U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Spent Fuel and Waste Science and Technology (SFWST)

Clear SAND2020-11671C

Report on Potential Coatings for Use as Mitigation and Repair Strategies for SCC on SNF Canisters

Andrew Knight[1], Rebecca Schaller[1], Charles Bryan[1], TJ Montoya[1], Alana Parey[1], Jacob Carpenter[1], Makeila Maguire[1], and Ken Ross[2]

[1]Sandia National Laboratories, [2]Pacific Northwest National

EPRI ESCP Fall Workshop

Virtual Meeting

November 11, 2020

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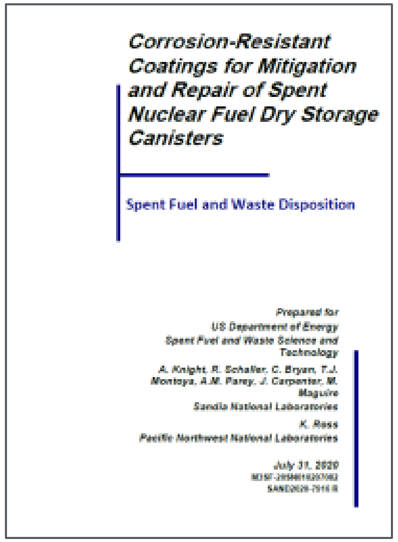
Prevention, Mitigation and Repair Strategies For SCC


Corrosion-Resistant Coatings for Mitigation and Repair of Spent Nuclear Fuel Dry Storage Canisters

Spent Fuel and Waste Disposition

Prepared for
US Department of Energy
Spent Fuel and Waste Science and Technology

A. Knight, R. Schaller, C. Bryan, T.J. Montoya, A.M. Parey, J. Carpenter, M. Maguire
Sandia National Laboratories

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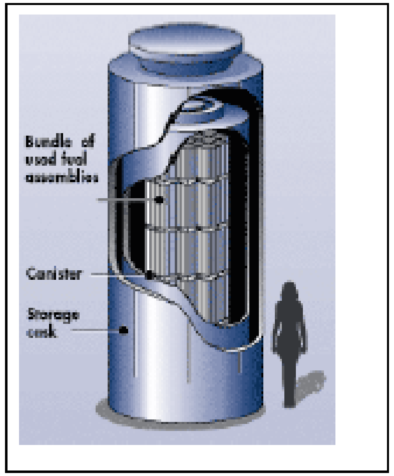
July 31, 2020

Goal: 1) Systematically evaluate coating options in order to identify promising candidates and 2) Develop a methodical testing plan for coating mitigation and repair strategies

There are a number of unique factors (elevated temperatures profile, high radiation levels, application challenges due to geometry) that must be considered when identifying potential prevention, mitigation, and repair strategies.

	In situ Repair	**Ex situ Prevention**	**Ex situ Prevention**
Shared Attributes of a Good Strategy	• Offers long term protection from corrosion and CISCC • Mechanically tough enough to withstand some physical damage • Easy to monitor and reapply if needed • Adherent enough to stay on the canister despite disturbances • Resistant to radiation • Chemically stable • Thermally stable over the range of interest • Affordable • TRL sufficiently high • Ability to seal existing crack		
Unique Attributes For Implementation	• Requires minimal surface treatment • Minimal edge effects (if applied as a patch)	• Requires minimal surface treatment • Minimal edge effects • Resistance to physical damage during canister handling	• Withstand high temperatures during loading (200 C or higher) • Resistant to physical damage from both shipping and handling



Classes of Coatings Considered

Polymers: **Great versatility and great chemical and mechanical stability. One major drawback is susceptibility to radiation damage**

Ceramics: Consisting of metal oxides deposited onto the SS surface. Great chemical and radiological stability, can be prone to scratching and brittle failure.

Conversion: Formed by reaction of an inorganic solution with the base metal to create a mechanically strong and electrically non-conductive coating.

	Attribute	Implementation		
Coating Name	*Properties/Degradation*	*In situ repair*	*Ex situ repair*	*Ex situ prevention*
Air Dry Epoxy	Susceptible to radiolytic degradation; not stable above 130°C	Minimal surface preparation; Requires T< 130° C	Minimal surface preparation; Requires T< 130° C	Susceptible to radiolytic degradation; Requires T< 130° C
Polyethylene	Chemically and mechanically stable; radiolytically sensitive; unknown thermally; multiple layers application can increase time to degradation	Can be easily applied as short term patch due potential radiolytically degradation	Can be easily applied as short term patch due potential radiolytically degradation	Poor radiolytic stability
Rubber	Robust but susceptible to permeation but can be improved with multiple layers; stable to high temperatures	Can be painted or sprayed on	Can be painted or sprayed on	Can be painted or sprayed on
Sol-gel	Chemically, thermally, radiolytically and mechanically stable; adhesion and application depends on additives and surface finish, prone to brittle failure	Can be applied by spray or brush methods	Prone to scratching and brittle failure, but can be improved with additives	Prone to scratching and brittle failure, but can be improved with additives
Phosphate Conversion	Chemically, thermally, radiolytically and mechanically stable; great adhesion; Complex application and reapplication process	Complex application and reapplication process	Complex application and reapplication process	Effective coating if applied during prior to SNF fuel loading
Cold spray*	Robust and great adhesion; surface modification effects on corrosion must be demonstrated	Can be applied locally with robotic crawler	Can easily be applied locally	Can be easily applied

*Cold spray is already being considered (PNNL/SNL)

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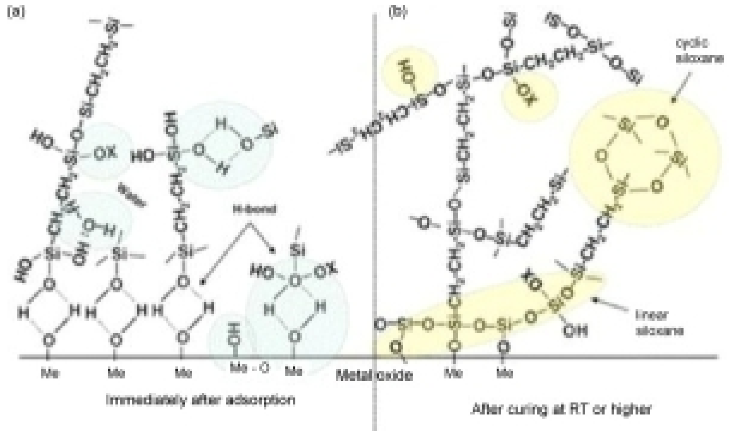

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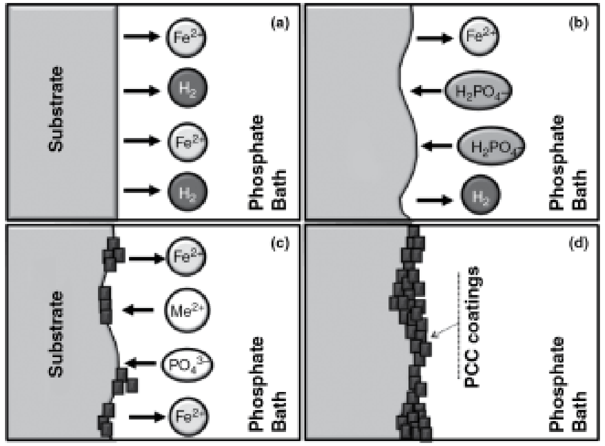

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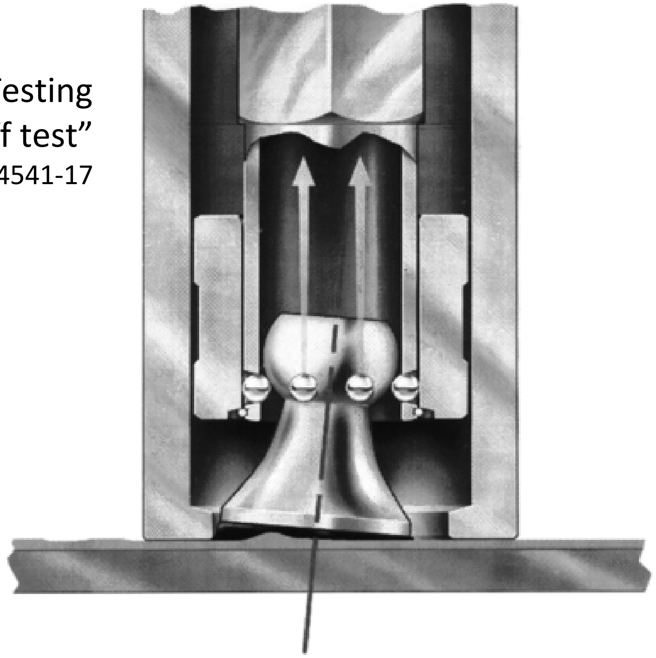
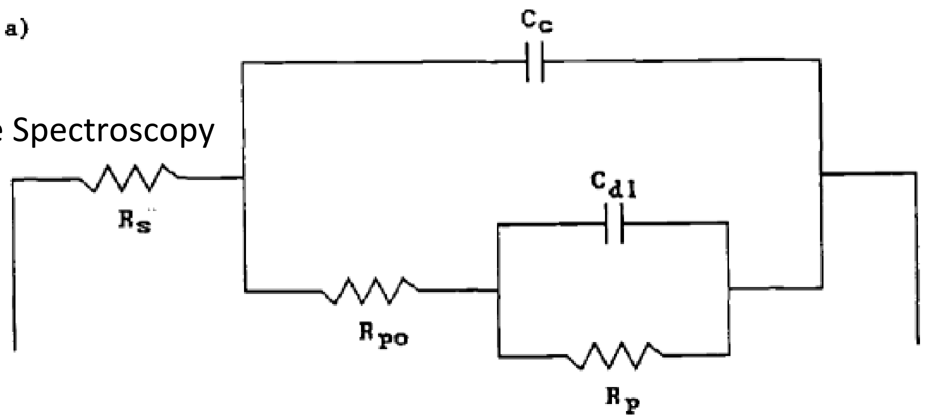
Initial Testing

