Effects of Water Chemistry on Internal Corrosion of Pipelines
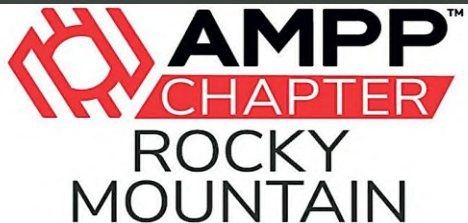
Hamed Mansoori

Western Midstream

AMPP – Rocky Mountain

January 18th, 2024

Corrosion products (FeCO$_3$)

Steel substrate

Speaker

Hamed Mansoori, *Ph.D.* in Chemical and Corrosion Engineering
Corrosion Engineering Supervisor, Western Midstream, The Woodlands, TX

- **Started the journey with the oil industry in 2003**
  - Operation and Engineering roles
- **Joined Ohio University's Corrosion Center in 2015**
  - Scholarship, full-time, *Ph.D.* Studies/Research
- **Worked for Anadarko/Oxy/Western Midstream, since 2019**
  - External corrosion
 - Internal corrosion
  - Specialty Chemical

Outline

Effect of Water Chemistry on Internal Corrosion of Pipelines

- **Introduction**

- **Literature Review**

- **Experimental Setup & Methodology**
  - Controlled water chemistry
  - Well-defined mass transfer

- **Experimental Results & Descriptive Models**

  - Influence of Ca^{2+} - containing solutions and $CaCO_3$ scale on corrosion mechanism (various ionic strengths, $[Ca^{2+}]$, pH)

  - Effect of Mg^{2+} - containing solutions on corrosion mechanism (various ionic strengths, $[Mg^{2+}]$, pH)

  - Electrolytes with simultaneous presence of Ca^{2+} and Mg^{2+}
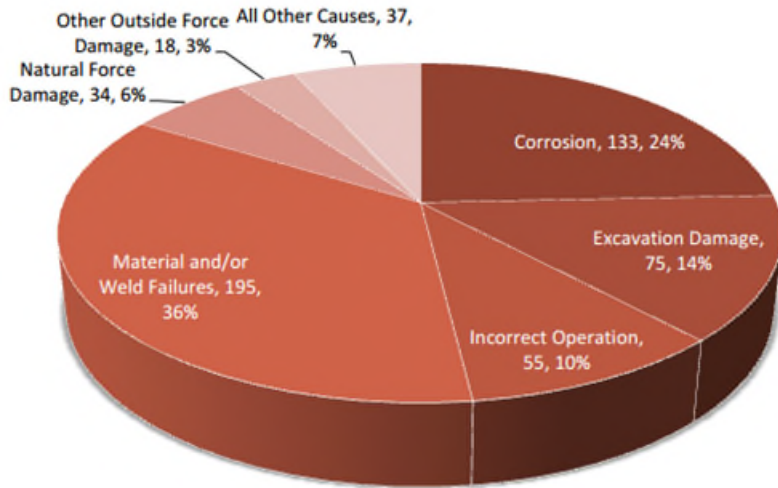
- **Conclusions**

Introduction

Pipelines Are Primary Means of Hydrocarbon Transportation

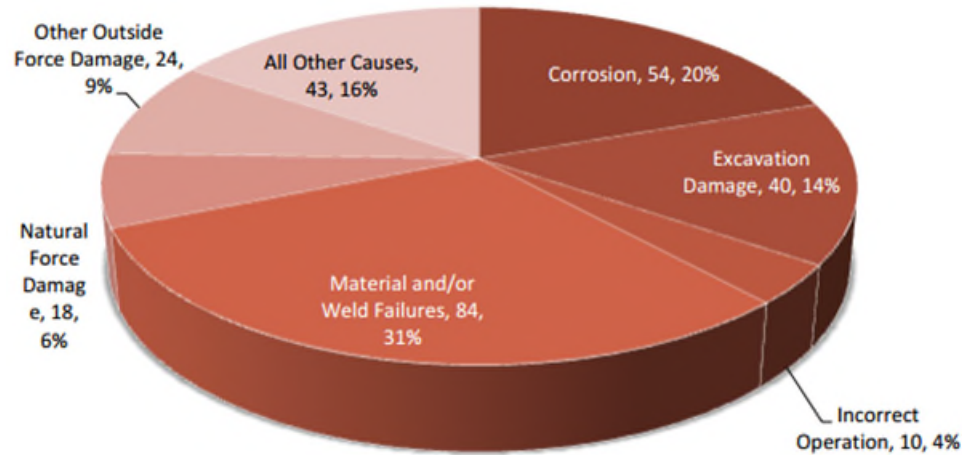**U.S. Natural Gas Pipelines**

Interstate
Intrastate
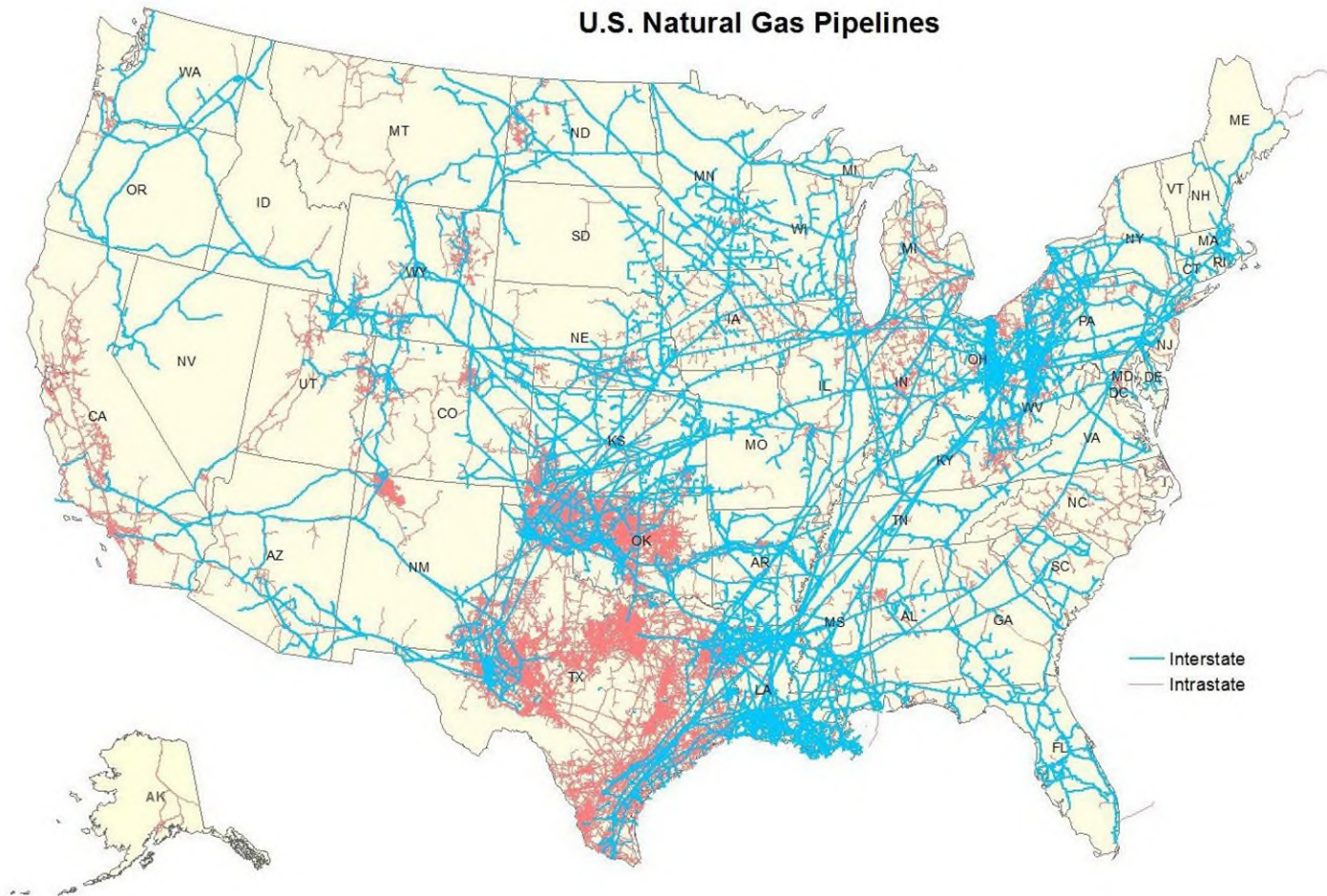
Source: American Energy Mapping (AEM) 2013

Oil and Gas Pipeline Failure Due to Corrosion

Failure statistics from 2006 to 2010 in USA: 24% (liquid pipeline) and 20% (gas pipeline)

Causes of Significant Onshore Hazardous Liquid Pipeline Incidents (2006 – 2010)[1]

Other Outside Force Damage, 18, 3%
All Other Causes, 37, 7%
Natural Force Damage, 34, 6%
Corrosion, 133, 24%
Material and/or Weld Failures, 195, 36%
Excavation Damage, 75, 14%
Incorrect Operation, 55, 10%

Causes of Gas Transmission Pipeline Significant Incidents (2006 – 2010)[1]

Other Outside Force Damage, 24, 9%
All Other Causes, 43, 16%
Corrosion, 54, 20%
Natural Force Damage, 18, 6%
Material and/or Weld Failures, 84, 31%
Excavation Damage, 40, 14%
Incorrect Operation, 10, 4%

1- R. Stover, "The State of the National Pipeline Infrastructure", *US Department of Transportation* report, 2013

2- H. Mansoori, R. Mirzaee, A. H. Mohammadi, and F. Esmaeelzadeh, "Acid Washes, Oxygenate Scavengers Work Against Gas Gathering Failures," *Oil Gas J.*, vol. 111, no. 7, pp. 106–111, 2013.

