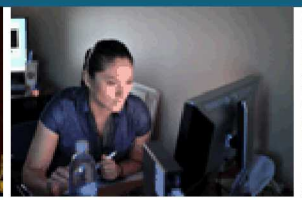
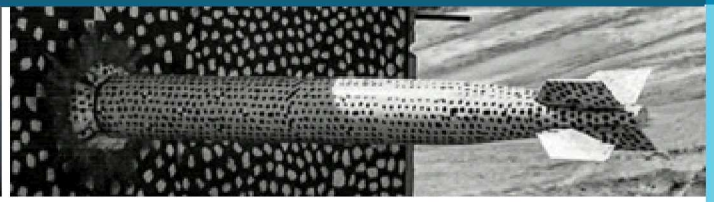
SAND2020-9741C

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





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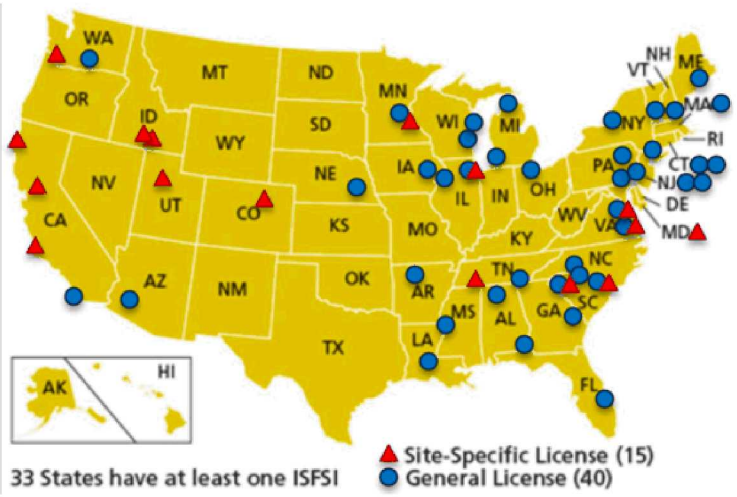
SAND 2020-xxxx

Factors the Affect Risk of SCC on Spent Nuclear Fuel Canisters

Spent nuclear fuel is currently stored in welded stainless steel canisters across the country at ISFSIs

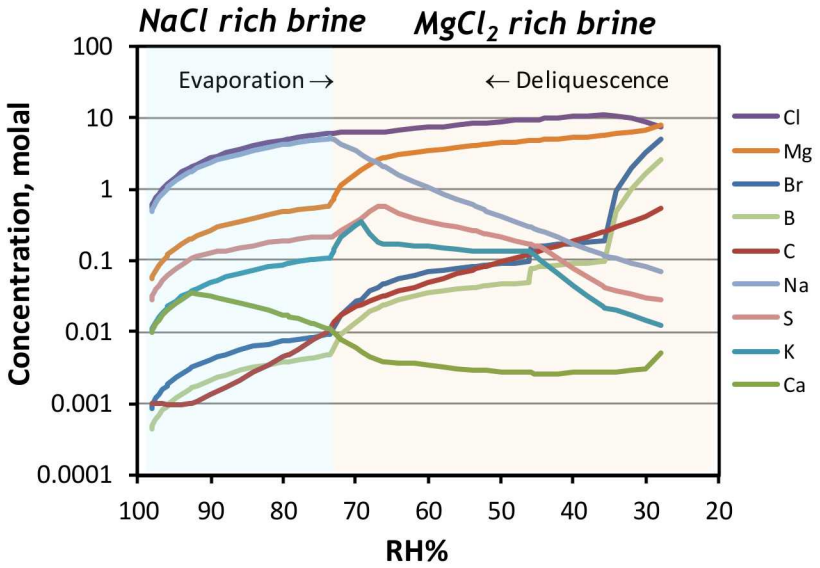
In near-marine applications, deposition of aggressive (commonly chloride-containing) sea salt aerosols is possible

- As canisters cool, deliquescence of sea salts can form a corrosive brine
- Criteria are met for the risk of chloride induced stress corrosion cracking

