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Anoxic Corrosion of Low-Carbon Steel at Elevated Temperatures—Effects of Sulfide

PRESENTED BY

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History of Anoxic Corrosion at Waste Isolation Pilot Plant

US DOE Waste Isolation Pilot Plant (WIPP)

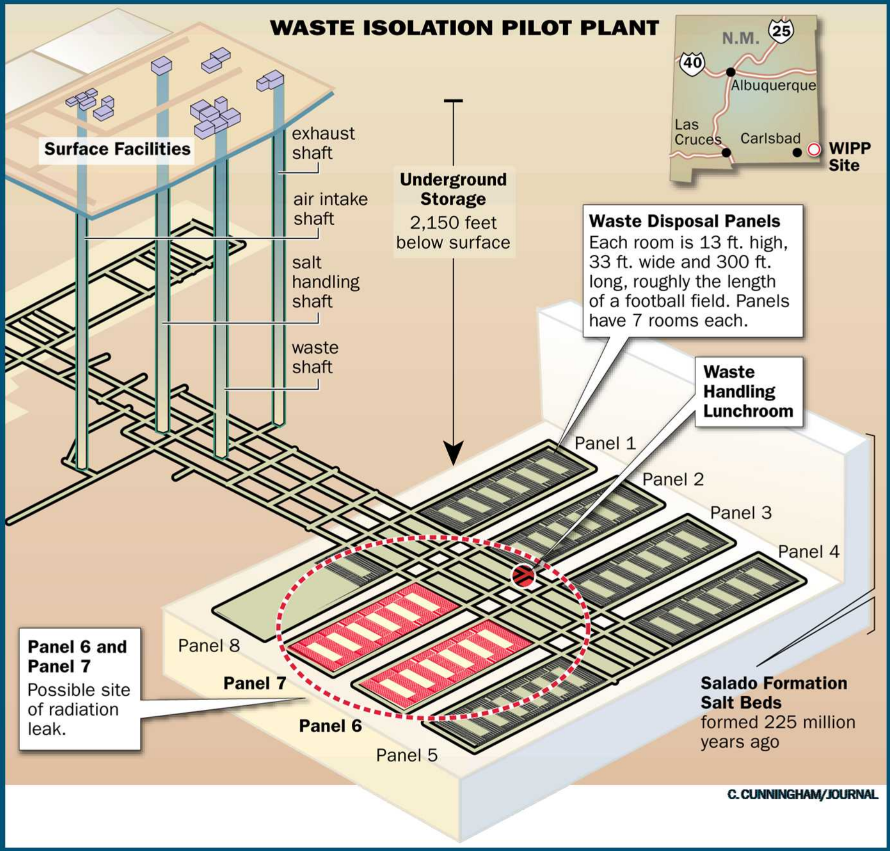
- Nation's only deep geological repository for defense nuclear waste

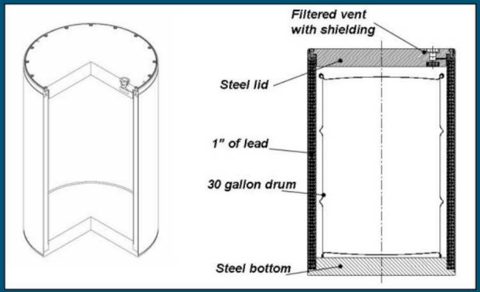
Sandia National Laboratories

- Scientific and technical advisor to the DOE

Iron (Fe) in WIPP

- Waste itself
- Low Carbon Steel Containers used for waste emplacement
- 1.6 x 10^7 kg Iron metal waste





Chloride and Sulfide in WIPP

- Chloride-sulfate Brines
- Halite

*Anoxic conditions expected approximately 100 yrs after WIPP closure.

Objective

Quantify the dissolution rate of the low-carbon steel (C1018) in the presence or absence of chlorides (NaCl and $MgCl_2$) or sulfides (NaHS) at 90°C and pH(25°C) = 9.

- Single-Pass Flow-Through (SPFT) experiments.
- Static experiments.
- Use of polished coupons (50 mm×50 mm× 6 mm).

Rates and chemical composition were determined by:

- Interferometry on coupons (novel application).
- Assay of Fe^{2+}(aq) using UV-Vis (ferrozine method)
- Assay of total Fe by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (still awaiting results)
- Release of H_2(g) from steel coupon. (still awaiting results)
- Weight loss of coupons.
- Scanning Electron Microscopy and Electron Dispersive X-Ray spectroscopy
- X-Ray Diffraction Spectroscopy
- Raman Spectroscopy

Experimental Details

Experiments performed in a glove box (200 ppb< O_2 < 400 ppb).

Temperature set to 90 ^{0} C, solutions set to pH(25 ^{0}C) = 9.0

Background solution:

- Simplified Generic Weep Brine (SGWB):
  - $NaCl_2$ + $MgCl_2$

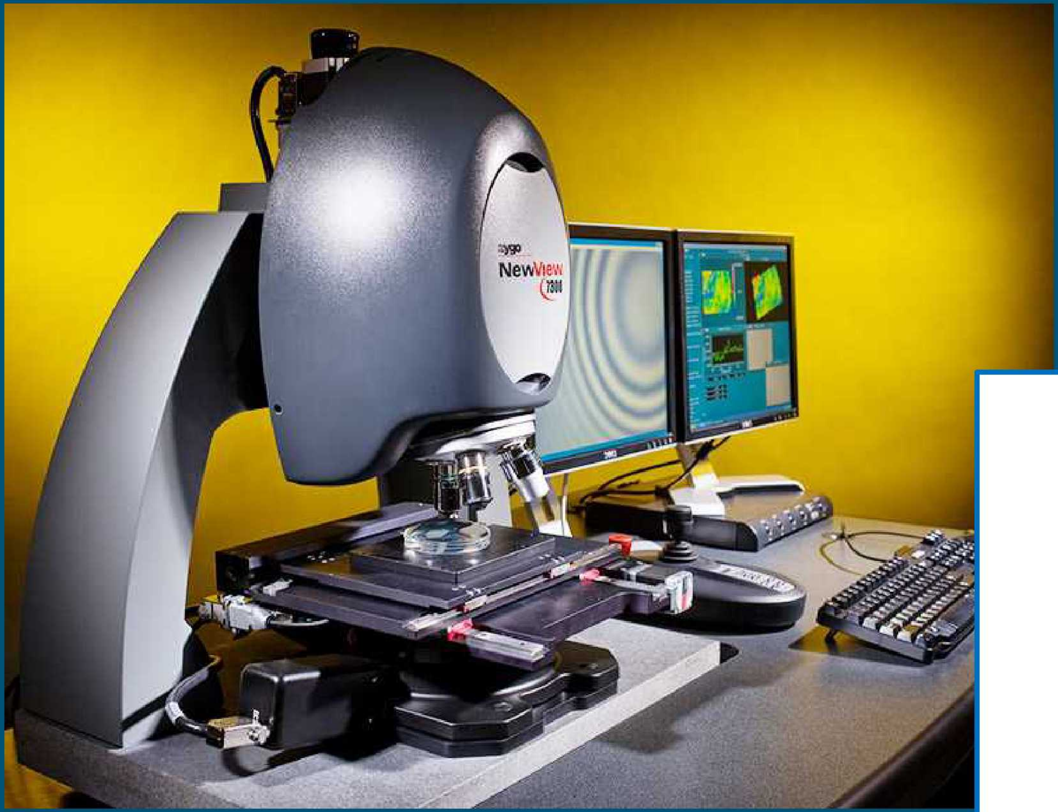
Subdivided into sulfide-free or sulfide-bearing:

