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Determination of Key Marine Environment Effects on Maximum Pit Size Predictions

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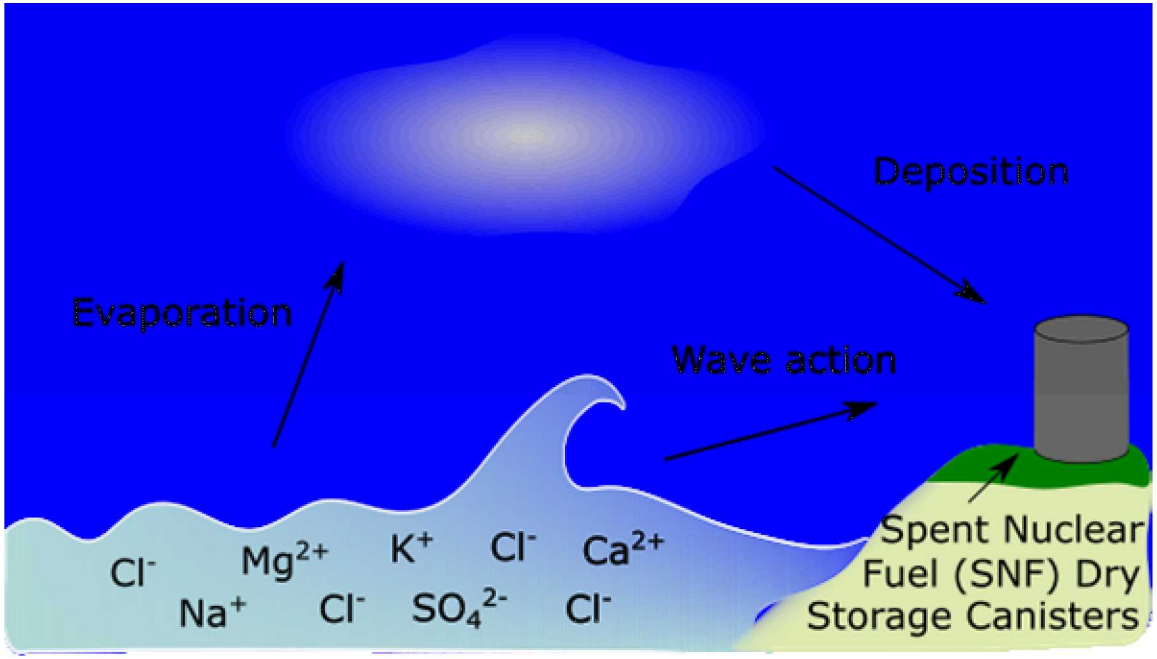
SAND #: 1103579

Background – Marine Environments

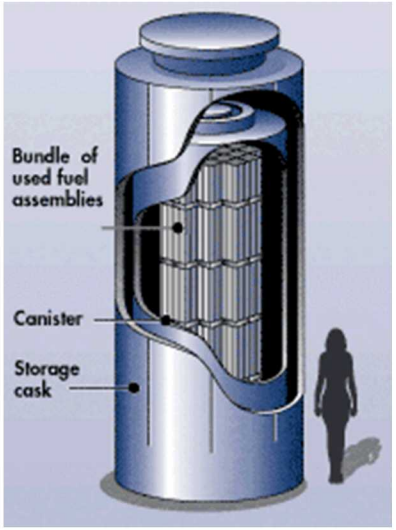


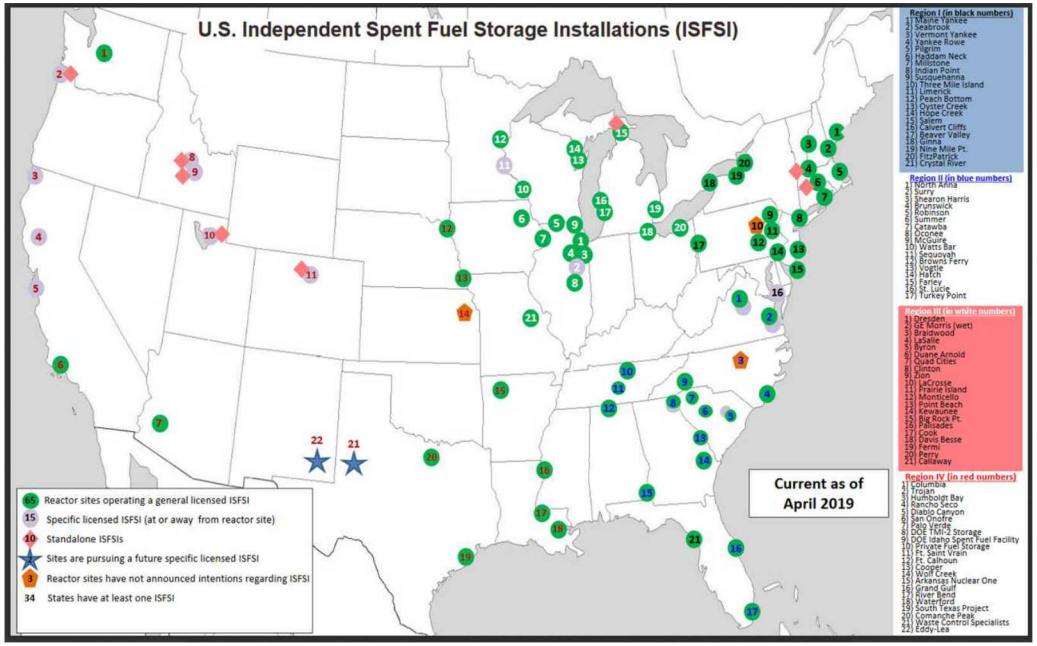
- In near-marine applications, deposition of aggressive (commonly chloride-containing) sea salt aerosols is possible
  - Spent nuclear fuel (SNF) dry storage canisters are one such example

Background – Spent Nuclear Fuel

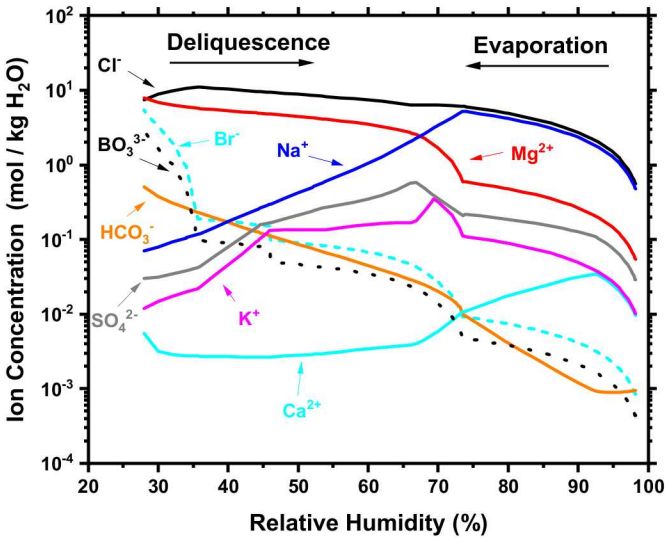
- US has over 80,000 metric tons of Spent Nuclear Fuel (SNF)
  - > 3000 stainless steel (SS) canisters
  - > 70 storage sites
- Historically licensed for 20 years with an additional 20 years upon recertification
  - 15-20 sites will have to be recertified in the next 10 years
- US has no permanent disposal pathway for SNF

SNF in SS canister inside concrete overpack

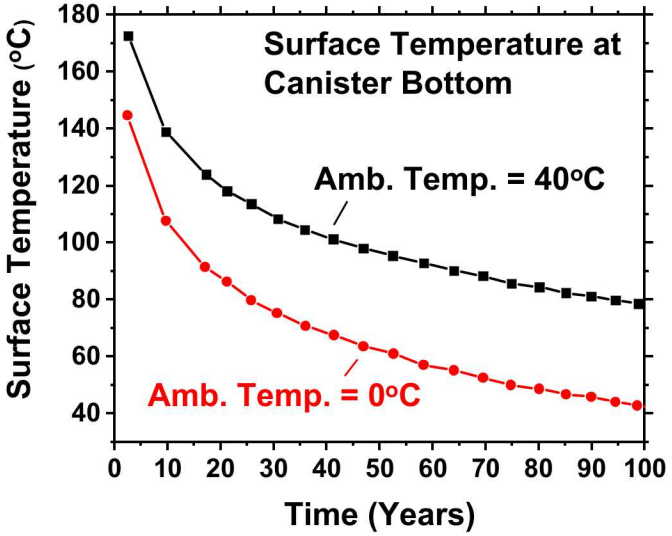




Background



Composition of Evaporated Seawater [2]



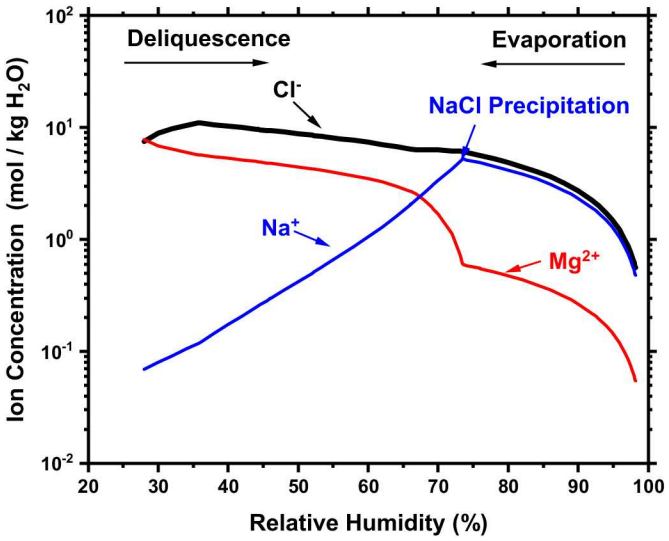
Canister temperature at various ambient temperatures [1]

- High chloride concentrations and elevated temperatures can be seen
  - Seldom explored in corrosion

[1] Enos, D. G., et al. *Data Report on Corrosion Testing of Stainless Steel SNF Storage Canisters*, p. 1–103, 2013

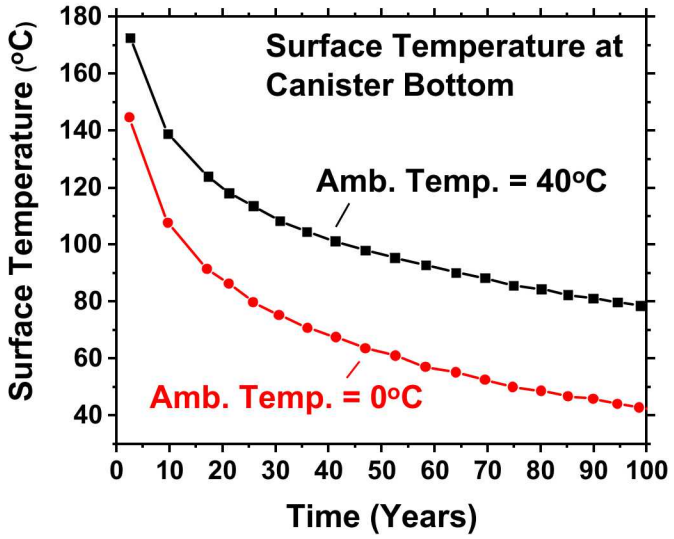
[2] Bryan, C. R. and Schindelholz, E. J., *Corrosion*. Paper 10516. 2018

Background



Composition of Evaporated Seawater [2]

- High chloride concentrations and elevated temperatures can be seen
  - Seldom explored in corrosion
- Localized pitting corrosion highly probable in such environments



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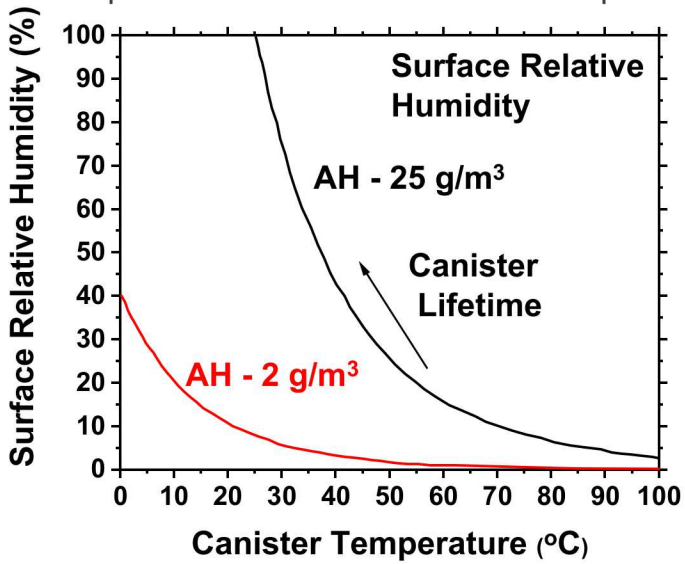

Surface relative humidity (RH) as a function of temperature and ambient RH (AH) [1]