- Characterization of coating performance will include the following tests:
  - **Adhesion**
    - **Pull Off Test**
      - **ASTM D4541-17**
  - **Permeability**
    - **Electrical Impedance Spectroscopy**
      - **ASTM STP 1188**
  - Thermal cycling and degradation
  - Radiation degradation
    - Gamma Irradiation Facility (SNL)
  - Corrosion testing
    - Accelerated testing
    - Long term canister-relevant tests

Adhesion Testing
"Pull off test"
ASTM D4541-17



Permeability Testing
Electrical Impedance Spectroscopy
ASTM STP 1188



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In-situ Raman Analysis of Precipitates Formed by Cathodic Polarization To Study Atmospheric Corrosion in Marine Relevant Environments

Andrew Knight[1], Ryan Katona[1,2], Rebecca Schaller[1], and Charles Bryan[1]

[1]*Sandia National Laboratories*, [2]*University of Virginia*

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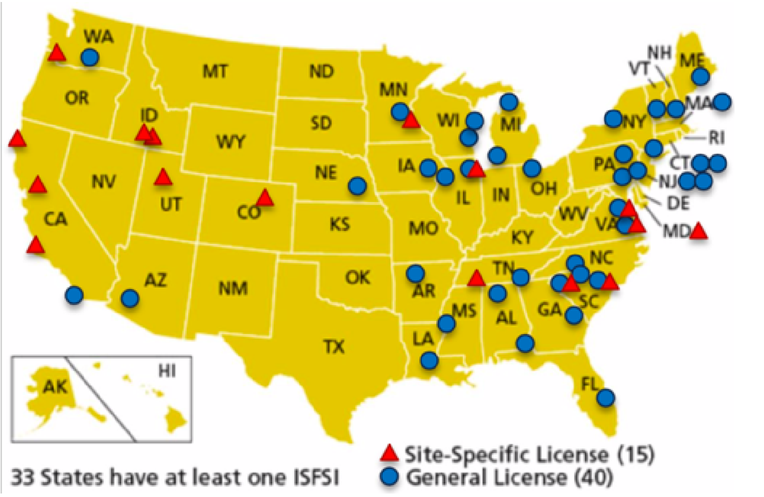
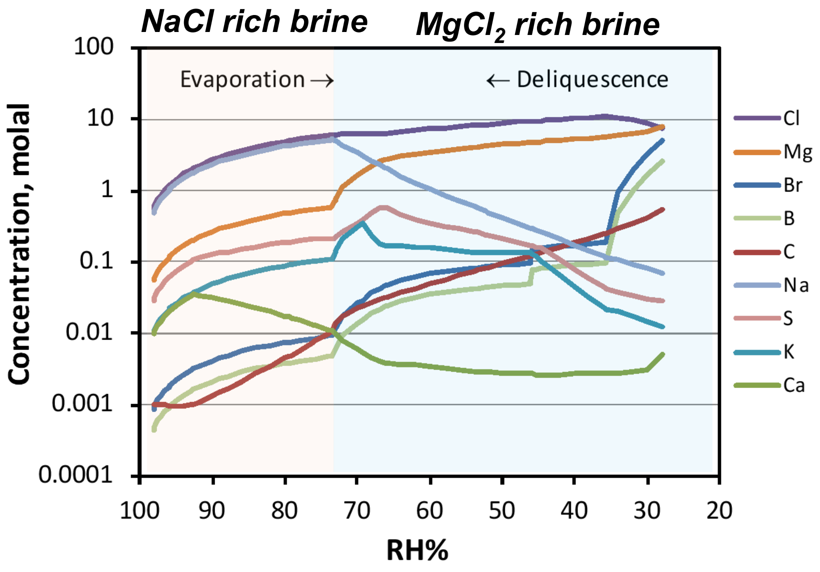
Factors that Affect Risk of SCC on Spent Nuclear Fuel Canisters

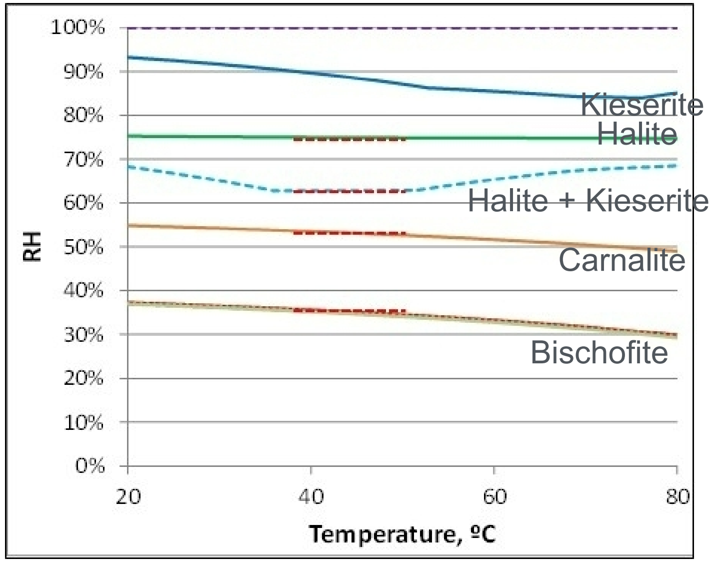
- Spent nuclear fuel is currently stored in welded stainless steel canisters across the country at independent spent fuel storage installations (ISFSI).
- In near-marine applications, deposition of aggressive (commonly chloride-containing) sea salt aerosols is possible
  - As canisters cool, deliquescence of sea salts can form a corrosive brine
  - Criteria are met for the risk of CISCC