3- H. Mansoori, R. Mirzaee, F. Esmaeelzadeh, and D. Mowla, "Altering CP Criteria Part of Unified Anti-SCC Approach," *Oil Gas J.*, vol. 111, no. 12, pp. 88–93, 2013.

Corrosion Costs

- Corrosion imposes significant cost of repair and replacement of infrastructures, operational losses, environmental damage and risk to life.

- Annual corrosion cost in the US $500.7 billion equivalent to 3.1 % of the nation's Gross Domestic Product (GDP)[1]

- Oil and gas related corrosion accounted for $7 billion of annual corrosion costs[1]

- However, the costs associated with corrosion can be reduced significantly if appropriate corrosion mitigation programs are applied.

1. G. Koch, J. Varney, N. Thompson, O. Moghissi, M. Gould, and J. Payer, "International measures of prevention, application, and economics of corrosion technologies study," NACE International IMPACT Report, 2016

Literature Review

What is Water Chemistry?

- **Concentration of dissolved ions**
  - ❑ **Total Dissolved Solids, TDS (conductivity, resistivity, individual ion activities)**
  - ❑ **pH ($[H^+]$)**
  - ❑ **Corrosive components like H_2S, CO_2, O_2, *etc.***
  - ❑ **Scale-forming ions such as Ca^{2+}/ Mg^{2+}/Fe^{2+} and CO_3^{2-}, Fe^{2+} and S^{2-}, Ba^{2+}/ Sr^{2+} and SO_4^{2-}**
  - ❑ **$[Cl^-]$**

$Ca_xFe_yCO_3$, $x+y=1$ FeS $Ba_xSr_ySO_3$, $x+y=1$

- **Bacteria** (SRB, APB, etc)
- **Suspended solids** (sand, scales, paraffin, etc.)
- **Suspended liquid hydrocarbon** (very important in produced water systems)
- **Temperature, pressure?**
- **Flow regime?**

Why is Water Chemistry Important?

- **Understand/Control Internal Corrosion**
  - ❑ **Predict corrosion rate, using corrosion models such as Ohio University, OLI**
  - ❑ **Choose the proper chemical to control or mitigate corrosion**

Brine Chemistry

Origin of Scales in Oil Production

- Brine (formation water) is co-produced with oil and gas from reservoirs.

- Brine has dissolved ions such as sodium, chloride, calcium, magnesium, strontium, barium, etc.

- Scaling happens when solid solubility limits are exceeded.

- Most of CO_2 corrosion studies have been performed in NaCl electrolytes.

Which Scales Are Relevant for CO_2 Corrosion?

1) Calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) are dominant, strontium and barium sulfates occur less frequently.

2) $CaCO_3$ and $MgCO_3$ can coexist with $FeCO_3$, impacting layer protectiveness against corrosion. Due to isostructurality between these calcite-type metal carbonates, Ca^{2+} and Mg^{2+} cations can incorporate into the lattice of $FeCO_3$.

Controversy on the Influence of Ca^{2+} & Mg^{2+} on CO_2 corrosion
Literature Review

- <u>General corrosion</u>:
  Tavares *et al.* and Eriksrud *et al.*[1,2] have claimed, respectively, that presence of Ca^{2+} & Mg^{2+} can enhance the protectiveness of $FeCO_3$, and other researchers claimed the opposite[3,4].

- <u>Pitting corrosion</u>:
  Hua *et al.* and Esmaeely *et al.*[5,6] reported pitting corrosion attacks in presence of Ca^{2+} and $CaCO_3$ scale while Jiang *et al.*[7] claimed Ca^{2+} could postpone pit initiation.

[1] L.M. Tavares, *et al.*, "Effect of Calcium Carbonate on Low Carbon Steel Corrosion Behavior in Saline CO_2 High Pressure Environments", *Appl. Surf. Sci.*, vol. 359, pp. 143–152, Dec. 2015.
[2] E. Eriksrud and T. Sontvedt, "Effect of Flow on CO_2 Corrosion Rates in Real and Synthetic Formation Waters", *Proc. Corros. Symp. CO_2 Corros. Oil Gas Ind. NACE*, vol. 1, pp. 20–38, 1984.
[3] C. Ding, *et al.*, "Effect of Ca^{2+} on CO_2 corrosion properties of X65 pipeline steel", *Int. J. Miner. Metall. Mater.*, vol. 16, no. 6, pp. 661–666, Dec. 2009.
[4] S.N. Esmaeely, *et al.*, "Effect of Calcium on the Formation and Protectiveness of Iron Carbonate Layer in CO_2 Corrosion", *Corrosion*, vol. 69, no. 9, pp. 912-920, May 2013.
[5] Y. Hua, *et al.*, "Protectiveness, morphology and composition of corrosion products formed on carbon steel in the presence of Cl^-, Ca^{2+} and Mg^{2+} in high pressure CO_2 environments," *Appl. Surf. Sci.*, vol. 455, pp. 667–682, Oct. 2018.
[6] S. N. Esmaeely, *et al.*, "Effect of Incorporation of Calcium into Iron Carbonate Protective Layers in CO_2 Corrosion of Mild Steel," *Corrosion*, vol. 73, no. 3, pp. 238–246, Nov. 2016.
[7] X. Jiang, *et al.*, "Effect of Calcium Ions on Pitting Corrosion and Inhibition Performance in CO_2 Corrosion of N80 Steel," *Corros. Sci.*, vol. 48, no. 10, pp. 3091–3108, Oct. 2006.

Contributing Factors to the Discrepancies in Literature
Literature Review

- Inadequate design of experimental procedures and setups
  - Change of water chemistry over time[1]
  - Undefined mass transfer conditions[2]

- Misleading comparison of experimental conditions using initial $[Ca^{2+}]$ & $[Mg^{2+}]$ without considering precipitation during the experiment[3]

- Insufficient reporting of information regarding water chemistry (e.g., pH, $CaCO_3$ and $FeCO_3$ saturation level) [4]

[1] L.M. Tavares, *et al.*, "Effect of Calcium Carbonate on Low Carbon Steel Corrosion Behavior in Saline CO_2 High Pressure Environments", *Appl. Surf. Sci.*, vol. 359, pp. 143–152, Dec. 2015.
[2] S.N. Esmaeely, *et al.,* "Effect of Calcium on the Formation and Protectiveness of Iron Carbonate Layer in CO_2 Corrosion", *Corrosion*, vol. 69, no. 9, pp. 912-920, May 2013.
[3] C. Ding, *et al.,* "Effect of Ca^{2+} on CO_2 corrosion properties of X65 pipeline steel", *Int. J. Miner. Metall. Mater.*, vol. 16, no. 6, pp. 661–666, Dec. 2009.
[4] G. X. Zhao, *et al.,* "Effect of Ca^{2+} and Mg^{2+} on CO_2 Corrosion Behavior of Tube Steel," J. Iron Steel Res. Int., vol. 12, no. 1, pp. 38–42, 2005.

Scenarios Observed in Oilfields

Motivation

- Brine is typically saturated with respect to $CaCO_3$/$MgCO_3$ for various Ca^{2+}/Mg^{2+} concentrations. [1]

- Precipitation of $CaCO_3$/$MgCO_3$ scale will occur from a temporarily supersaturated brine (due to change of operational conditions). After precipitation, the brine should remain saturated with respect to $CaCO_3$.[1]

1- J. E. Oddo, M. B. Tomson, and others, "Why Scale Forms in the Oil Field and Methods to Predict It," SPE Prod. Facil., vol. 9, no. 01, pp. 47–54, 1994.

Experimental Setup & Methodology

Optimized Experimental Setup

Controlled Mass Transfer System-Equipped with Rushton-Type Impeller

Controlled Water Chemistry System

Fe^{2+} Control loop
by Na-form
ion-exchange resin
(Amberlite® IR 120)