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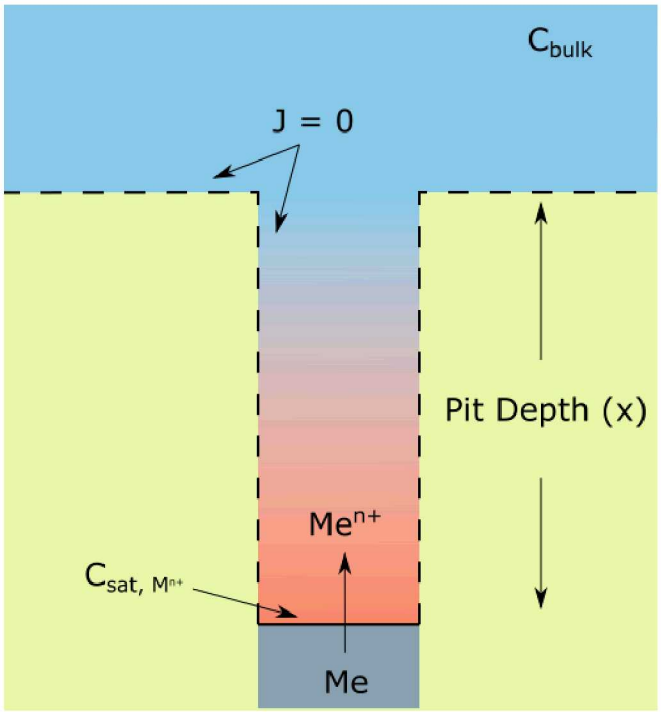
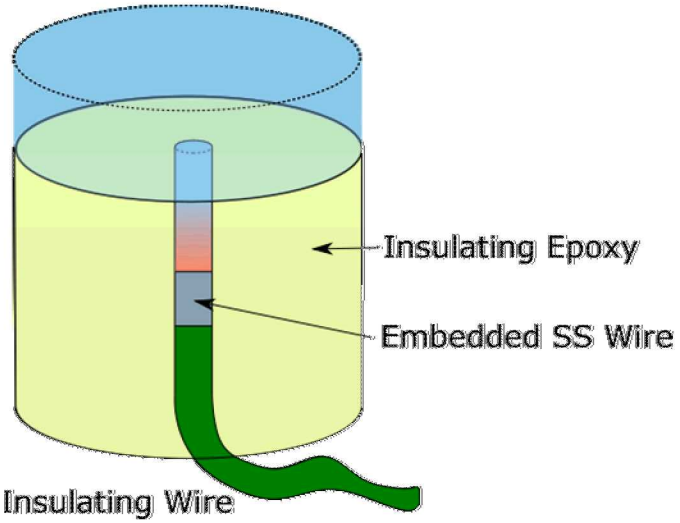
Background – Pit Propagation



Schematic of 1-D scenario with active alloy surrounded by no flux (J) boundary (J=0)

Studied through lead-in-pencil experiments under a salt film (full saturation) [1]



- Battle between outward ion diffusion and maintaining critical environment
- Galvele 1-Dimensional analysis yielded a pit stability product $(i \cdot x)$ [2]
  - Where i is current density and x is the pit depth

[1] Srinivasan, J. and Kelly, R. G., *Corrosion*, Vol. 73, 2017, p. 613–633
[2] Galvele, J. R.,, *Corrosion Science*, Vol. 21, 1981, p. 551–579

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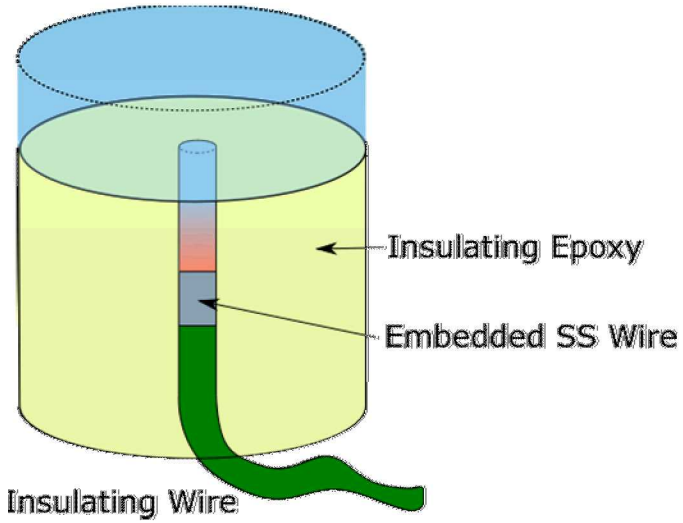
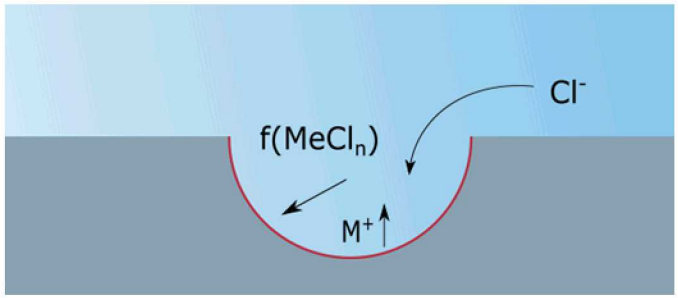


Converted to hemisphere by a geometric factor of 3



- To sustain pitting, the current (I) at a given radius (r) must satisfy

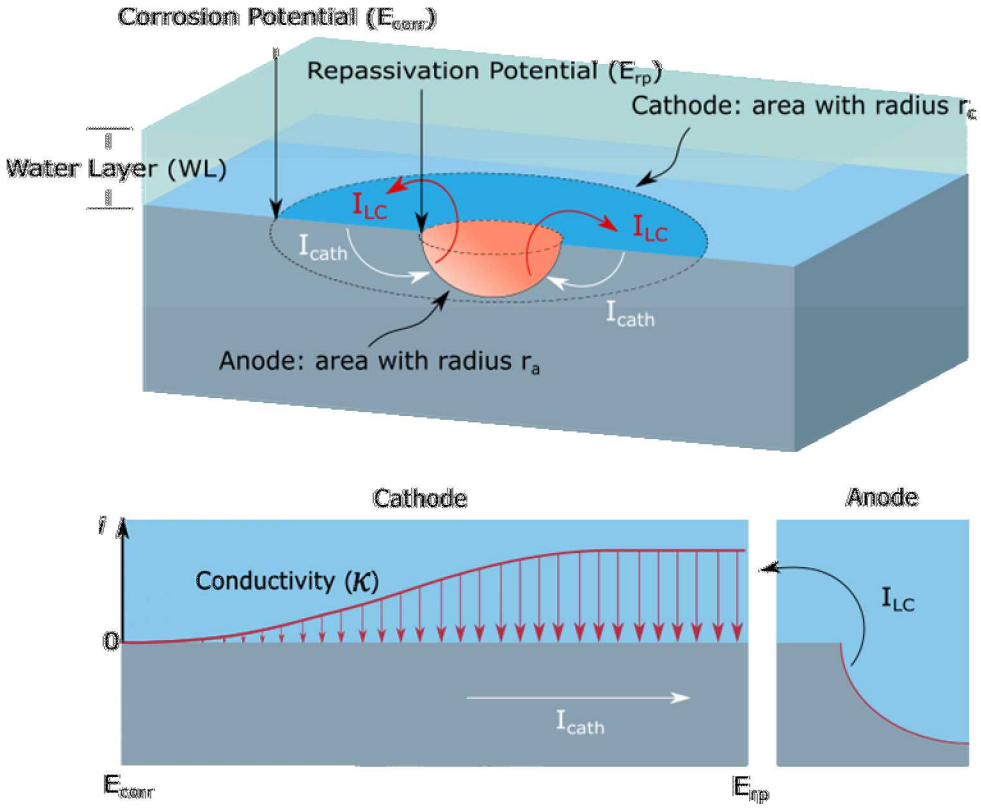
$$\left(\frac{I}{r}\right) \geq \left(\frac{I}{r}\right)_{crit}$$

- Critical value ~50% of full saturation of salt film needed

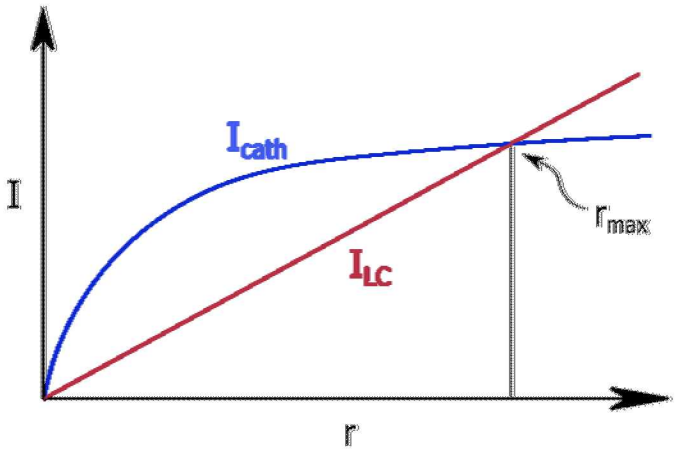
- Limiting anodic current demand (I_{LC}):

$$I_{LC} = \left(\frac{I}{r}\right)_{crit} r_{anode}$$

Background – Cathodic Reduction Reaction



- Pit must be supported by cathodic reduction reaction forming an inherent galvanic couple
- In finite water layers, cathode limited by ohmic drop [1]
  - Finite cathode → Finite anode →



Key Assumptions:
- hemispherical pit
- Un-suppressed cathode kinetics

[1] Chen, Z. Y. and Kelly, R. G., *J. of The Electrochemical Society*, Vol. 157, 2010, p. C69–C78

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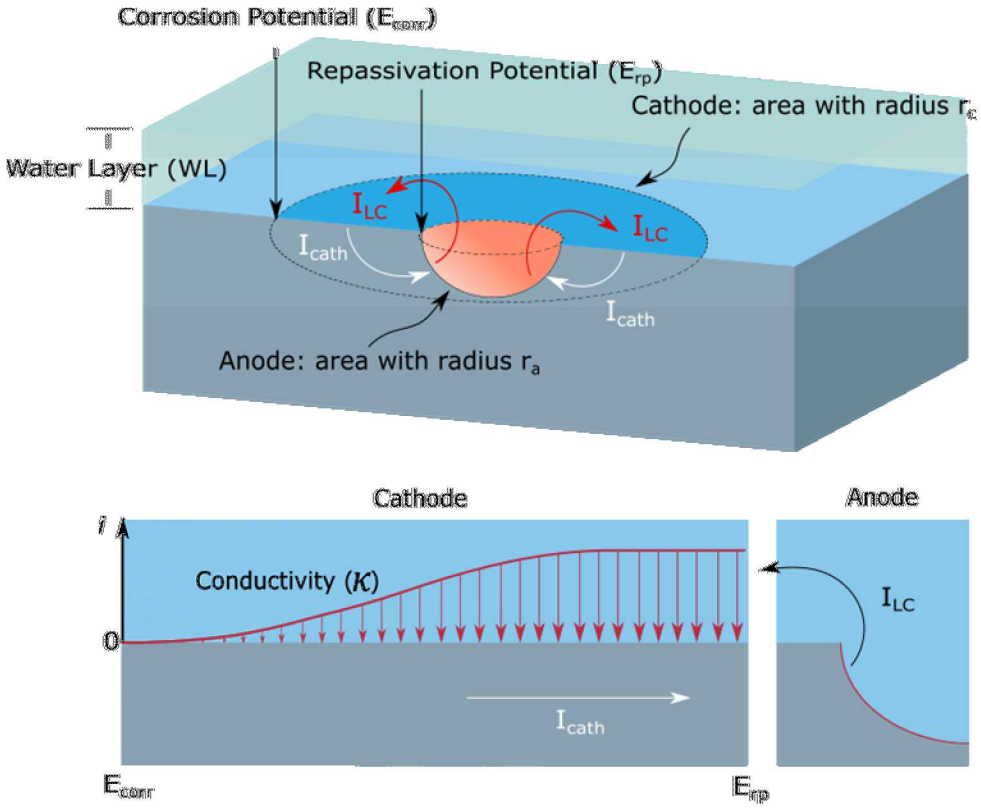

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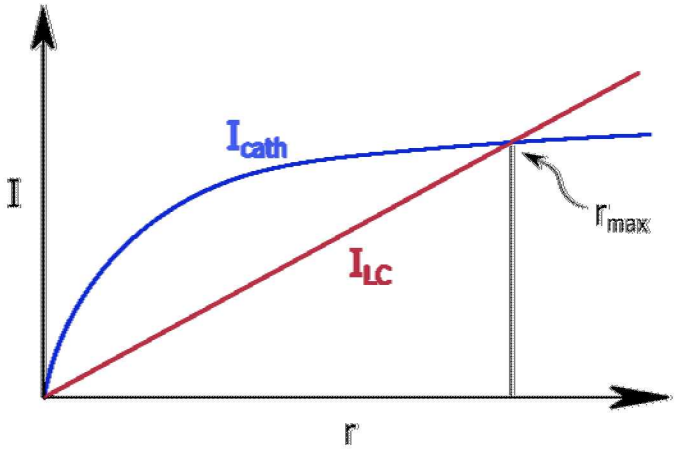

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Background – Cathode Properties

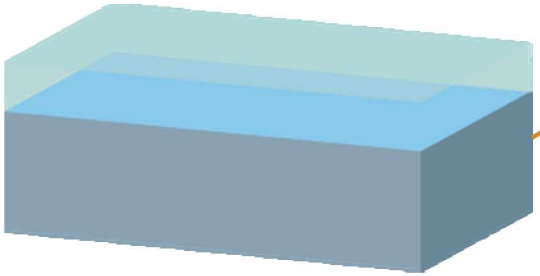
- Substantial pH rise possible in the cathode region

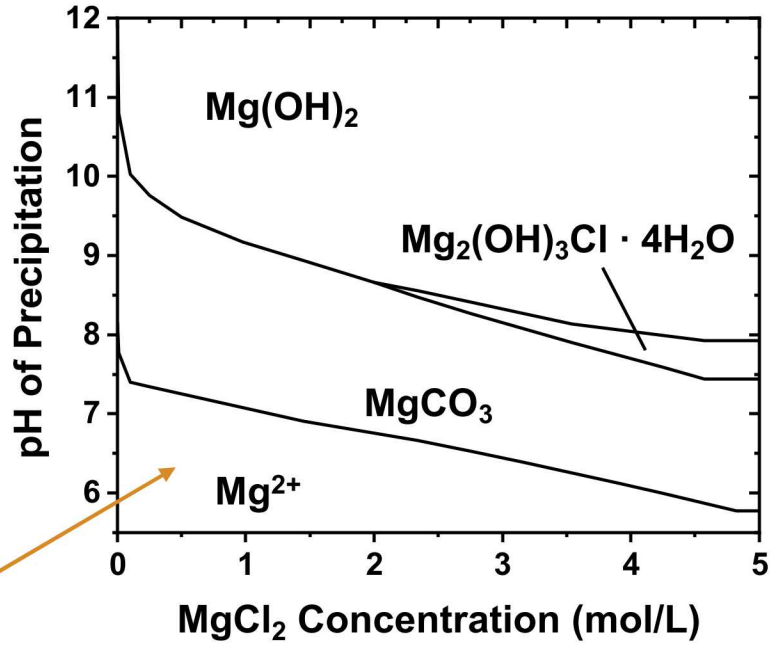
$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

