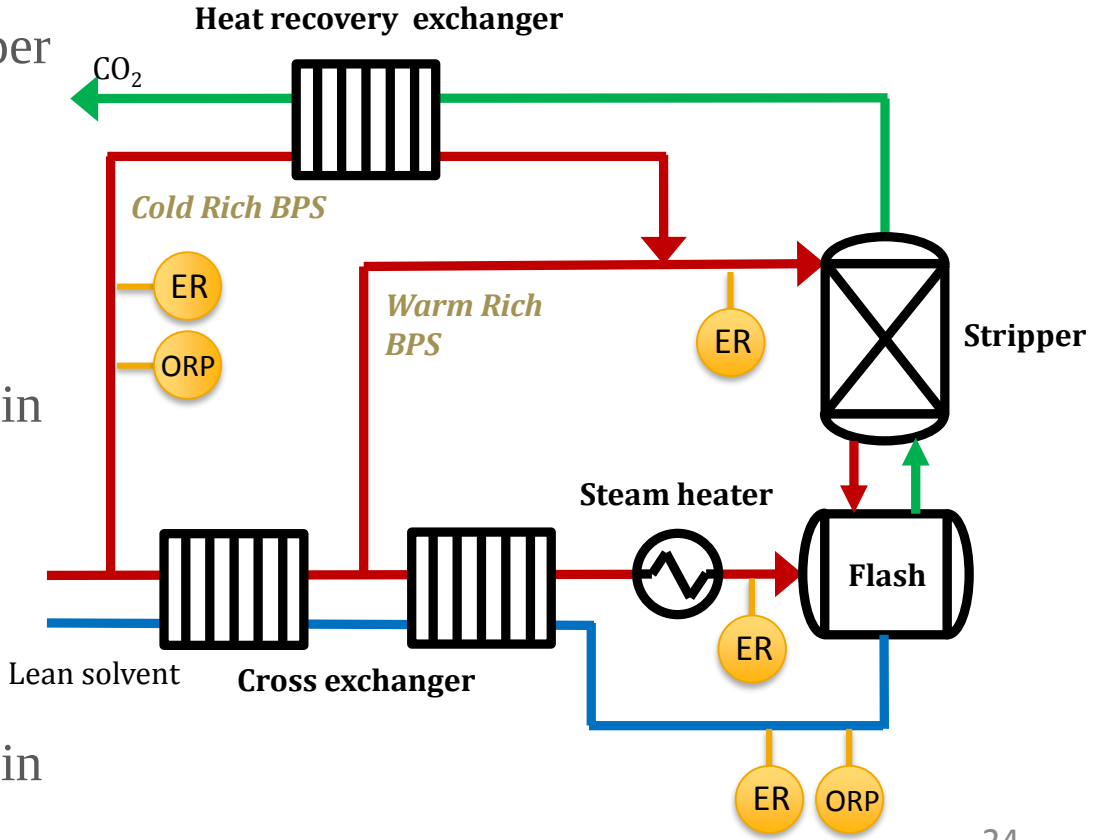
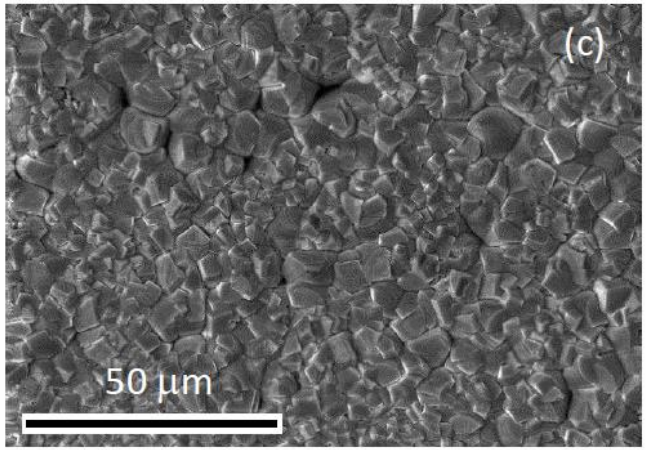
Backup Slides

Planned work at NCCC-November 2017

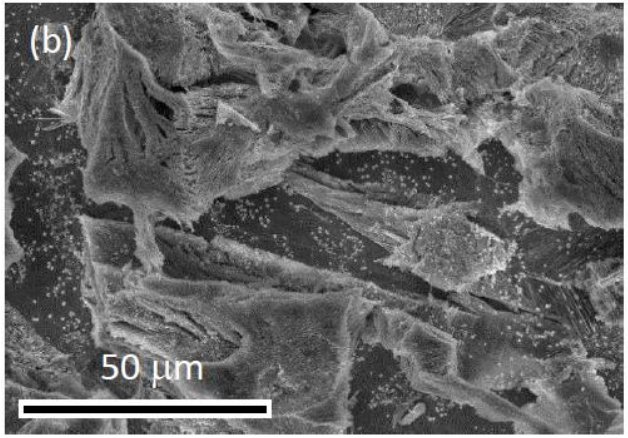
- 4 ER probe locations in stripper
  - Several probes:1010 CS, 316L SS
  - Probes will be swapped around
- 5 corrosion coupon locations in stripper
- 2 ORP probes
- In addition, 2 ER probes in absorber (1010 CS)
- 4 corrosion coupon locations in absorber



PZ forms protective $FeCO_3$ layer



30 wt % PZ -- $FeCO_3$ layer



30 wt % MEA – Fe_3C layer

- A106 Carbon Steel, 0.43 mol CO_2/mol alkalinity, 80°C, ~150 hr. (Zheng, Landon and Matin, et al. 2014)

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