on/off timer

pump
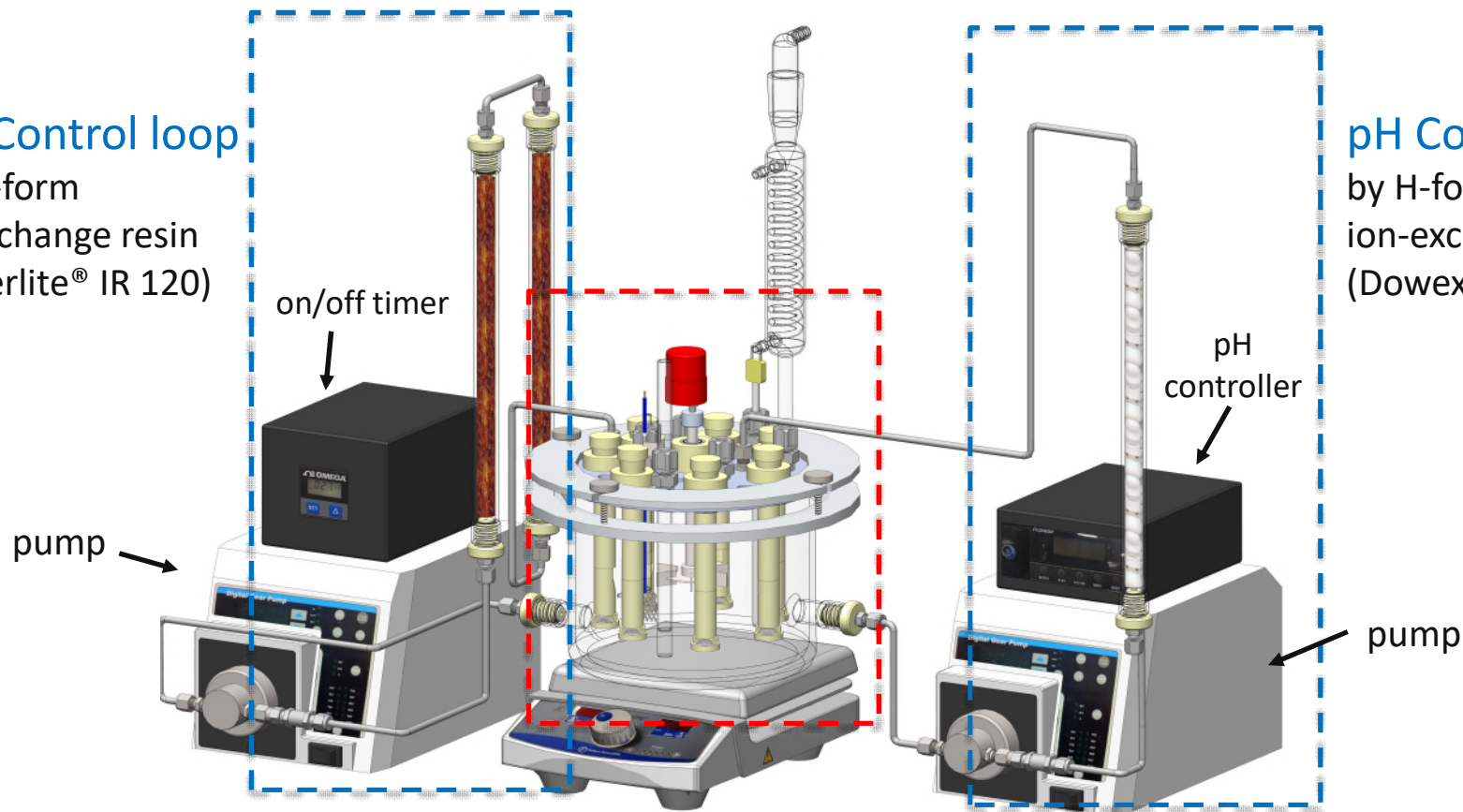
pH Control loop
by H-form
ion-exchange resin
(Dowex® G26)

pH
controller

pump

Image by Cody Shafer

Controlled Mass Transfer System

Specimen at Fixed Distance from Impeller

Specimen Removable During Experiment

Top View

Specimen Holder

Metal Specimen
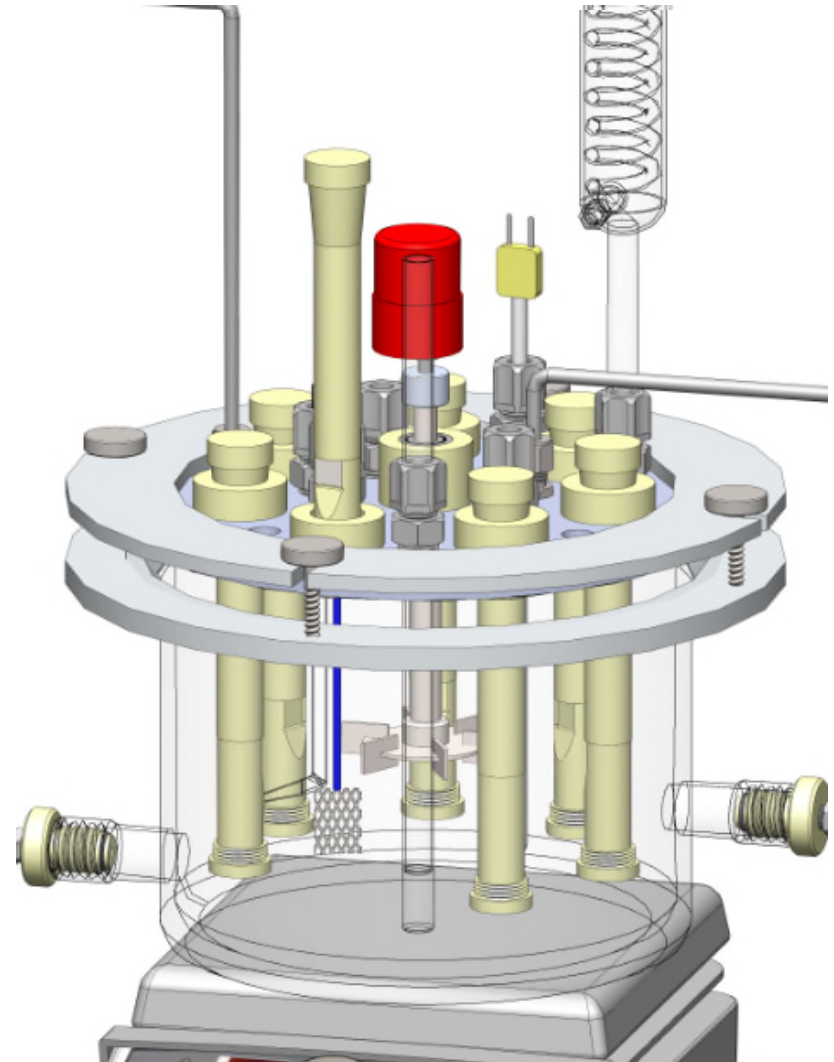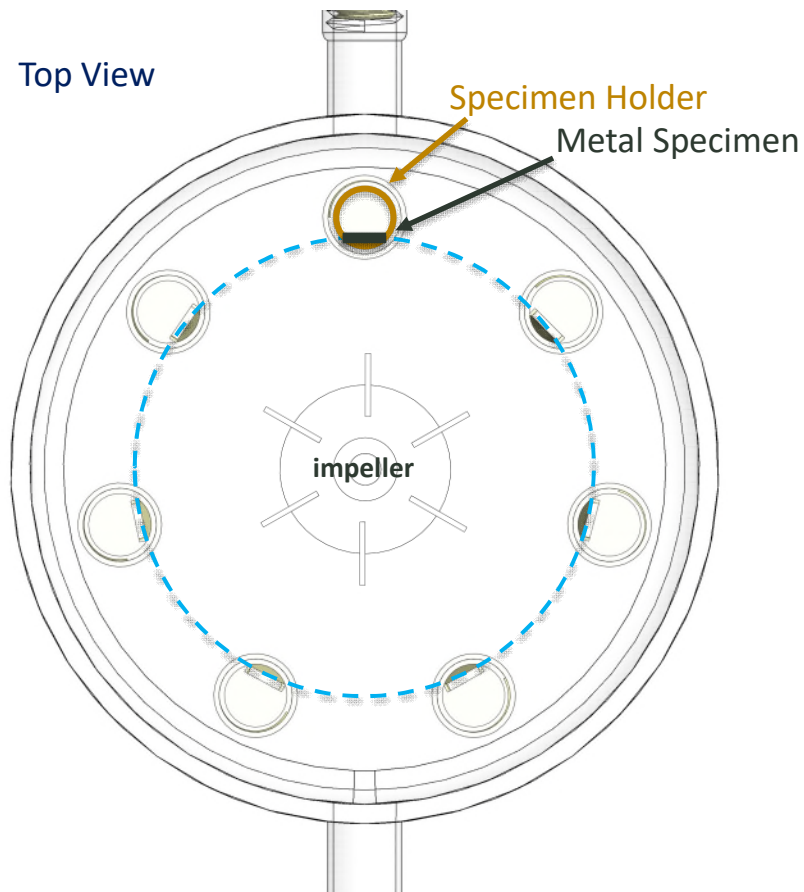
impeller

Images by Cody Shafer

Corrosion Measurements

Weight Loss/Surface Characterization Specimen Holder (6)

Electrochemical Specimen Holder (1)