- With pH increase, stable precipitates can form in the cathodic region

Bulk Solution pH

Mg^{2+} soluble





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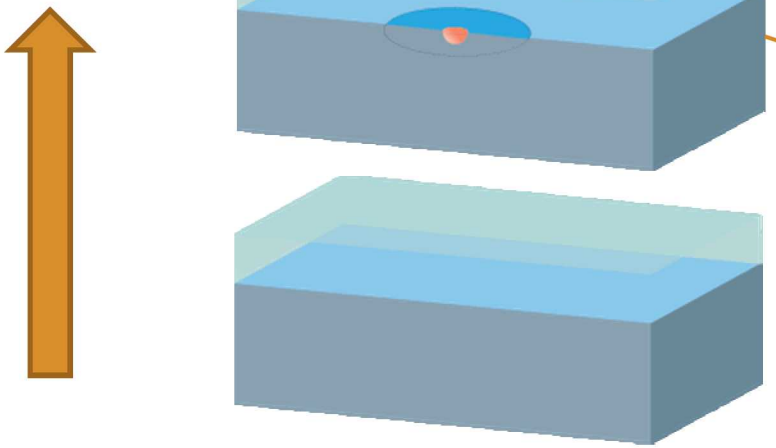
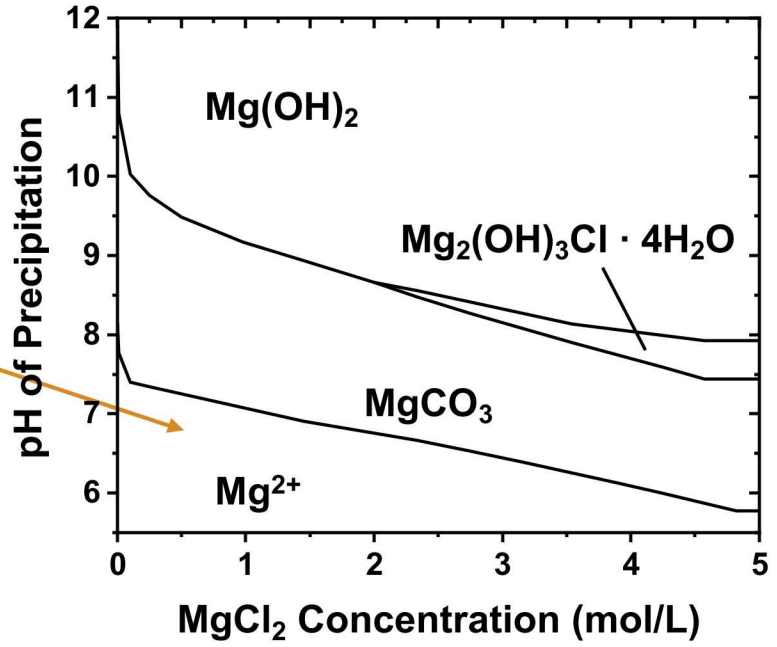
Increased cathode pH

Pit size





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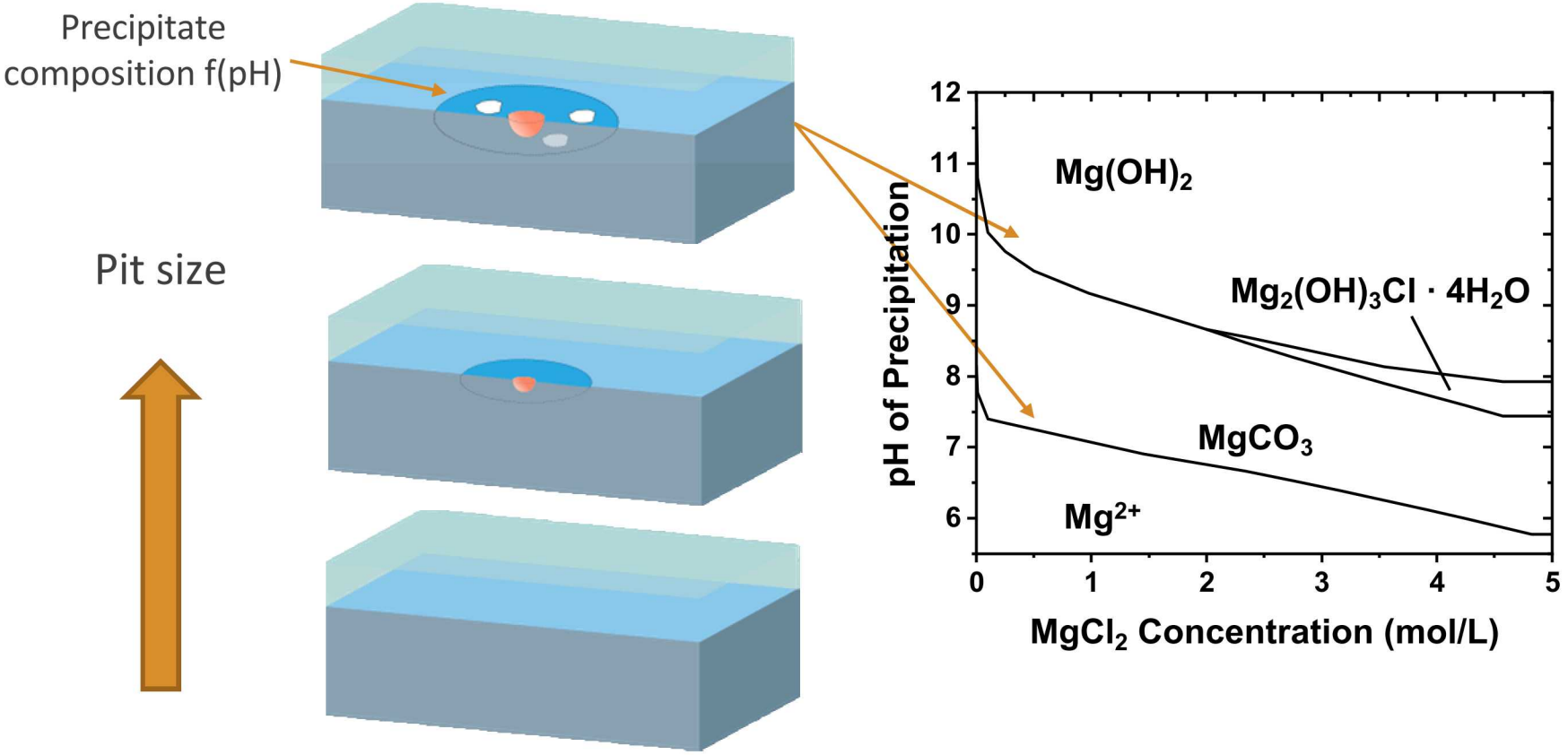
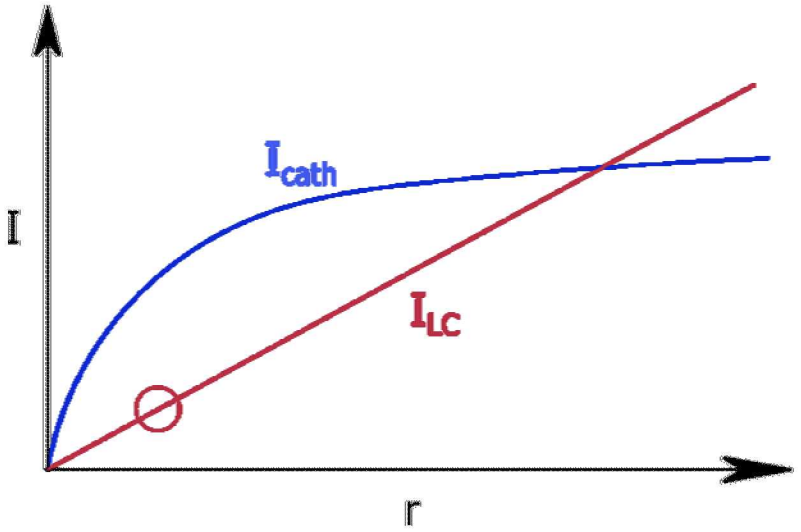
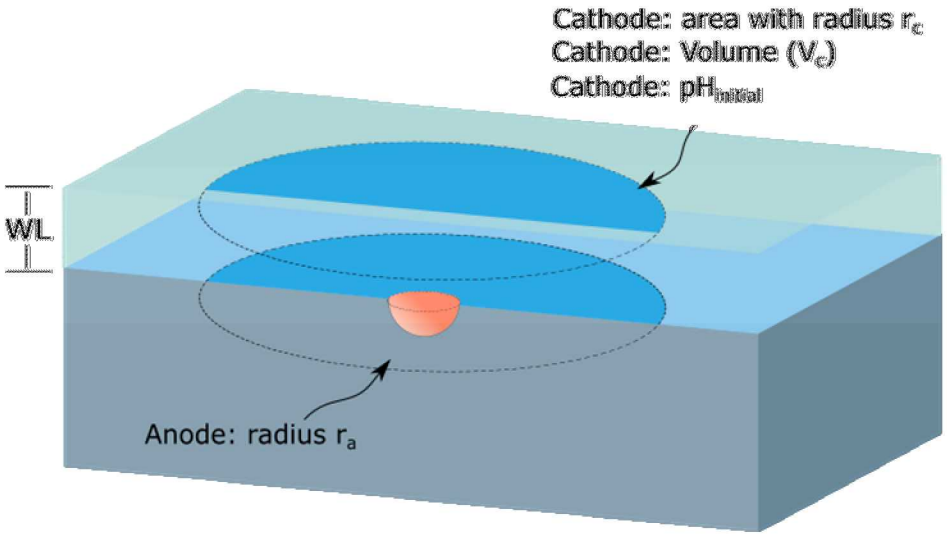


Modeling Cathode Precipitates

- Cathodic reactions produce hydroxyl causing pH rise
- Can calculate OH^- production at a given pit depth and convert to a pH

$$M_{OH^-} = \frac{\left[\frac{2}{3}(r_a)^3\right]\left[\frac{\rho_{SS} * e^-_{SS}}{MW_{ss}}\right]}{V_{cath}}$$





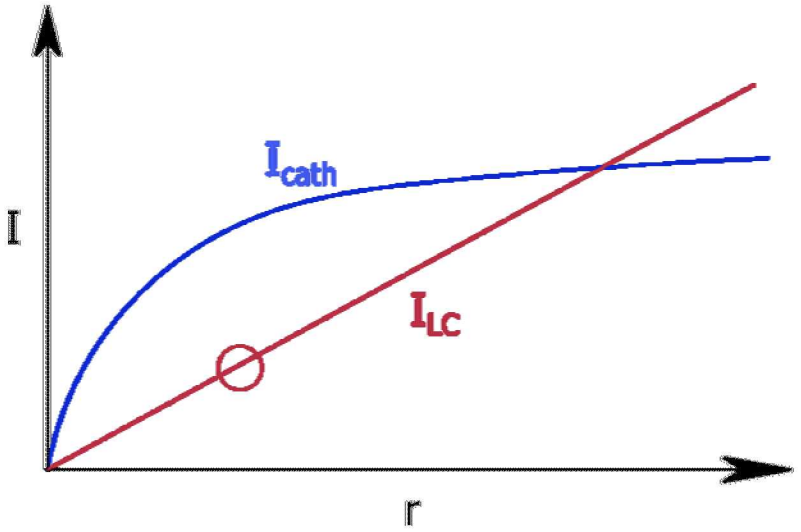
Modeling Cathode Precipitates

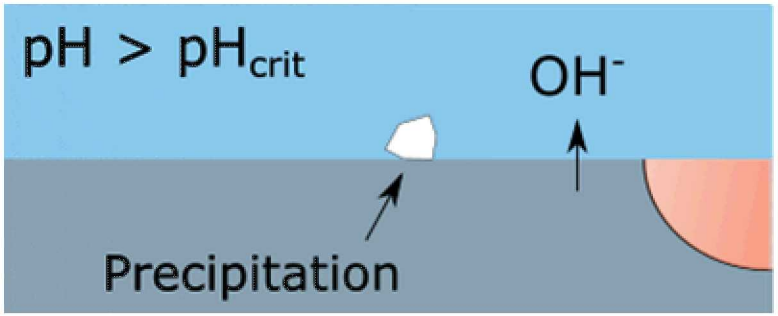
- Once the critical pH is reached, conductivity updated based on Bruggeman's Equation

$$\kappa_{eff} = k\left(1 - \frac{V_{precip}}{V_{solution} + V_{precip}}\right)^{\frac{3}{2}}$$

$$I_{cath,updated} = f(\kappa_{eff})$$

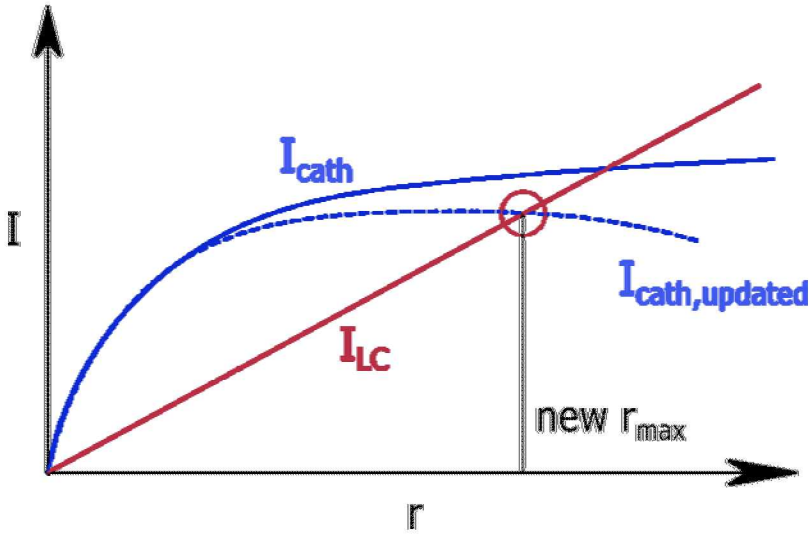
- Cathodic current is re-calculated based on decreased conductivity from precipitation formation, until maximum pit is reached