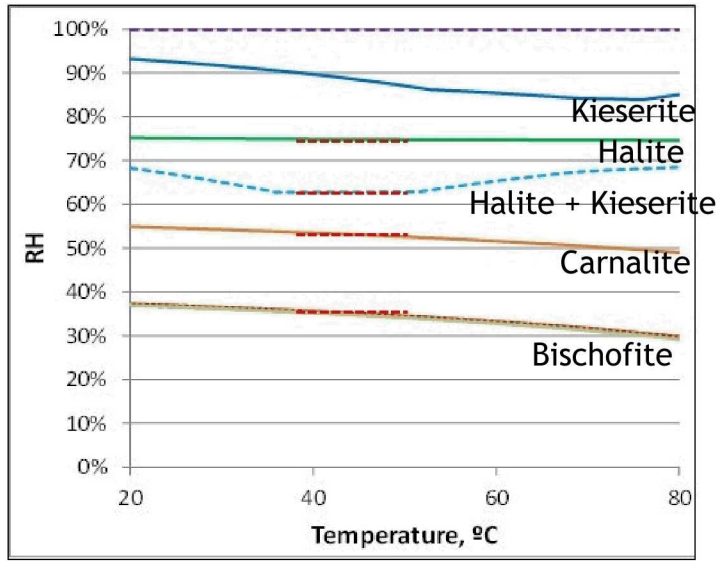


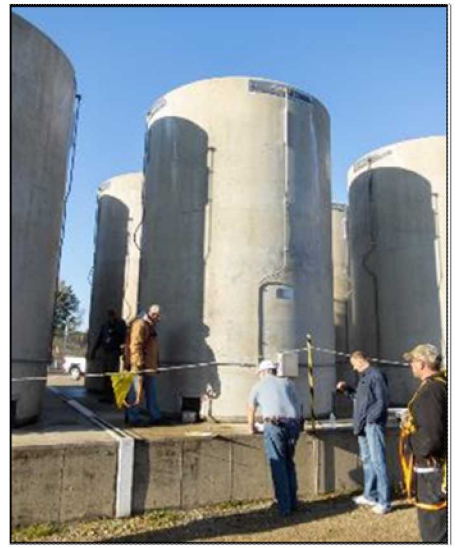
ISFSI locations

Sea Salt Brine Evolution



Deliquescent Sea Salts



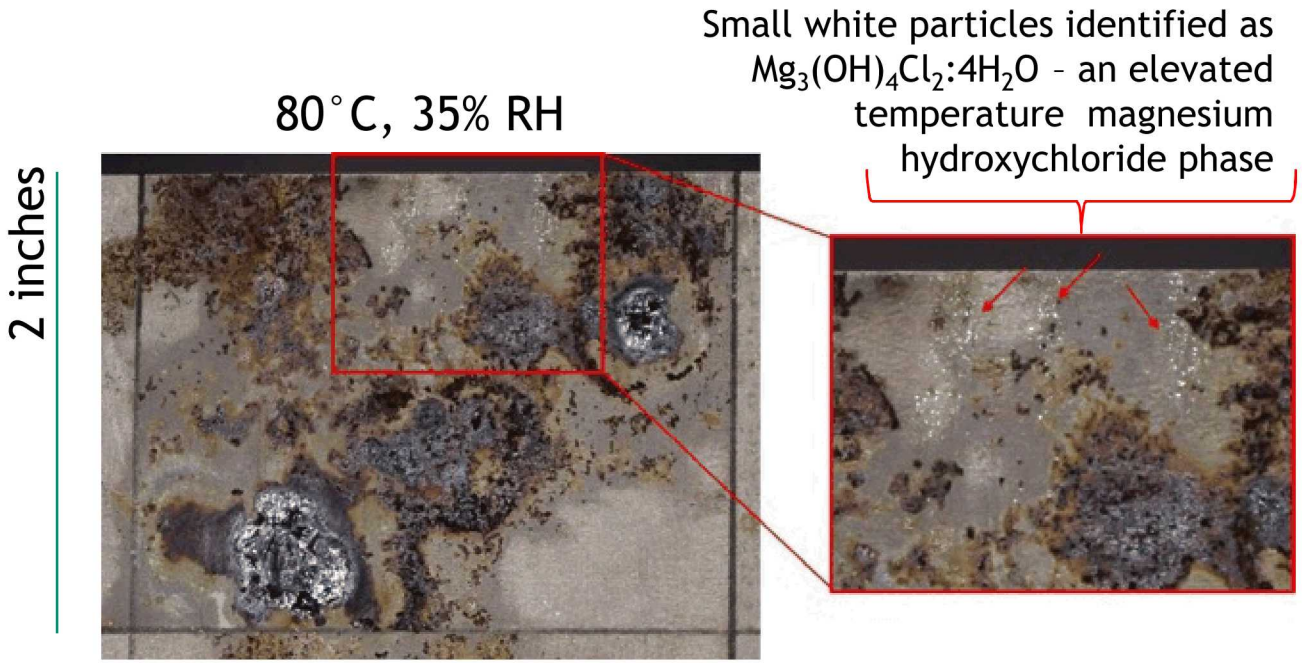


Brine Stability and Reactions

Temperature and Relative Humidity dictate which salts deliquesce

Brines can react to form less deliquescent salts

- Leads to brine dry-out under deliquescent conditions



Brine Stability and Reactions

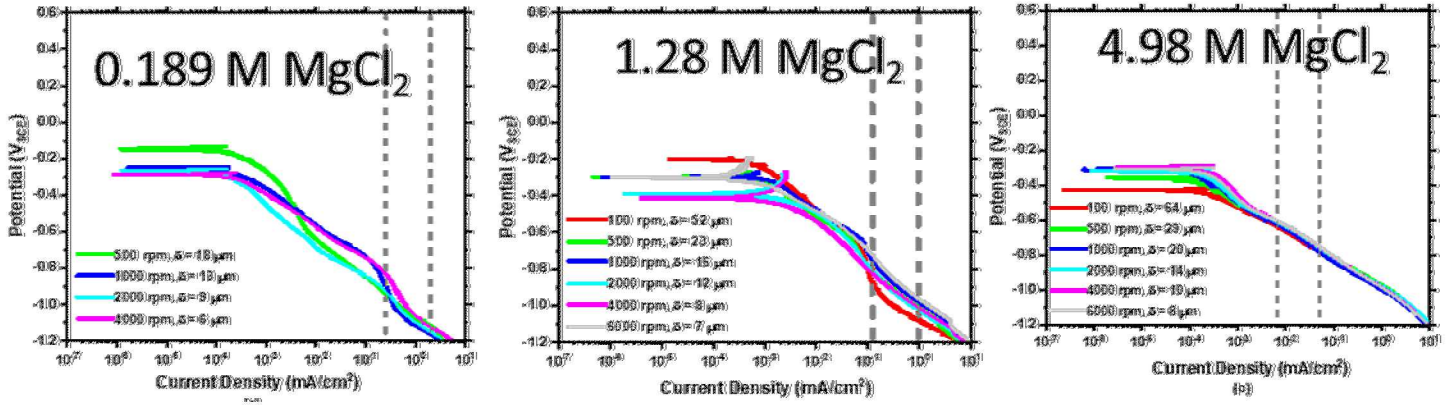
Temperature and Relative Humidity dictate which salts deliquesce

Brines can react to form less deliquescent salts

- Leads to brine dry-out under deliquescent conditions

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

R.M. Katona et al., Corros. Sci. 177 (2020) 108935.

How can we Identify Mg-precipitated films in-situ?

Objective

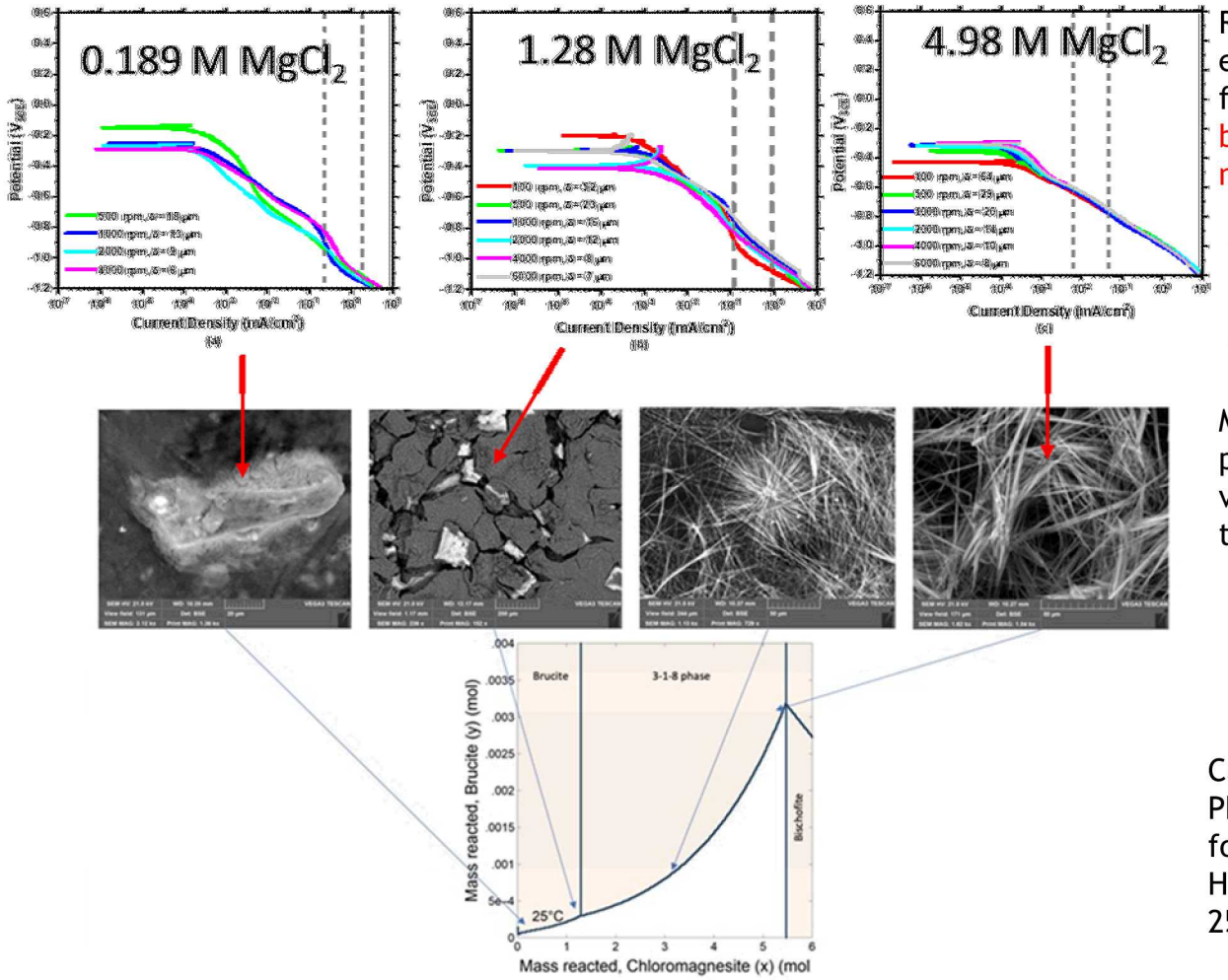
- Determine why cathodic scans of MgCl brines on SS experience abnormal behavior by establishing the conditions where specific Mg-films precipitate

Why?

- The identity of the Mg-film controls the brine stability as well as the electrochemistry, and therefore plays an important role in understanding the corrosion of SS in the presence of $MgCl_2$ – rich brines (including seawater)

In-situ Raman

- We hypothesize that collecting Raman measurements during the cathodic scan, will allow for us to simulate atmospheric environments and identify the films that forms on the surface in-situ
  - What is the effect of flow rate?



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

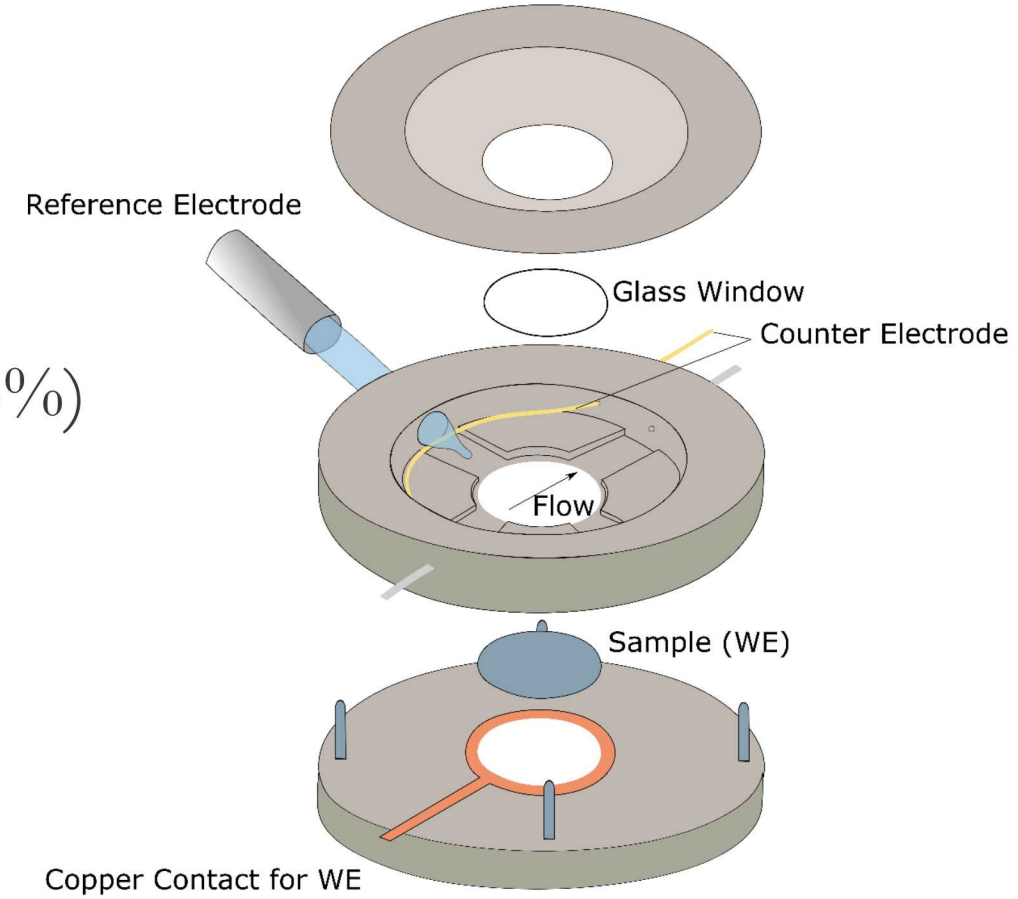
Flow experiments allow for us to mimic RDE measurements while maintaining the ability to probe the precipitating film directly