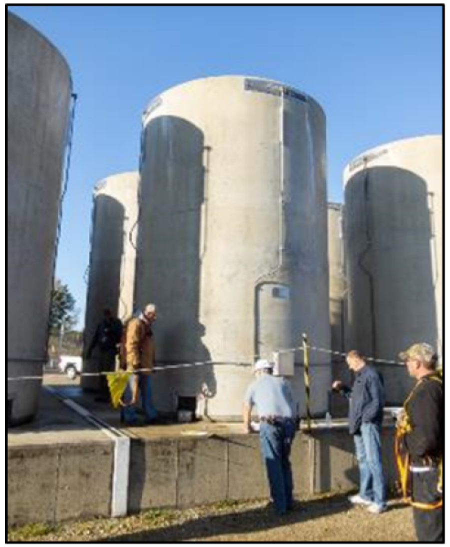
Sea Salt Brine Evolution



Deliquescent Sea Salts



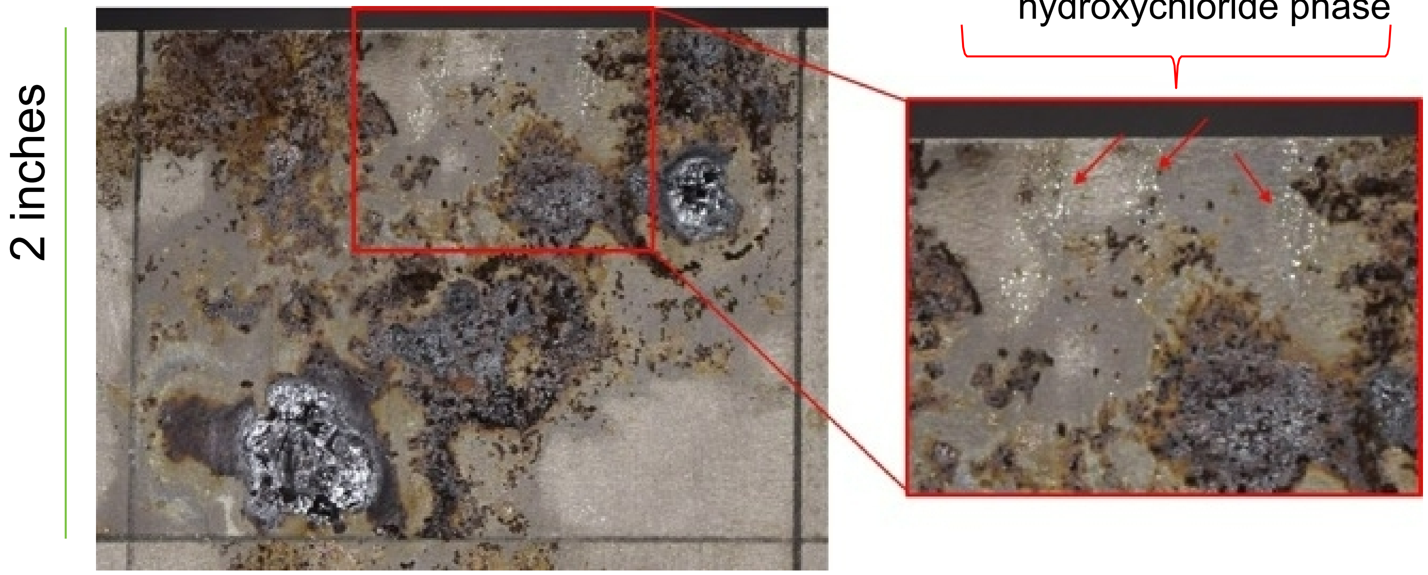
ISFSI locations



Brine Stability and Reactions

Salt deliquescence is a function of T and RH. Once formed, brines can react to precipitate less deliquescent salts, potentially resulting in brine dry-out:

- Degassing
- Corrosion reactions



Mg-chloride brines convert to Mg-hydroxychloride in response to degassing or corrosion reactions

Brine Stability and Reactions

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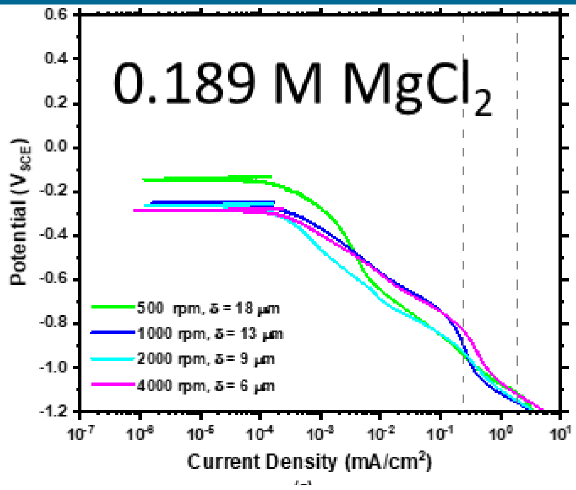
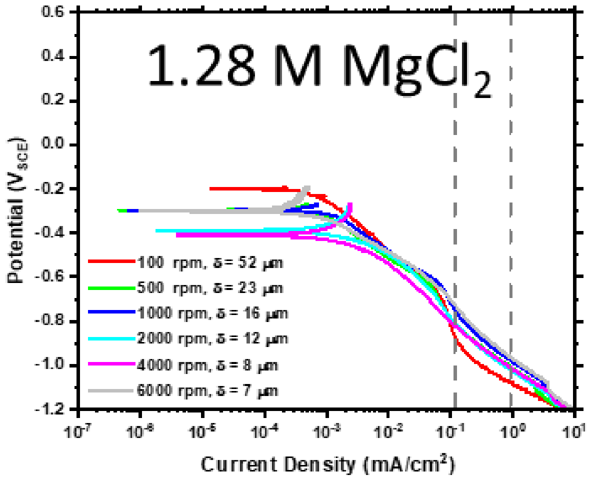
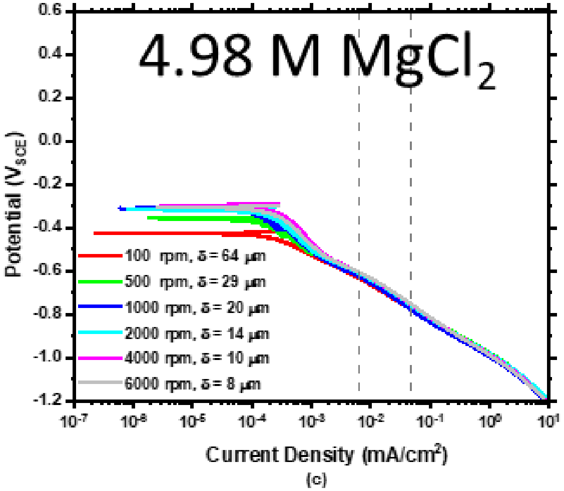
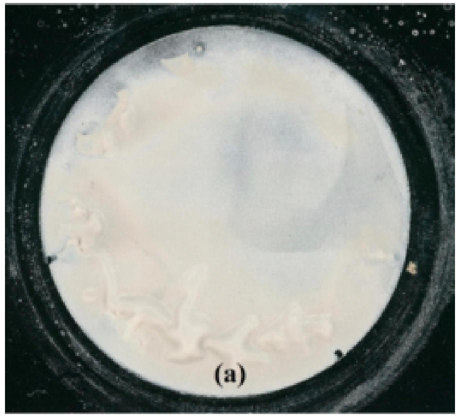
RDE experiments show unexpected results due to film precipitation at the cathode.

- Specifically in Mg-rich brines





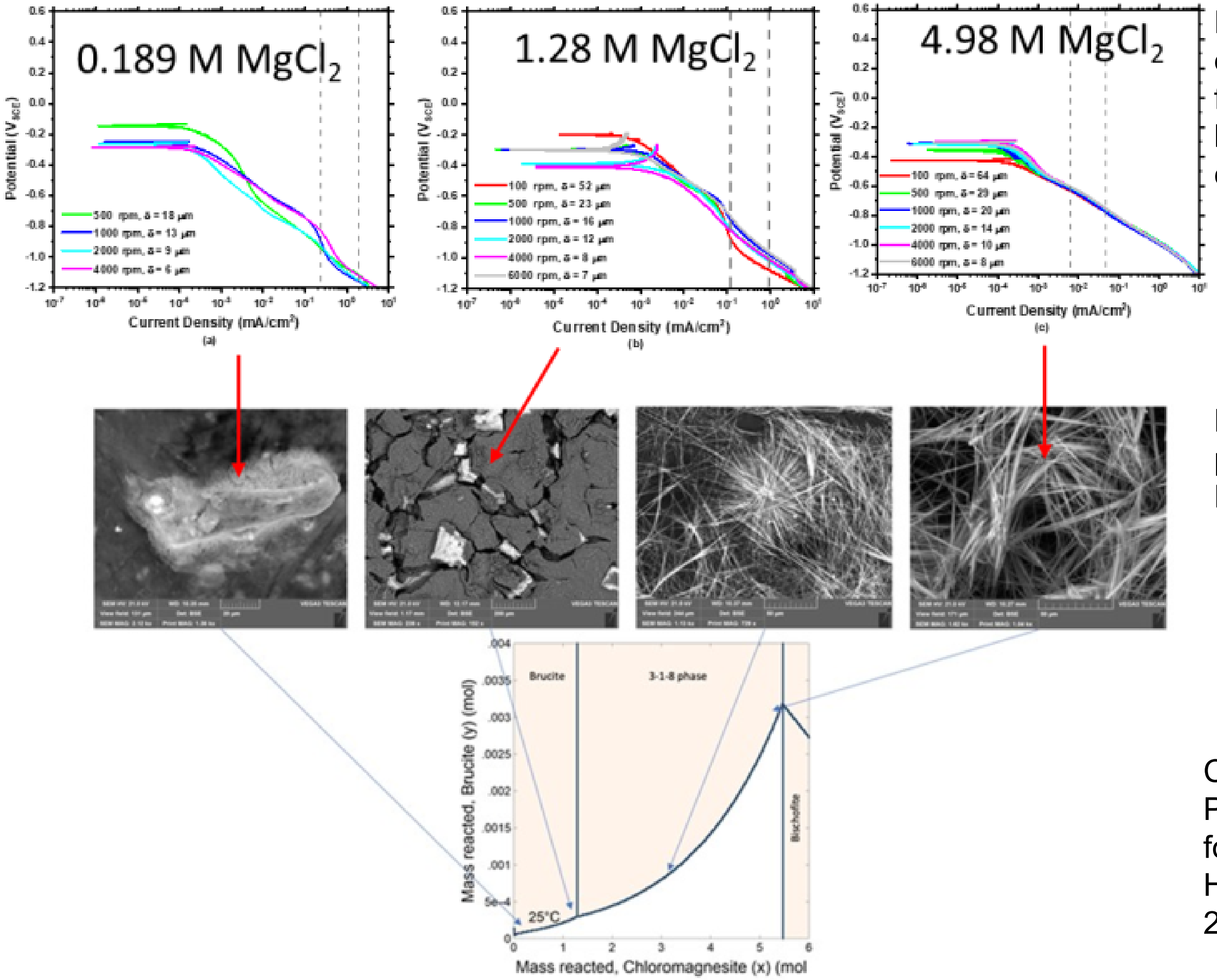




Film analyses, after RDE experiments, have been challenging; therefore the identity of the film has not been confirmed

Can we Identify Mg-precipitates in-situ?

