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Impact of salt deliquescence on the humidity-dependence of atmospheric corrosion

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ECS 228th Meeting
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University of Virginia School of Engineering

Sandia National Laboratories

Overview

Topics

- What is deliquescence?
- Hygroscopic behavior of sea salt simulants
- Effect of RH on corrosion response of steel contaminated with simulants

Tools

- Inkjet printing for rigorous, high-throughput contaminant loading
- Interdigitated microelectrode array for study of hygroscopic particles

Deliquescence

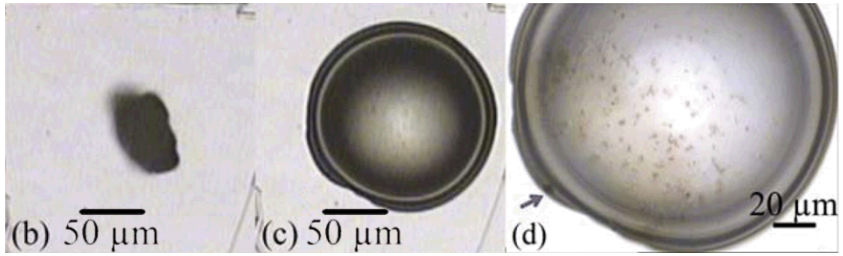
When is a surface wet enough for considerable corrosion rate?

DRH- RH at which solid→ liquid phase transformation occurs

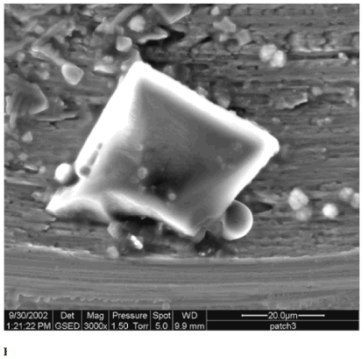
$V_{deliquesced} >> V_{sorbed}$

DRH as Critical Humidity

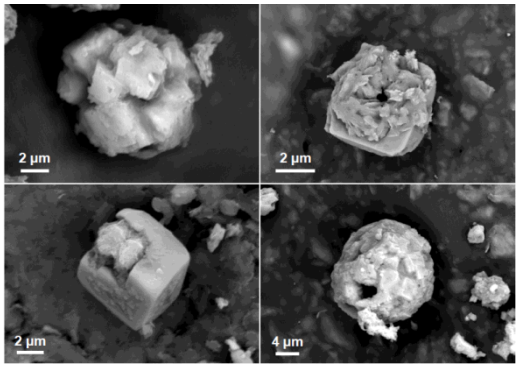
TOW = TOW(DRH)



Li, 2012



Cole, 2004

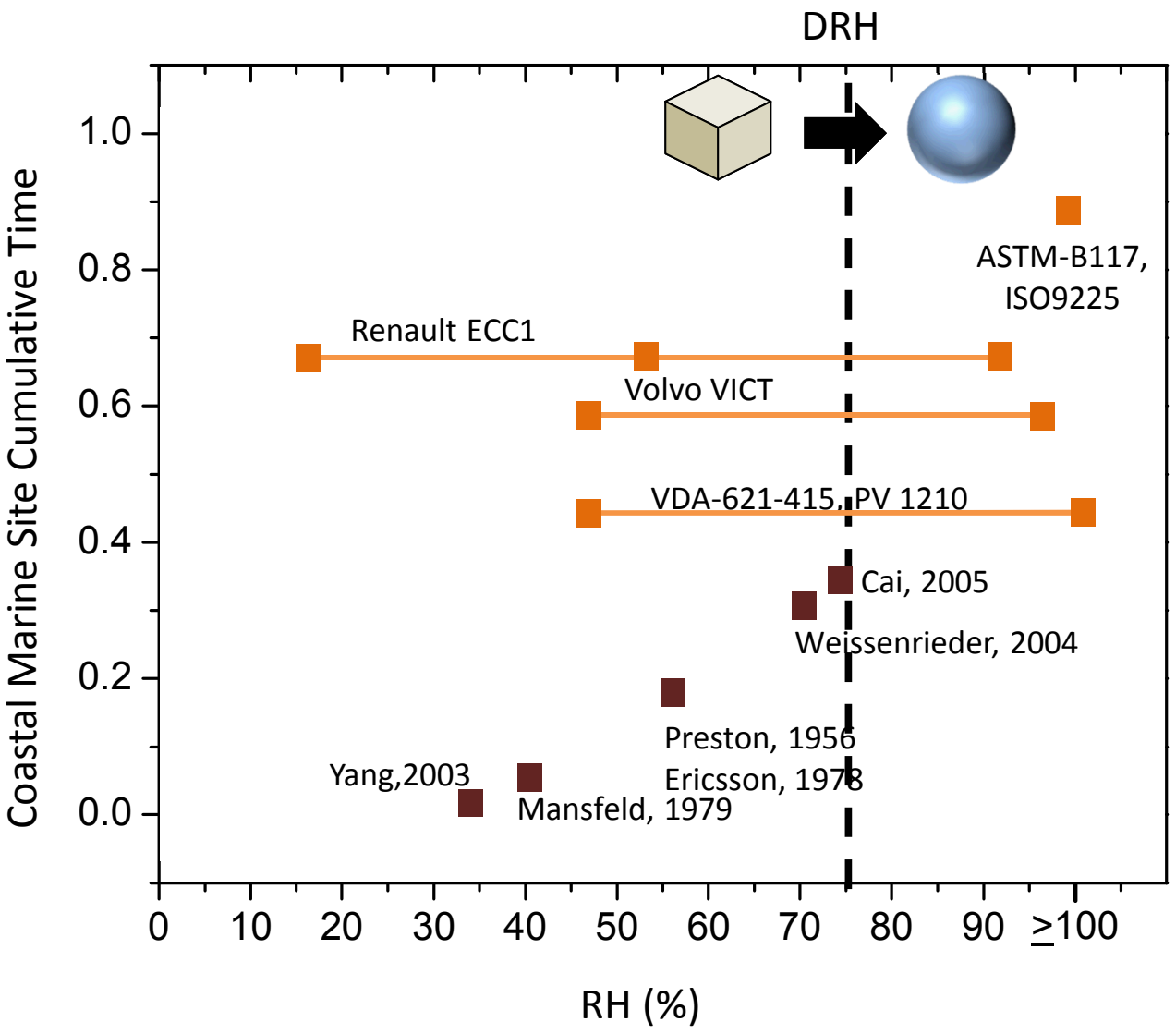


Bryan, 2014

$$\log(rate) = -0.739 + 3.26(TOW) + 5.02(SO_2) + 6.71(Cl)$$

Roberge, 2012

RH and NaCl


DRH
Coastal Marine Site Cumulative Time
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
80
90
≥100
RH (%)
ASTM-B117, ISO9225
Renault ECC1
Volvo VICT
VDA-621-415, PV 1210
Cai, 2005
Weissenrieder, 2004
Preston, 1956
Ericsson, 1978
Yang,2003
Mansfeld, 1979

Driving Questions

- What is relationship between deliquescence and humidity dependence of corrosion rate and damage distribution?