Electrical connection

0.5" x 0.5" x 0.08"
Removable Weight Loss Specimen

Electro-chemical Specimen
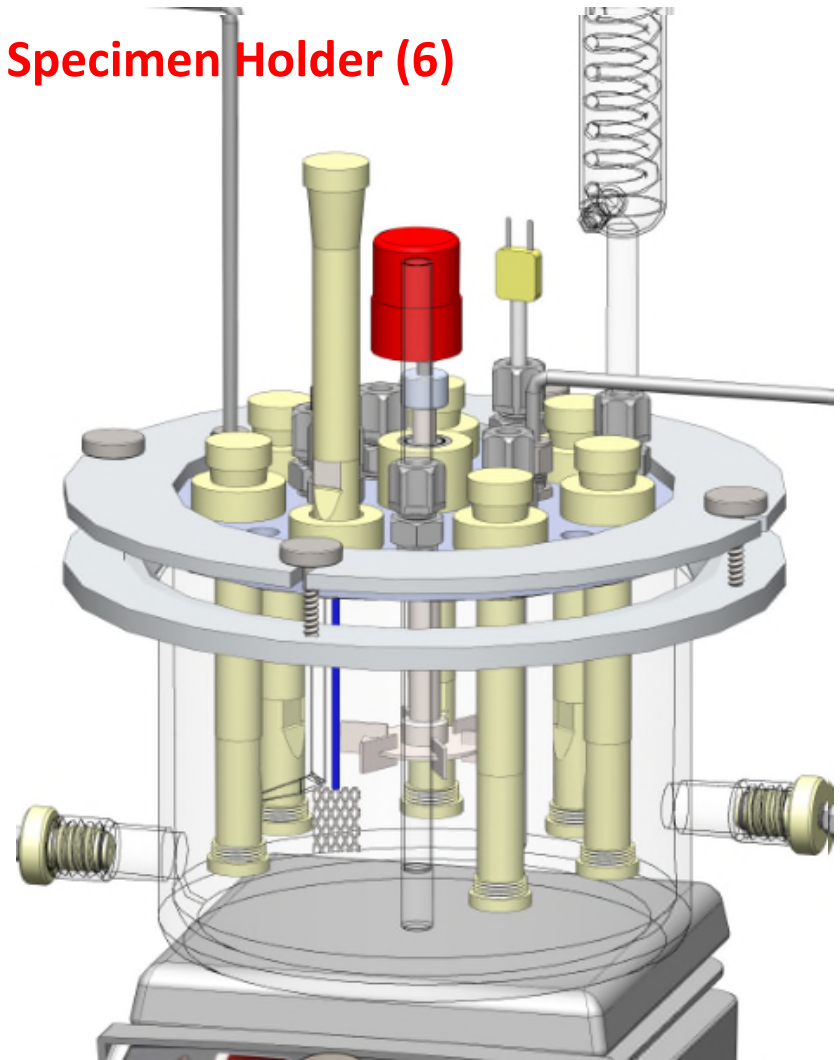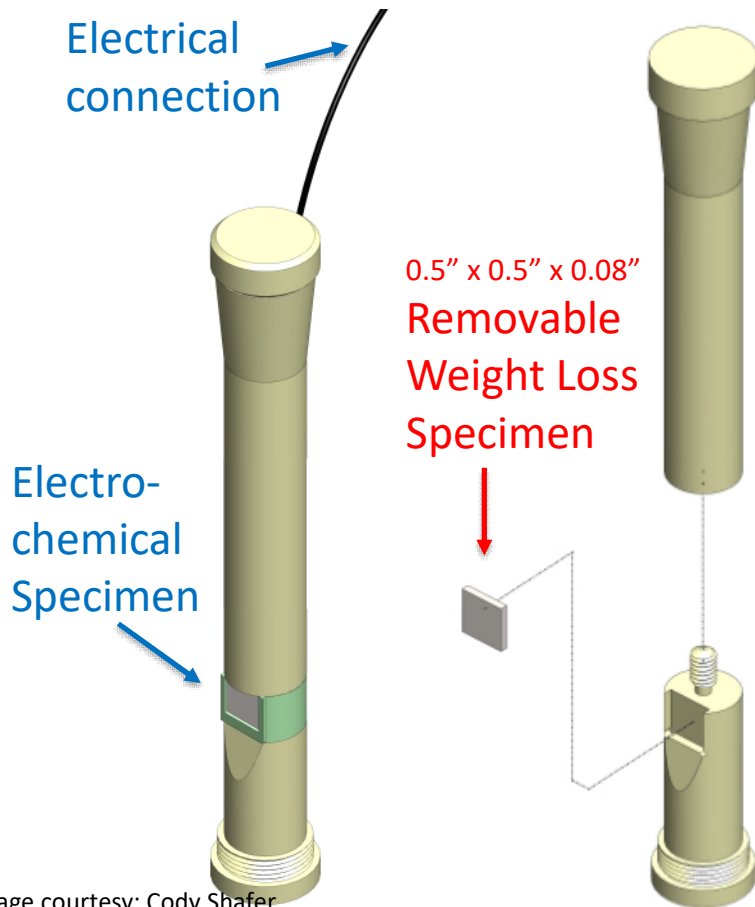
Image courtesy: Cody Shafer

Impeller Rotation Speed vs. Pipe Velocity

Equivalent Mass Transfer Coefficient for a Pipe with 0.1m ID Based on *Berger & Hau* Correlation

$$Sh = 0.0165 \, Re^{0.86} Sc^{0.33}$$ **Berger & Hau correlation for pipes**

$$Sh = 0.47 \, Re^{0.62} Sc^{0.33}$$ **Obtained correlation for current experimental setup**

$$V = \left(24.48 \times N^{0.62} \times d_{pipe}^{0.14} \times d_{imp}^{0.24} \times v^{0.24}\right)^{1.162}$$

Where,
N = impeller rotational speed (rpm)
d_{pipe} = diameter of pipe (m)
d_{imp} = diameter of impeller (m)
v = kinematic viscosity (m²/s)
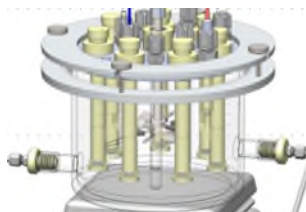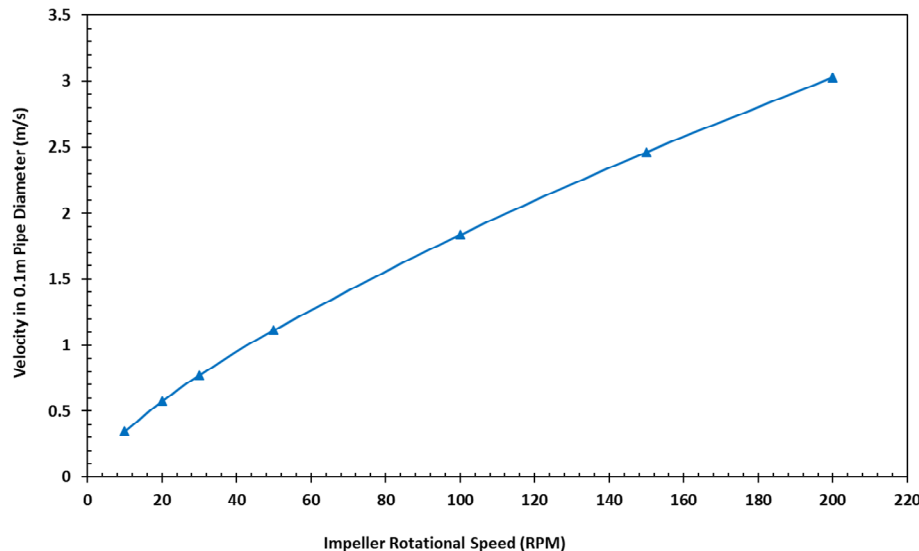
Experimental Results:

Ca^{2+}- containing solutions

Carbon Dioxide (CO_2) Corrosion Mechanisms

Electrochemical reactions happing at the metal surface

Chemical reactions happing in the bulk solution

Carbon dioxide dissolution

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$

Carbon dioxide hydration

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

Carbonic acid dissociation

$$H_2CO_{3\ (aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

Bicarbonic acid dissociation

$$HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Anodic reaction

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$

Cathodic reactions

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

Corrosion Product

(can be protective, lower corrosion rate)

$$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3(s)}$$

Chemical reaction, can happen at the metal surface and bulk solution

Experimental Design – Study of $Fe_xCa_yCO_3$ layers

Varying $CaCO_3$ saturation level (at different [Ca^{2+}], and pH)

Baseline

Working electrode

$S_{CaCO_3}=0$
[Ca^{2+}]=0
pH 6.2 & 5.5
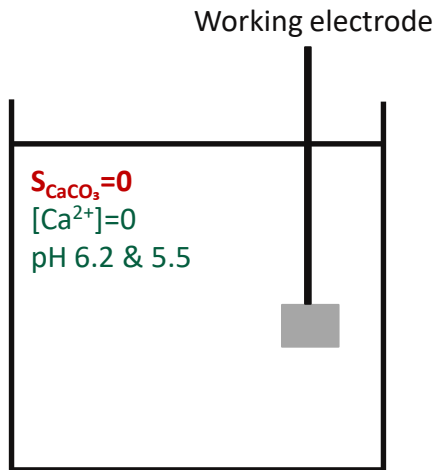
Blank solution

Effect of Ca^{2+}

$S_{CaCO_3}=1$
[Ca^{2+}]~160 & 6000 ppm
pH 6.2 & 5.5

Ca^{2+}

$CaCO_3$ in excess
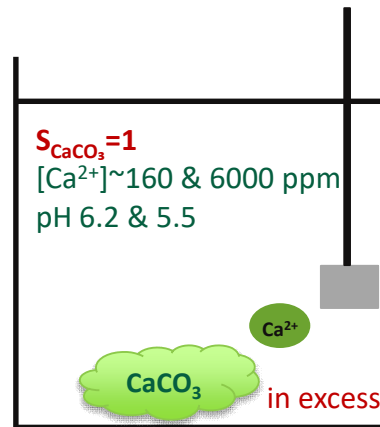
Saturated
solution

**Effect of
$CaCO_3$ scale**

S_{CaCO_3}>>1000 then 1
[Ca^{2+}]~160 & 6000 ppm
pH 6.2 & 5.5

Ca^{2+}

$CaCO_3$ in excess
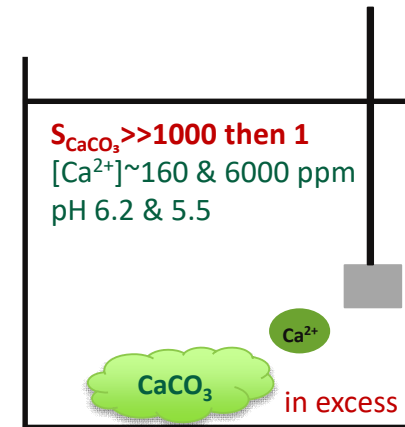
Temporarily supersaturated
solution