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

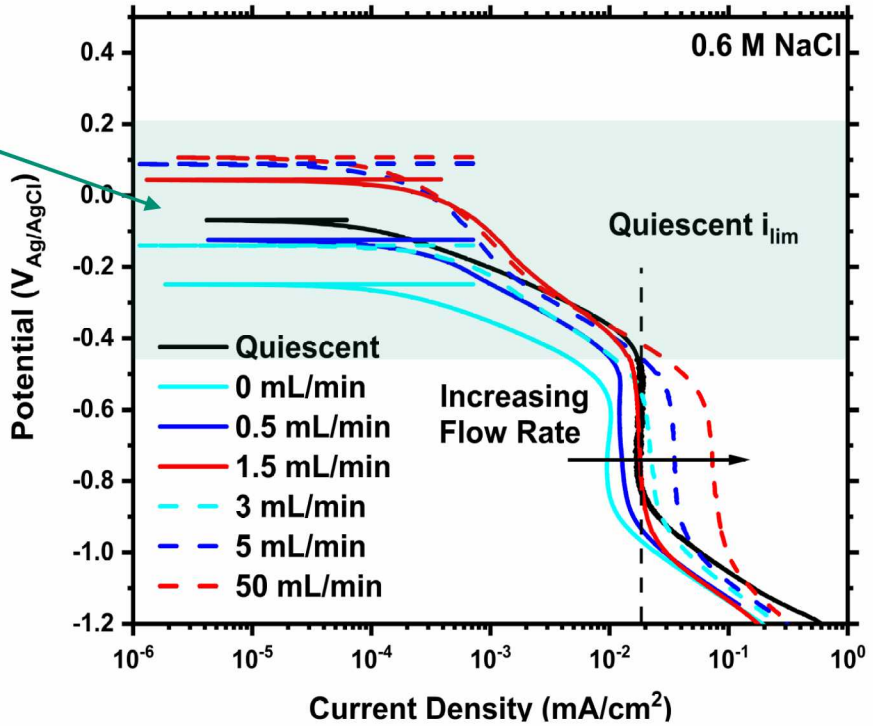


Flow-through Raman Cell

Flow and O_2 Depletion – 0.6 M NaCl

As flow rate (Q) increases, the limiting current density increases

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

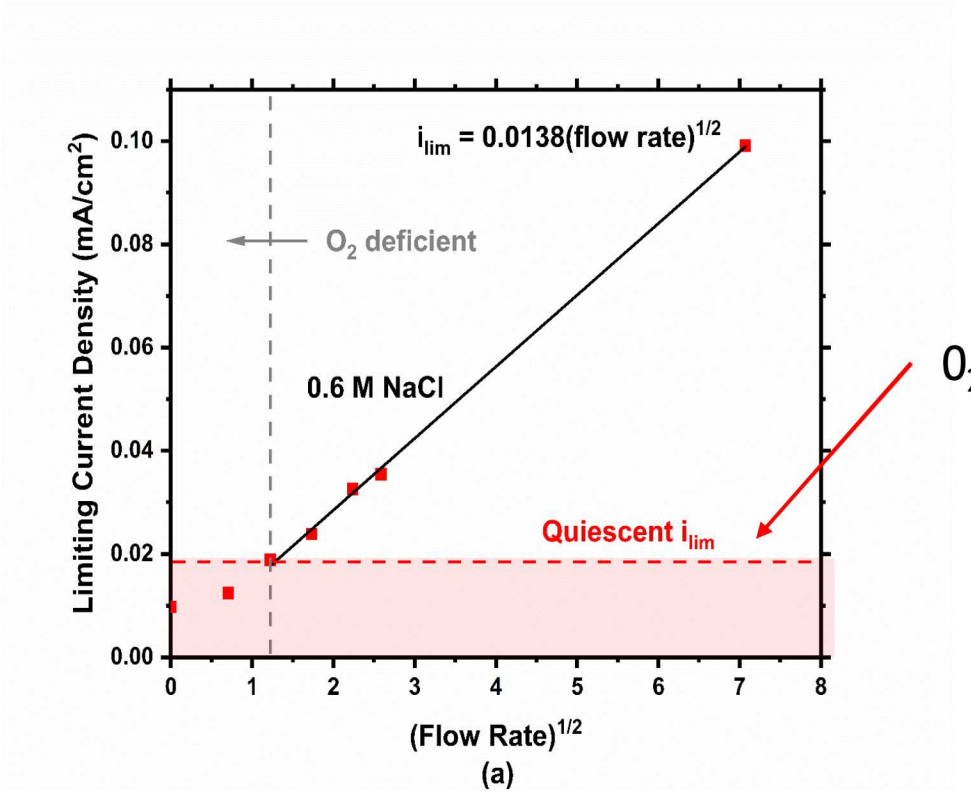


Flow and O_2 Depletion – 0.6 M NaCl

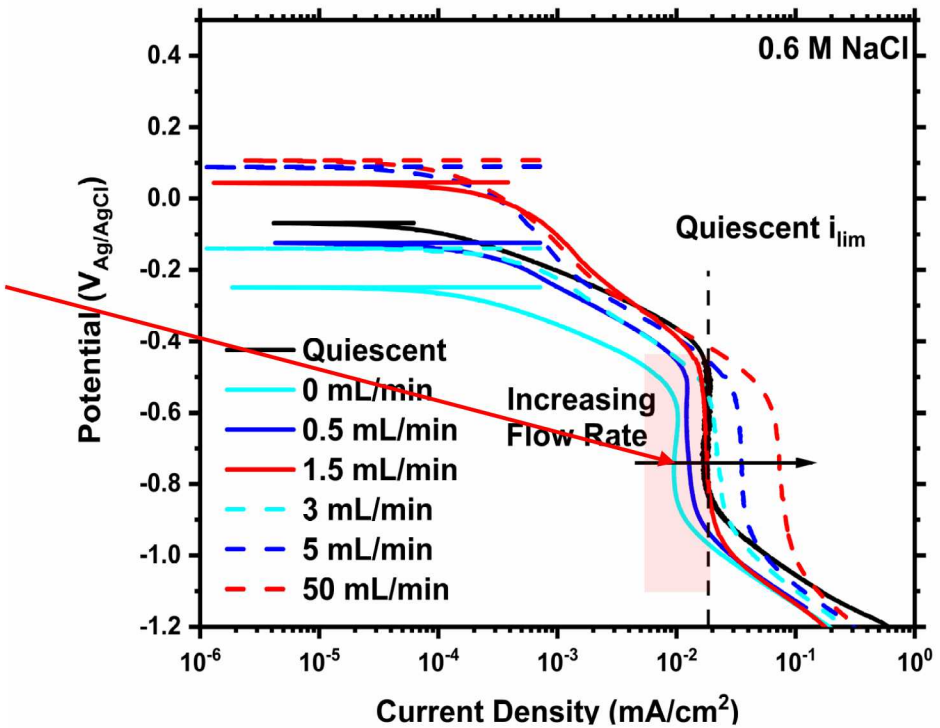
- As flow rate (Q) increases, the limiting current density increases
  - Q < 1.5 mL/min: i_{lim} flow < i_{lim} for a quiescent