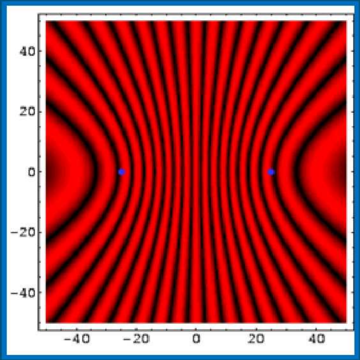
- Sulfide-bearing consisted of 1, 5 or 10 mmol NaHS

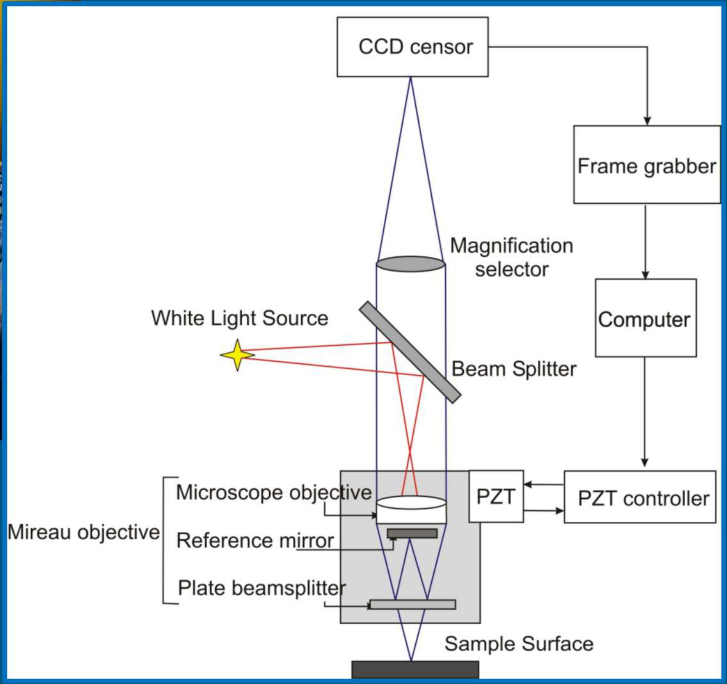
Flow-rate set to ~60 mL/day (exchange of 1 reactor volume every other day).

Ran for 5 months' duration.