Experiment Matrix (pH 5.5, high [Ca^{2+}])

Parameter	Description		
Material Specimens	UNS G10180 with **Ferritic-Pearlitic** Structure Flat Square Sample (A = 1.5 cm²)		
Temperature	80°C		
pCO$_2$	0.53 bar		
pH	5.5 (controlled)		
Electrolyte	Baseline	Effect of Ca²⁺	Effect of CaCO$_3$ scale
	1 wt.% **NaCl** **+NaHCO$_3$+NaClO$_4$** (Ionic Strength~0.6 M)	1 wt.% **NaCl** **+CaCO$_3$** (Ionic Strength~0.6 M)	1 wt.% **NaCl** **+CaCO$_3$+Ca(OH)$_2$** (Ionic Strength~0.6 M)
[Ca^{2+}]	0	6000 ppm	6020 (at pH 11) then 6000 ppm (at pH5.5)
S$_{CaCO_3}$	0	1	>> 1000 then 1
S$_{FeCO_3}$	0 to 11		
Dissolved O$_2$	<5 ppb		
Reference Electrode	Saturated Ag/AgCl		
Impeller Rotation Speed	20 rpm		
Mass Transfer Conditions	Equivalent to 0.58 m/s in a 0.1m ID pipe		
Electrochemical Techniques	LPR, OCP, EIS, Potentiodynamic sweeps		
Surface Analysis Techniques	XRD, SEM/EDS		

pH Variation over Time

Identical water chemistry for different CaCO$_3$ saturation levels (pH 5.5, high [Ca^{2+}])

Note: error bars

1. $Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$
2. $2OH^-_{(aq)} + 2H^+_{(aq)} \rightleftharpoons 2H_2O_{(l)}$
3. $Ca^{2+}_{(aq)} + H_2CO_{3(aq)} \rightleftharpoons CaCO_{3(s)} + 2H^+_{(aq)}$
4. $Ca(OH)_{2(aq)} + H_2CO_{3(aq)} \rightleftharpoons CaCO_{3(s)} + 2H_2O_{(l)}$
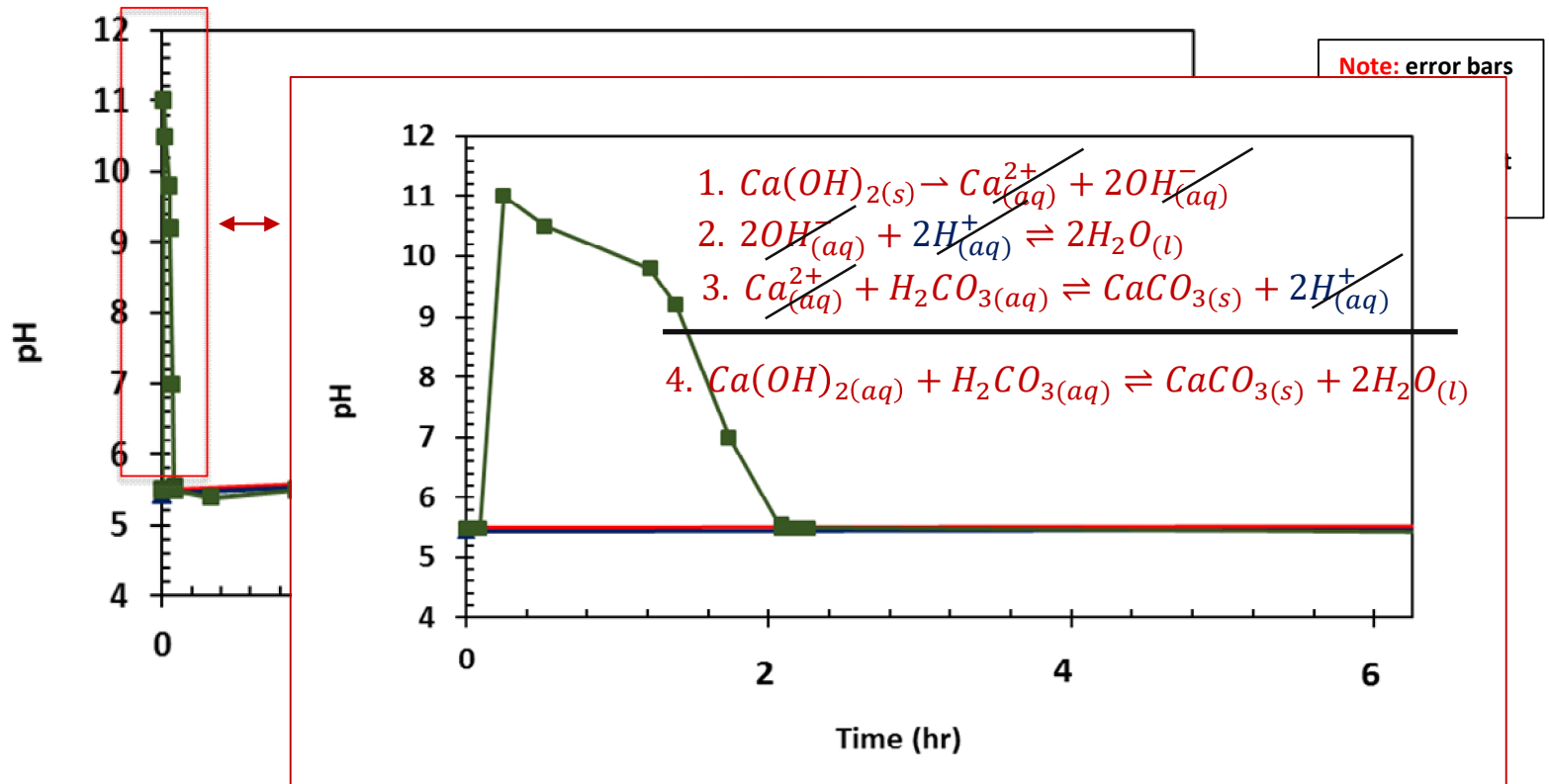
LPR Corrosion Rate Trend

Effect of CaCO₃ saturation level (pH 5.5, high [Ca²⁺])
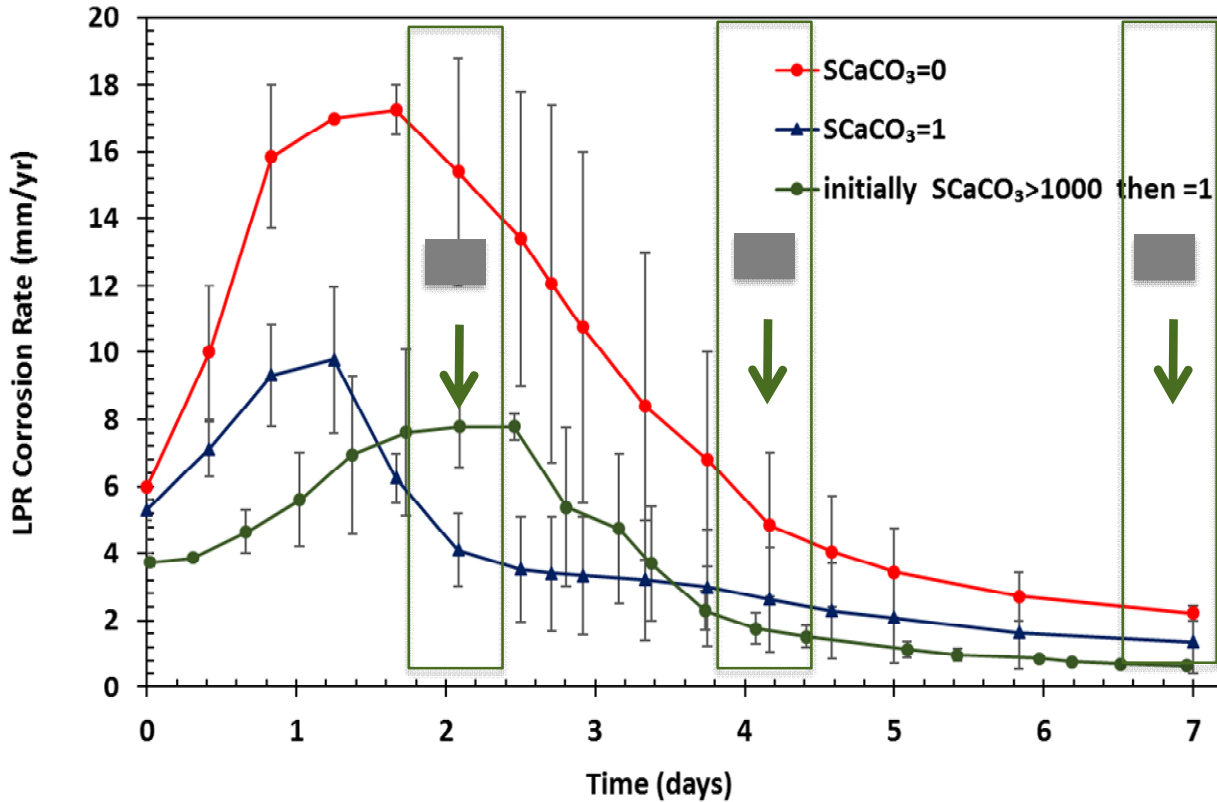
Note: error bars represent max and min values of two different tests