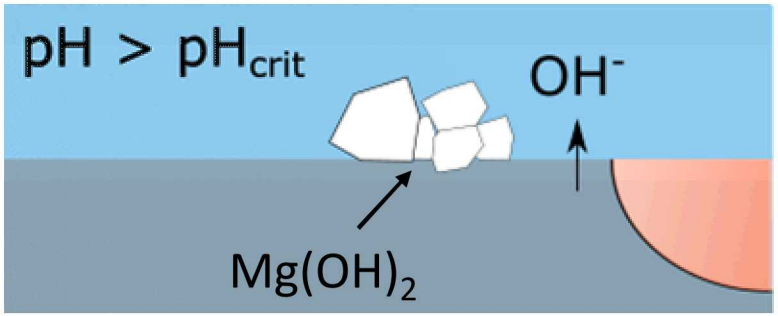


Modeling Cathode Precipitates

- Based on the decreased conductivity, a new, decreased cathodic current is present
- Solutions of interest
  - $MgCl_2$

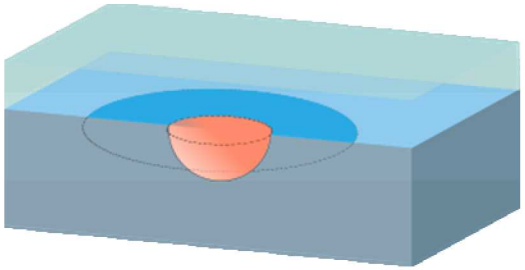


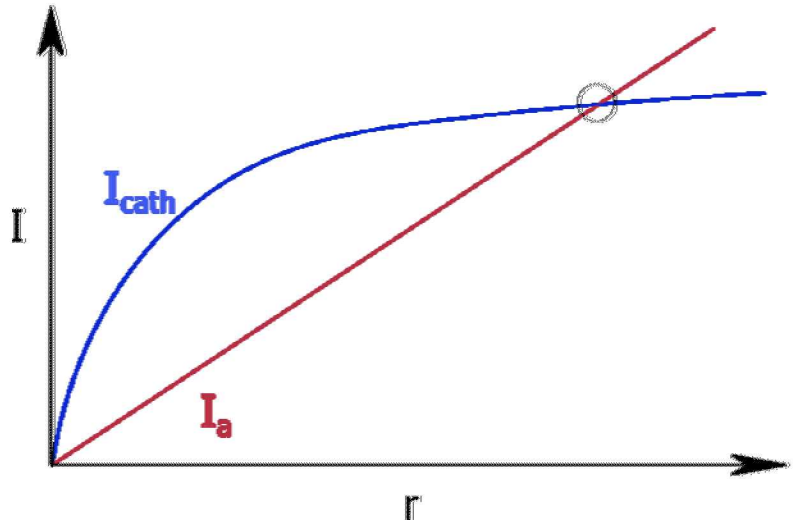
- Assumptions
  - (1) no mass transport
  - (2) the cathode and anode are separate
  - (3) no metal hydroxide precipitation from the pit



Objective and Approach

- Understand the quantitative impacts on maximum pit size predictions
- Determine governing factors for marine atmospheric corrosion





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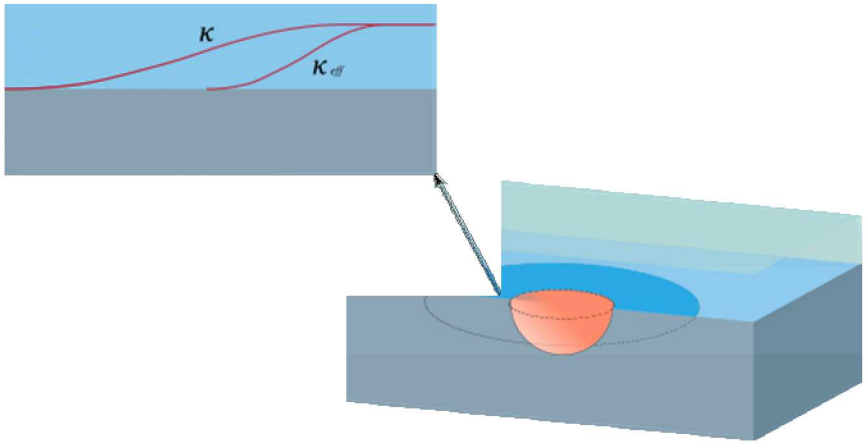

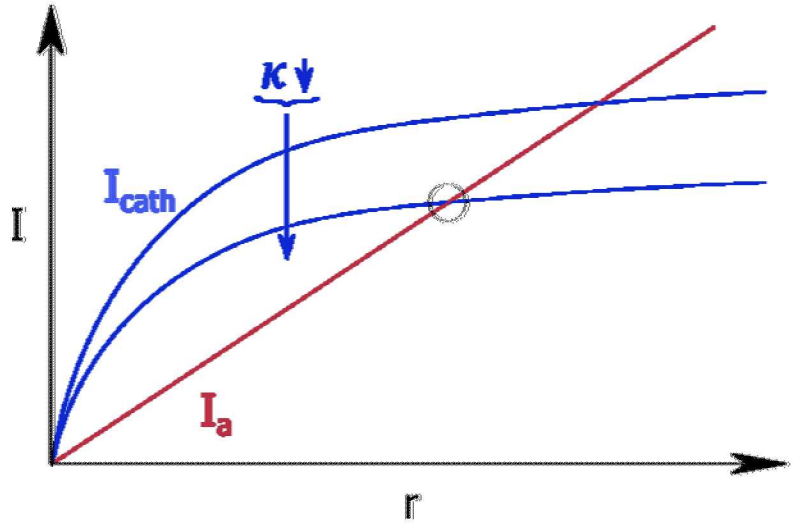

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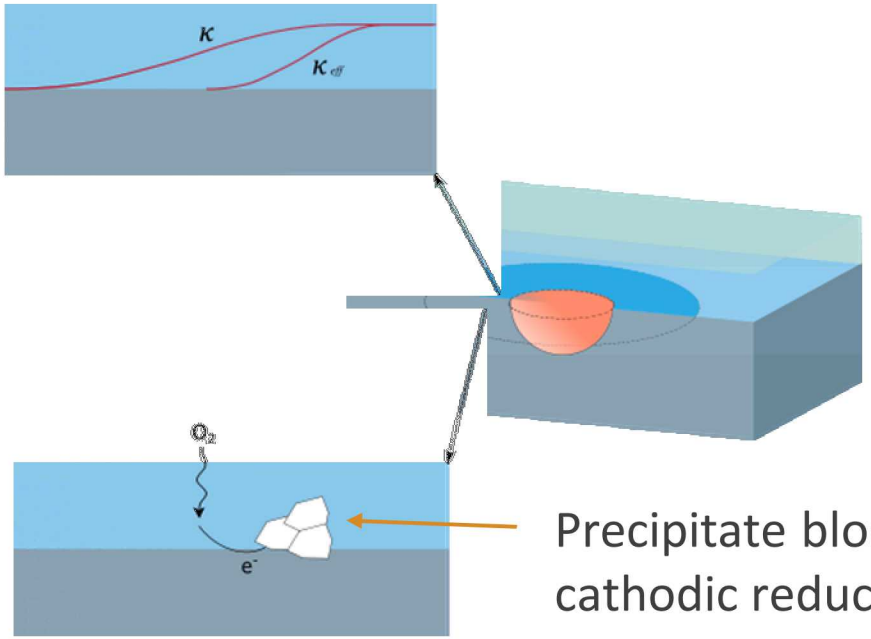
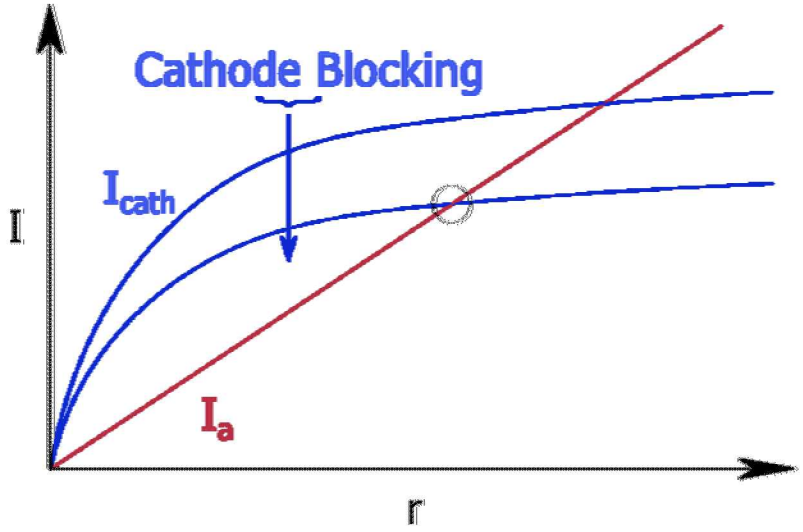


Precipitate blocking cathodic reduction site



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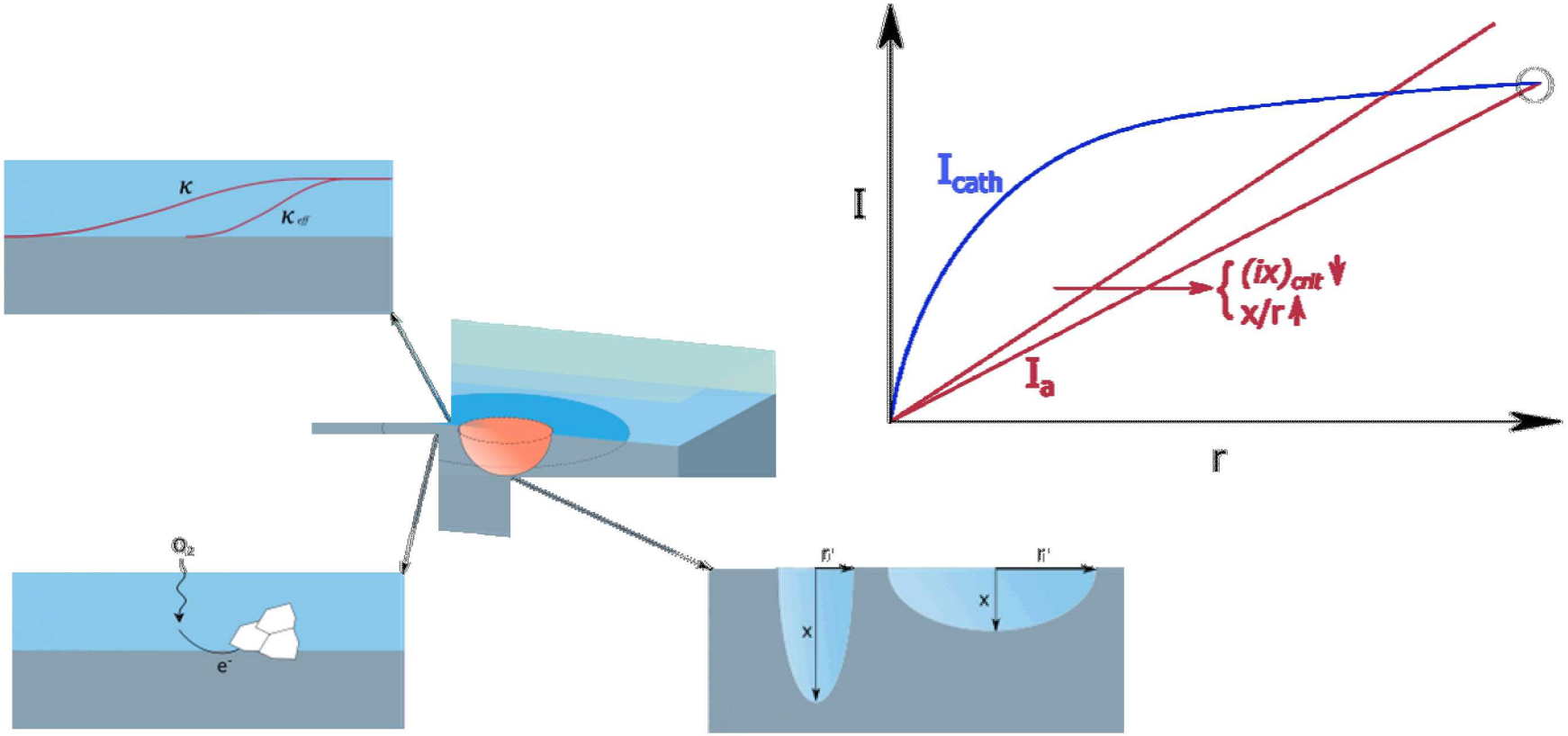