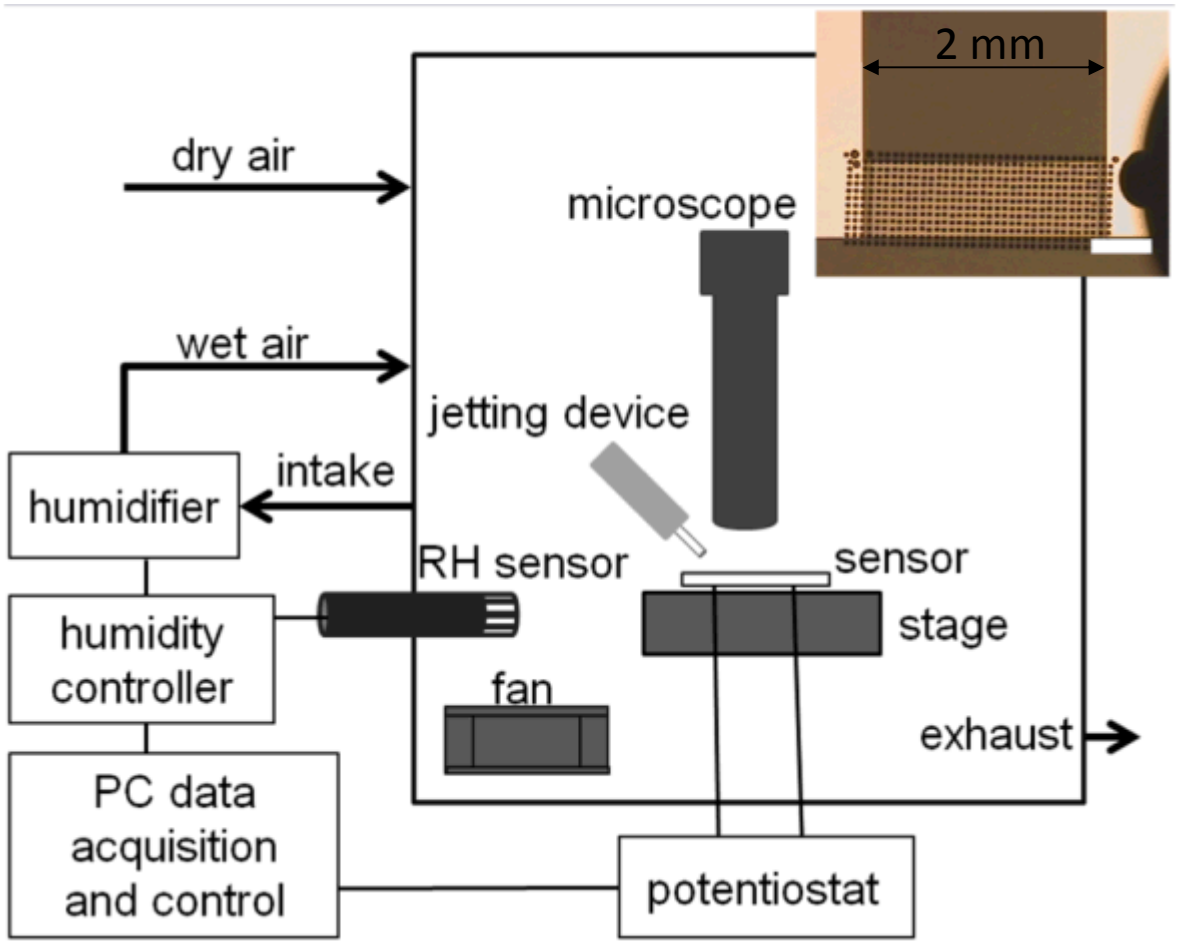
- What is the state of electrolyte below the deliquescence point?

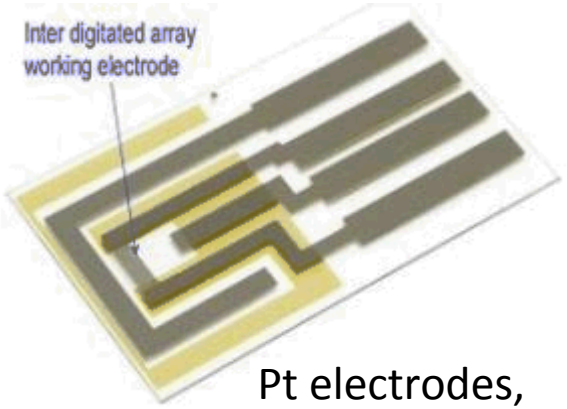
Approach

Characterize wetting and drying behavior of sea salt simulants and relate to corrosion behavior of steel under isohumidity conditions