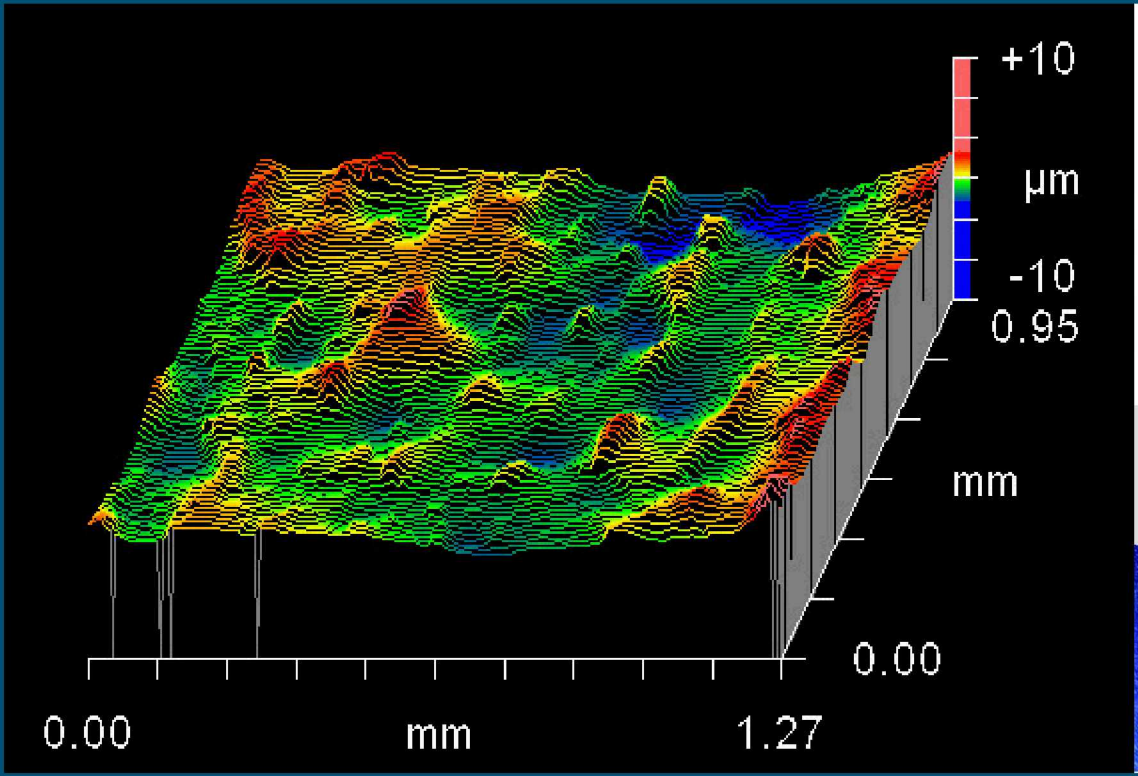
Interferometry Measurements

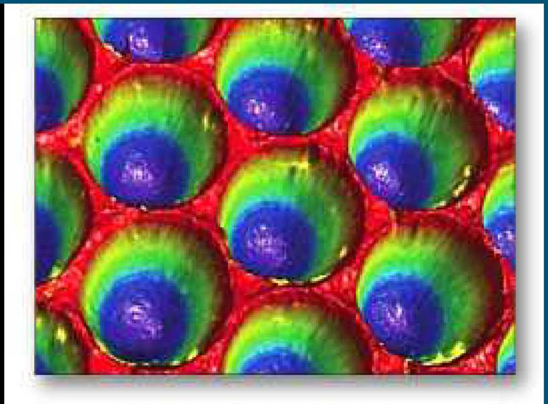


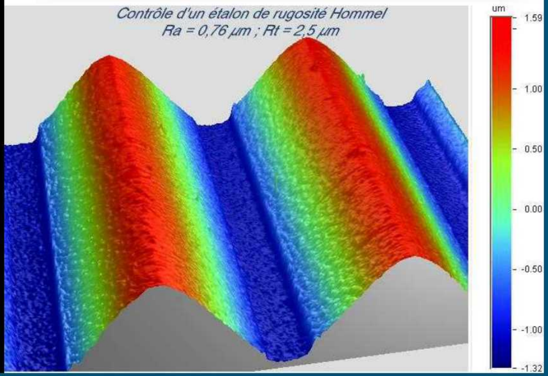




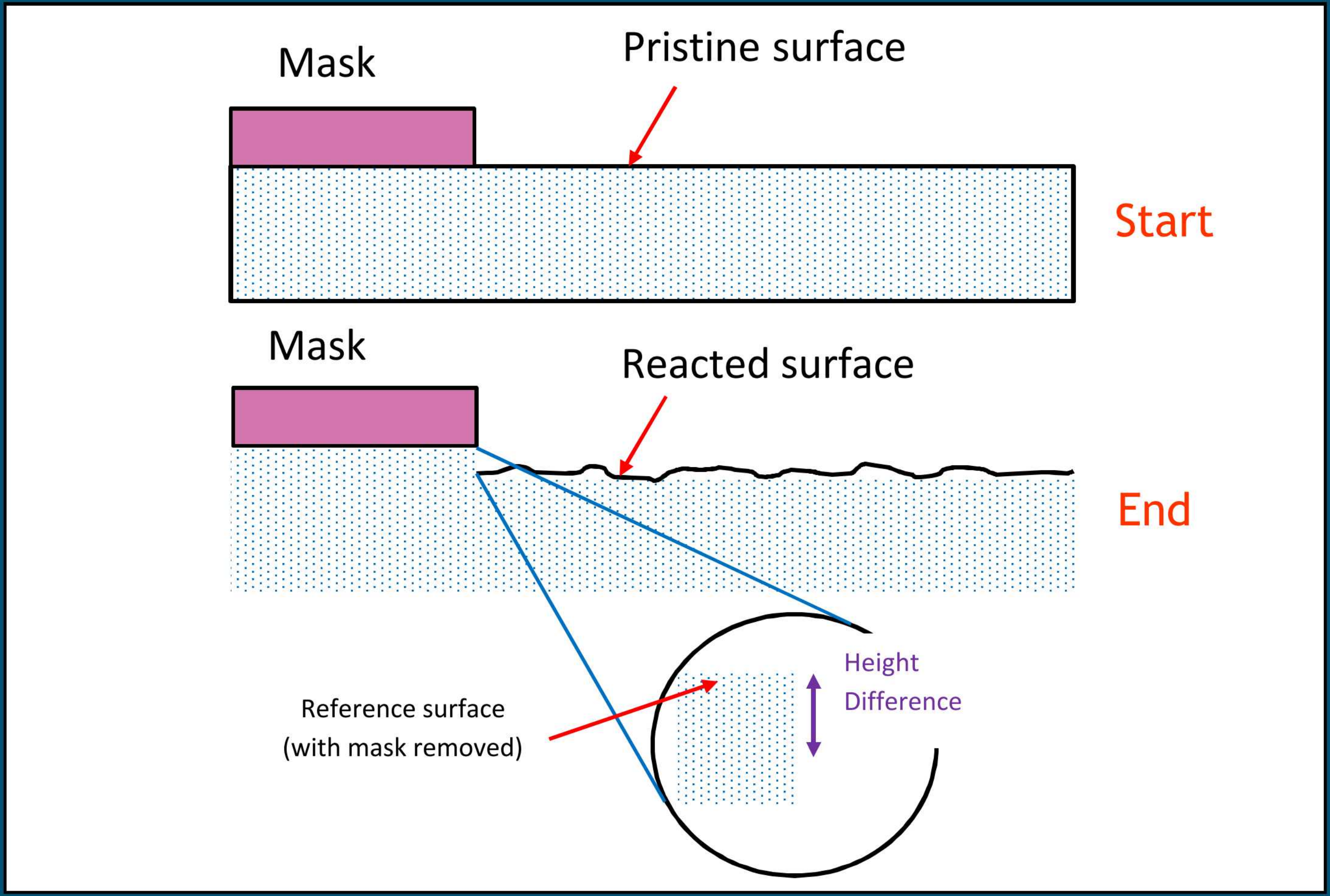
3-D Mapping of a surface







Summary of interferometry strategy



Interferometer Rates

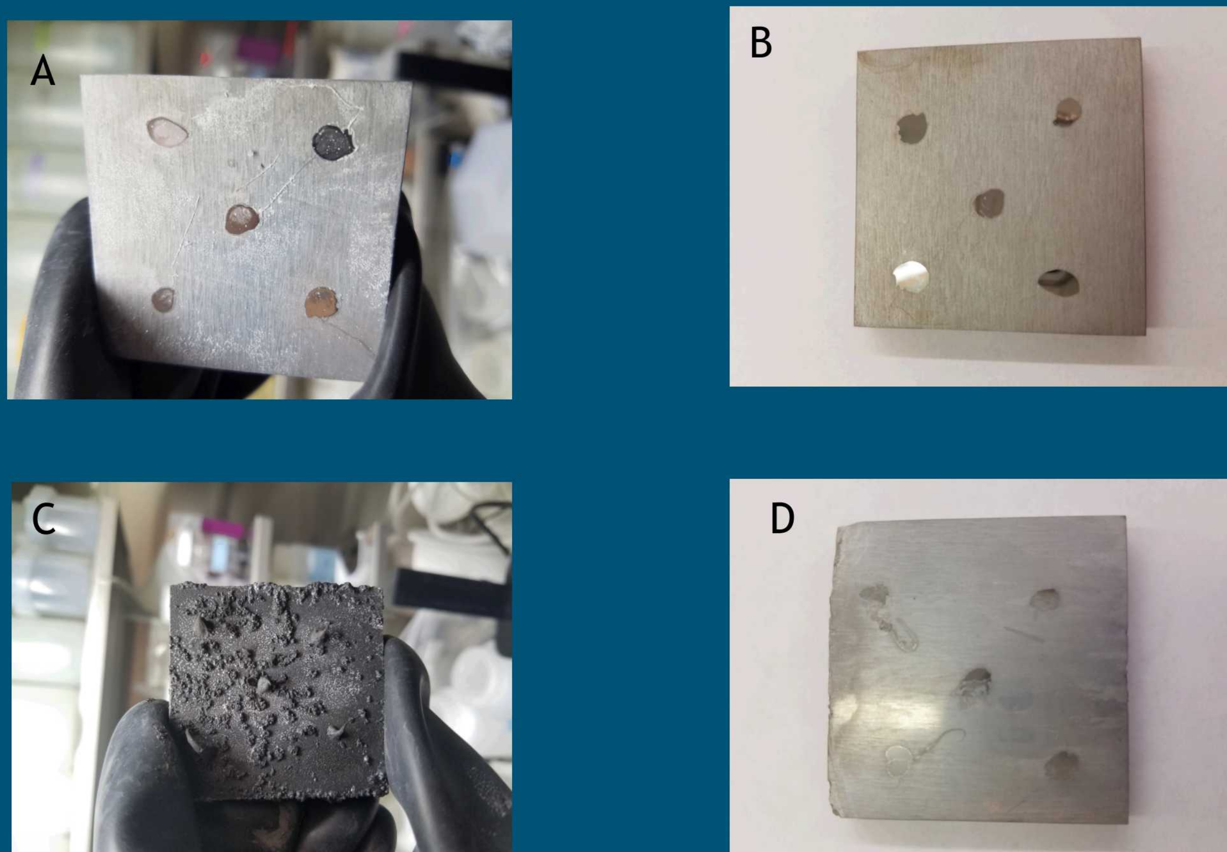
$$Rate = \frac{\Delta h}{\Delta t}$$

$\Delta \boldsymbol{h}$ is the height difference between the reference and reaction surfaces

$\Delta \boldsymbol{t}$ is elapsed time

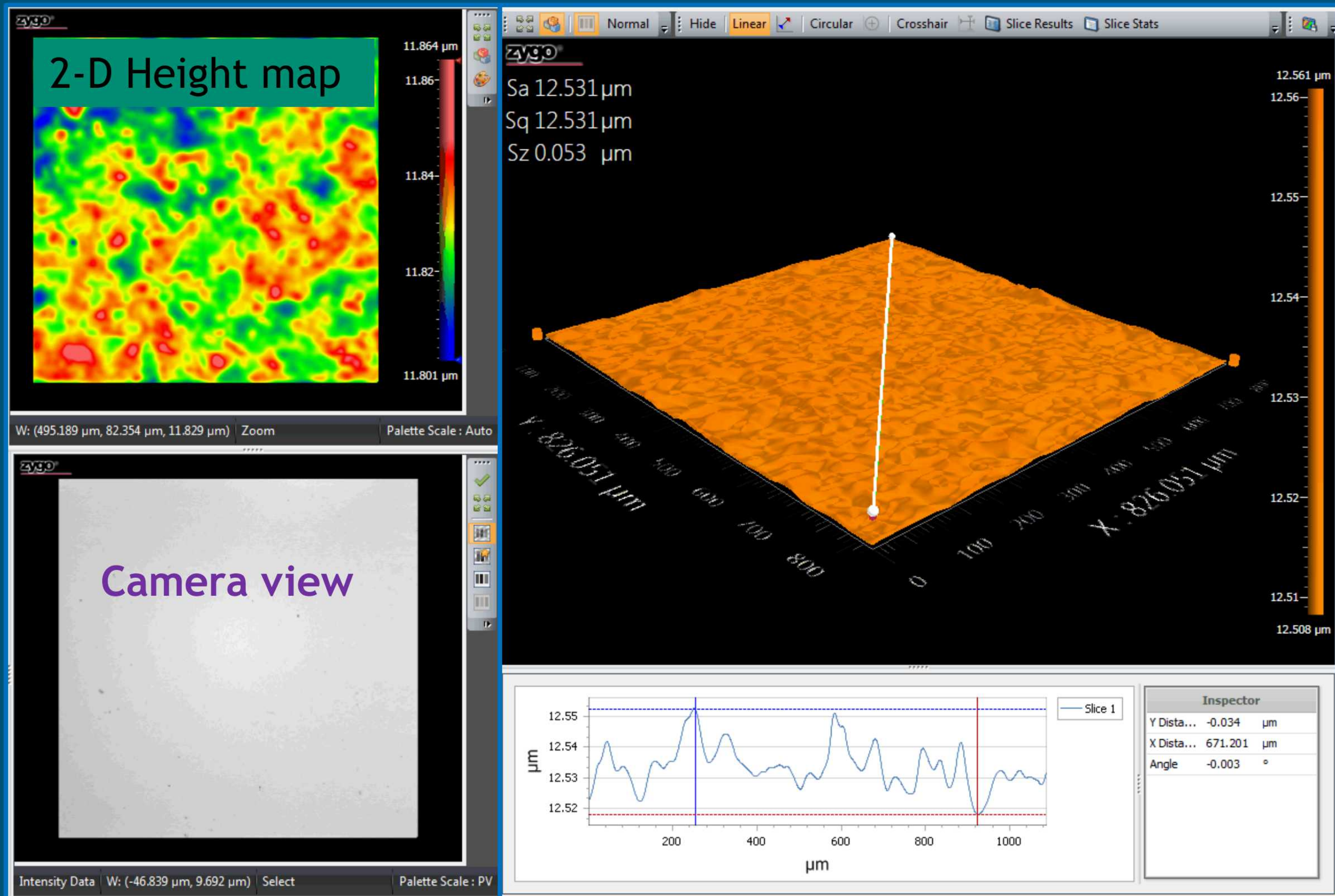
- Cut and polish steel coupons.
- Measure coupon dimensions using electronic calipers.
- "Mask" a small portion of the coupon.
- Expose coupon to solution in flow-through reactor.
- Remove coupon from reactor, remove mask, measure the change in height between reference and reaction surface.

Summary of interferometry strategy



Photographs of post-experiment steel coupons. A. Coupon 113 (SGWB) before cleaning. B. Coupon 113 after cleaning. C. Coupon D (SGWB + NaHS) before cleaning. D. Coupon D after cleaning.