- <u>Objective</u>
  - Determine how and why cathodic behavior of SS in $MgCl_2$ brines changes in response to surface reactions
- <u>Why?</u>
  - The identity of the Mg-precipitate controls the brine stability and electrochemistry, and is important in understanding SS corrosion in the presence of $MgCl_2$-rich brines (including seawater) under field-relevant conditions
- <u>In-situ Raman</u>
  - Utilizing in-situ Raman during the cathodic scan will allow for us to simulate atmospheric environments and identify the precipitates that form on the metal surface



RDE experiments, film formed but identity not confirmed

Mg-phase precipitation via NaOH titration

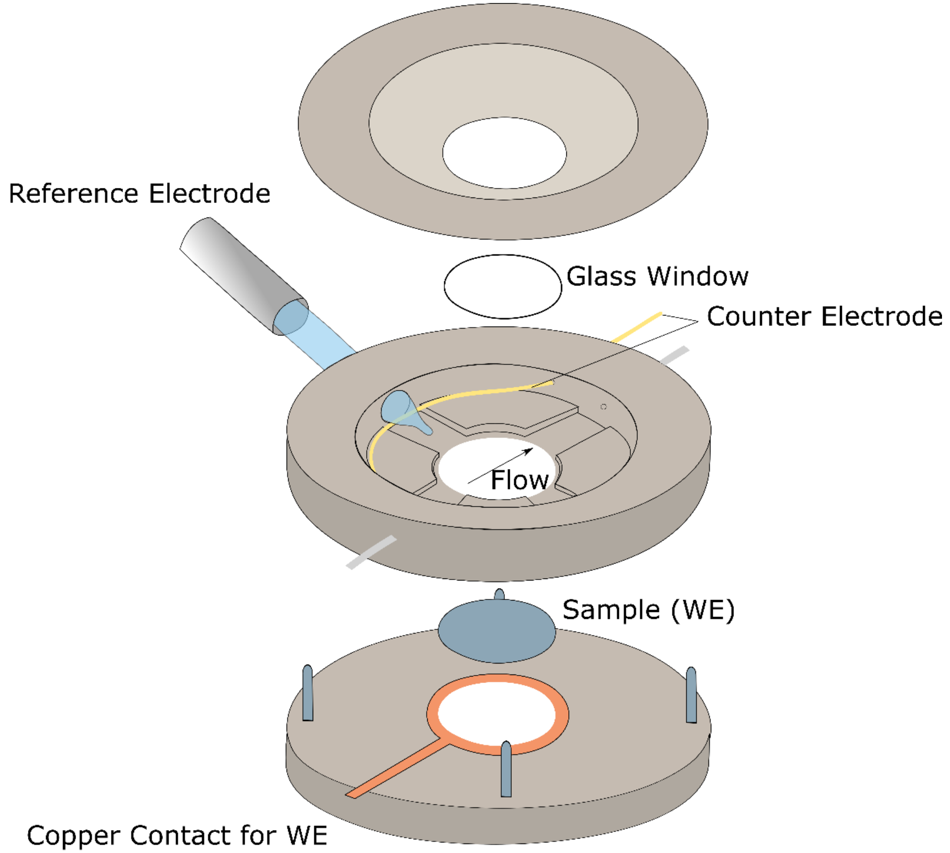
Calculated Phase diagram for Mg-OH-Cl-H2O system at 25 C

Flow Experiments

Rotating disc electrode (RDE) experiments are used to simulate atmospheric corrosion under thin brine films. In-situ flow cell mimics RDE measurements while maintaining the ability to probe the precipitating film directly

- In-situ Raman cell specifications
  - Cell volume = 4.5 mL
  - Electrolyte thickness = 2.25 mm
  - Flow rate: 0 mL/min – 50 mL/min (+/- 0.25%)
    - Compared to quiescent scans in standard flat cell (~350 mL)
- Electrochemical Measurements:
  - 1-hour OCP
  - Cathodic scan: OCP to -1.4 $V_{Ag/AgCl}$
    - Scan rate = 0.167 mV/sec.
    - Solution flowing continuously during experimentation

What is the effect of flow rate?



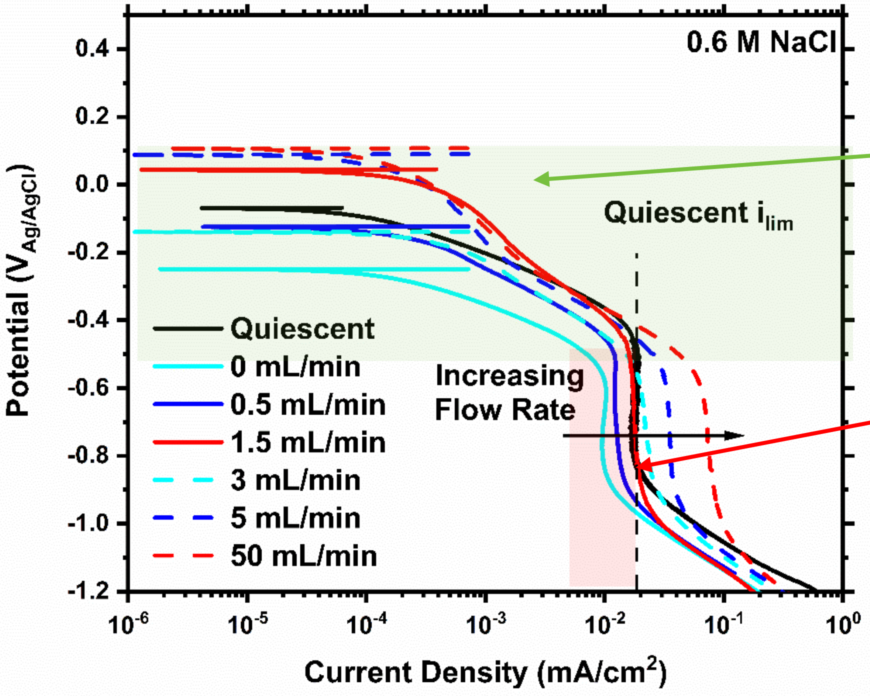
Flow-through Raman Cell

Flow and O_2 Depletion – 0.6 M NaCl

- As flow rate (Q) increases, the limiting current density increases
  - Q < 1.5 mL/min: i_{lim} flow < i_{lim} for a quiescent
  - Q =1.5 mL/min: i_{lim} flow = i_{lim} for a quiescent

$$i_{lim} \sim D_{O2}^{\frac{2}{3}} C_{O2}$$

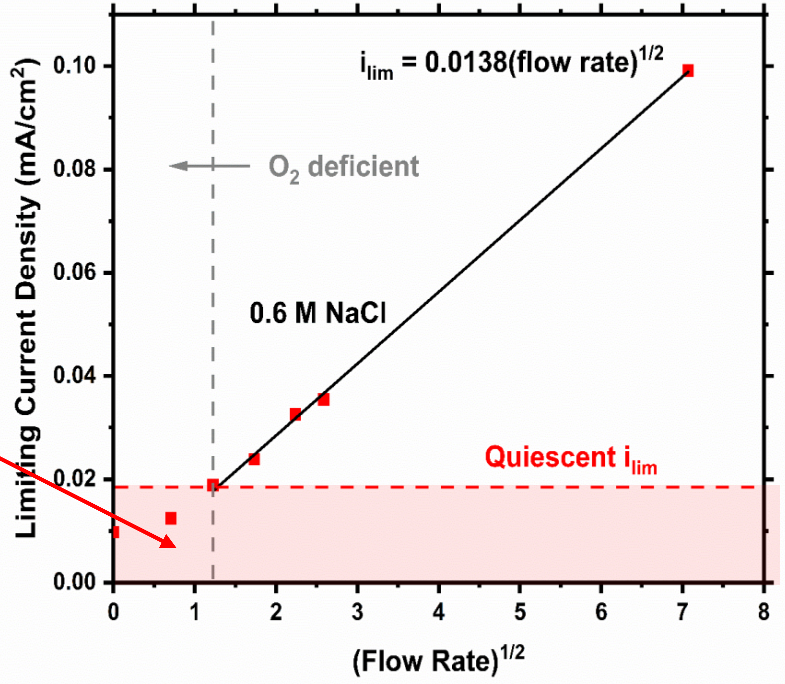
i_{lim}: limiting current density
D_{O2}: oxygen diffusivity (cm^2/second)
C_{O2}: oxygen concentration (mol/cm^3)