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

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

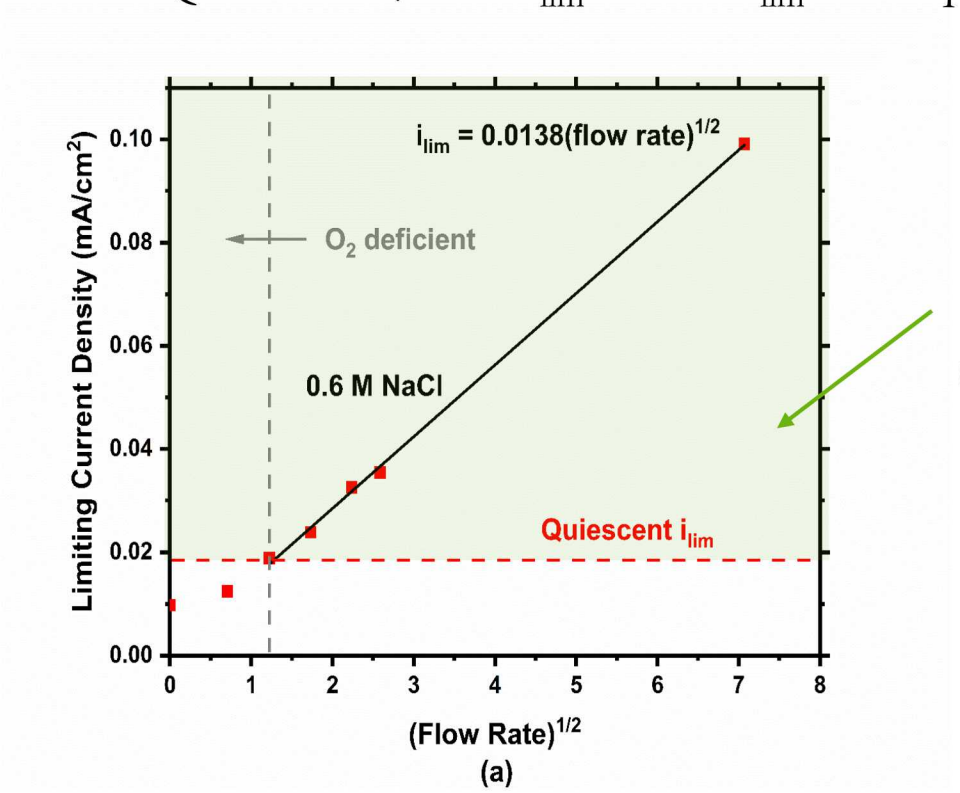


0_2 deficient region

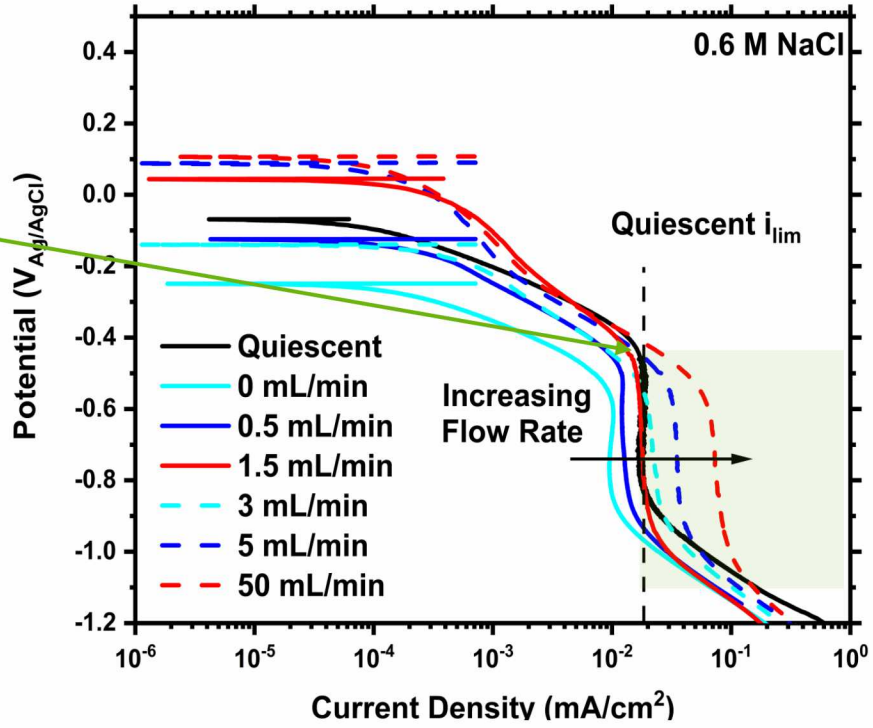


Flow and O_2 Depletion – 0.6 M NaCl

- 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
- 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 $V_{Ag/AgCl}$)

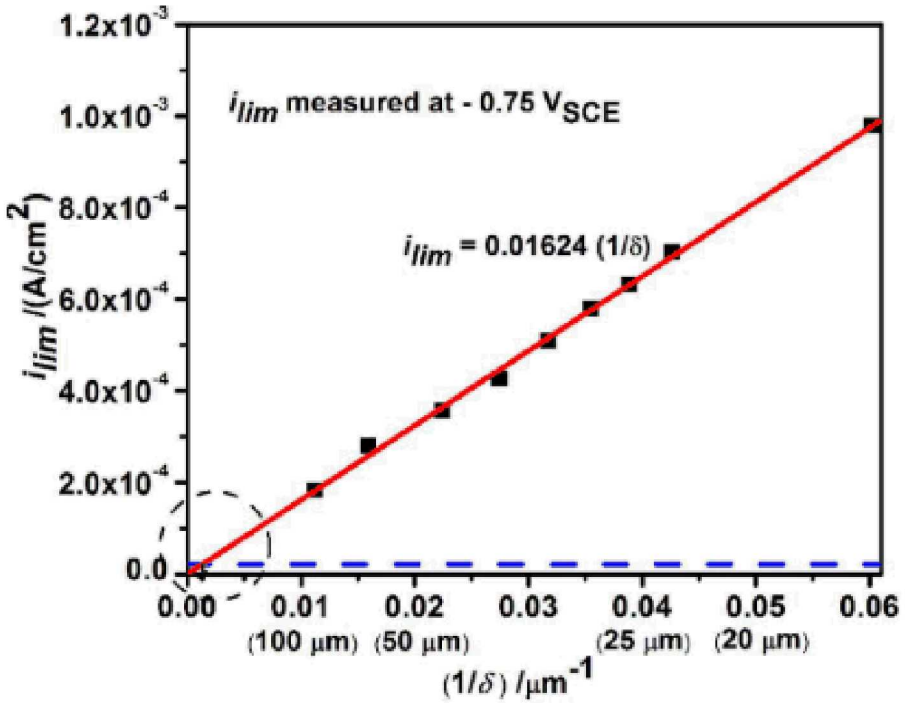


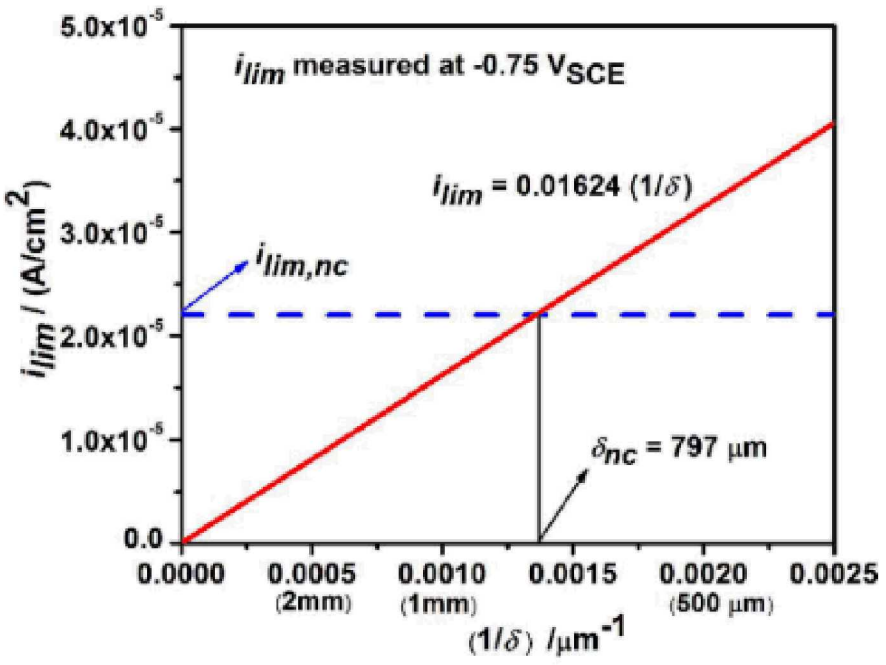
This result demonstrates that flow rate determines O_2 concentration, and solution regeneration is required to prevent O_2 deficiencies. Also, like RDE experiments, flow rate is proportional to the limiting current density

i_{lim} and Estimation of Boundary Layer Thickness

Previous RDE studies demonstrated Levich behavior in 0.6 M NaCl, where

$$i_{lim} = \frac{nFD(C_{\text{bulk}} - C_{\text{surface}})}{\delta}$$





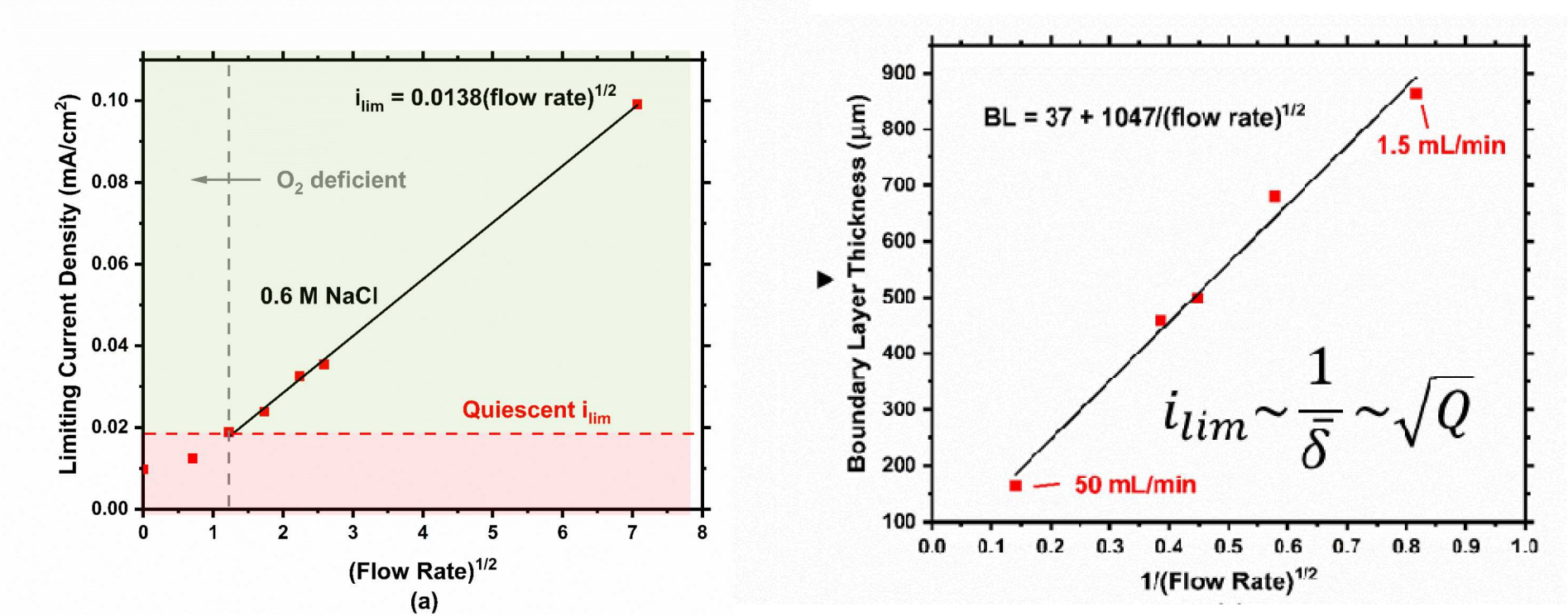
C. Liu, J. Srinivasan, R.G. Kelly, E. J. Electrochem. Soc. 164 (2017) C845-C855.