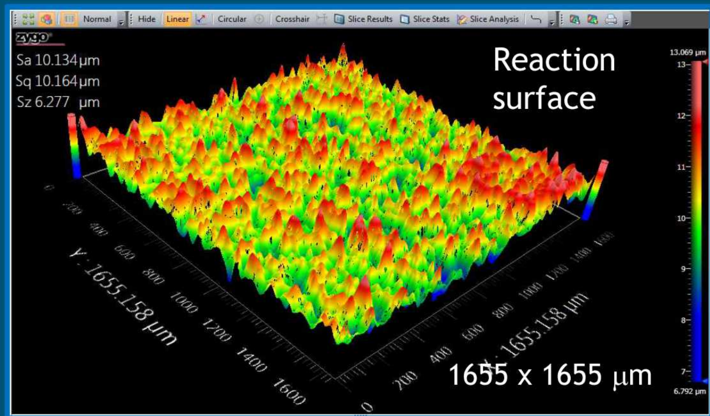
Polished coupons (unreacted)

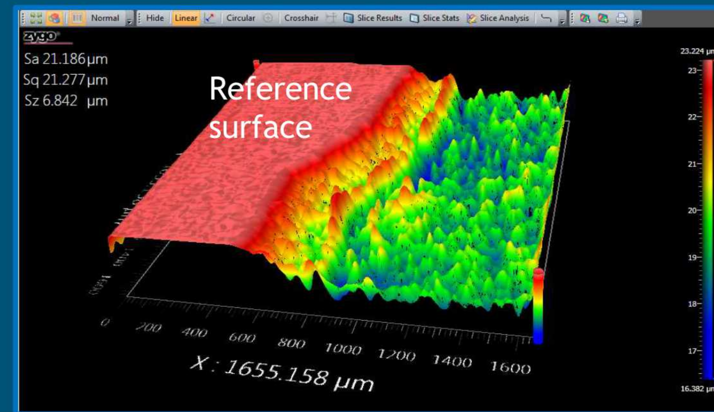


Small height differences across the surface (average of ~35nm)

Simplified Generic Weep Brine (reacted)

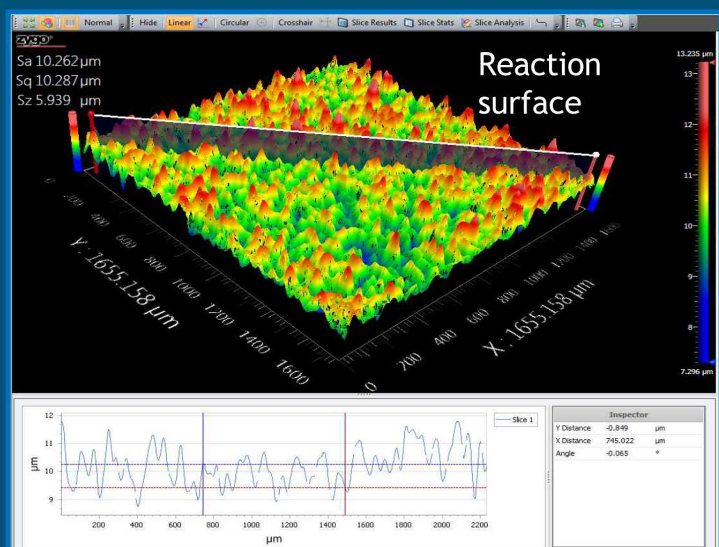
5 months, 60 mL/d flow-rate

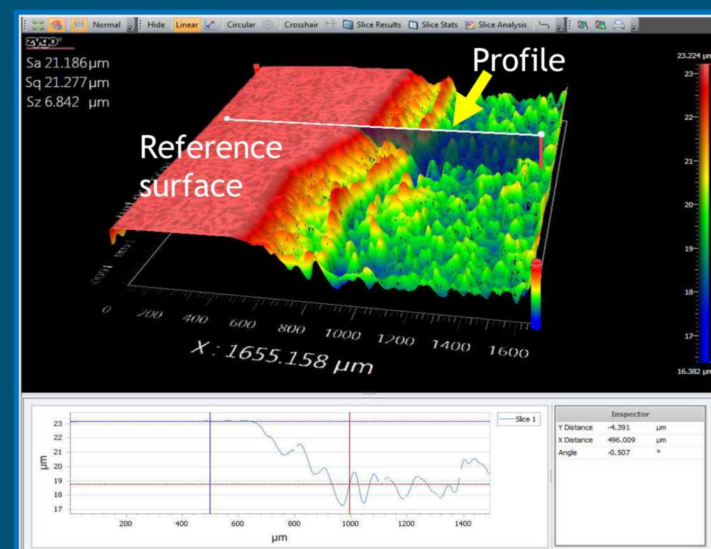




Reaction surface showing an increase in surface roughness

~4.4 μm difference in height can be observed between Reaction and Reference surface