Hygroscopic Behavior of Sea Salt Simulants

NaCl, $MgCl_2$, ASW

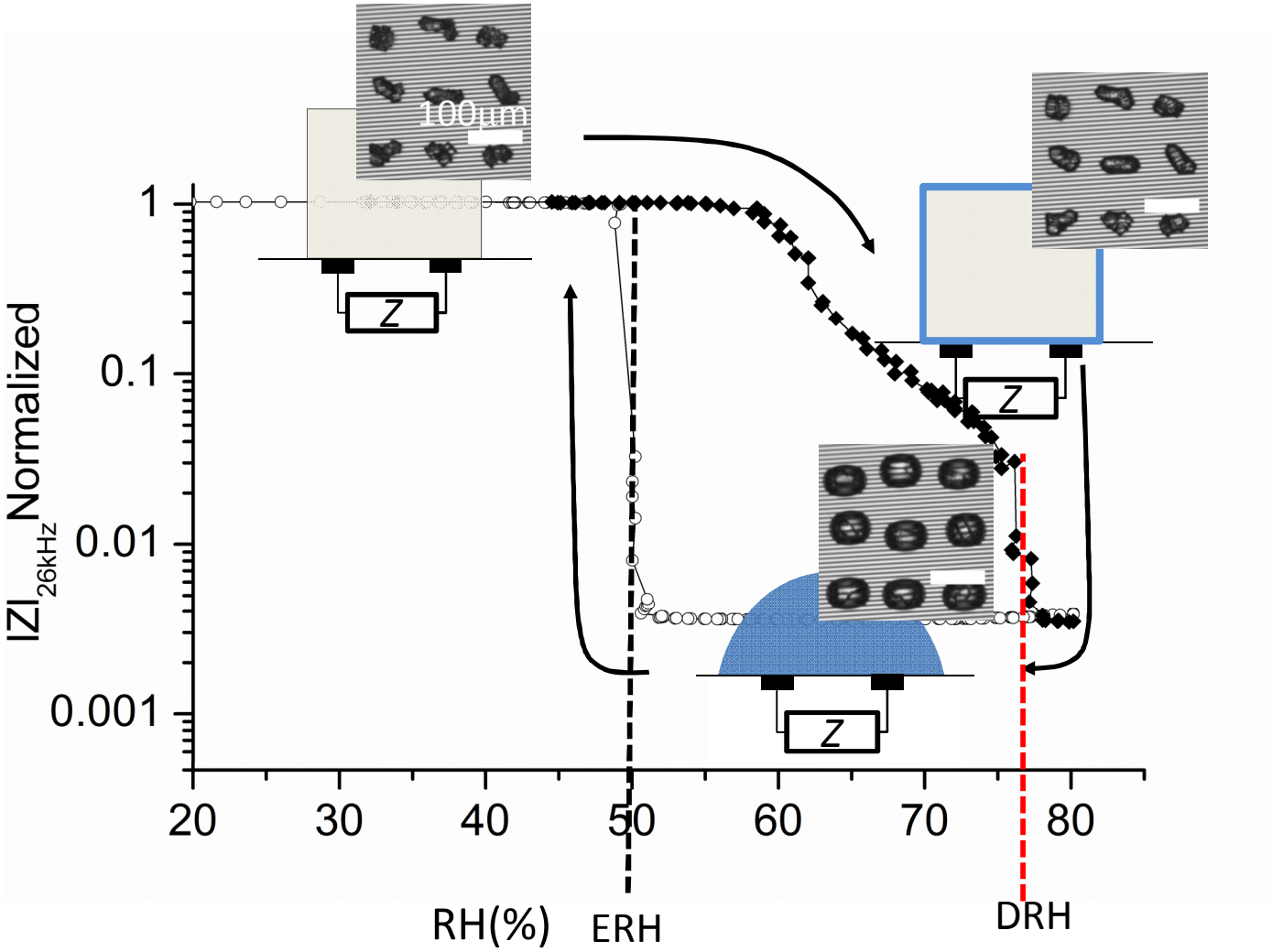




Pt electrodes, 3μm spacing

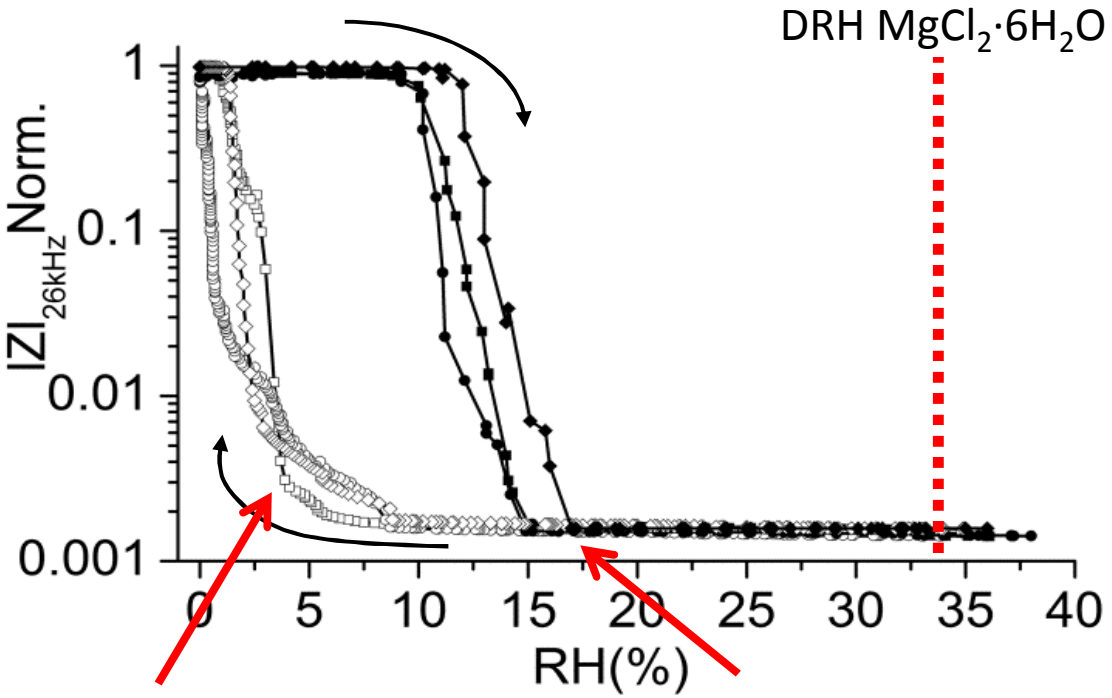
Hygroscopic Behavior

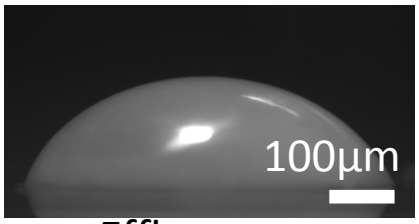
NaCl



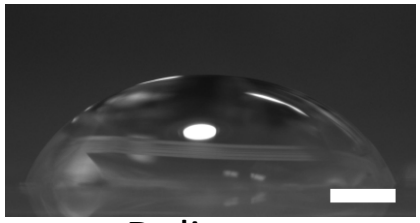
Hygroscopic Behavior

$MgCl_2$





Effloresce



Deliquesce

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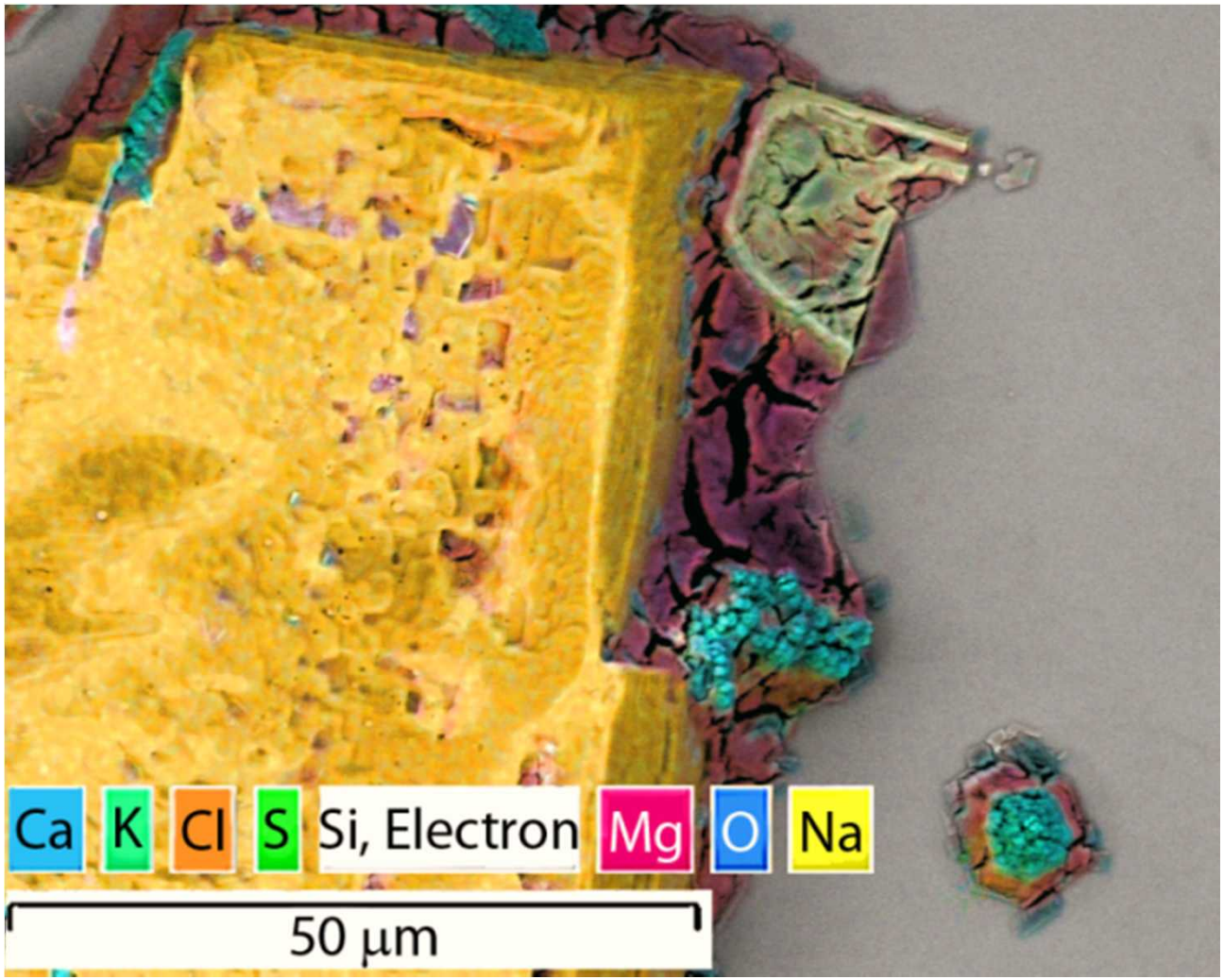
Hygroscopic Behavior: ASW