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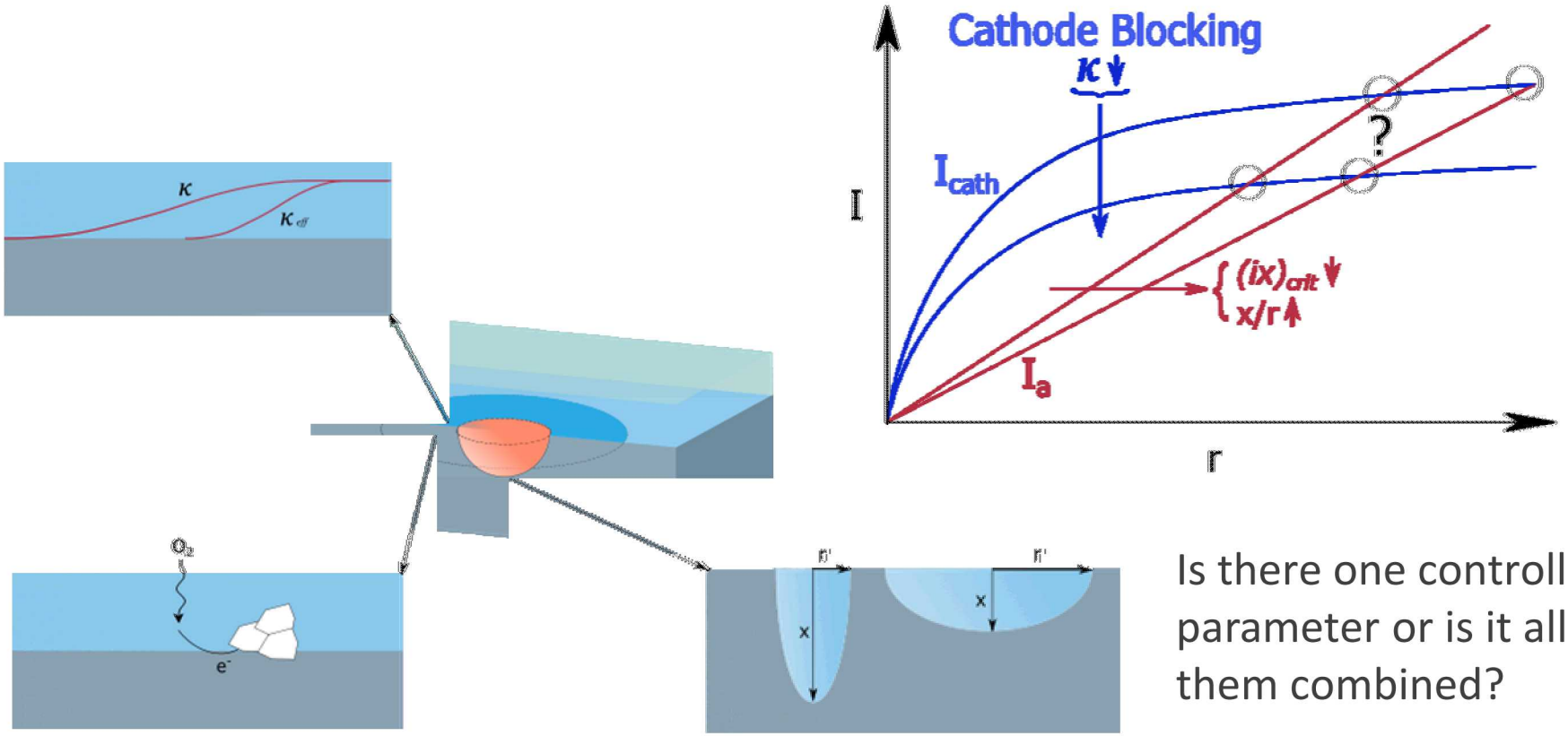

Is there one controlling parameter or is it all of them combined?

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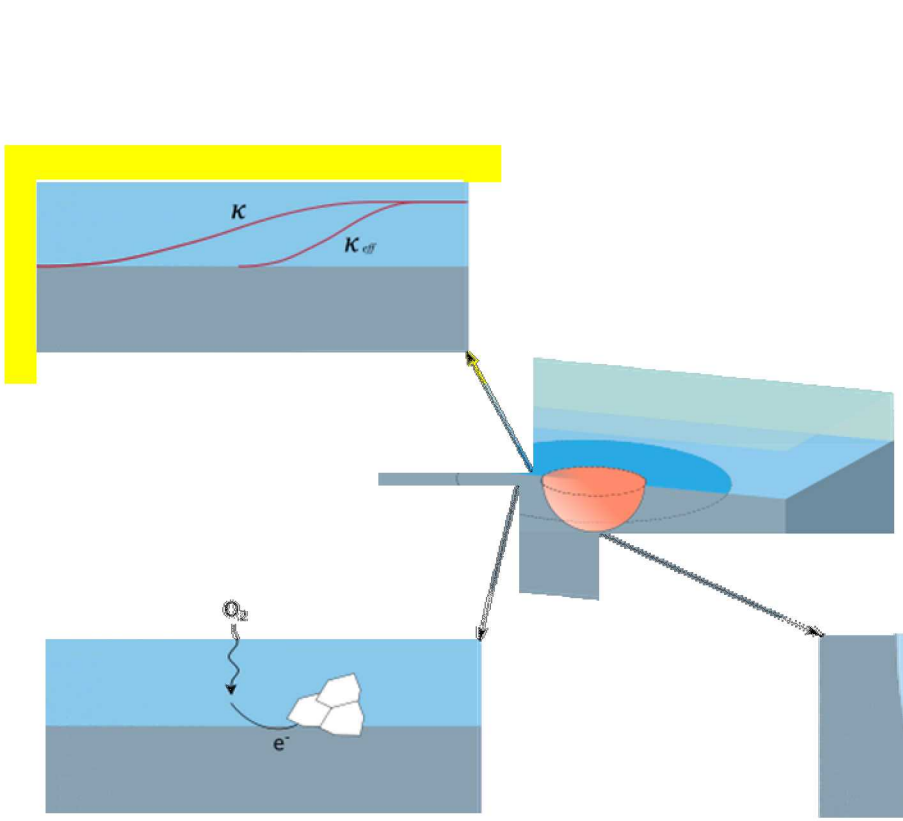
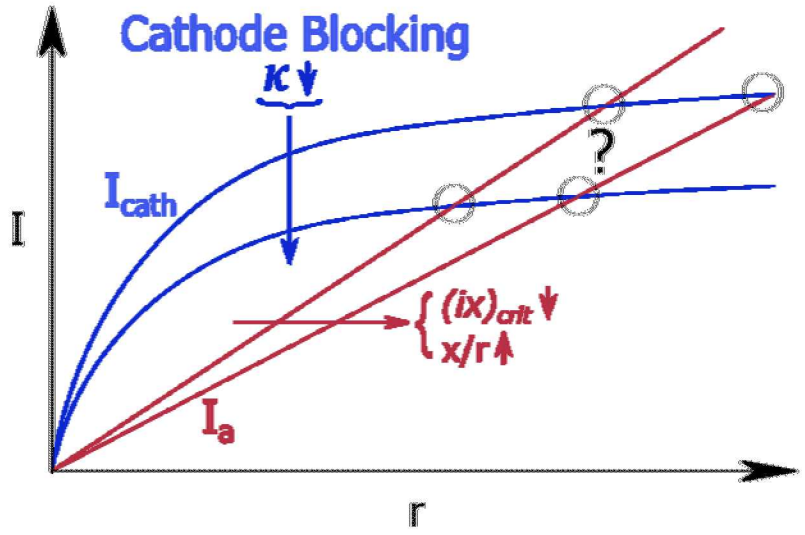
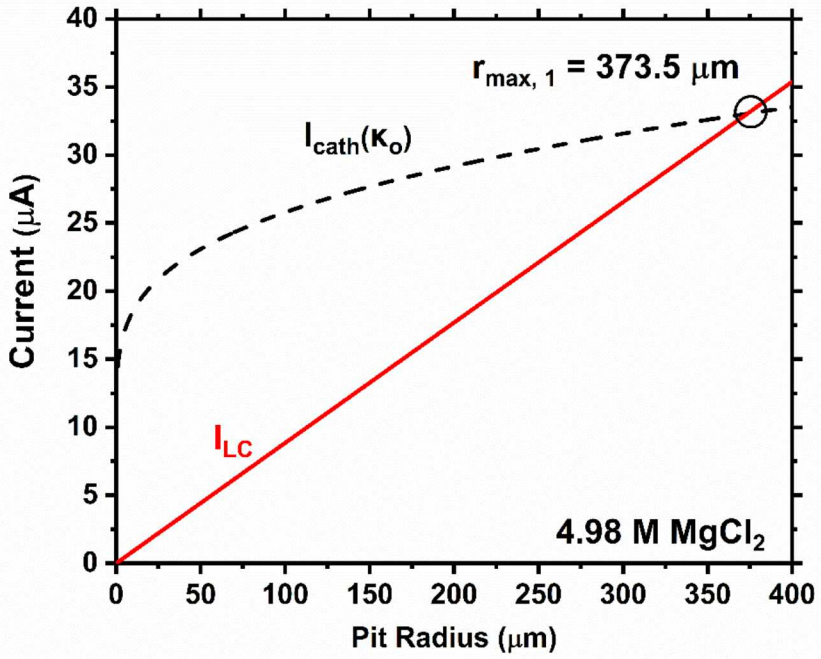


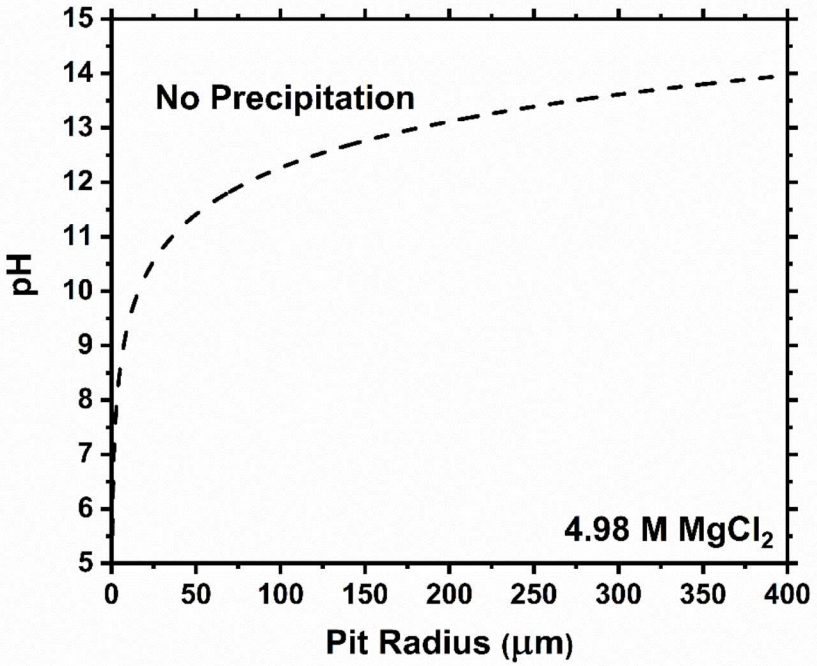


Is there one controlling parameter or is it all of them combined?

Maximum Cathode Current Decreases with Increasing Pit Size with Precipitation

- Maximum pit size predictions without precipitation for saturated $MgCl_2$ (4.98 M, RH = 38 %) at 25°C
- I_{LC} is that needed to maintain concentration of 50% of saturation

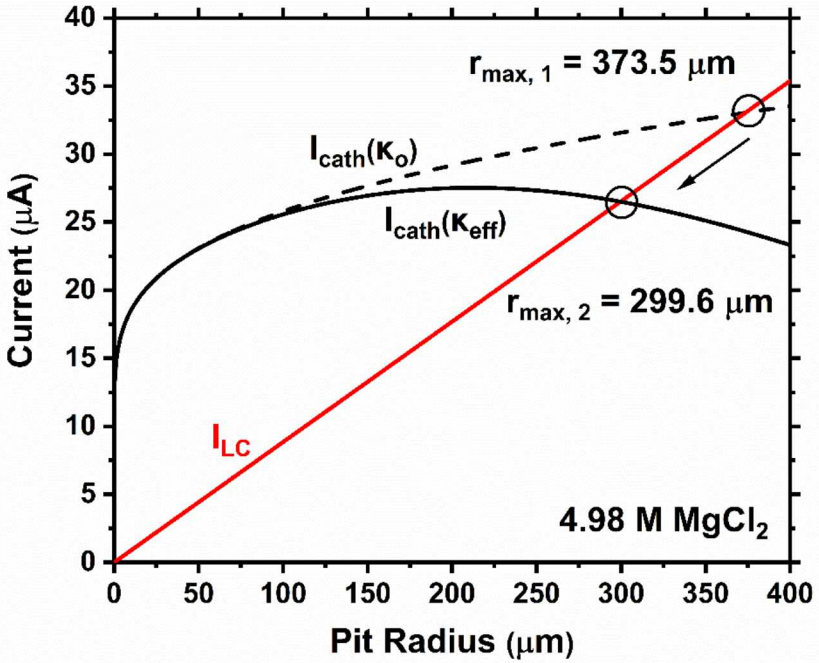


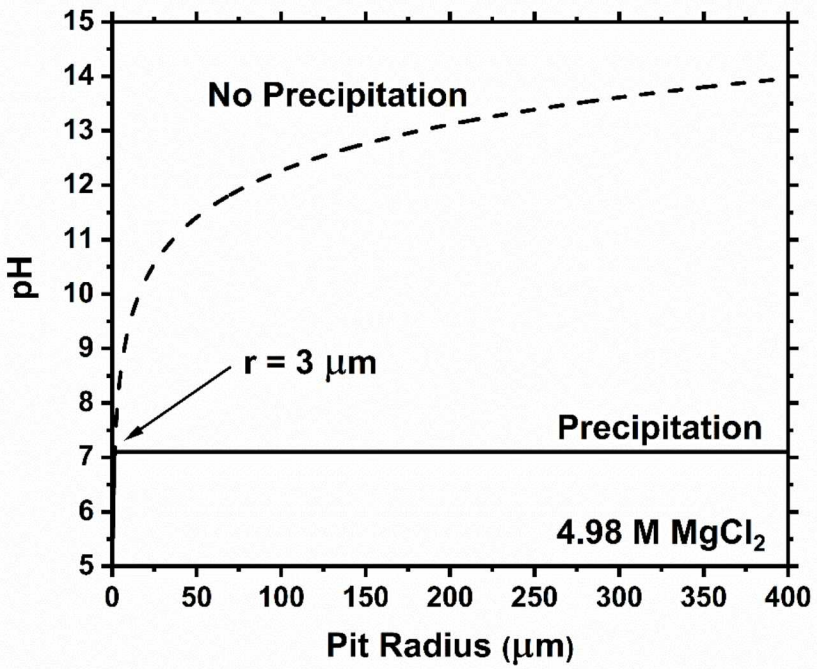


$[MgCl_2]$ = 4.99 M DD = 3 g/m^2 WL = 8.56 μm i_{eq} = 1.91·10^{-7} A/cm^2

Maximum Cathode Current Decreases with Increasing Pit Size with Precipitation

- With increased pit size, the cathode pH remains constant, increasing Mg species precipitation and decreasing cathodic current