EDS LineScan Analysis; 7-Day Exposure, Cross-Section

Effect of CaCO$_3$ saturation on surface layer characteristics (pH 5.5, high [Ca^{2+}])
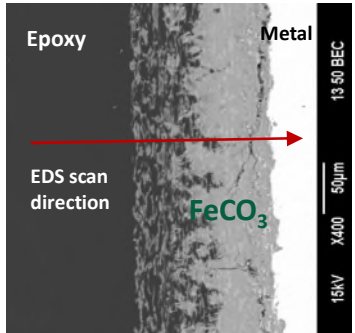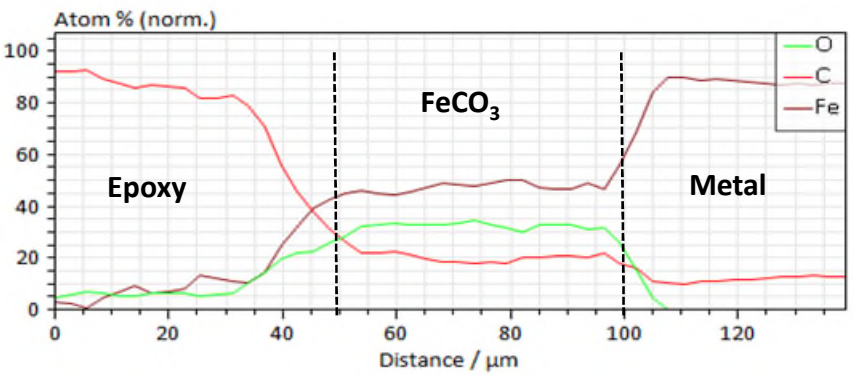
Electrolyte
S$_{CaCO_3}$=0
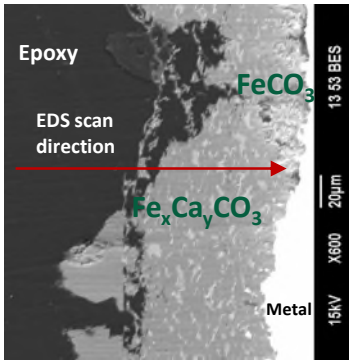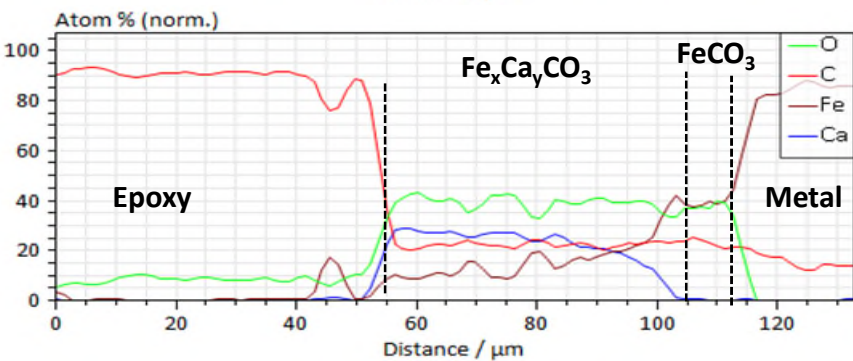
Electrolyte
S$_{CaCO_3}$=1
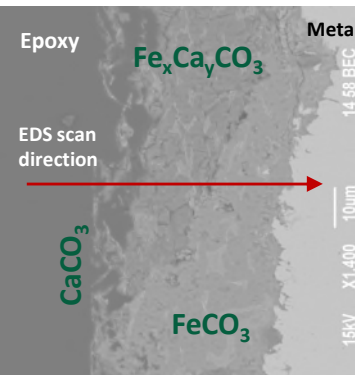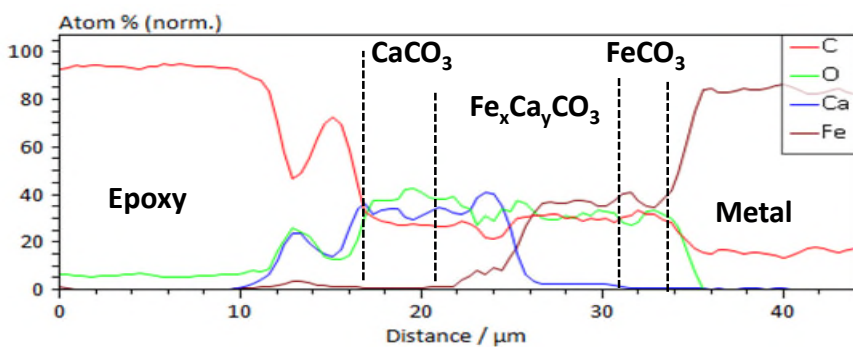
Electrolyte initially
S$_{CaCO_3}$>1000 then =1

EDS Mapping Analysis; 7-Day Exposure, Cross-Section View

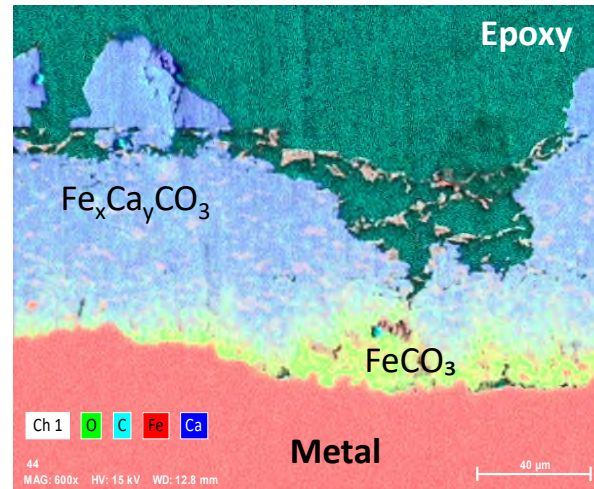**Precipitation of $FeCO_3$ adjacent to the steel (pH 5.5, high $[Ca^{2+}]$)**

$S_{CaCO_3}=0$
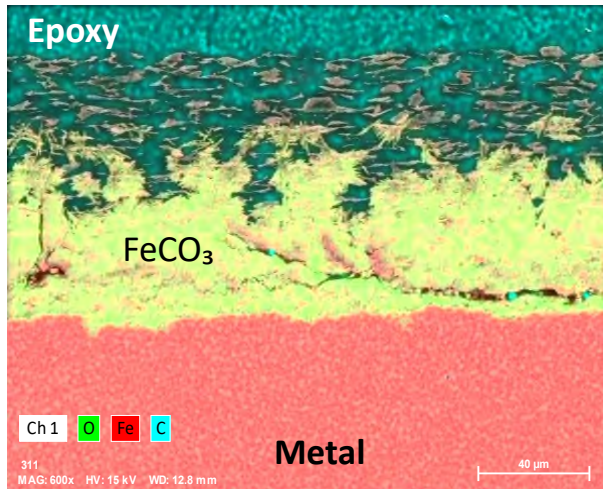
Surface layer thickness ~ 105 μm