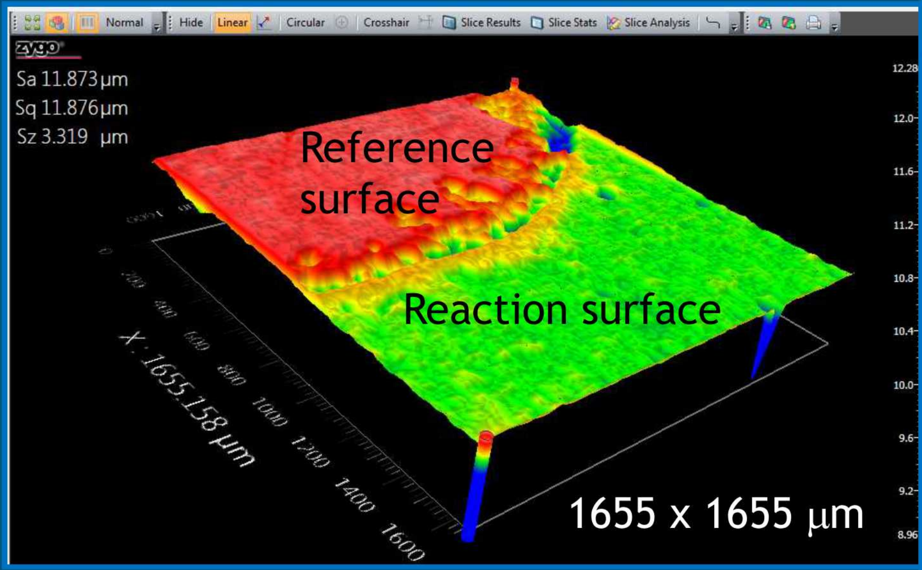


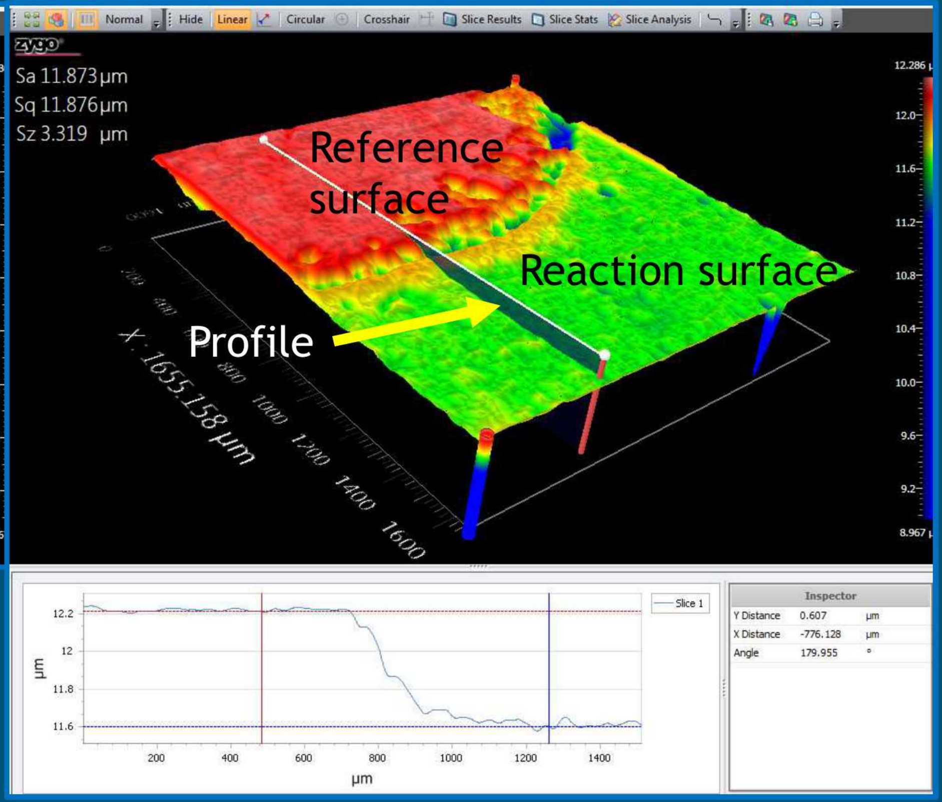


Simplified Generic Weep Brine + 10 mmol NaHS

5 months, 60 mL/d flow-rate

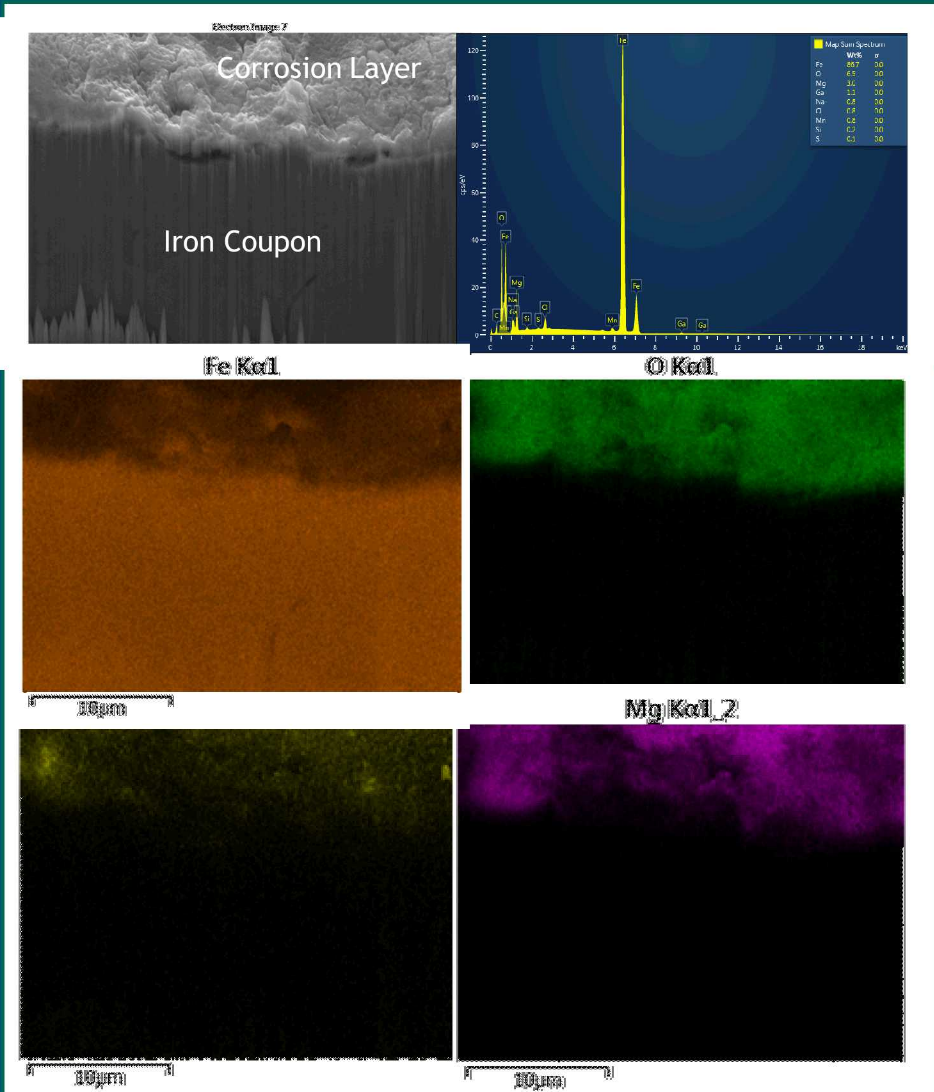
Both reference and reaction surfaces displayed