i_{lim} and Estimation of Boundary Layer Thickness

0.6 M NaCl:

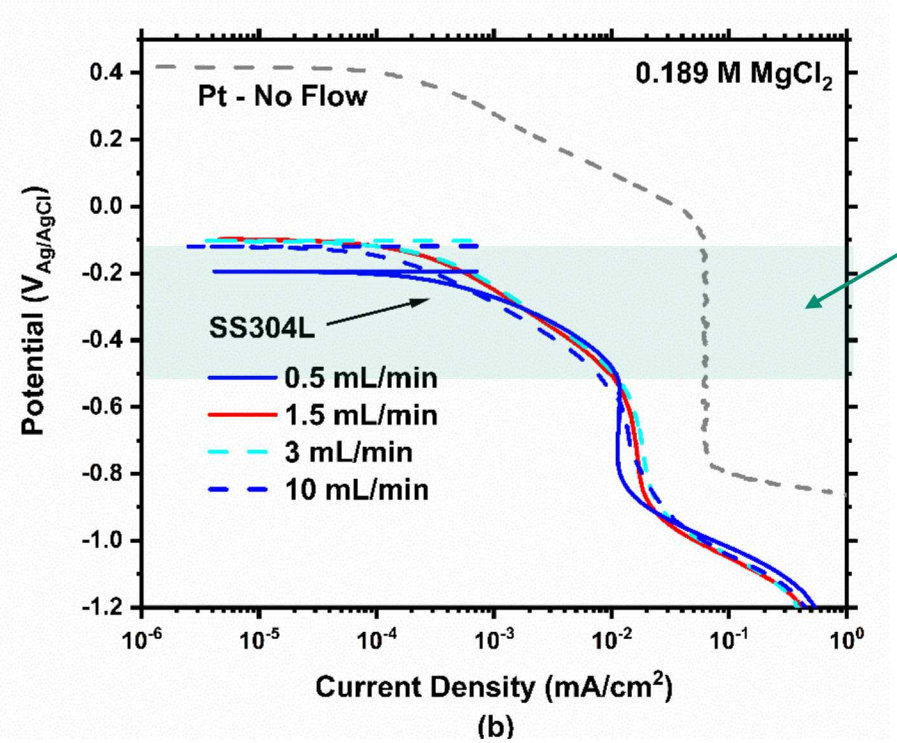
i_{lim} vs $\sqrt{flow\ rate}$ is linear

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 $MgCl_2$

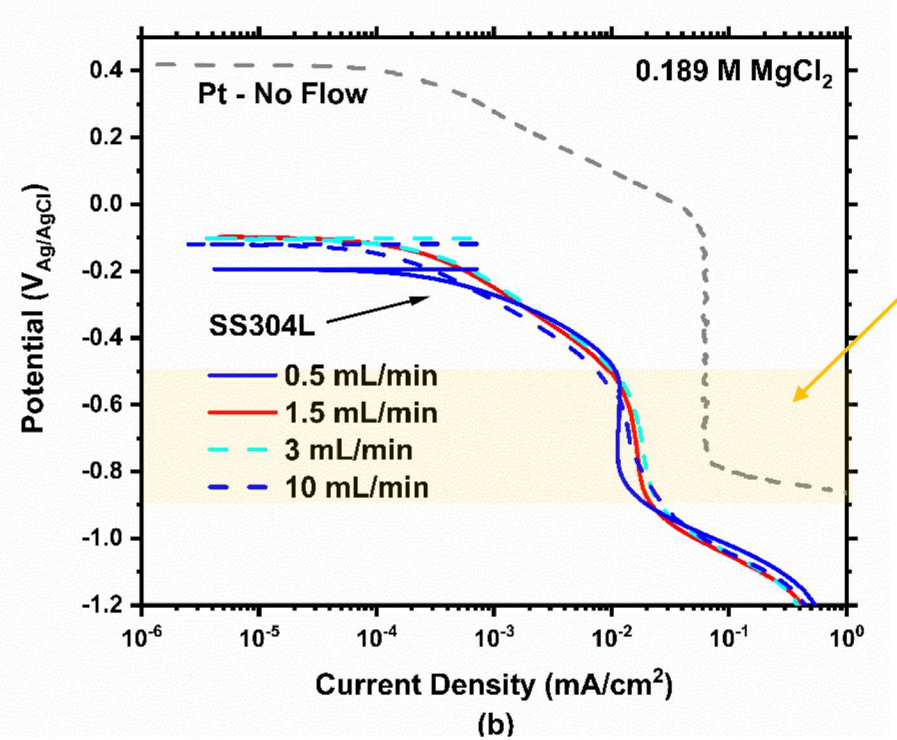


Activation controlled region (OCP to ~0.5 $V_{Ag/AgCl}$)

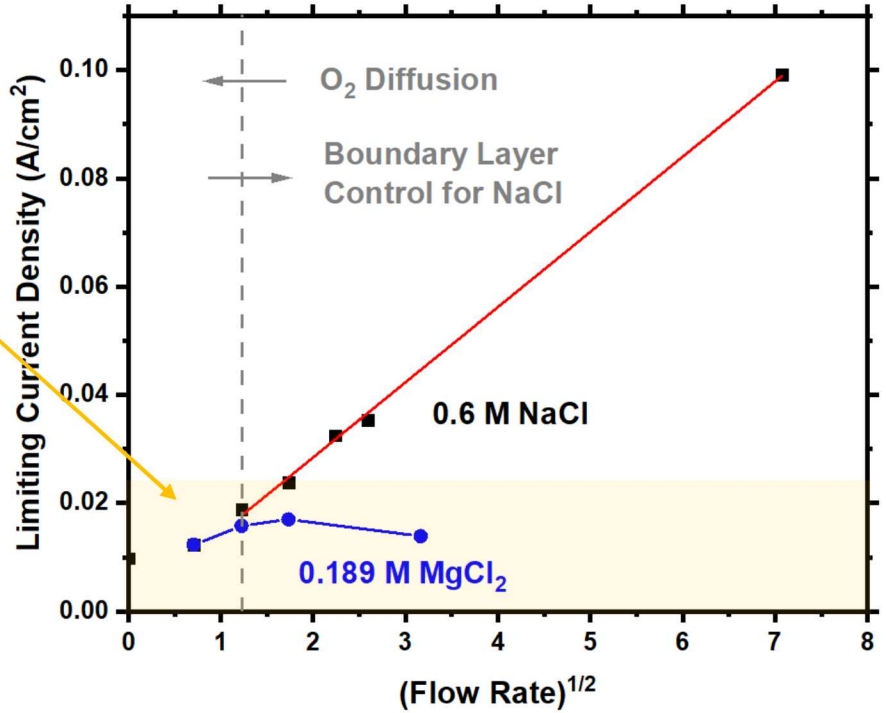
Flow and O_2 Depletion – 0.189 M $MgCl_2$

No dependence between flow rate and limiting current density

- No value of Q reaches the i_{lim} for expected quiescent ORR (displayed on Pt)



Mass transfer controlled



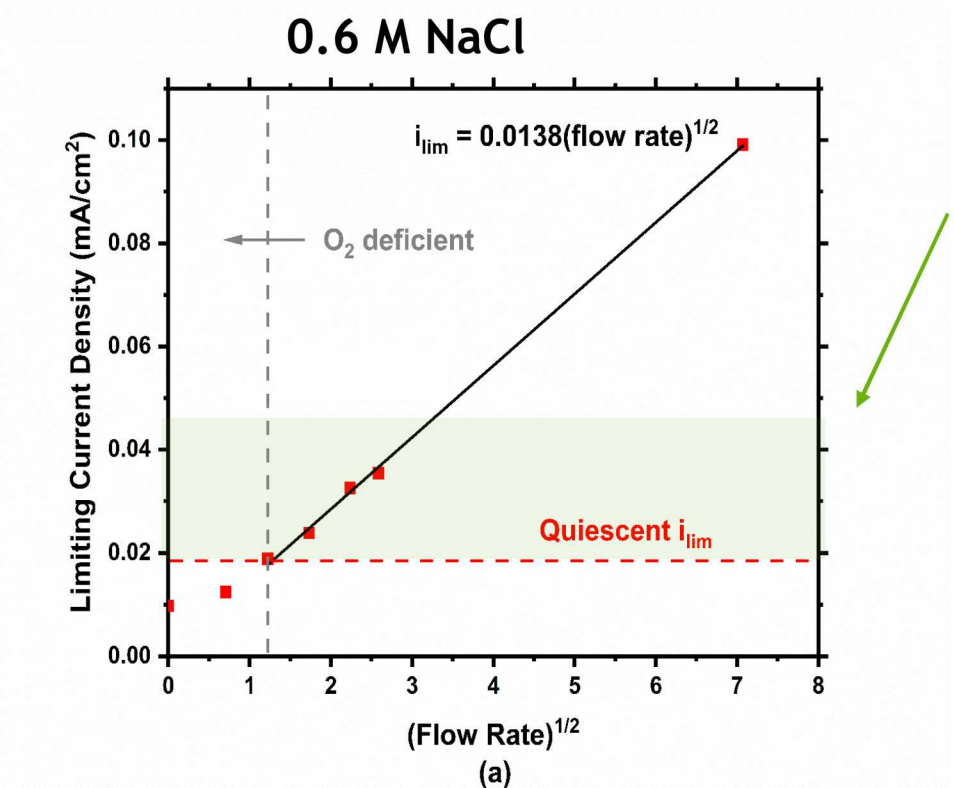
This result is consistent with RDE experiments, where boundary layer thickness could not be controlled by adjusting the rotation speed (R.M. Katona et al., Corros. Sci. 177 (2020) 108935).