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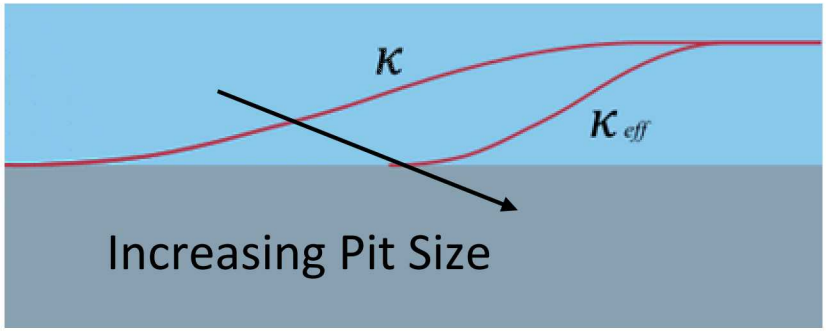
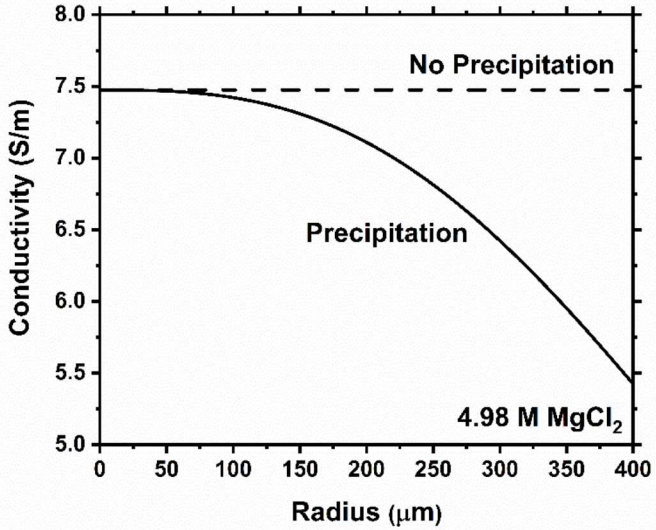
Ideal Cathode Radius Decreases with Increased Precipitation

- Conductivity decreases with increased precipitation, which is a result of increased pit size



- Increased ohmic drop, due to a lower conductivity, leads to the decrease in cathode size



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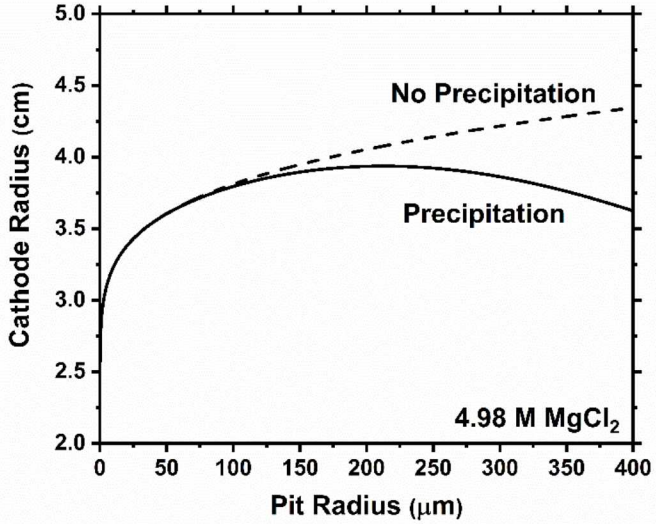
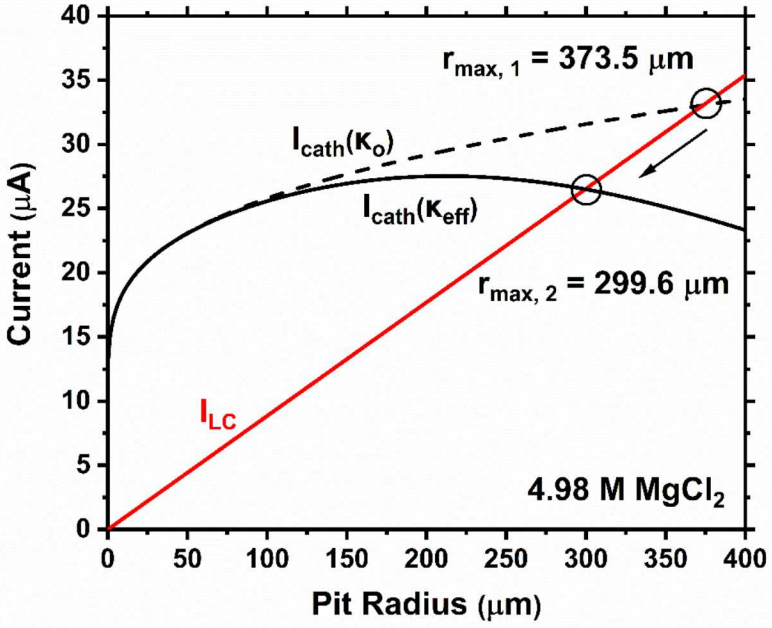
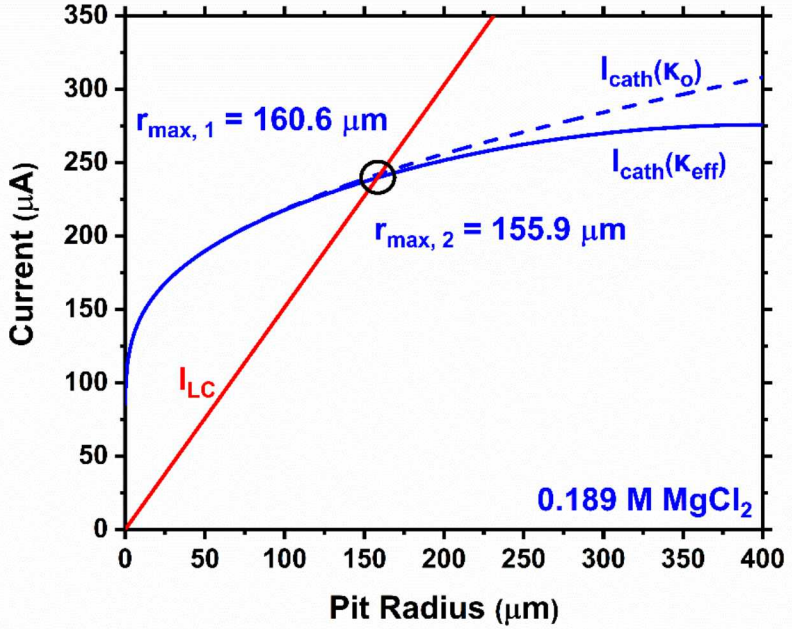


Cathodic Precipitation Affects Max Pit Size More in Concentrated Brines

- Larger pit differences seen at elevated concentrations of $MgCl_2$
- Water layer is orders of magnitude smaller in saturated solutions





$[MgCl_2]$ = 4.99 M RH = 38%

WL = 8.56 μm

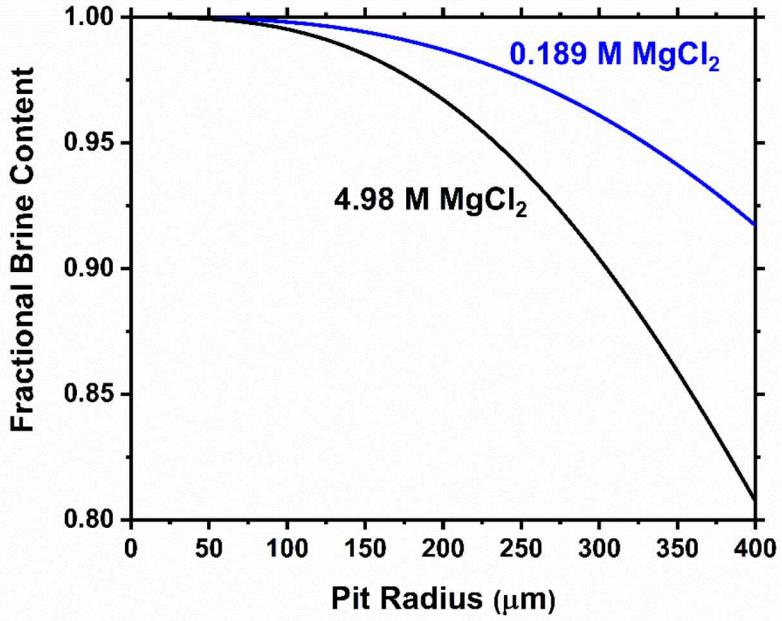
$[MgCl_2]$ = 0.187 M RH = 98%

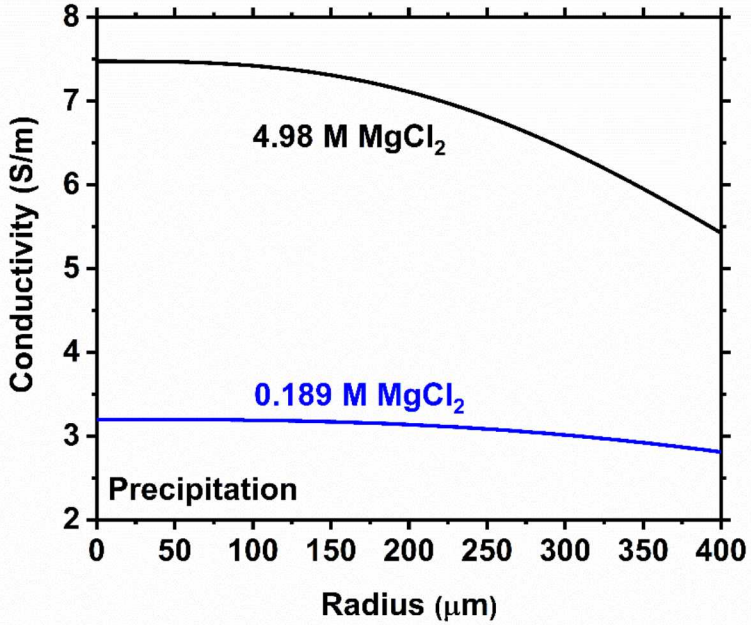
WL = 136.53 μm

Cathodic Precipitation Affects Conductivity More in Concentrated Brines

$$\kappa_{eff} = k\left(1 - \frac{V_{precip}}{V_{solution} + V_{precip}}\right)^{\frac{3}{2}}$$

- Fractional precipitate term influenced more in concentrated solutions due to smaller solution volume ($V_{solution}$)

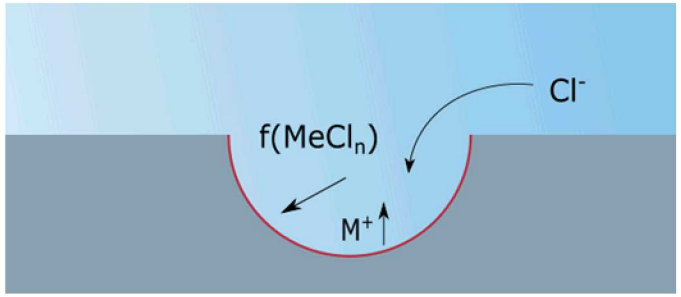


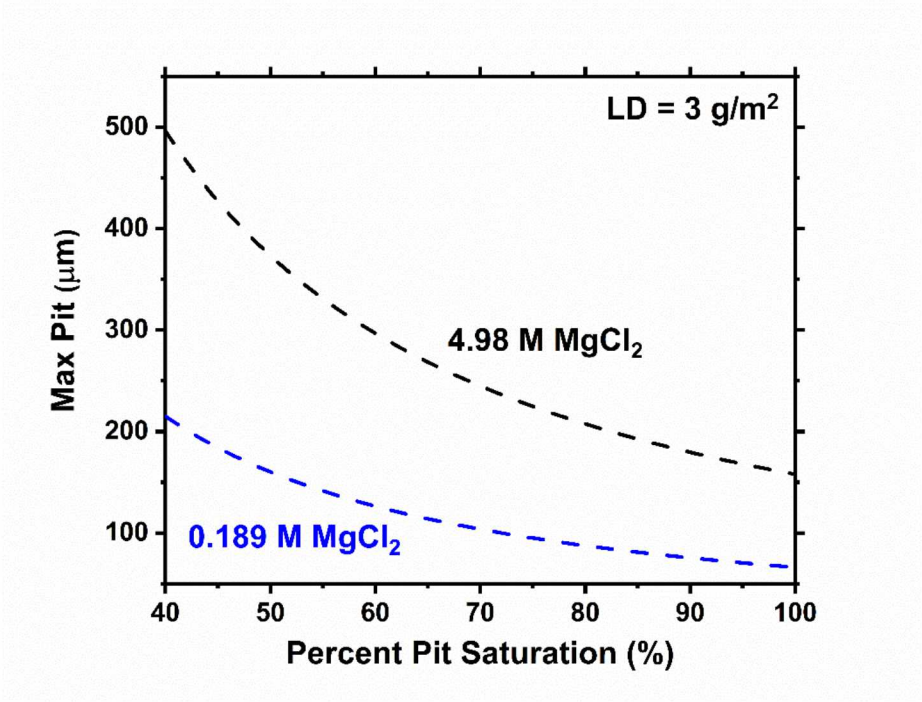


- More drastic change in conductivity and a lower $(i \cdot x)$ leads to a greater difference in maximum pit size

Larger Difference in Pit Radius at Lower Percentage of Saturation

- Critical current (I_{LC}) needed to maintain aggressive environment can be a fraction of saturation
  - Values can range from 45 % to 70 % [1-3]