Phase Segregation



Hygroscopic Study Summary

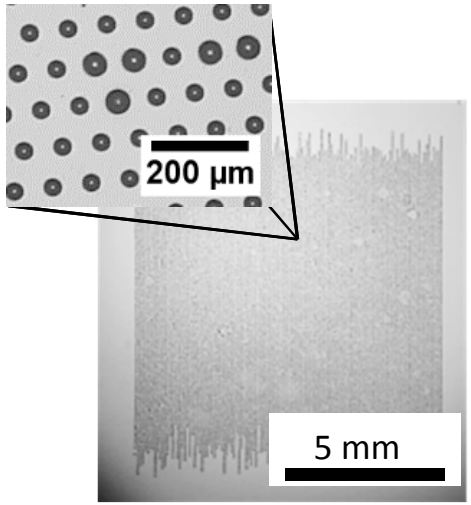
- Characterized and validated IDE microelectrode impedance method for microparticle interrogation

- $MgCl_2$ does not fully dry even after long times at low RH
  - fluid trapping
  - metastable hydrates

- ASTM seawater may not fully dry
  - identified key phase transition events
  - may be due in part to $MgCl_2$
  - Does TOW = 1 ?

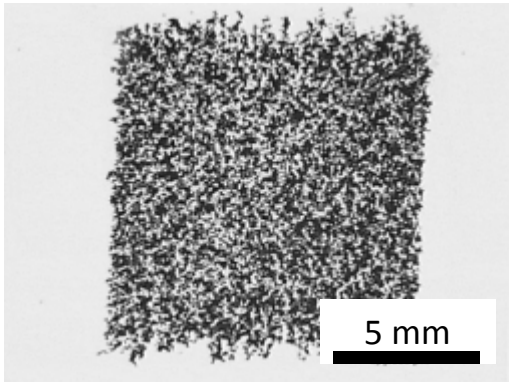
NaCl Particles: Corrosion Response

Experimental Approach



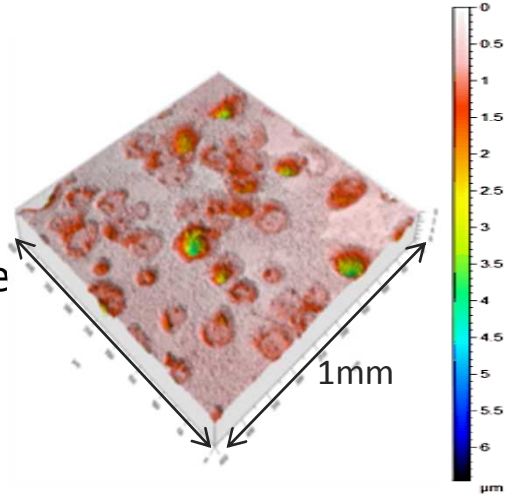
Deposit Sat. NaCl drops (9 µg/cm^2)

Fixed RH



Expose for 12hr, 24hr, 7days, 30days

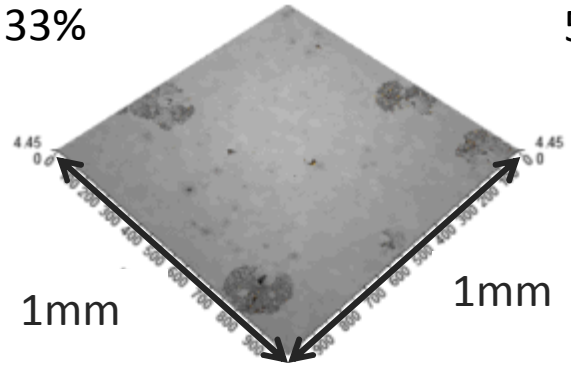
Remove Rust

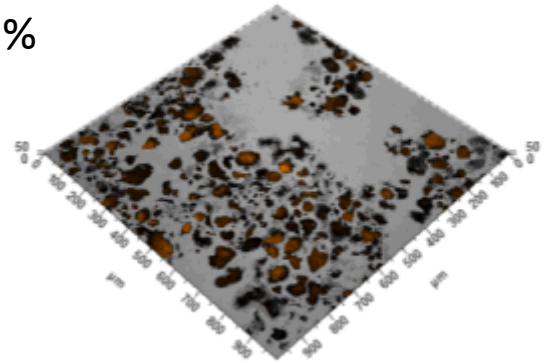


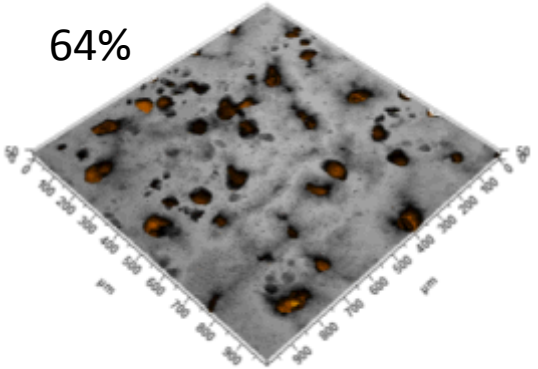
Quantify corrosion attack via profilometry

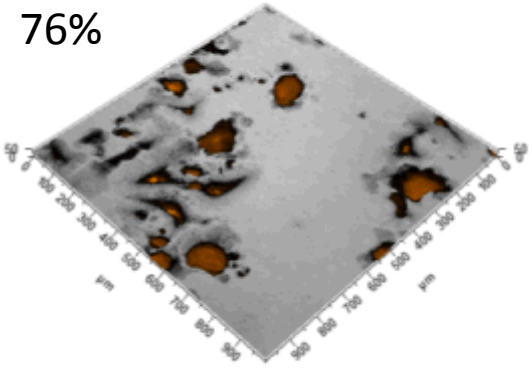
NaCl Particles: Corrosion Response

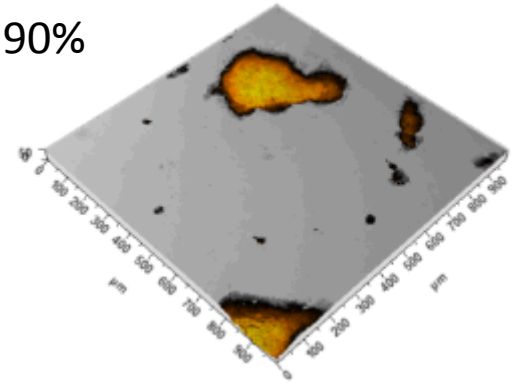
What is the effect of RH on attack morphology?