Flow and O_2 Depletion

In 0.6 M NaCl:

As flow rate increases, the i_{lim} 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
- Q > 1.5 mL/min: i_{lim} flow > i_{lim} for a quiescent

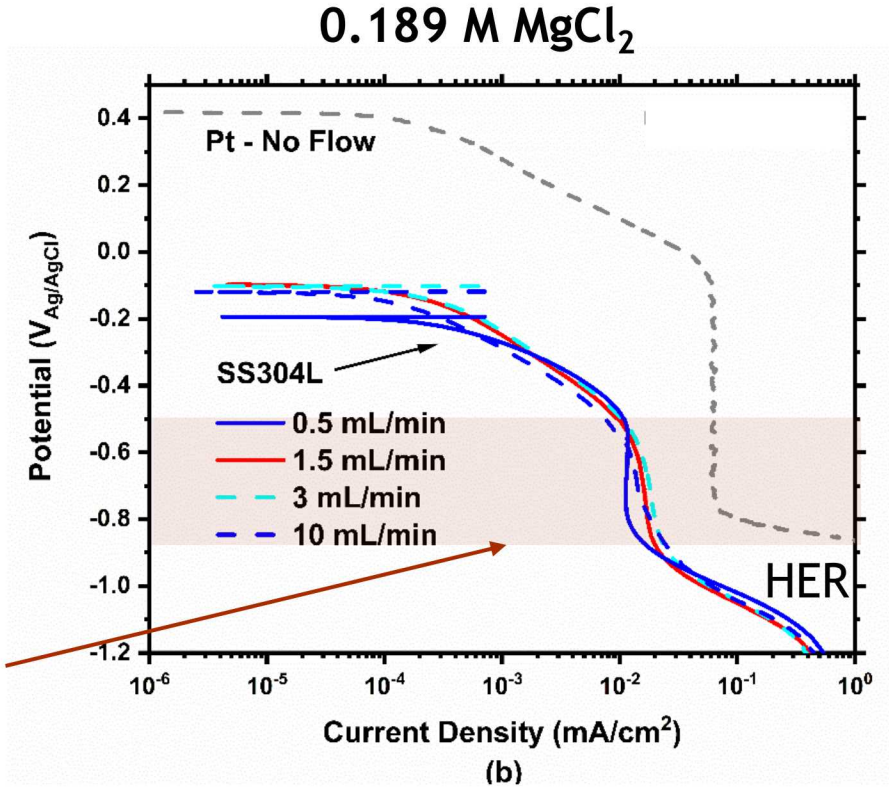


Mass transfer controlled region (~ 0.5 - 0.9 $V_{Ag/AgCl}$)

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

In 0.189 M $MgCl_2$:

No dependence between flow rate and i_{lim}



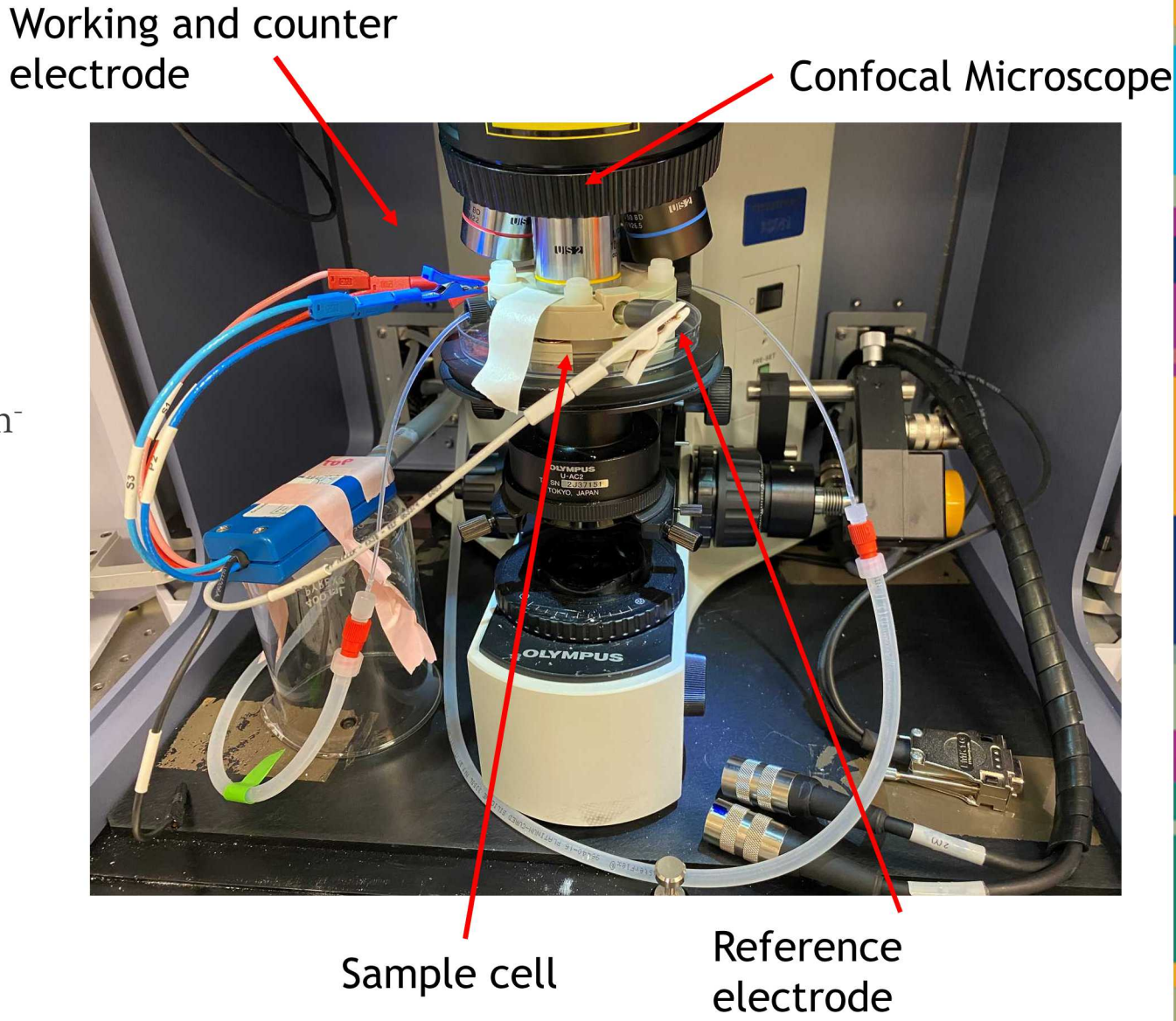
In-situ Raman Collection

Confocal XploRA Plus Raman microscope

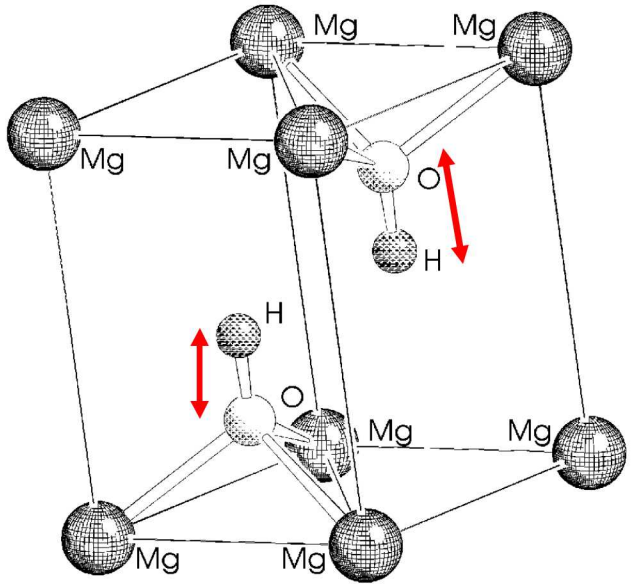
- 532 nm Laser
- Power = 100 mW (spectra collected at 50 % reduction)
- 10x magnification
- N_a = 0.25, and a 2.6 μm beam diameter.
- Scans collected every 2-5 mins over 2800 to 4000 cm^{-1}
  - Collected for 3 s and averaged over 10 consecutive scans.
  - The laser was turned off in between scans to reduce surface heating

Flow Rate 1.5 mL/min

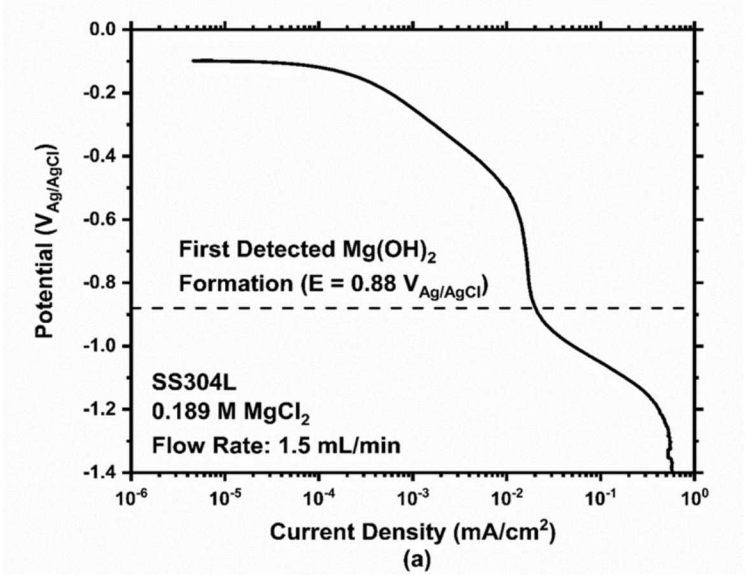
Monitored ingrowth of the $Mg\text{-}OH_{brucite}$ stretch at 3654 cm^{-1}