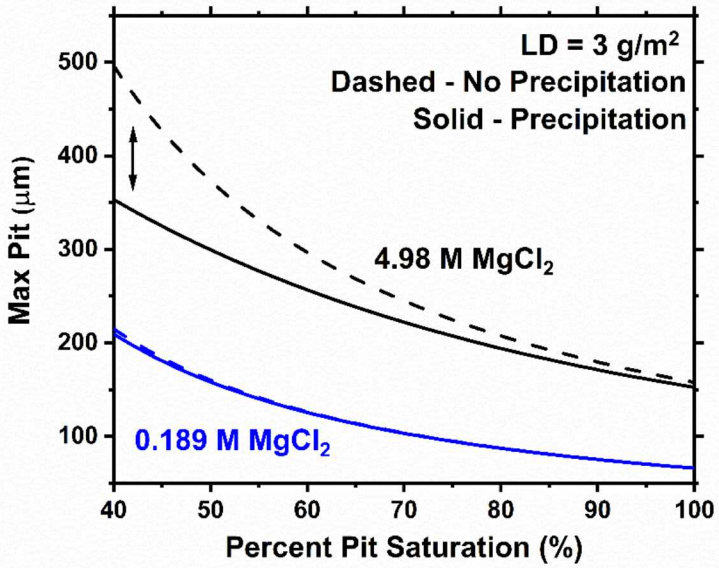


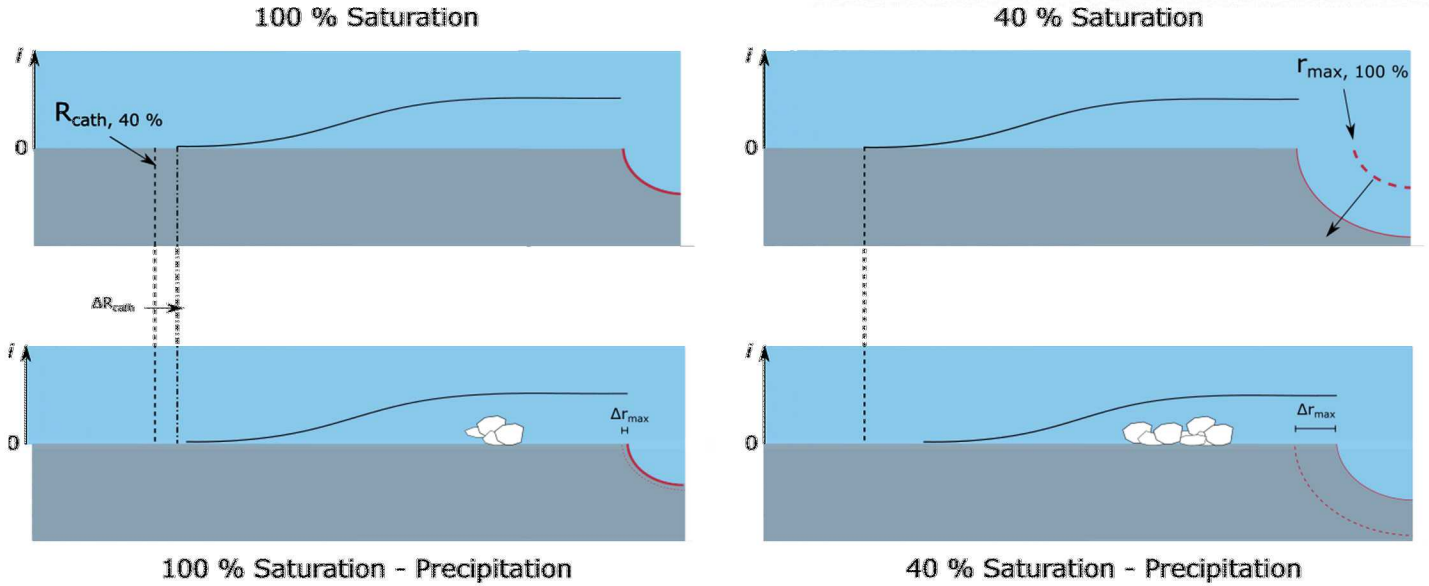


[1] Li, T., et al. *Journal of The Electrochemical Society*, Vol. 166, 2019, p. C3341–C3354
[2] Srinivasan, J. and Kelly, R. G., *Corrosion*, Vol. 73, 2017, p. 613–633
[3] Gaudet, G. T. et al., *AIChE Journal*, Vol. 32, 1986, p. 949–958

Larger Difference in Pit Radius at Lower Percentage of Saturation

- Percent saturation and precipitation influence concentrated solutions more drastically
- Precipitation reactions more influential at low values of pit saturation



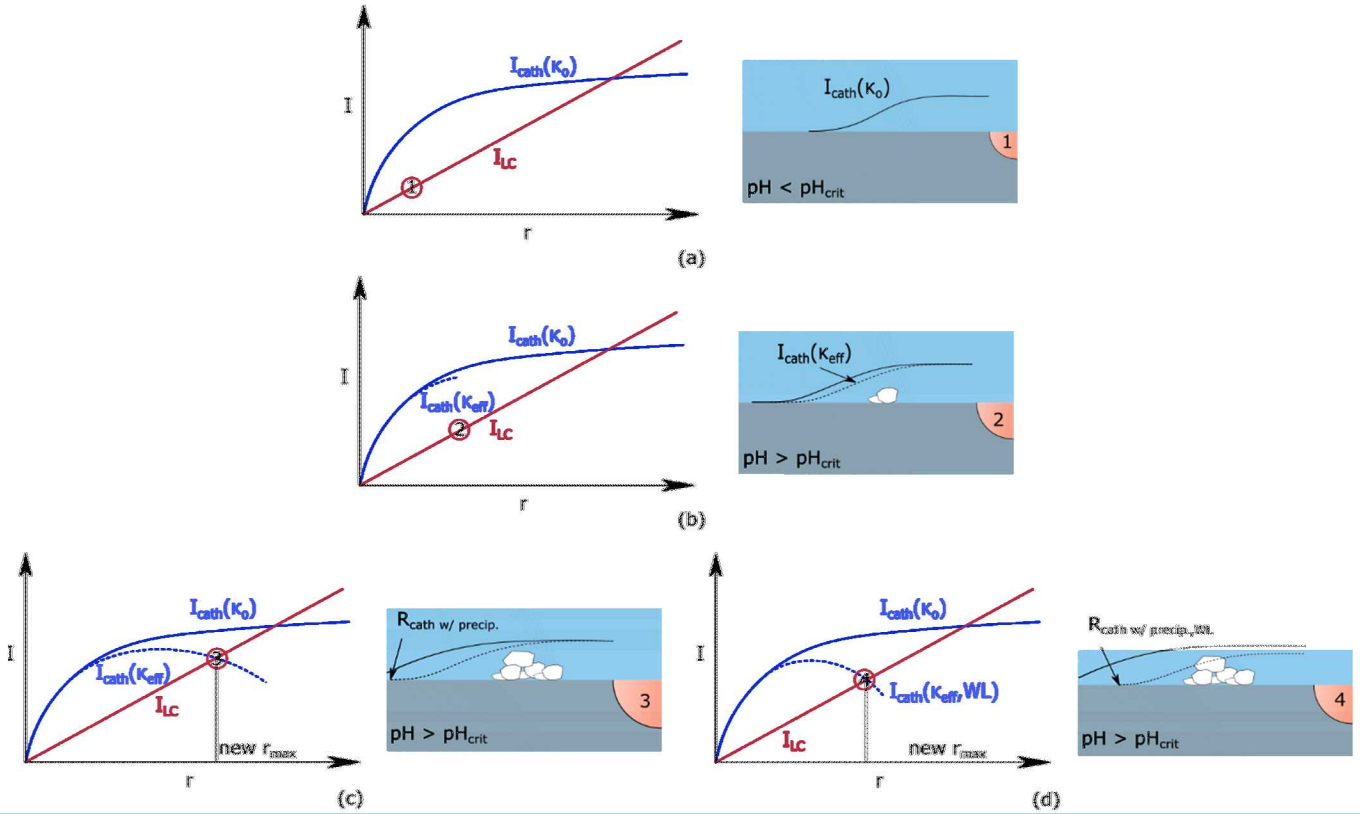


Conclusions

- Considering cathodic precipitation decreases calculated maximum pit sizes significantly
  - Pit sizes decrease by roughly 20% in saturated $MgCl_2$
- Cathode sizes decrease when considering precipitates due to increased ohmic drop
- Precipitation reactions influence pit sizes most in concentrated solutions and at low values of pit saturation

Future Work

- Further assumptions to be explored in max pit modeling:
  - No mass transport in cathode
  - No metal hydroxide precipitates
- Dehydration reactions



Acknowledgements

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Determination of Key Marine Environment Effects on Maximum Pit Size Predictions

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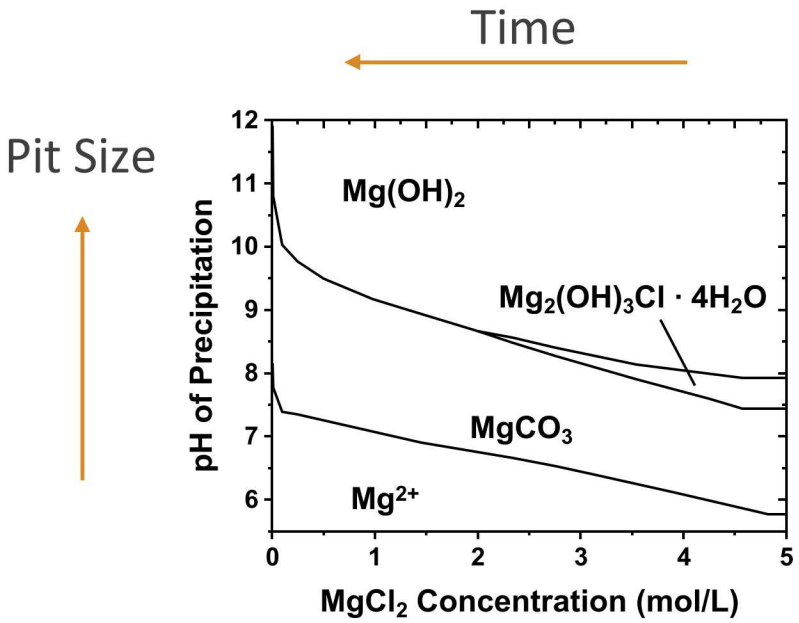
Back-up Slides

Background – Cathode Properties

- Substantial pH rise possible in the cathode region

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \qquad 2\mathrm{H_2O} + 2\mathrm{e^-} \rightarrow \mathrm{H_2} + 2\mathrm{OH^-}$$

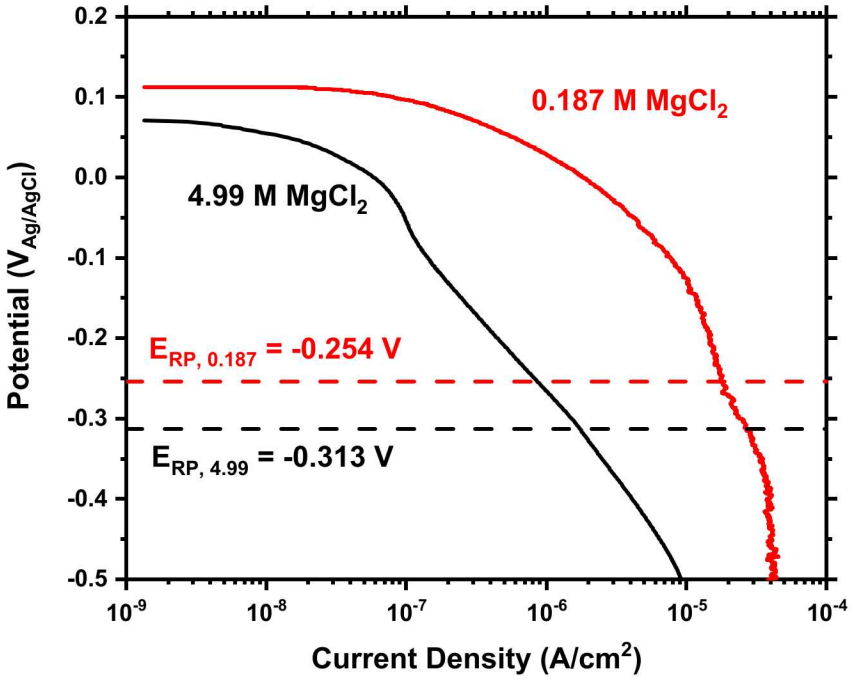
- With pH increase, stable precipitates can form in the cathodic region



- Multiple precipitates present in seawater brines
  - Still mainly Mg precipitates

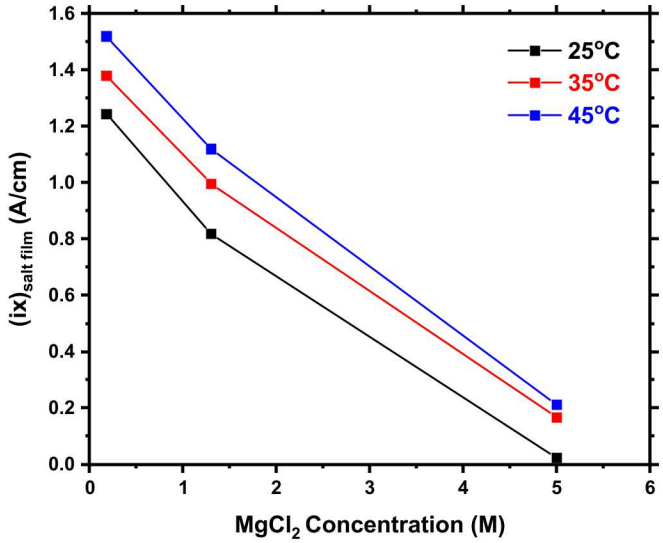
$MgCl_2$ and Seawater Polarization Scans