Final LPR corrosion rate ~ 2.2 mm/y

$S_{CaCO_3}=1$

Surface layer thickness ~ 75 μm

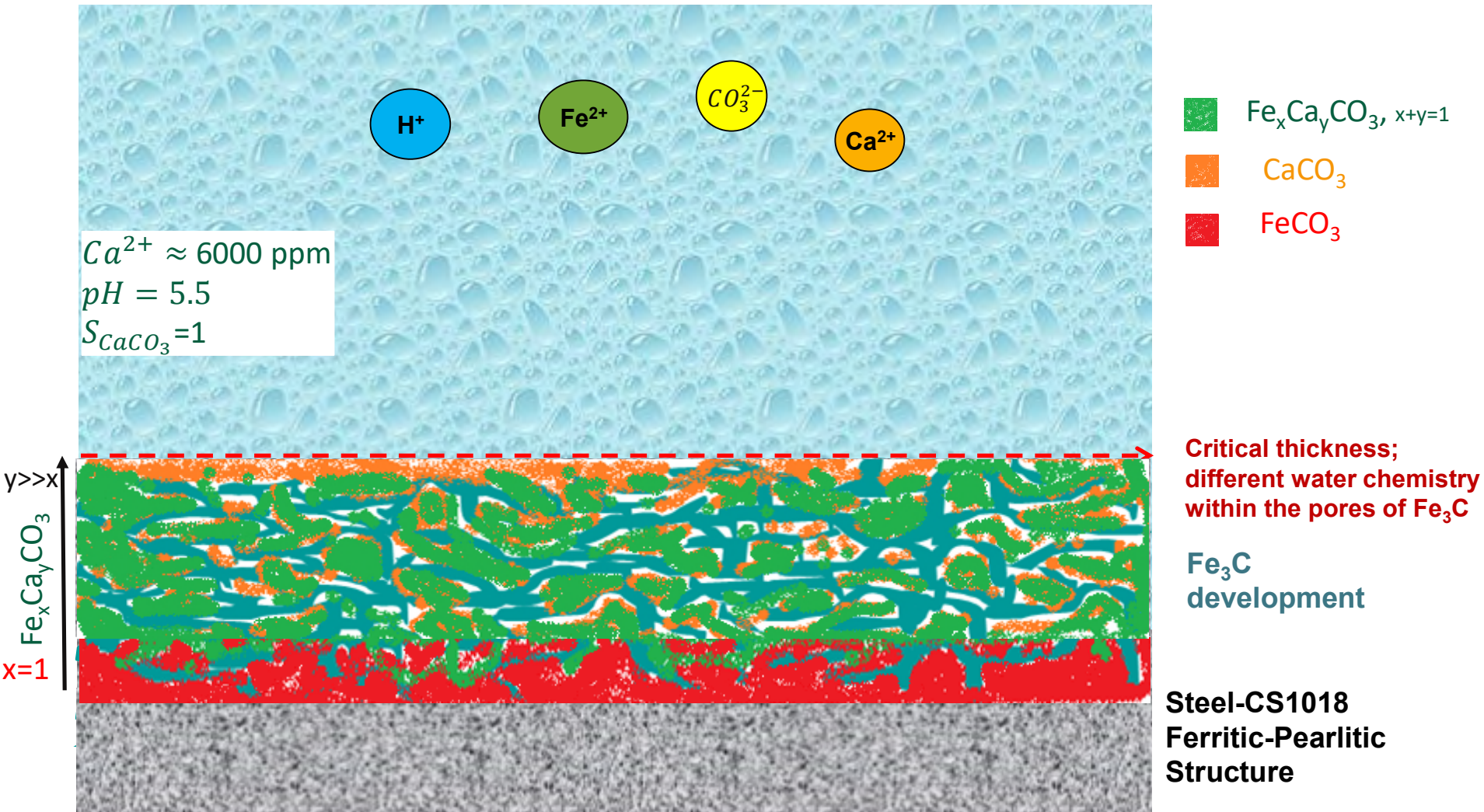Final LPR corrosion rate ~ 1.4 mm/y

Initially $S_{CaCO_3}>1000$ then $=1$
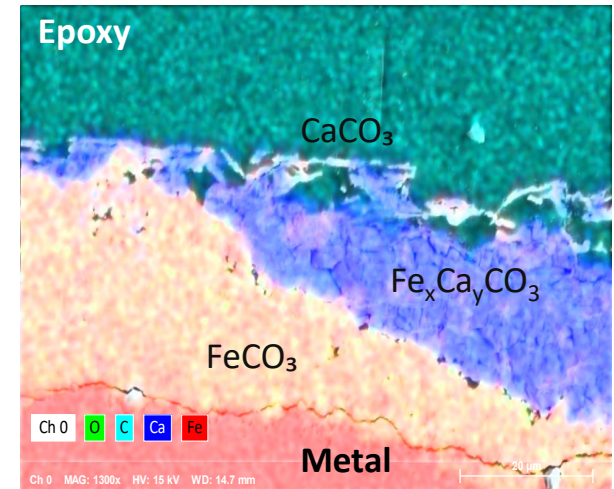
Surface layer thickness ~ 48 μm

Final LPR corrosion rate ~ 0.5 mm/y

A Descriptive Model (simplified)

(Mechanism of CO_2 corrosion in $CaCO_3$-saturated solution)

$Ca^{2+} \approx 6000$ ppm
$pH = 5.5$
$S_{CaCO_3} = 1$

H⁺ **Fe²⁺** CO_3^{2-} **Ca²⁺**

$Fe_xCa_yCO_3$, x+y=1
$CaCO_3$
$FeCO_3$

y>>x

$Fe_xCa_yCO_3$

x=1

**Critical thickness;
different water chemistry
within the pores of Fe_3C**

**Fe_3C
development**

**Steel-CS1018
Ferritic-Pearlitic
Structure**

XRD Patterns of the Top Surface After 7 Days

Effect of CaCO$_3$ saturation level on XRD patterns (pH 5.5, high [Ca^{2+}])
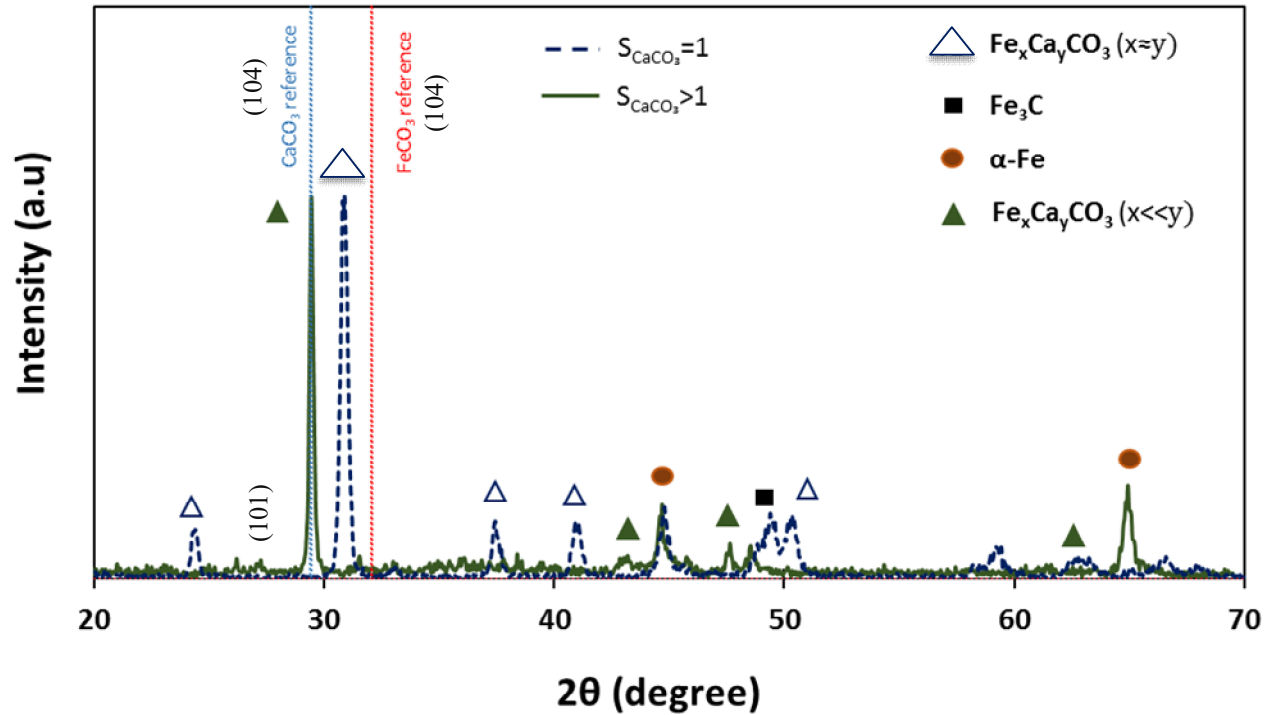
Conclusions

Conclusions

Effect of Water Chemistry on Internal Corrosion of Pipelines

- Water chemistry drives the corrosion rate of pipelines (general and localized)
- Ca^{2+} is an important component of water chemistry that should not be neglected in analysis
- When analyzing the effect of Ca^{2+}, always look for the system pH and saturation degree of $CaCO_3$
- Having high $[Ca^{2+}]$ in the brine is not scary and could be beneficial in formation of a protective $FeCO_3$ layer on the CS pipe
- When the bulk solution is super saturated with respect to $CaCO_3$, depends on how $CaCO_3$ precipitated on the surface, it could lead to localized corrosion and under-deposit corrosion. It is better to remove the scale using mechanical and chemical means.

Thank you for your attention!

AMPP™

Questions?

Backup Slides

Publications (google scholar: citation 357, h-index 11, i10-index 11)

PhD Dissertation

1. H. Mansoori, <u>Influence of Calcium and Magnesium Ions and Their Carbonate Scales on CO_2 Corrosion of Mild Steel</u>, **Ohio University**, PhD Dissertation, 2020.

Journal Papers

1. C. Prieto, H. Mansoori, B. Brown, M. Singer, D. Young, <u>'Mechanical Integrity of Iron (II) Carbonate Layers with Substitutional Calcium Atoms (FexCayCO3)'</u>, **Corrosion Science**, (190), 109625.

2. H. Mansoori, D. Young, B. Brown, S. Nesic, M. Singer, <u>'Effect of $CaCO_3$-Saturated Solution on CO_2 Corrosion in a Controlled Water Chemistry and Defined Mass Transfer System'</u>, **Corrosion Science**, (158), p: 108078, 2019.

3. H. Mansoori, D. Young, B. Brown, S. Nesic, M. Singer, <u>'Effect of $Fe_xCa_yCO_3$ and $CaCO_3$ Scales on the CO_2 Corrosion of Mild Steel</u>, **Corrosion**, 75 (12), p:1434-1449, 2019.

4. H. Mansoori, D. Young, B. Brown, S. Nesic, M. Singer, <u>'CO_2 corrosion of Mild Steel Exposed to $CaCO_3$-Saturated Aqueous Solutions'</u>, Poster Award Research Letter, **Corrosion**, 75 (11), p: 1281-1284, 2019.

5. H. Mansoori, D. Young, B. Brown, M. Singer, <u>'Influence of Calcium and Magnesium Ions on CO_2 Corrosion of Carbon Steel in Oil and Gas Production Systems-A Review'</u>, **Journal of Natural Gas Science and engineering**, (59), p: 287-296, 2018.

Conference Papers

1. H. Mansoori, B. Brown, D. Young, S. Nesic, M. Singer, <u>'Investigations on the CO_2 Corrosion of Mild Steel in the Presence of Magnesium and Calcium Ions</u>, **NACE2020**, Paper no. 14914, Houston, Texas.