(a)

Activation controlled region (OCP to ~-0.5 $V_{Ag/AgCl}$)

O_2 deficient region



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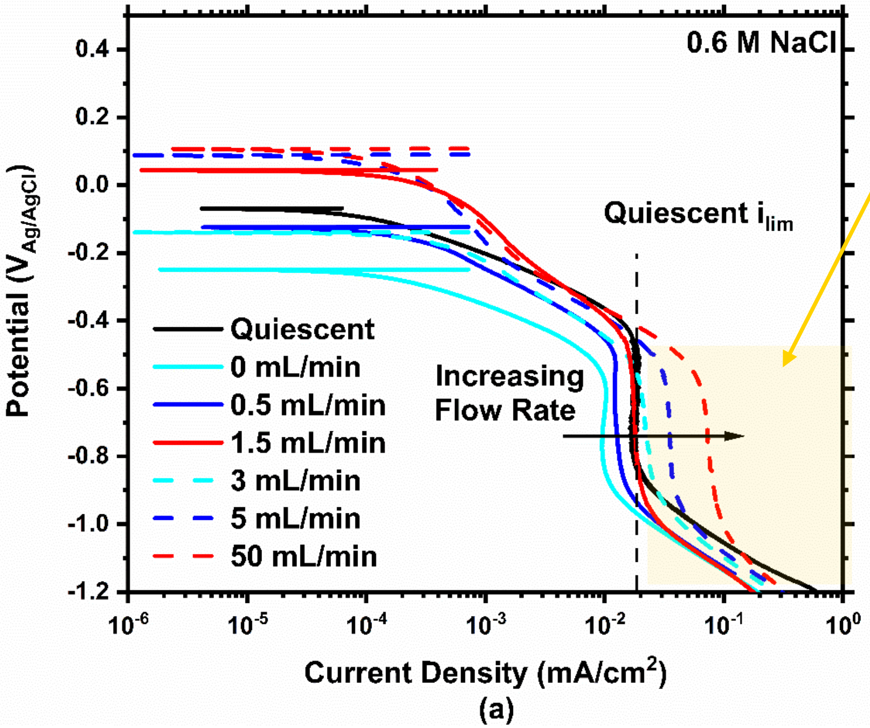
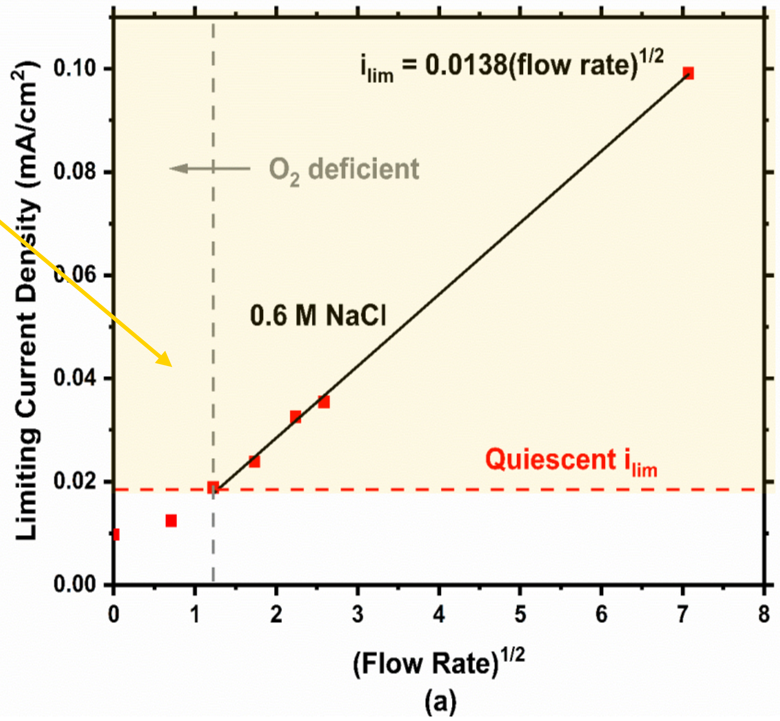
- Q > 1.5 mL/min: i_{lim} flow > i_{lim} for a quiescent
  - Representing a decreased δ.



Mass transfer controlled region (~ -0.5 – -0.9 $V_{Ag/AgCl}$)



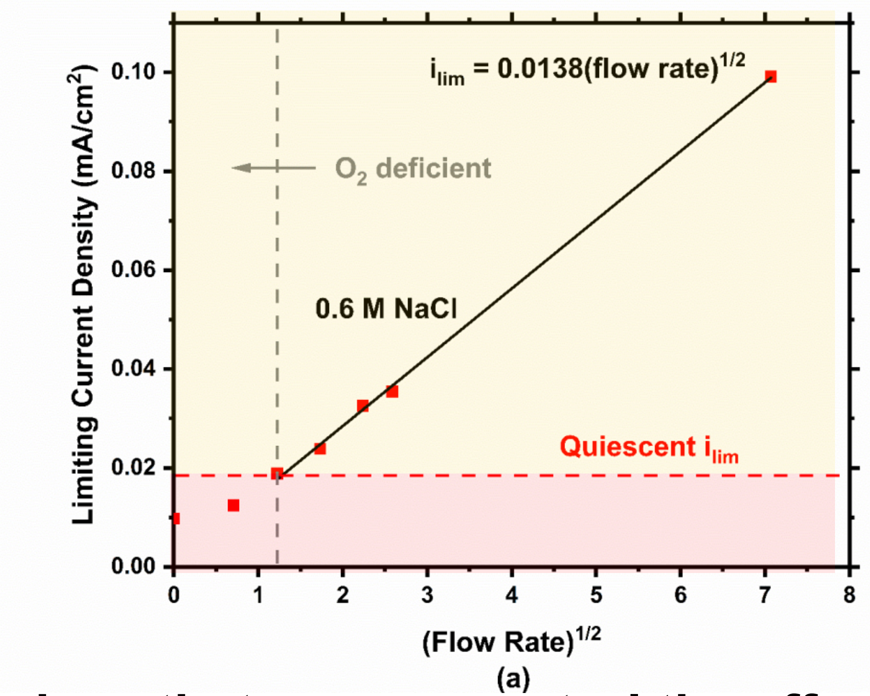
This demonstrates that flow rate determines [O_2] and solution regeneration is required to prevent O_2 deficiencies. Also, RDE, flow rate is proportional to the limiting current density

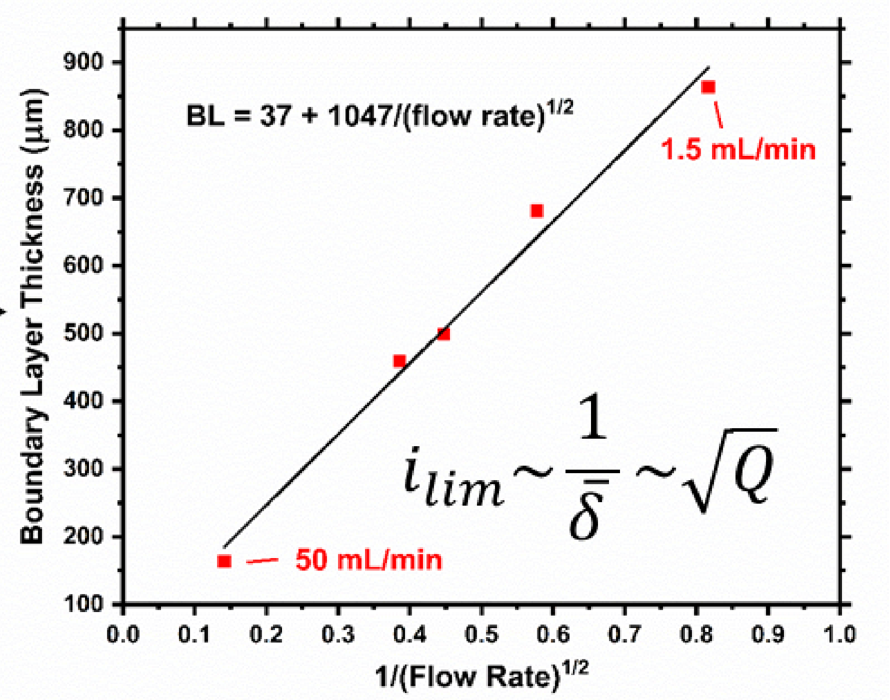
i_{lim} and Estimation of Boundary Layer Thickness