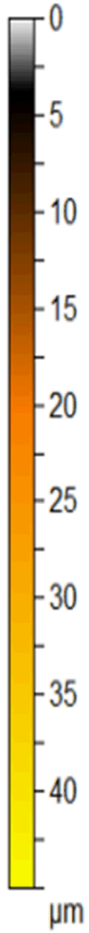








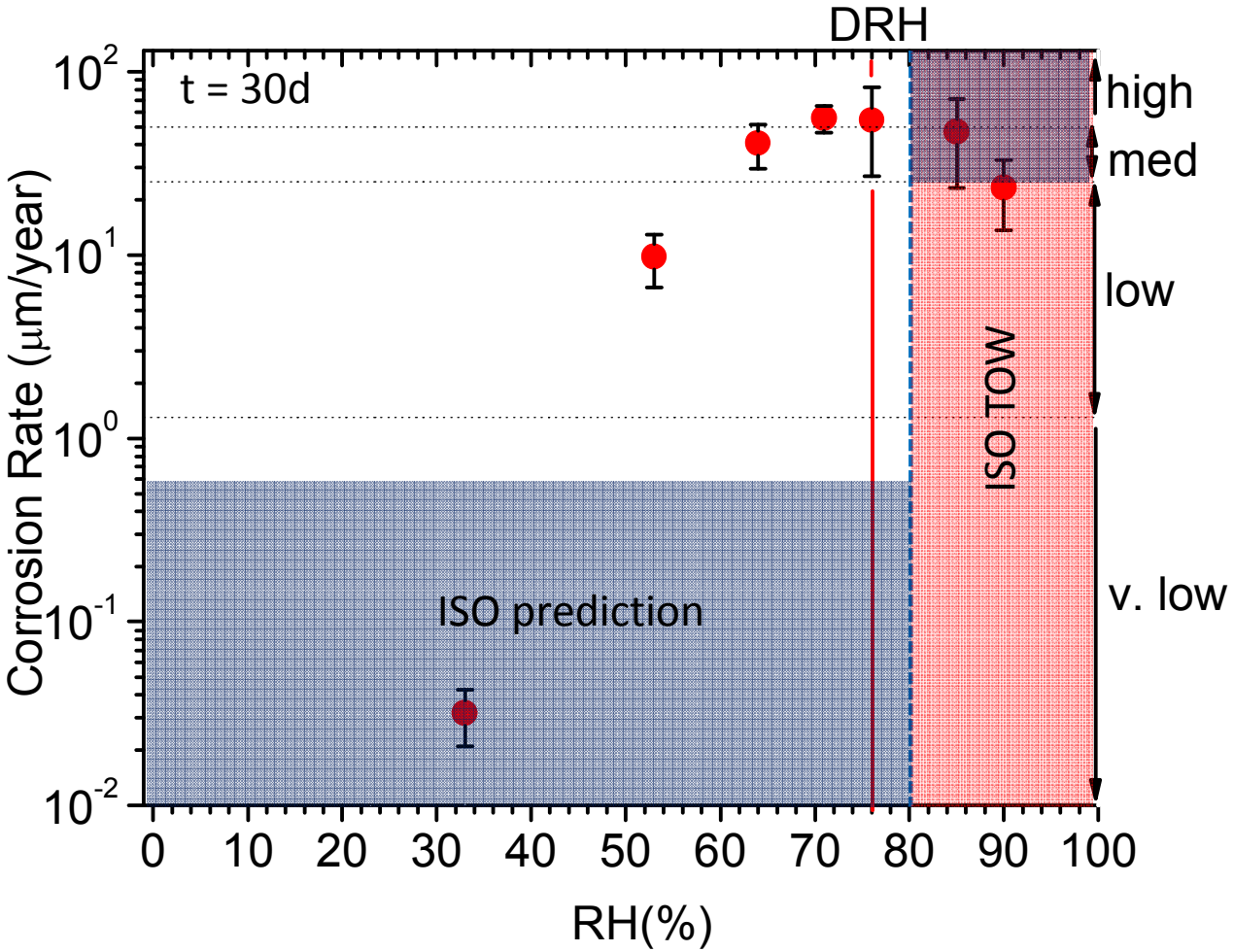




7 day exposure of
9 µg·cm^{-2} NaCl

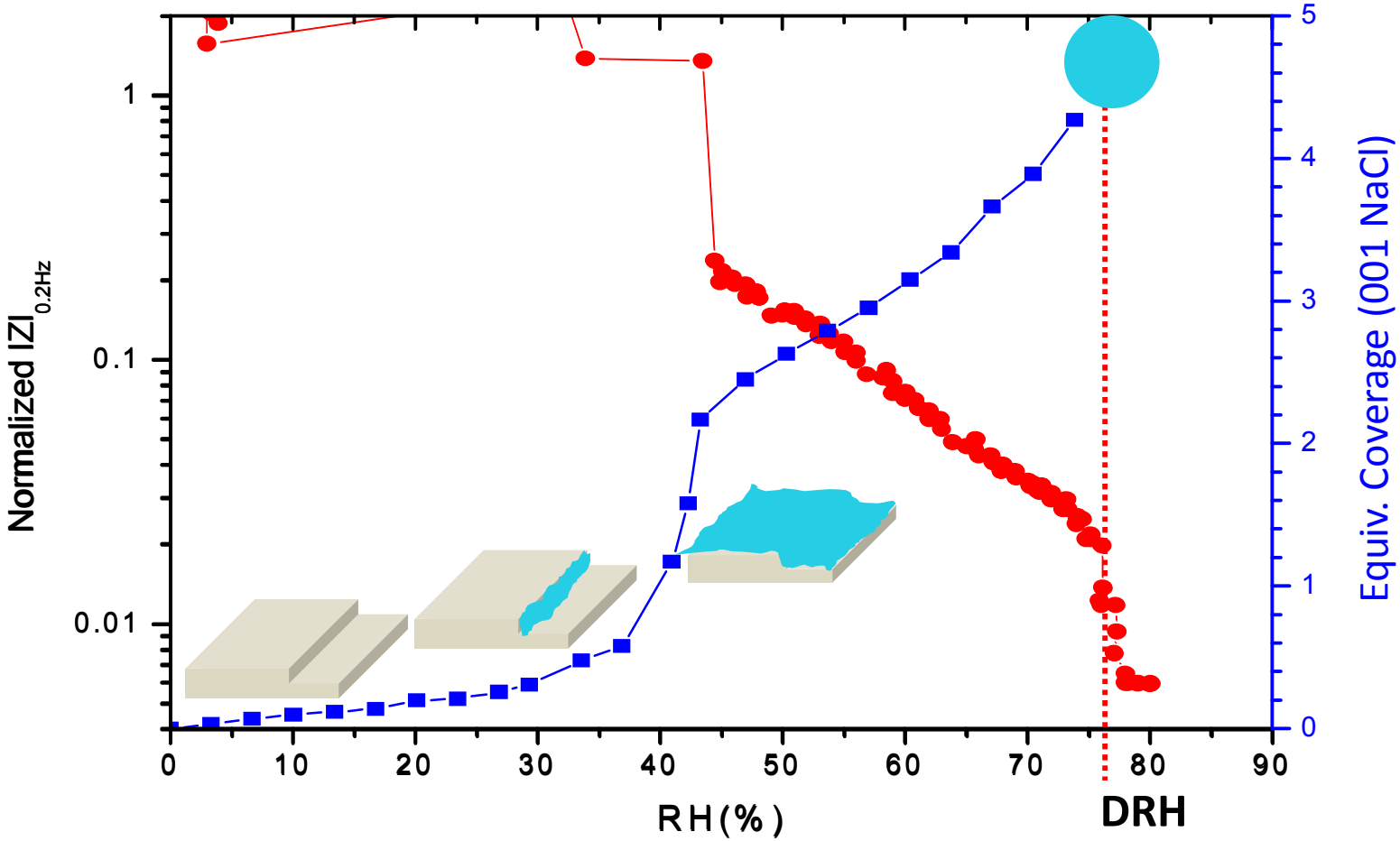
NaCl Particles: Corrosion Response

Under what RH range can corrosion be considered significant for plain carbon steel?