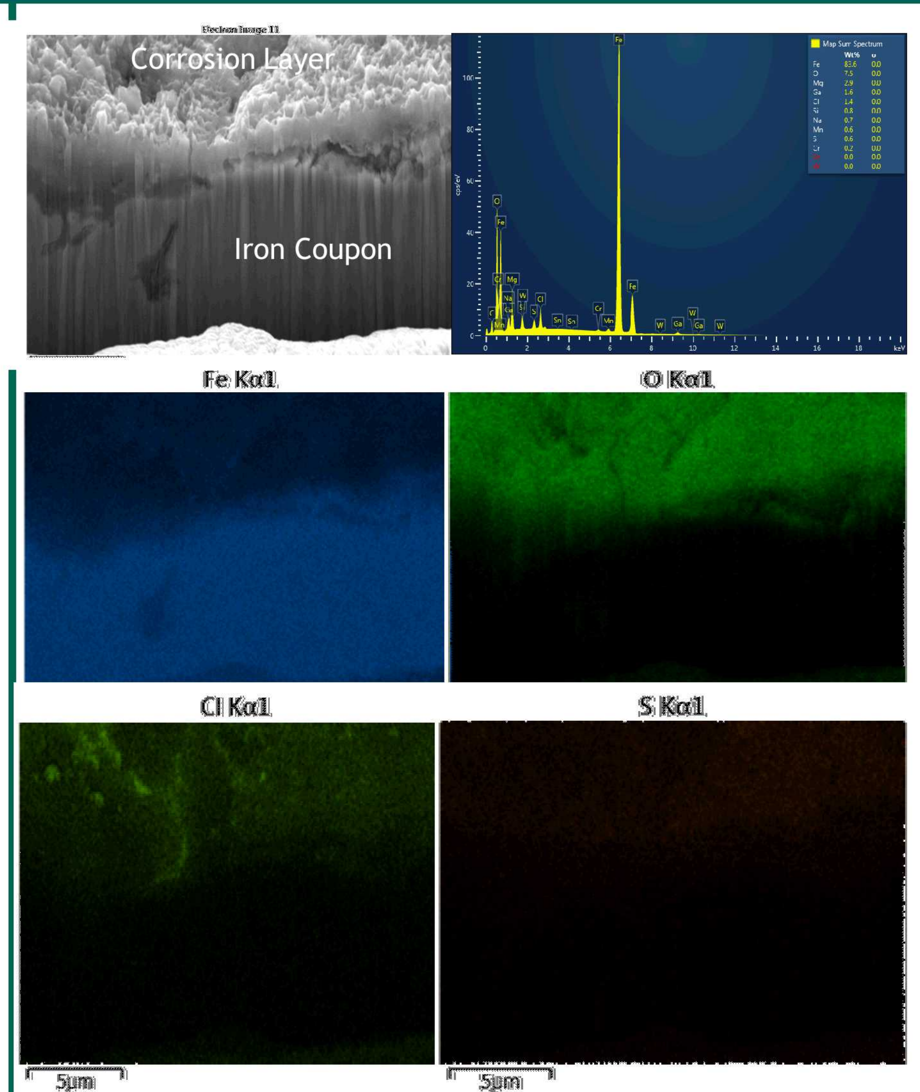


~0.61 µm difference in height can be observed.