In-situ Raman Analysis - 0.189 M $MgCl_2$



Zigan F, Rothbauer R (1967) Neues Jahr Mineral 137 143

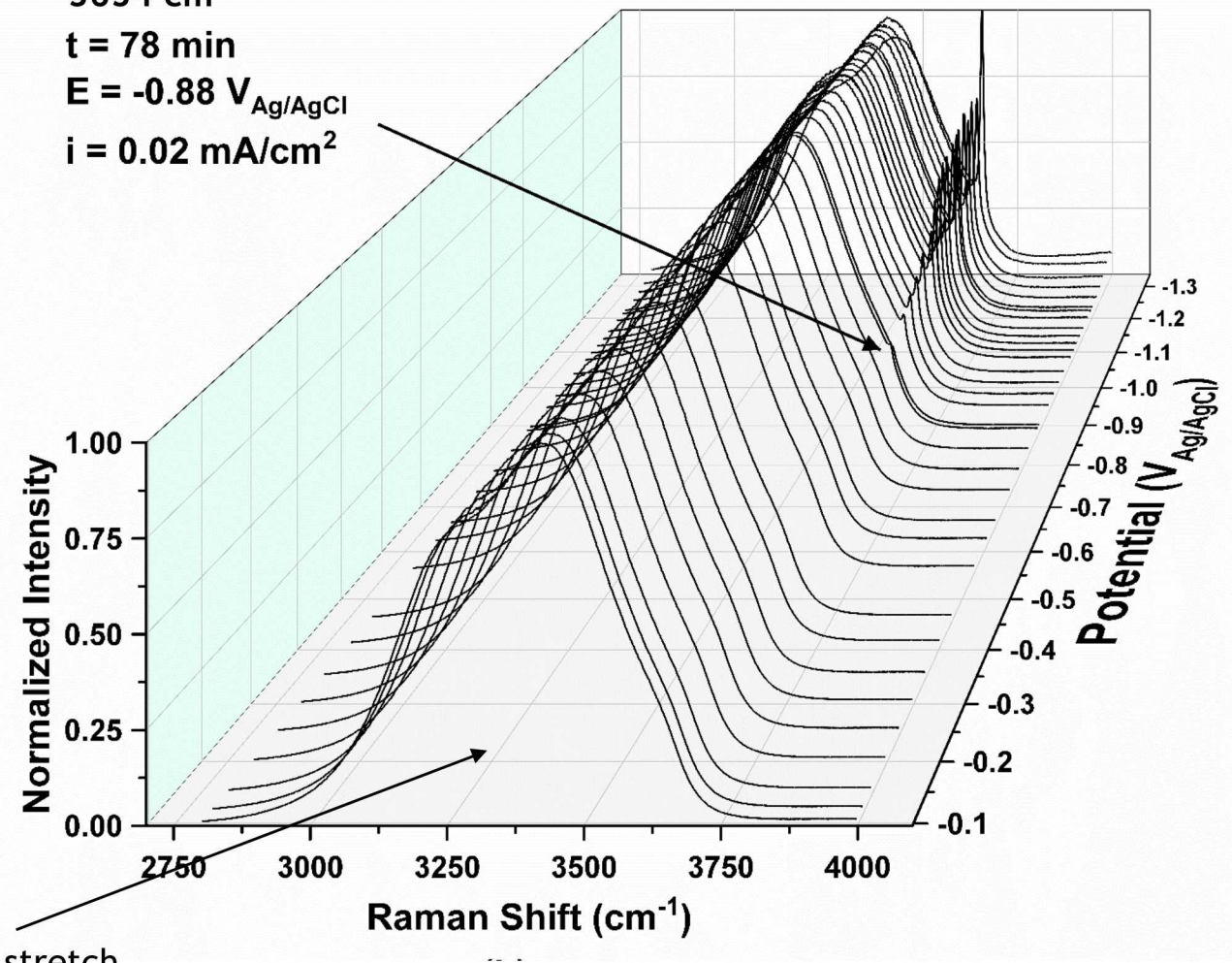


Microcrystalline A_{1g} O-H stretch in $Mg(OH)_2$ stretch at 3654 cm^{-1}

t = 78 min

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

i = 0.02 mA/cm^2



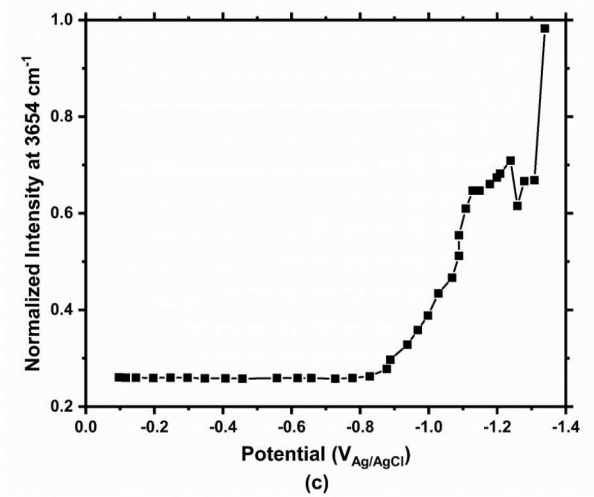
Water O-H stretch

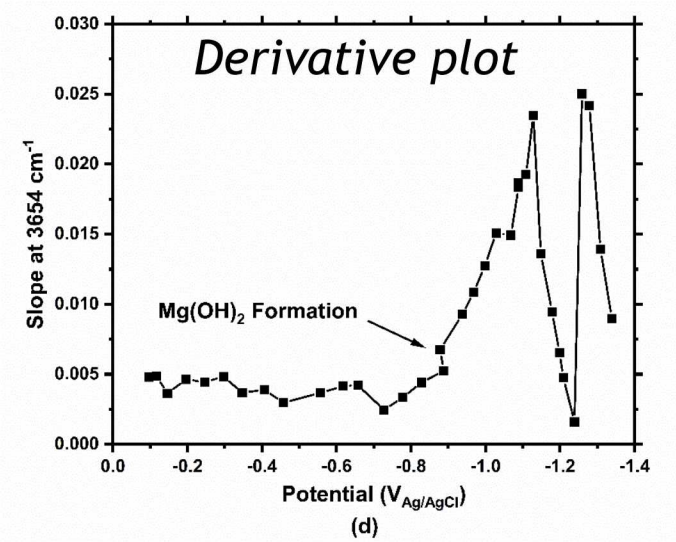
Under what conditions does precipitation occur?

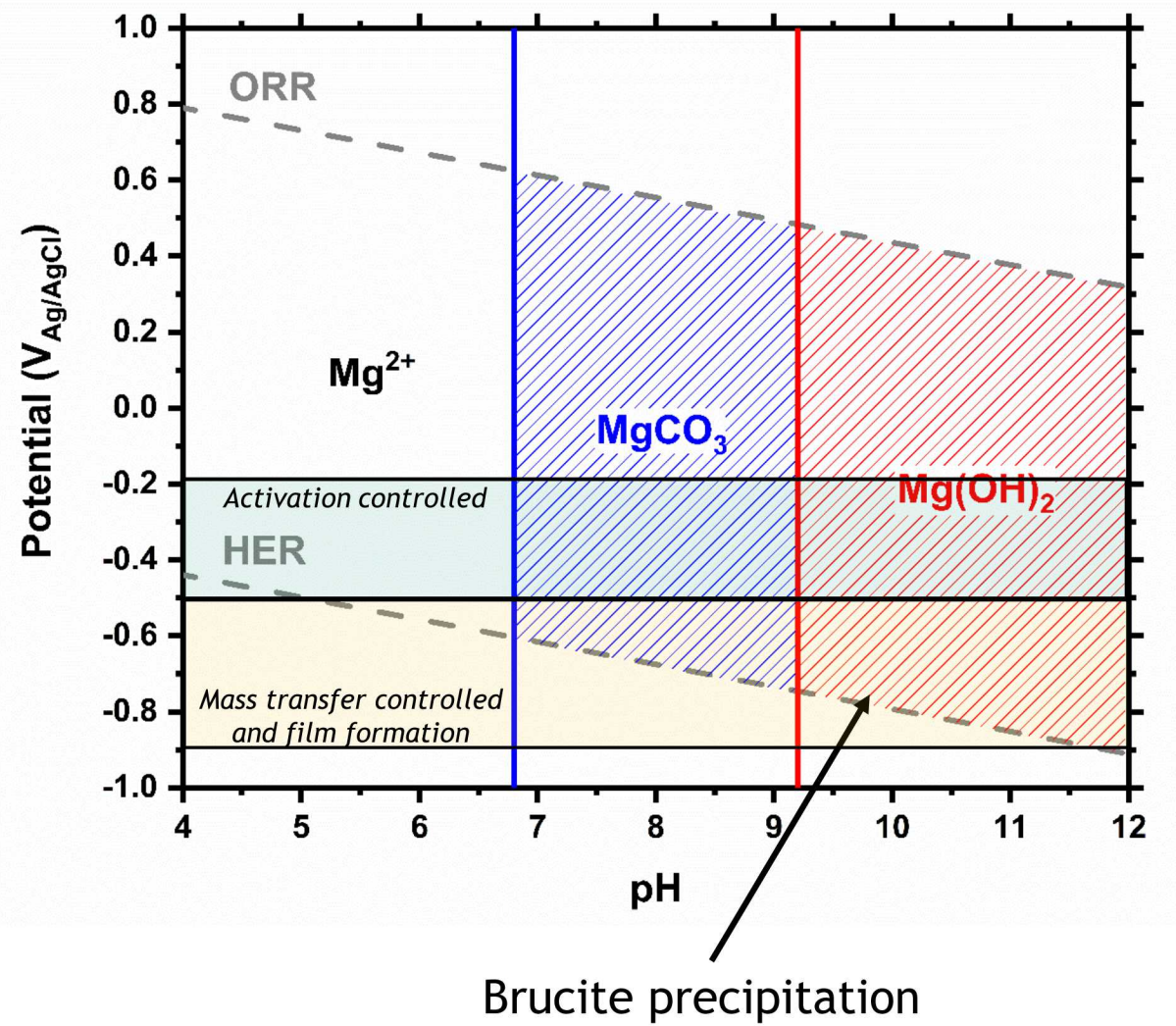
Brucite peak grows in starting at ~0.88 $V_{Ag/AgCl}$