Previous RDE studies demonstrated Levich behavior in 0.6 M NaCl, where boundary layer thickness is inversely related to the limiting current density

0.6 M NaCl: i_{lim} vs $\sqrt{flow\ rate}$ is linear

- Allows for an estimation of the boundary layer thickness

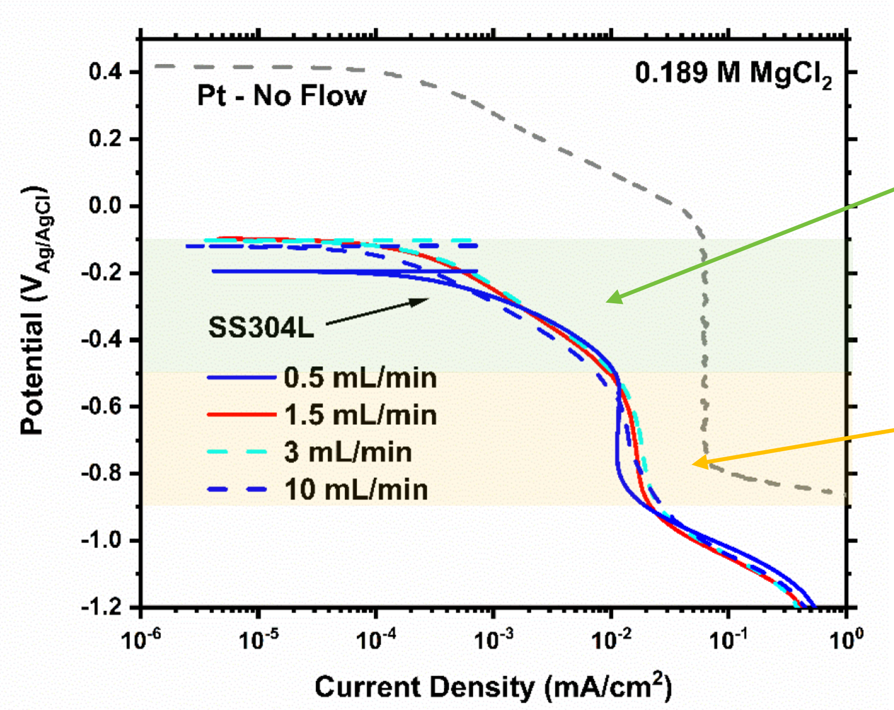




Here, we show that we can control the effective boundary layer thickness by adjusting the flow rate, this allows for investigations of atmospheric corrosion scenarios using flow cells.

Flow and O_2 Depletion – 0.189 M $MgCl_2$

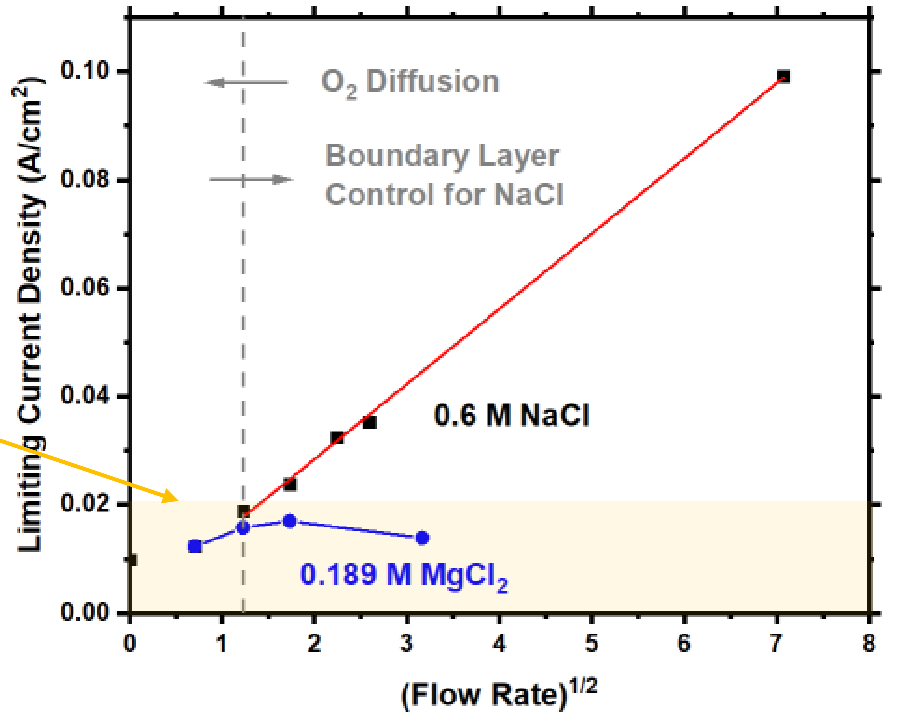
- **<u>No dependence</u>** between flow rate and limiting current density
  - No value of Q reaches the i_{lim} for expected quiescent ORR (displayed on Pt)



(b)

Activation controlled region (OCP to ~-0.5 $V_{Ag/AgCl}$)

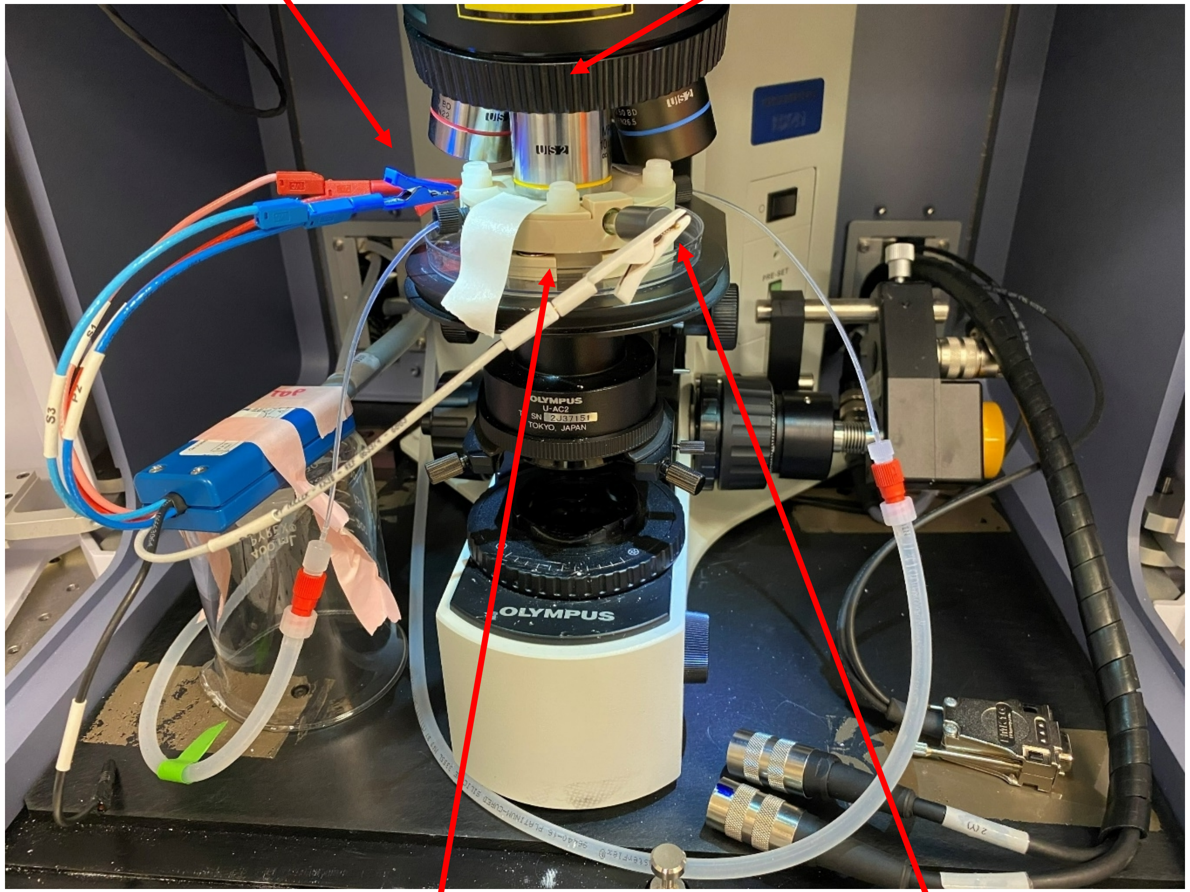
Mass transfer controlled



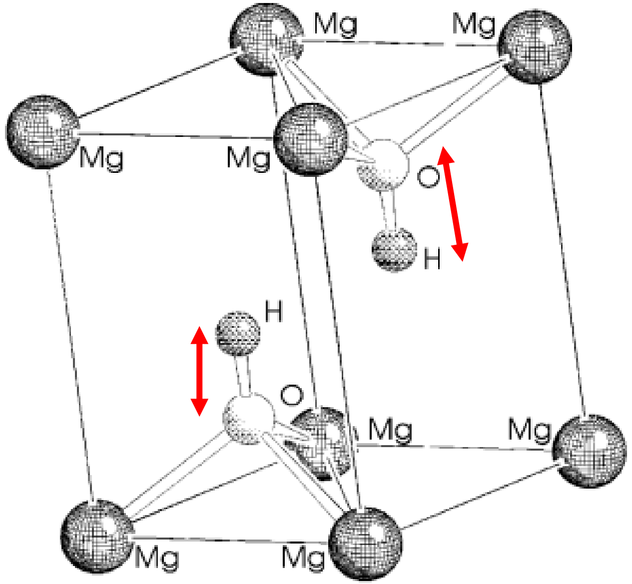
This result is consistent with RDE experiments, where boundary layer thickness could not be controlled by adjusting the rotation speed