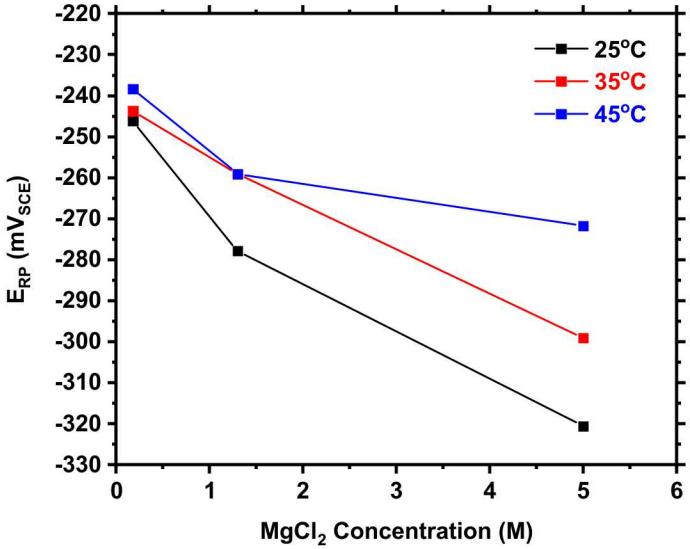
$MgCl_2$



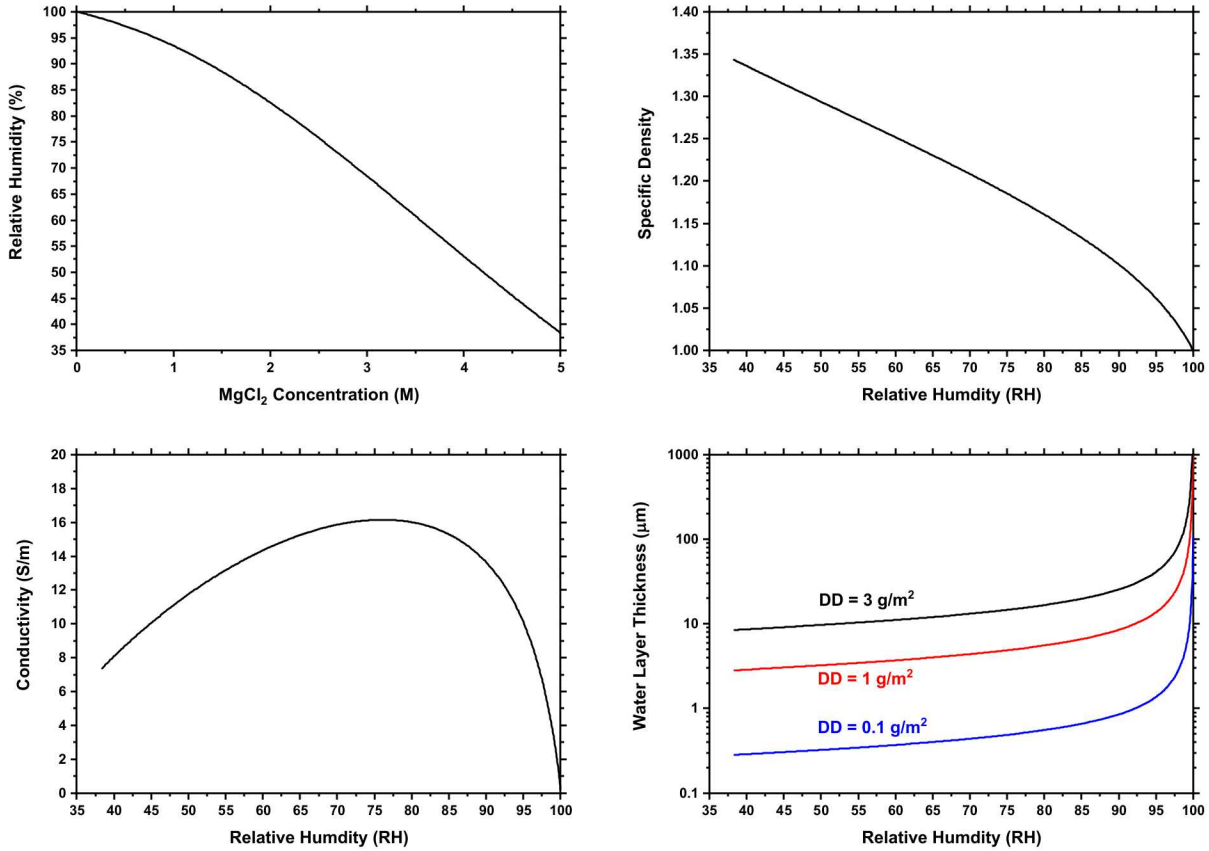
Pit Stability and Repassivation Potential

- Determined through the lead in pencil technique



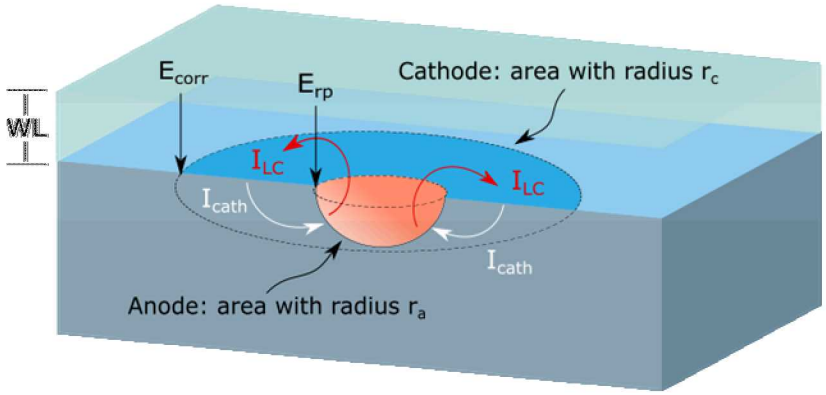


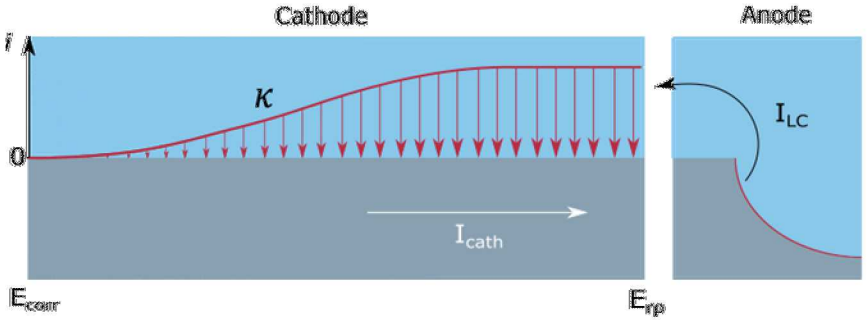
$MgCl_2$ Properties

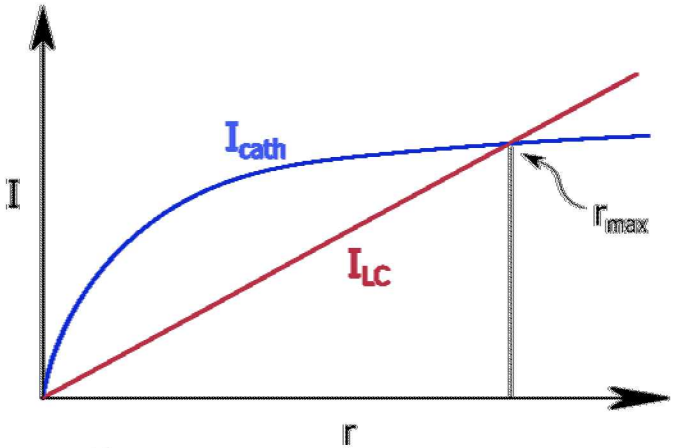


$$WL(in\ \mu m) = DD * \frac{-0.01253(RH)^3 + 2.232(RH)^2 - 171.39(RH) + 17473.660}{-3.76E^{-8} * (RH)^4 + 8.904E^{-8} * (RH)^3 - 7.741E^{-4} * (RH)^2 + 0.02295 * (RH) + 0.3102}$$

Calculating I_{cath}







Max. Cathode Current

Brine Conductivity

Brine Thickness

Cathodic Kinetics

$$\ln I_{c,max} = \frac{4\pi\kappa(\mathrm{WL})\Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (i_c - i_p)dE}{\Delta E_{max}}\right]$$

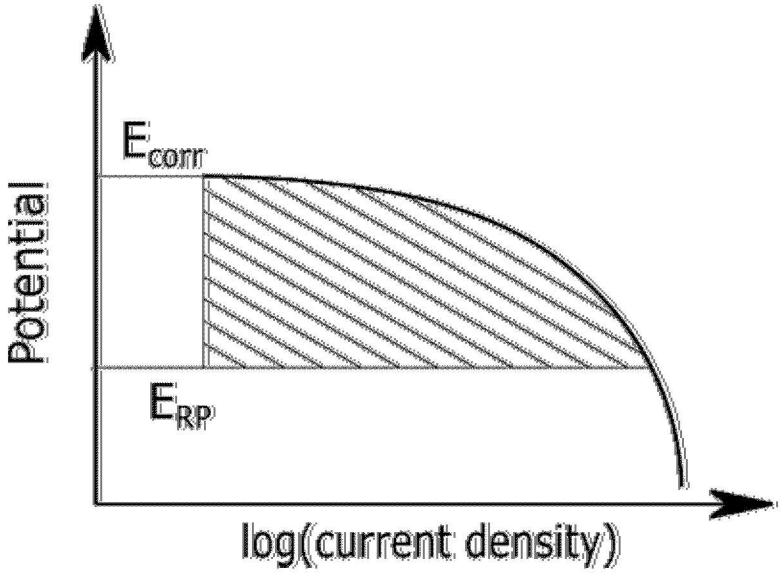
E_{rp} = Repassivation Potential

E_{corr} = Corrosion Potential

Limiting anodic current demand:

$$I_{LC} = \left(\frac{I}{r}\right)_{crit} r_{anode}$$

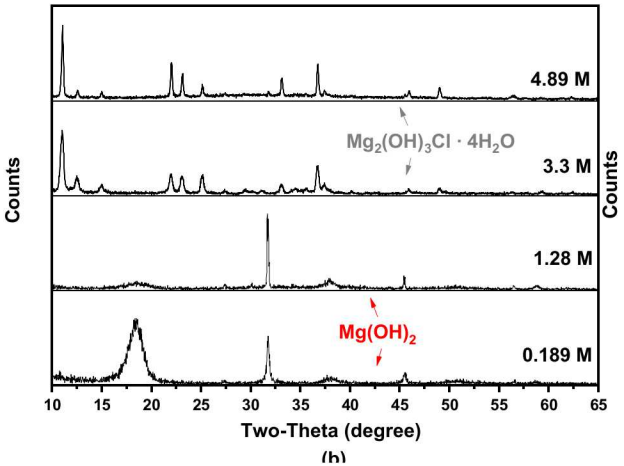
Calculating Equivalent Current Density

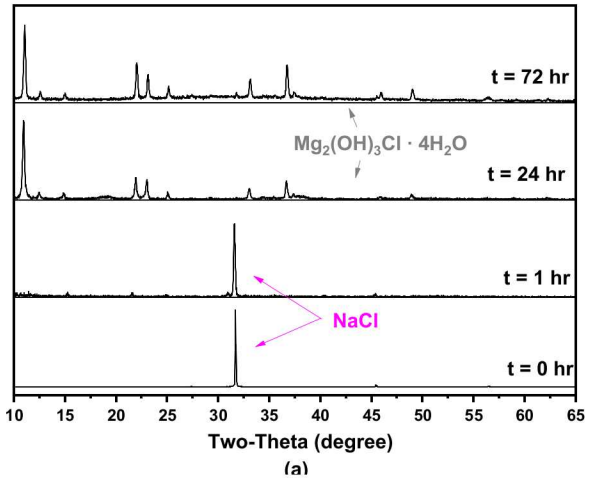


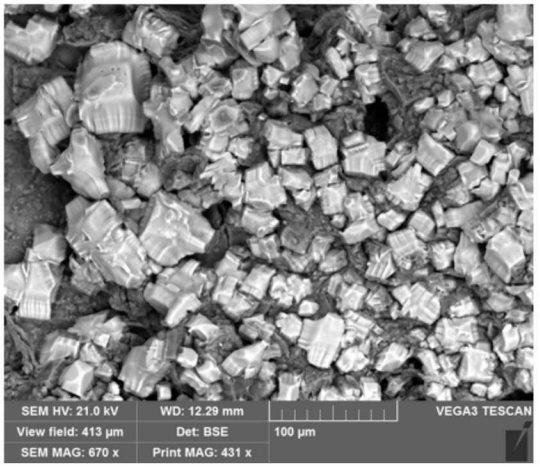
Cathodic Kinetics → $\int_{E_{corr}}^{E_{rp}} (i_c - i_p) dE$

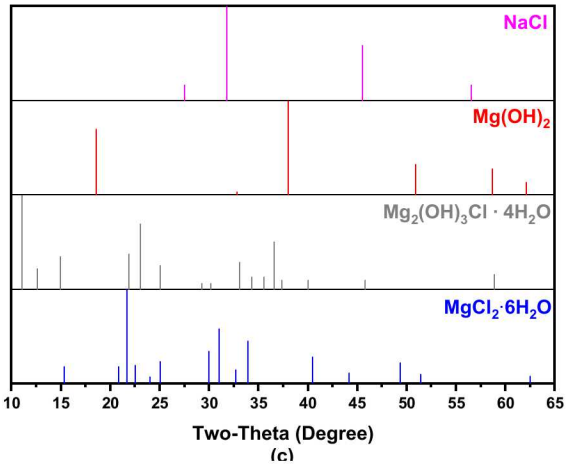
- Intersection of cathodic and anodic currents yields a maximum pit size

$MgCl_2$ precipitates









- Stable phases in the $MgCl_2$-NaOH-CO_2-H2O-O_2 system