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

- Consistent with literature, suggesting that kinetic inhibition prevents precipitation







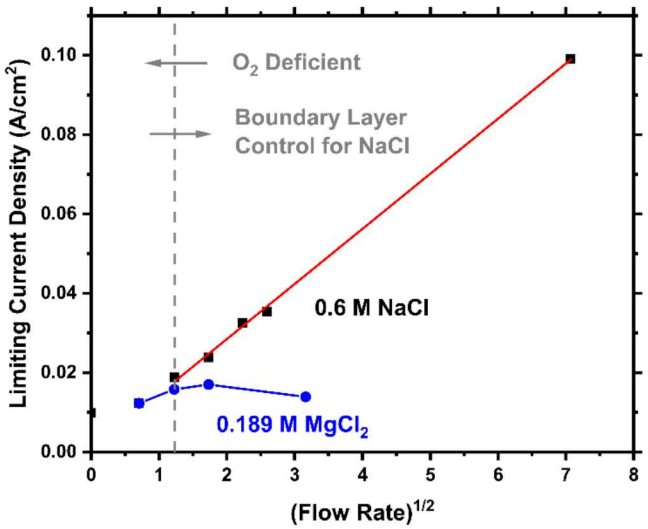
Summary and Conclusions

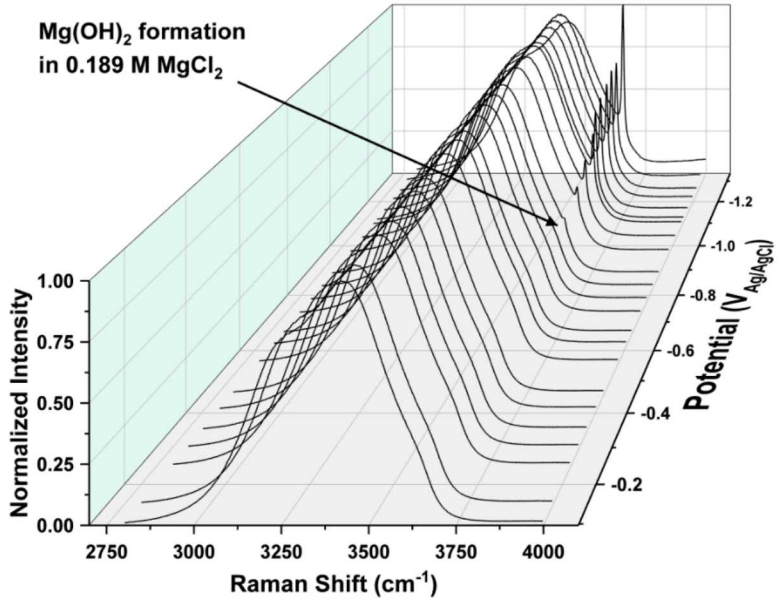
In-situ spectroelectrochemical systems, consisting of coupled Raman flow cells and cathodic potential scans, can be effective for for atmospheric corrosion investigations

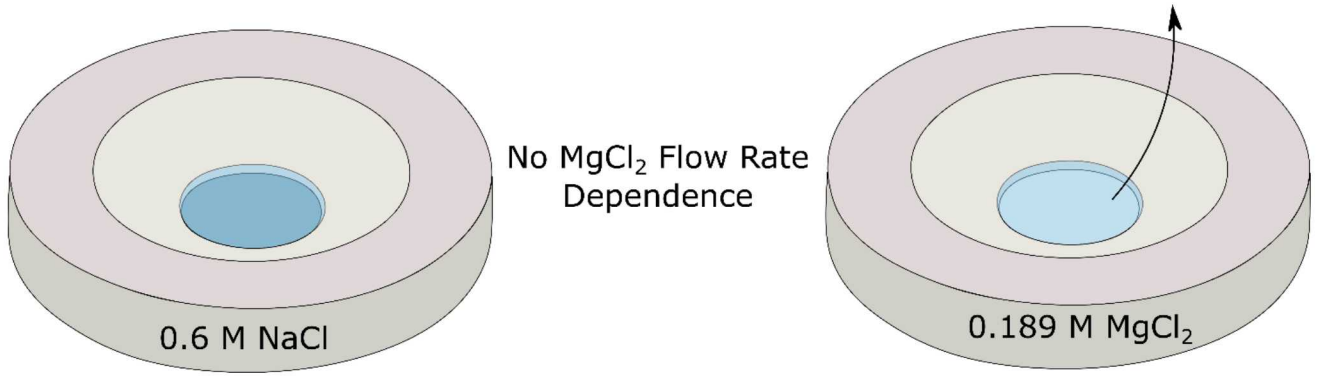
0.6 M NaCl: Solution regeneration is required to prevent oxygen deficiencies, boundary layer thickness is controlled by solution flow rate

0.189 M $MgCl_2$: boundary layer thickness is not related to flow rate

- Inhibited by the precipitation of Mg-hydroxide phases (brucite in this case)



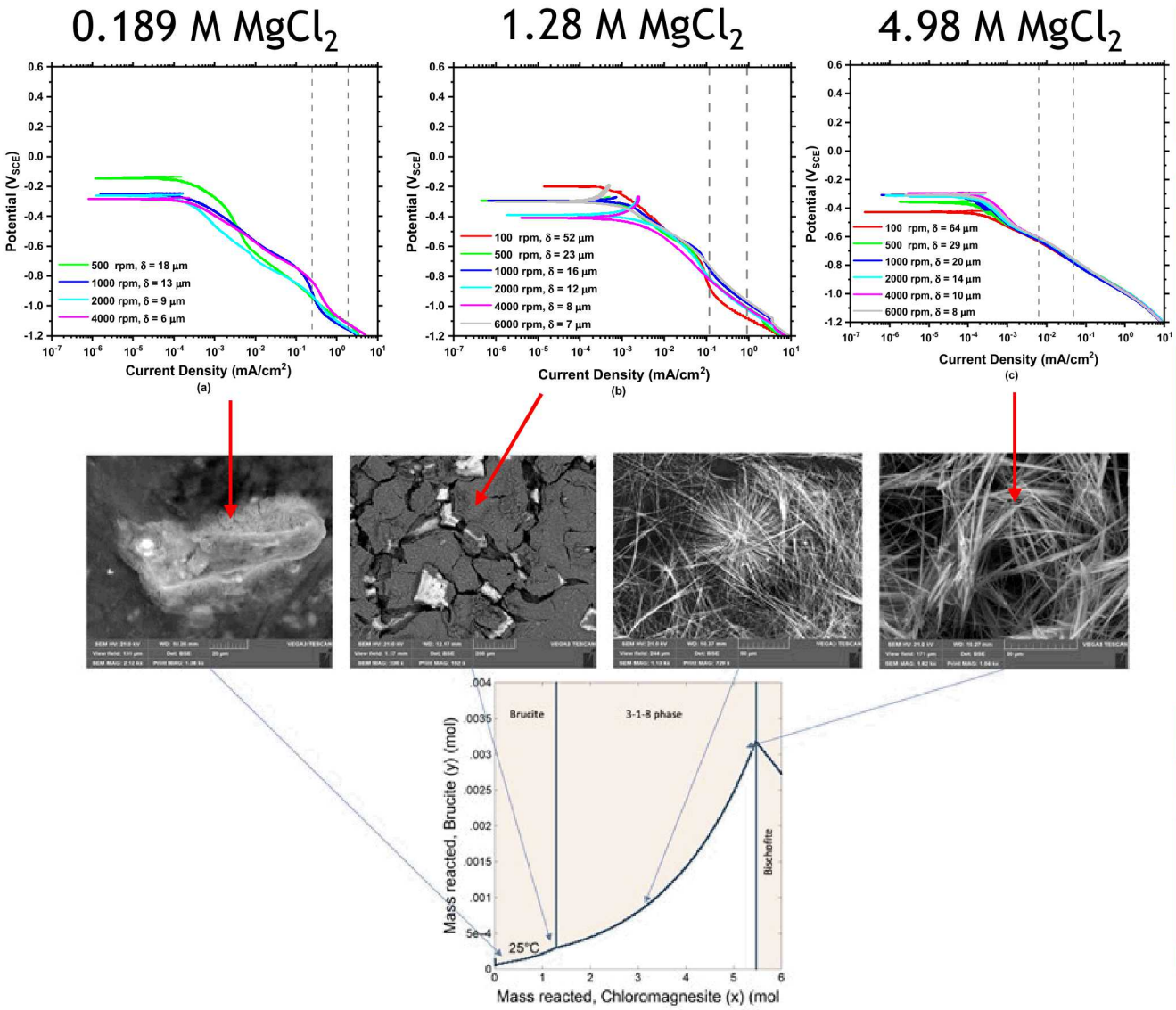




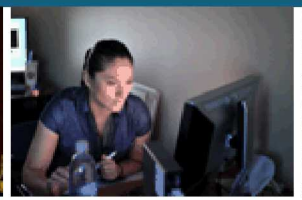
Future work

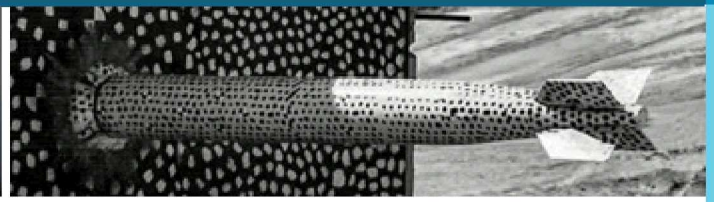
Use in-situ Raman analyses to identify the Mg-OH-Cl phases that form as a function of [$MgCl_2$] and temperature

Explore seawater solutions to identify thin film phase formation as a function of relative humidity and temperature



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





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