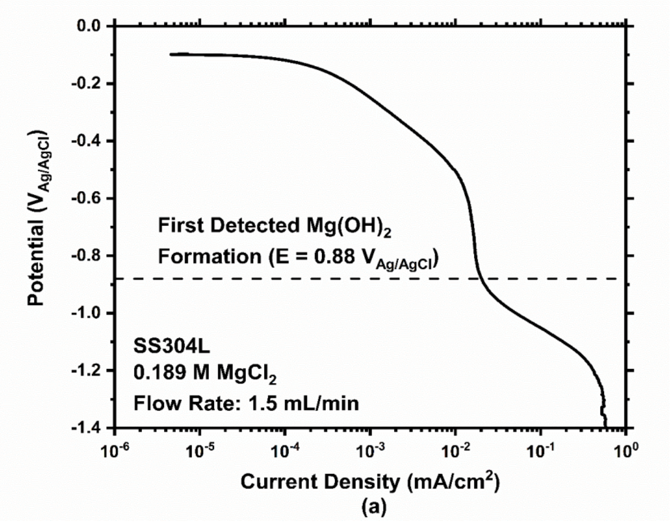
In-situ Raman Data Collection System

- *Next step: in-situ Raman analysis allows identification of phases precipitating due to cathodic reactions.*
- Confocal XploRA Plus Raman microscope
  - 532 nm Laser
    - Power = 100 mW (spectra collected at 50 % reduction)
  - 10x magnification
  - N_a = 0.25, and a 2.6 μm beam diameter.
  - Scans collected every 2-5 mins over 2800 to 4000 cm^{-1}
    - Collected for 3 s and averaged over 10 consecutive scans.
    - The laser was turned off in between scans to reduce surface heating
- Flow Rate 1.5 mL/min



In-situ Raman Analysis - 0.189 M $MgCl_2$



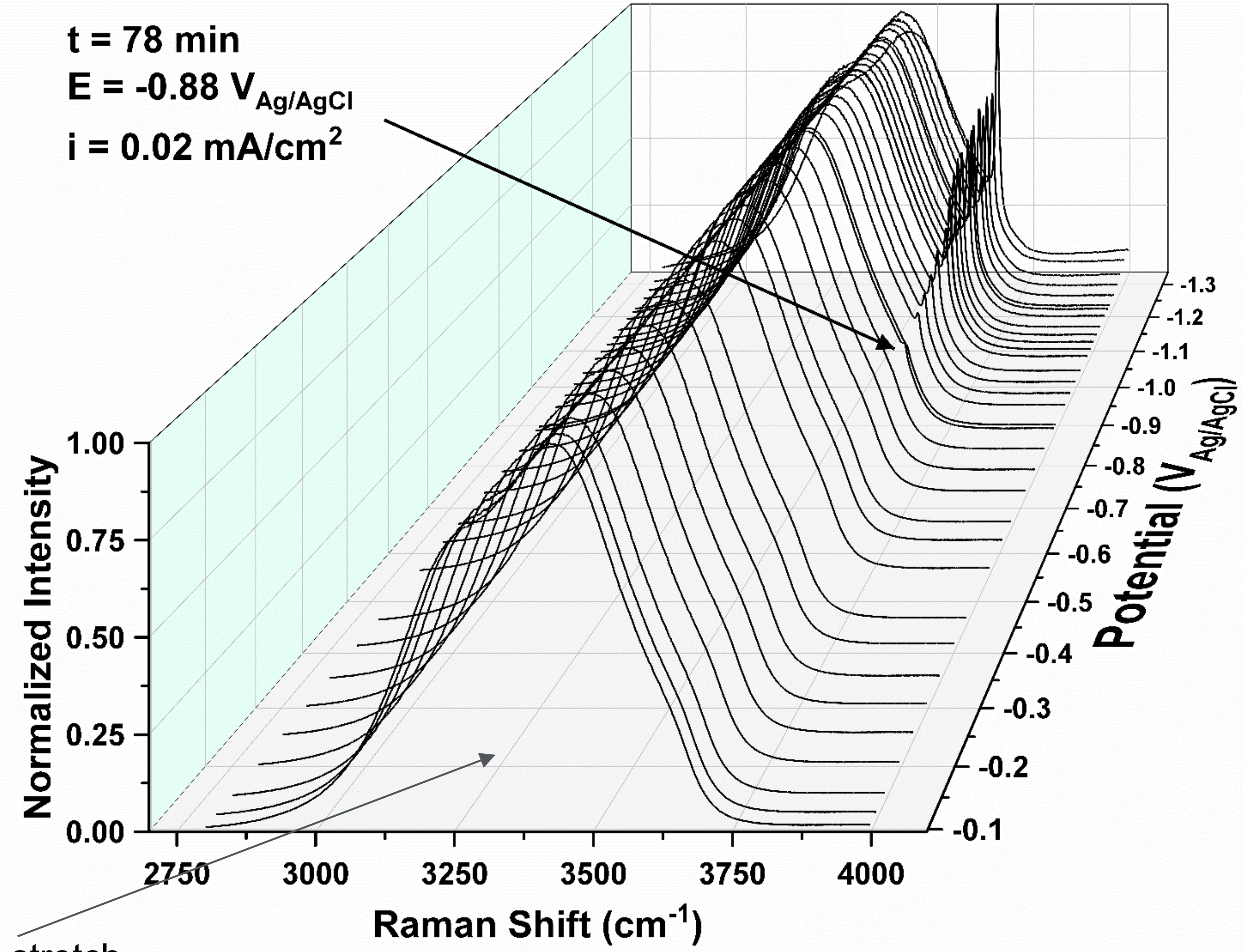


Monitored microcrystalline A_{1g} O-H stretch in $Mg(OH)_2$ stretch at 3654 cm^{-1}

t = 78 min

E = -0.88 $V_{Ag/AgCl}$

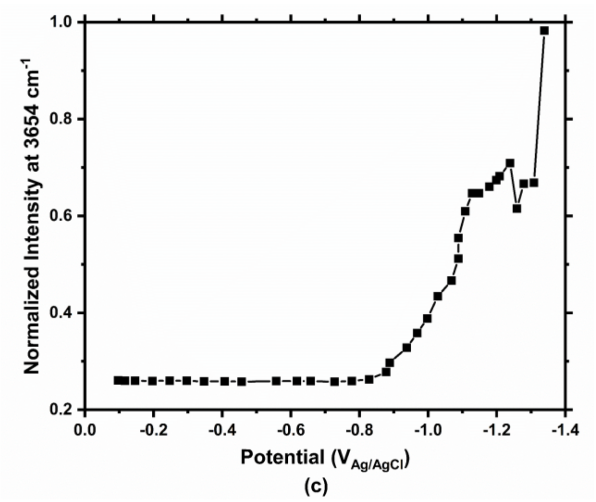
i = 0.02 mA/cm^2

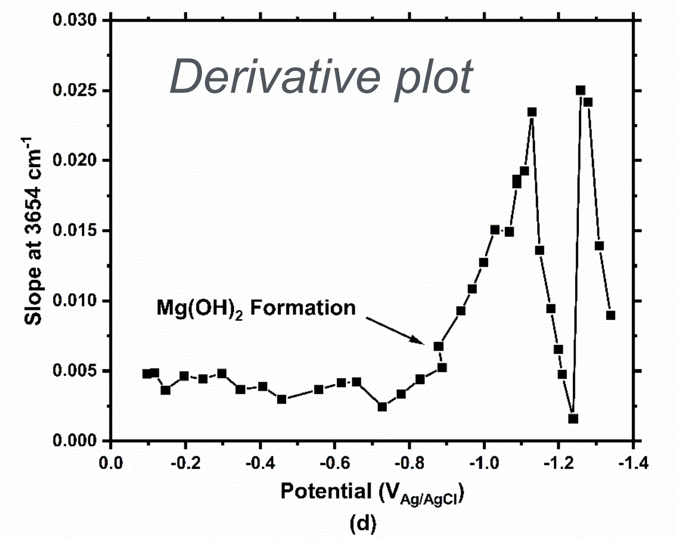


Water O-H stretch

Under what conditions does precipitation occur?