NaCl: Hygroscopic Behavior

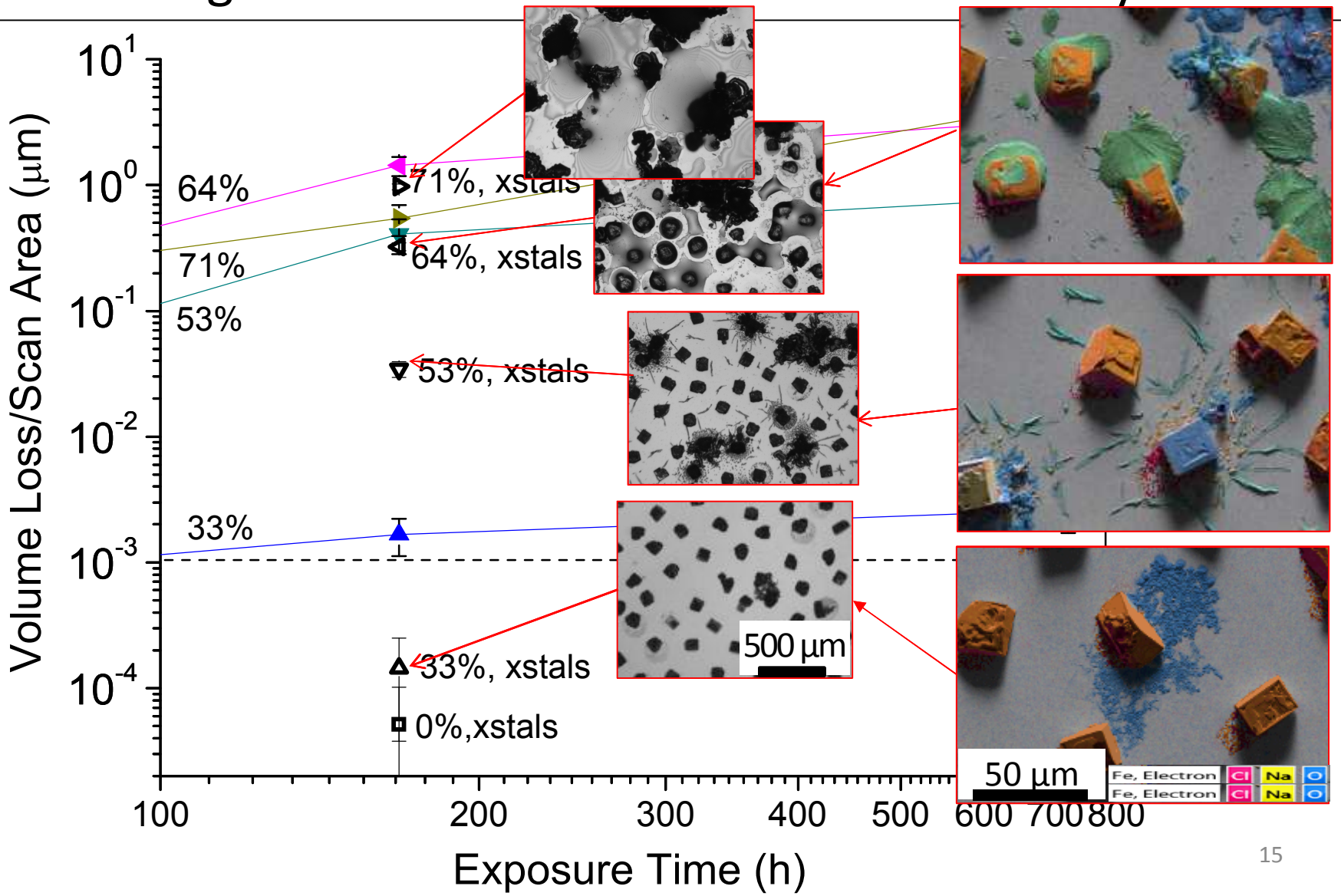
What enables corrosion below the DRH? Adsorbed Water?



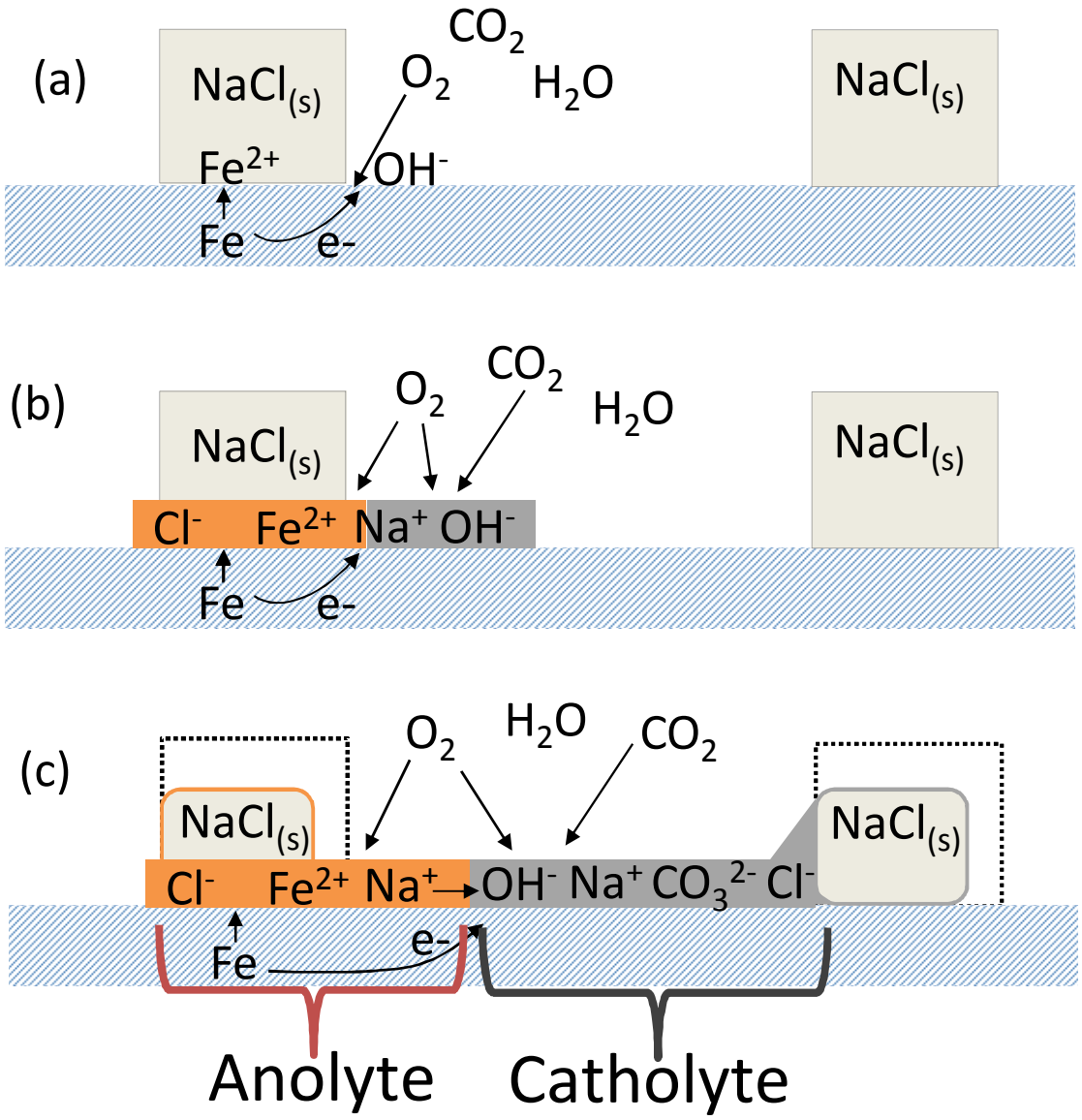
MC Foster and GE Ewing. 2000. J. Chem. Phys. 112:6817-6826
BJ Finlayson-Pitts. 2003. Chem. Rev. 103: 4801-4822
E. Schindelholz, L. Tsui, R.G. Kelly. 2014. J Phys. Chem. A. 118: 167-177