2. H. Mansoori, B. Brown, D. Young, S. Nesic, M. Singer, <u>'Effect of Calcium Ions and $CaCO_3$ scale on CO_2 Corrosion Mechanism of Mild Steel</u>, **NACE2019**, Paper no.13000, Nashville, Tennessee.

Experimental Design – Is pure CaCO$_3$ protective?

- CaCO$_3$ precipitation-electrochemically driven (temporarily supersaturated at metal/solution)
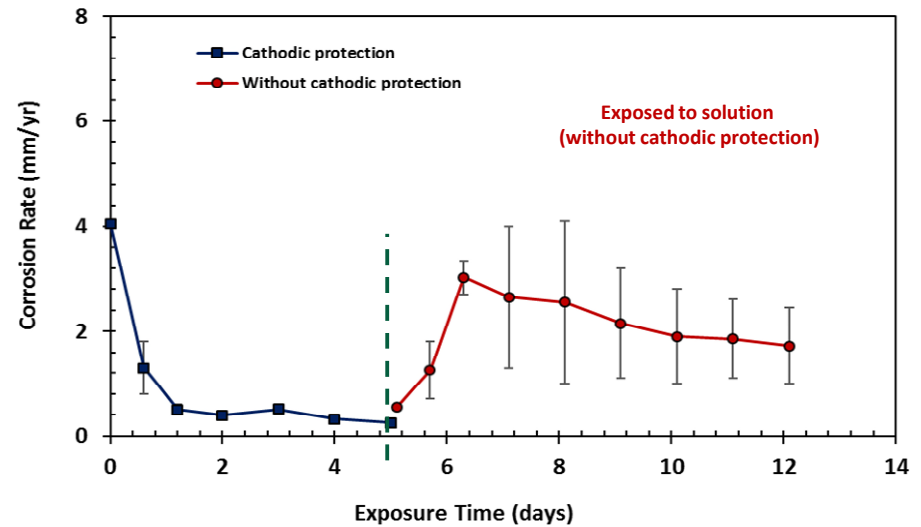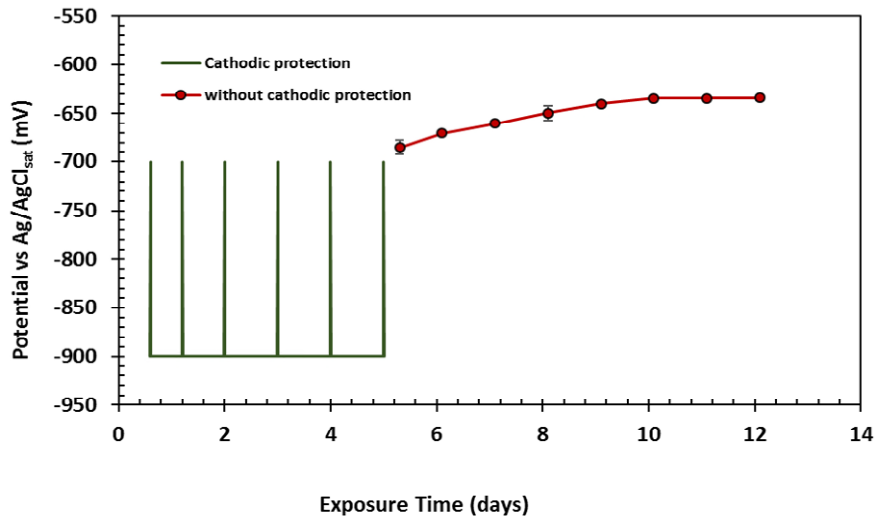

CaCO$_3$-Saturated Solution

$$Ca^{2+}, CO_3^{2-}$$
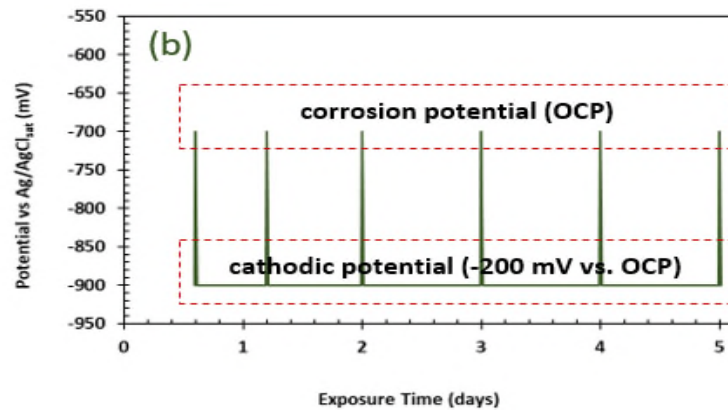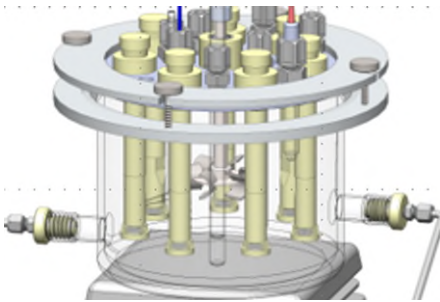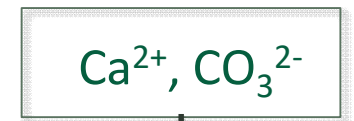
Precipitation of CaCO$_3$

Cathodic Polarization of WE:
1- prevent interference by Fe^{2+} in carbonate formation
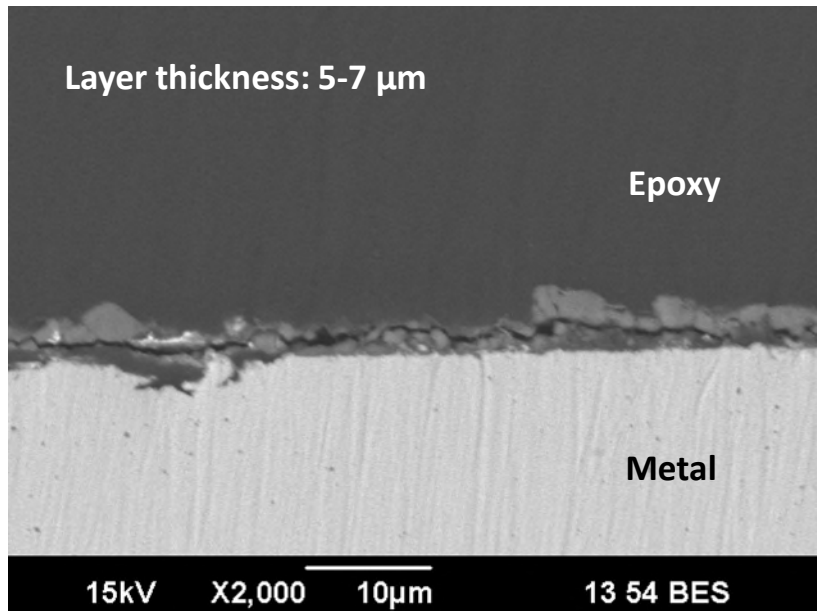2- promote precipitation of CaCO$_3$

Corrosion Rate & Potential over Time

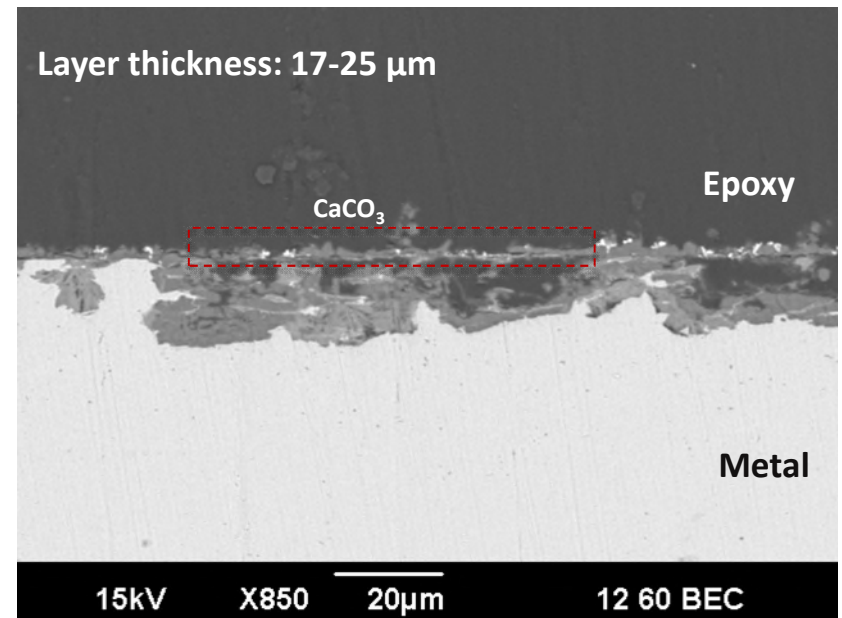- 80˚C, pCO_2 0.53 bar, pH 5.5, CS1018, 0.58 m/s, 1 wt.% NaCl, $CaCO_3$-saturated solution

Surface layer morphology after 7 days of exposure to solution (without cathodic polarization)

- 80˚C, pCO_2 0.53 bar, pH 5.5, CS1018, 0.58 m/s, 1 wt.% NaCl, $CaCO_3$-saturated solution

$CaCO_3$ formed during cathodic polarization

Cross-section view-active corrosion

Comparison: Pre-Scaled Specimen vs. Bare Specimen

- 80°C, pCO_2 0.53 bar, pH 5.5, CS1018, 0.58 m/s, 1 wt.% NaCl, $CaCO_3$-Saturated Solution