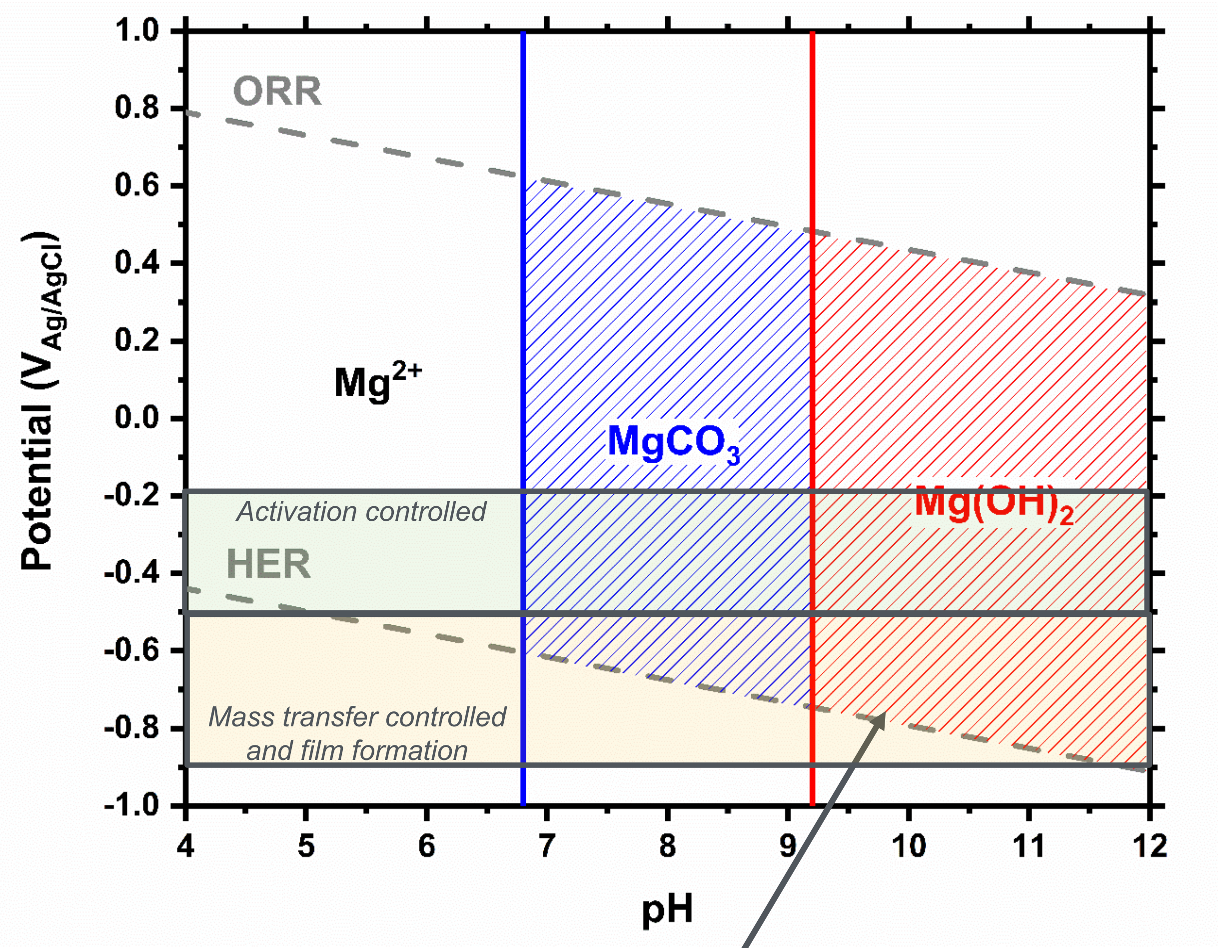
- Brucite peak grows in starting at ~-0.88 $V_{Ag/AgCl}$





No evidence of $MgCO_3$ forming (~1095 cm^{-1})

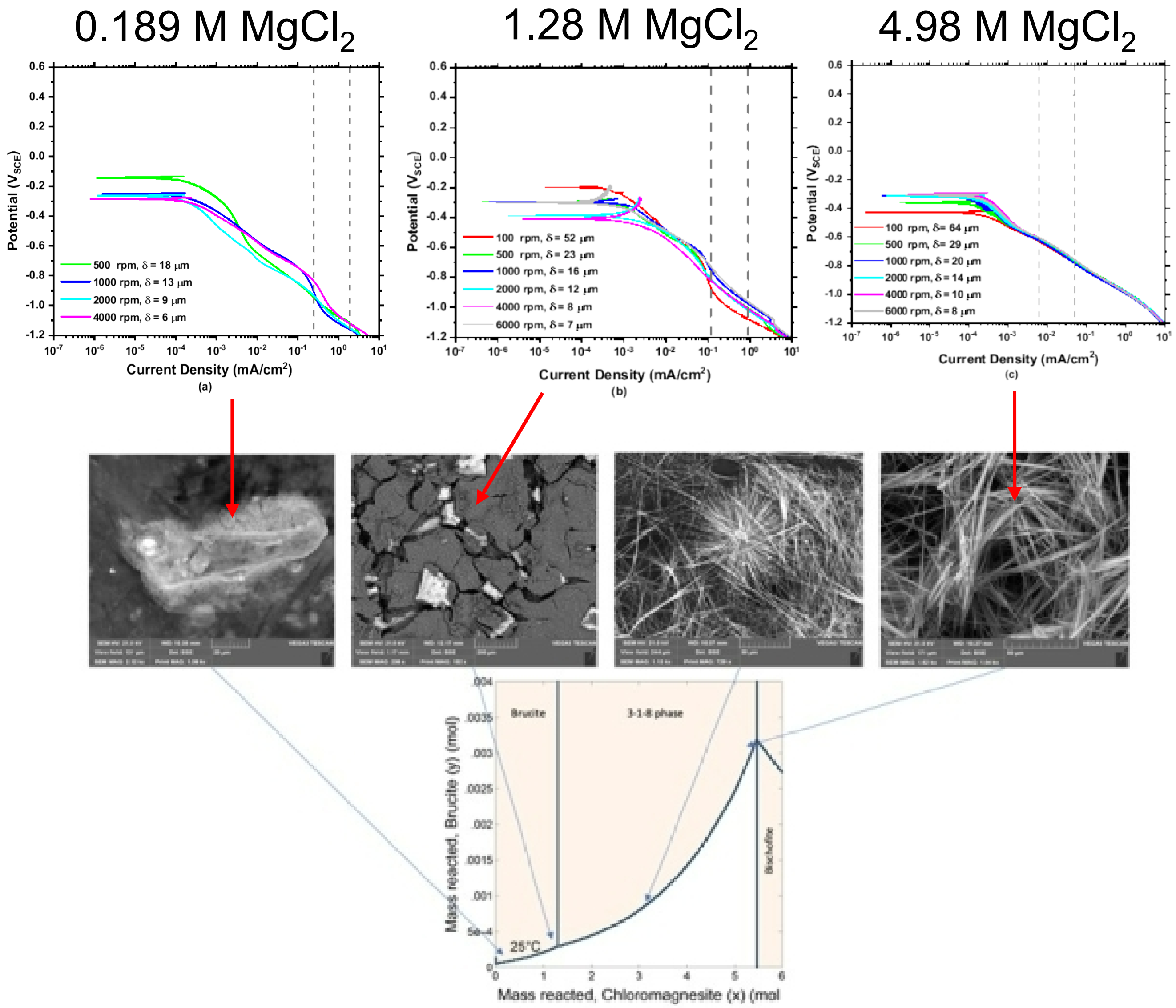
- Consistent with literature, suggesting that kinetic inhibition prevents precipitation



Brucite precipitation

Conclusions and Future Studies

- **Conclusions**
  - In-situ Raman spectroelectrochemical flow systems can be effective for for atmospheric corrosion investigations
    - 0.6 M NaCl: Requires solution regeneration to prevent O_2 deficiencies, δ is controlled by flow rate
    - 0.189 M $MgCl_2$: δ is not related to flow rate
      - Inhibited by the precipitation of Mg-hydroxide phases (brucite in this case)
- **Future work**
  - ***Incorporate effects of precipitation (reduced cathodic current and pit size; potential brine dryout) into SCC predictive models.***
    - Use in-situ Raman analyses to identify the Mg-OH-Cl phases that form as a $f([MgCl_2],T)$
    - Explore seawater solutions to identify precipitating phase formation as f(RH,T)



Questions?

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