NaCl Crystals: Corrosion Response

Can significant corrosion occur under NaCl crystals?



Mechanism and RH dependence



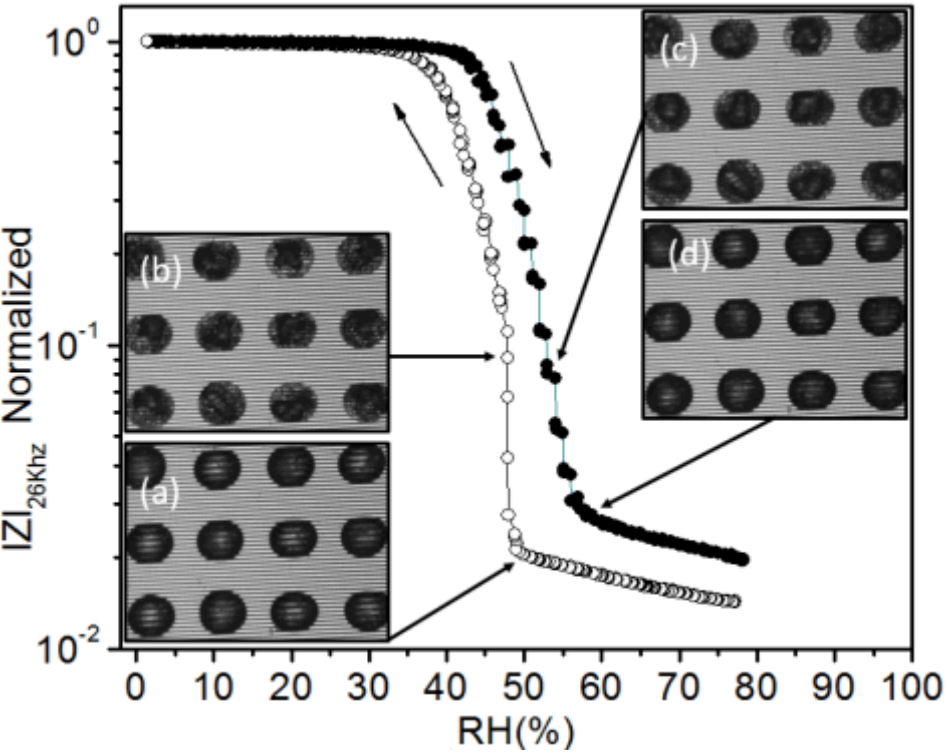
Compound	DRH
NaOH	6
$FeCl_3.7H_20$	40
$FeCl_2.4H_20$	64
NaCl	75
$Na_2CO_3.10H_20$	98

E. Schindelholz, et al. J. Electrochem. Soc. 2014. 161: C450-459

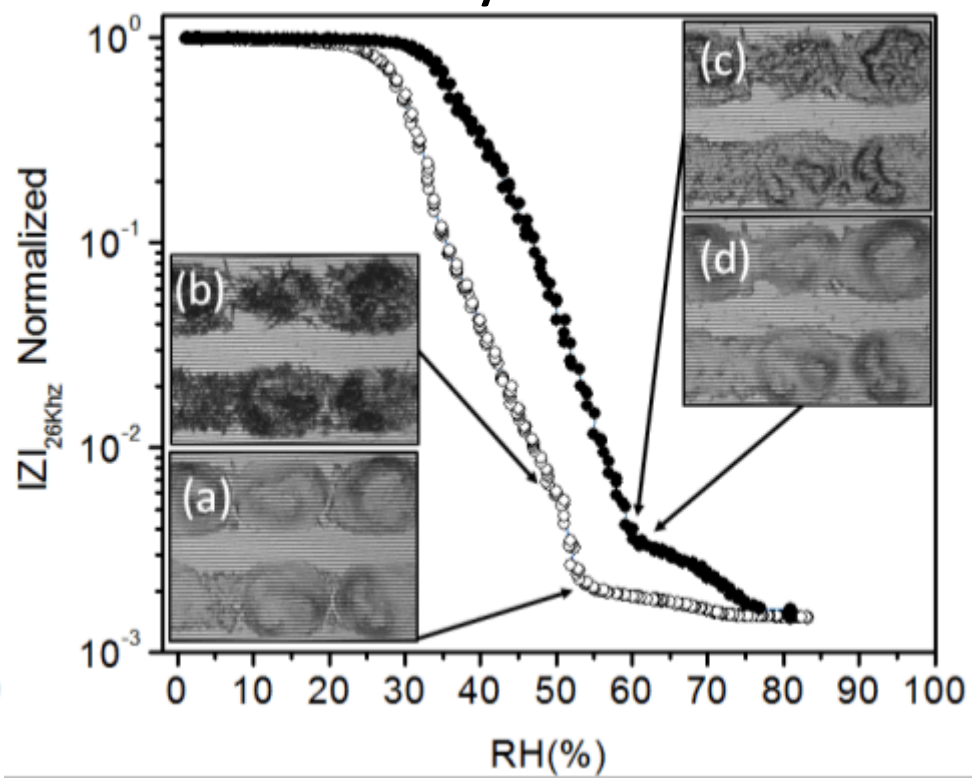
Corrosion Chemistry

What is the hygroscopic behavior?