Cross Sectional SEM & EDS images of iron coupon

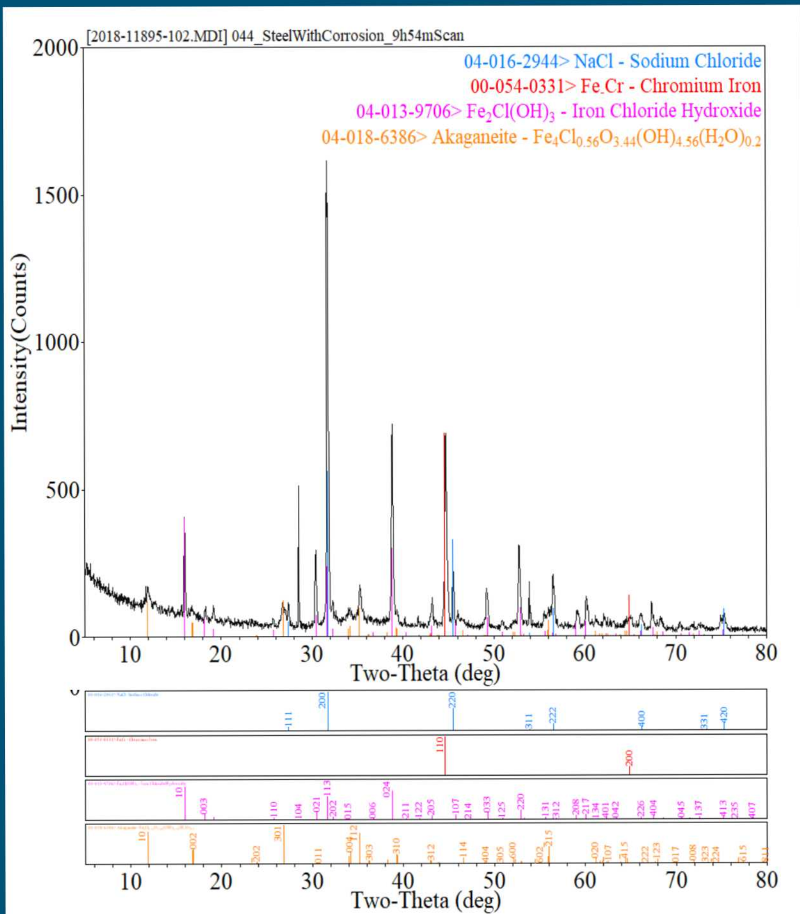


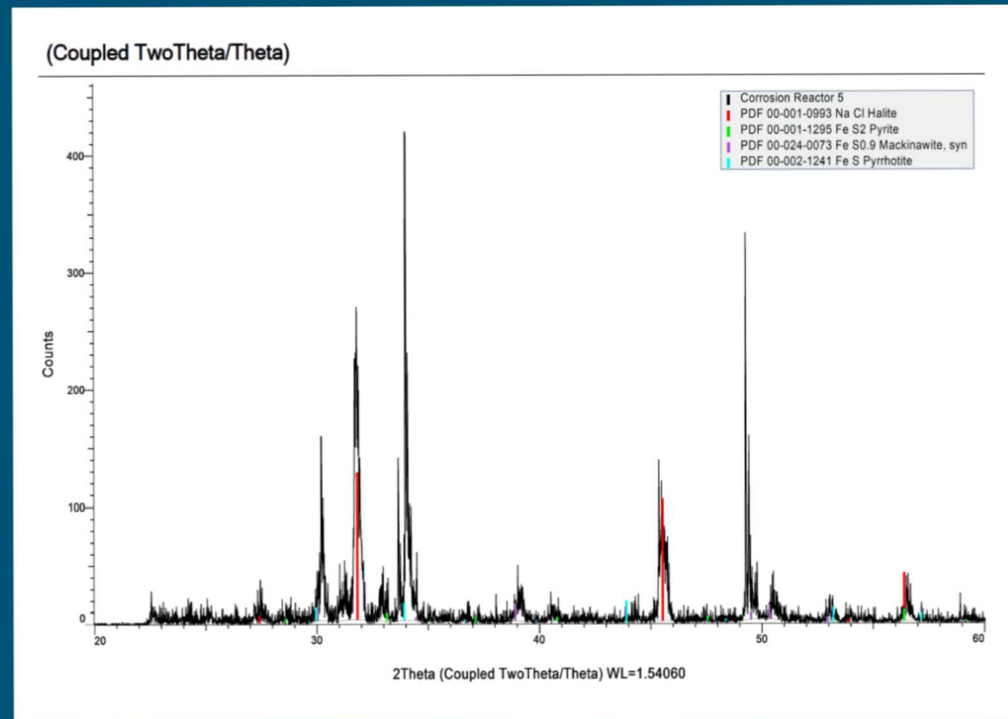
GWB



GWB + NaHS

Characterization of Corrosion Products-XRD





$$Fe^{\circ}(s) + H_2S(aq) = FeS(s) + H_2(g)$$

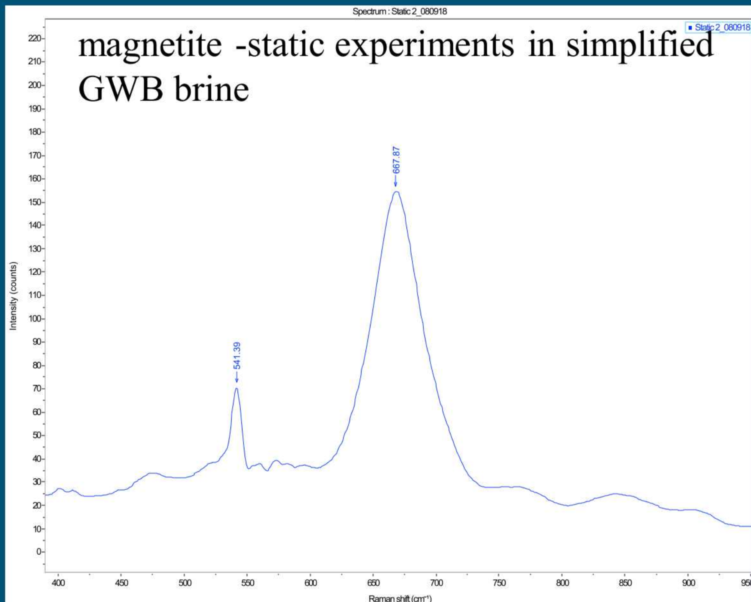
$$Fe^{\circ}(s) + 2H_2S(aq) = FeS_2(s) + 2H_2(g)$$

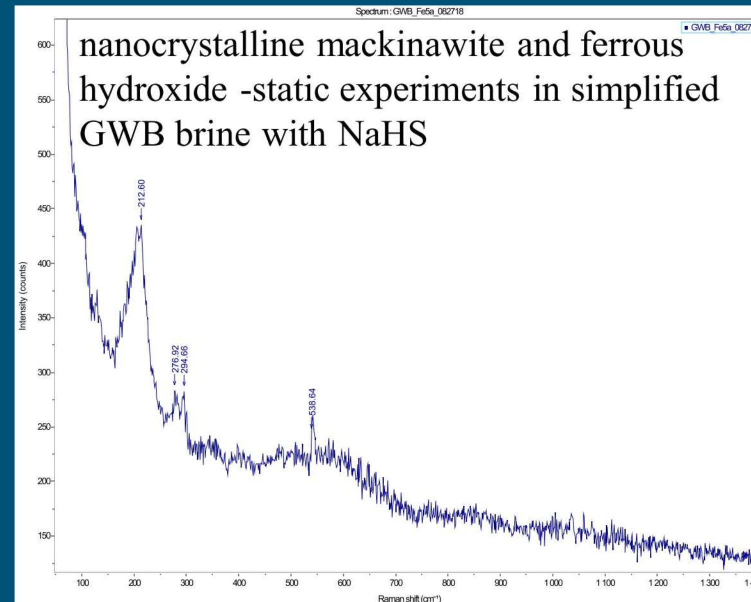
$$Fe^{\circ}(s) + 2H_2O(l) = Fe(OH)_2(s) + H_2(g)$$

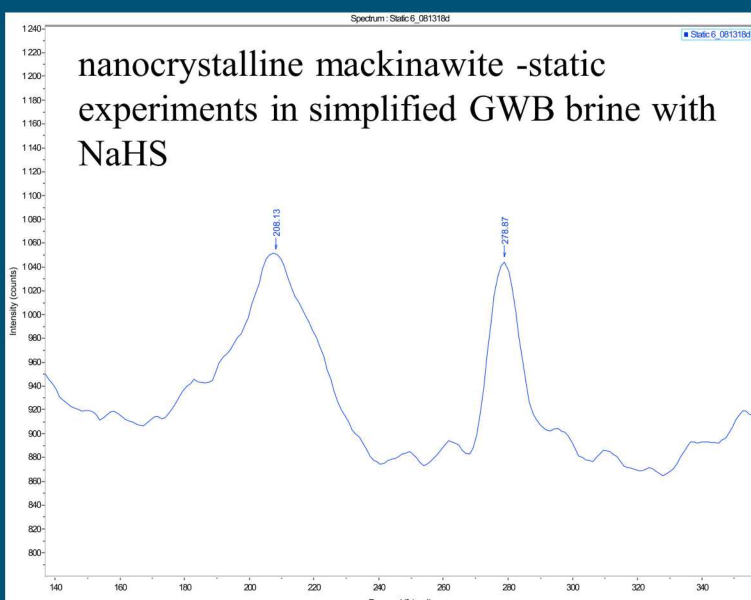
$$3Fe^{\circ}(s) + 4H_2O(l) = Fe_3O_4(s) + 4H_2(g)$$

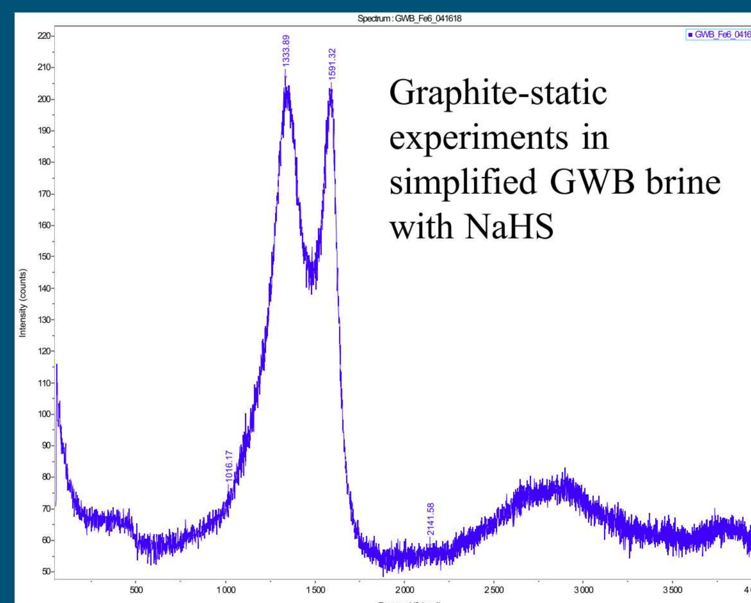
Looking at Fe to $H_2(g)$ ratio

Characterization of Corrosion Products-Raman Spectroscopy









Interferometer Rates

$$Rate = \frac{\Delta h}{\Delta t} = \frac{12\mu m}{yr}$$

Δh is the height difference between the reference and reaction surfaces

Δt is elapsed time

- Cut and polish steel coupons.
- Measure coupon dimensions using electronic calipers.
- “Mask” a small portion of the coupon.
- Expose coupon to solution in flow-through reactor.
- Remove coupon from reactor, remove mask, measure the change in height between reference and reaction surface.

Conclusions

- Steel coupons experienced fast dissolution (~12 μm/yr) in SGWB solutions at 90 ^{0}C and pH(25 ^{0}C) = 9.0.
- Coupons reacted in SGWB + NaHS also showed dissolution, but at much slower rates.
- These rates can be efficiently measured by interferometry.
- Interferometry, therefore, shows great promise in quantifying dissolution rates of steel.