Anolyte: $FeCl_2$-NaCl (1:1)



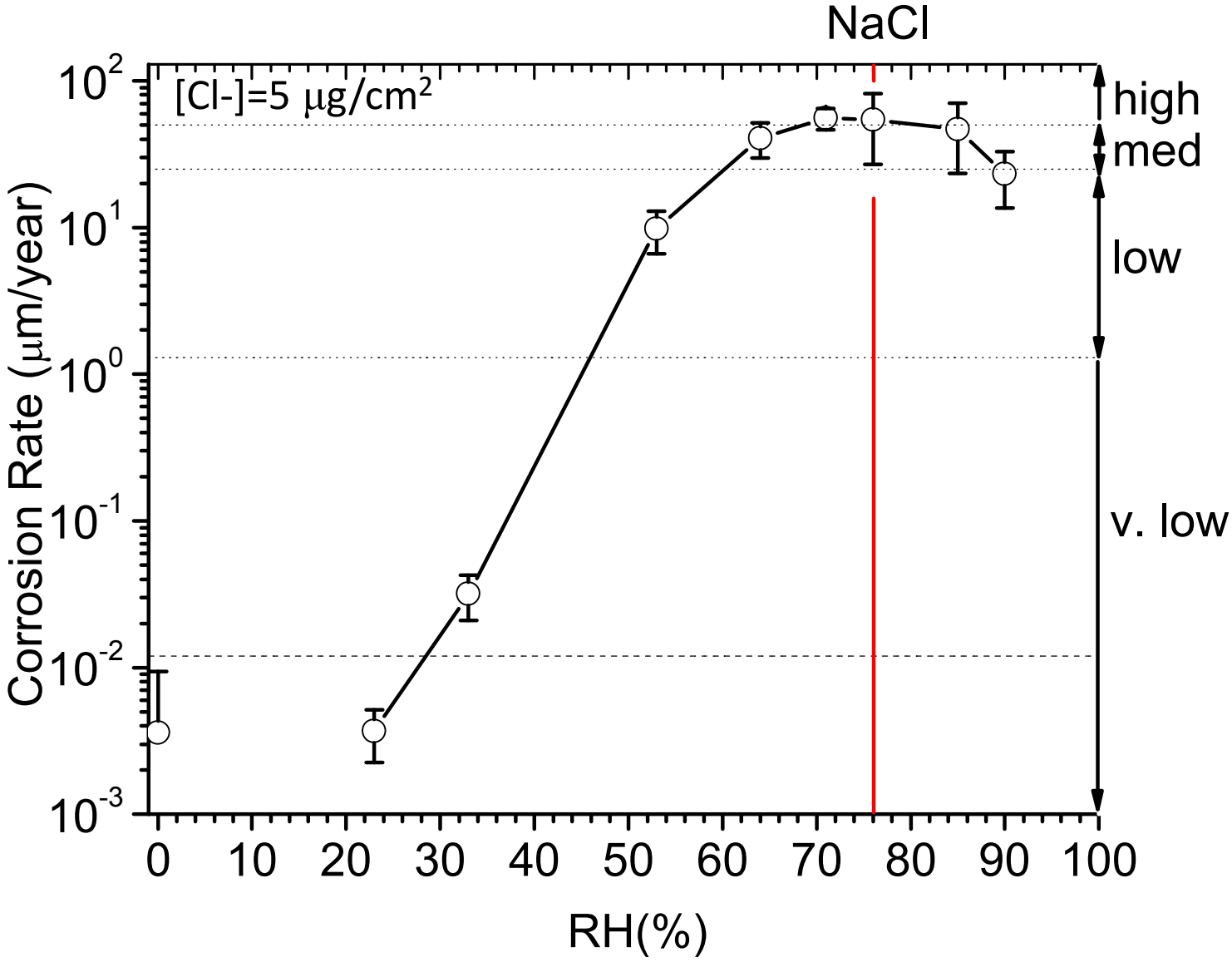
Catholyte: NaOH



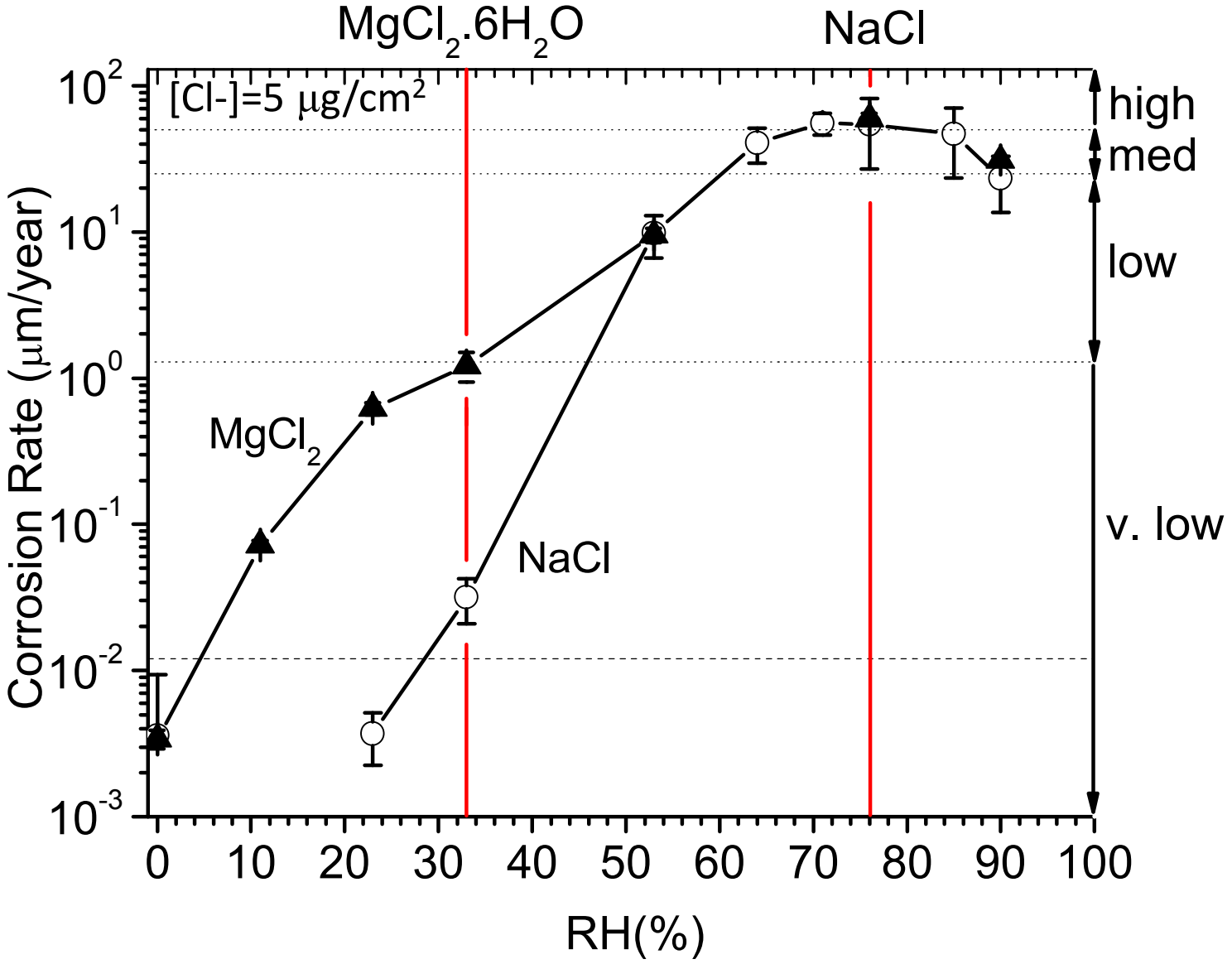
NaCl Study Summary

- Critical RH where corrosion is possible~ 33%RH
- Considerable corrosion occurs ≥ 53%RH
- Corrosion Below NaCl DRH Attributed to:
  - adsorbed water on NaCl crystals
  - corrosion chemistry
- Attack morphology can be controlled by RH

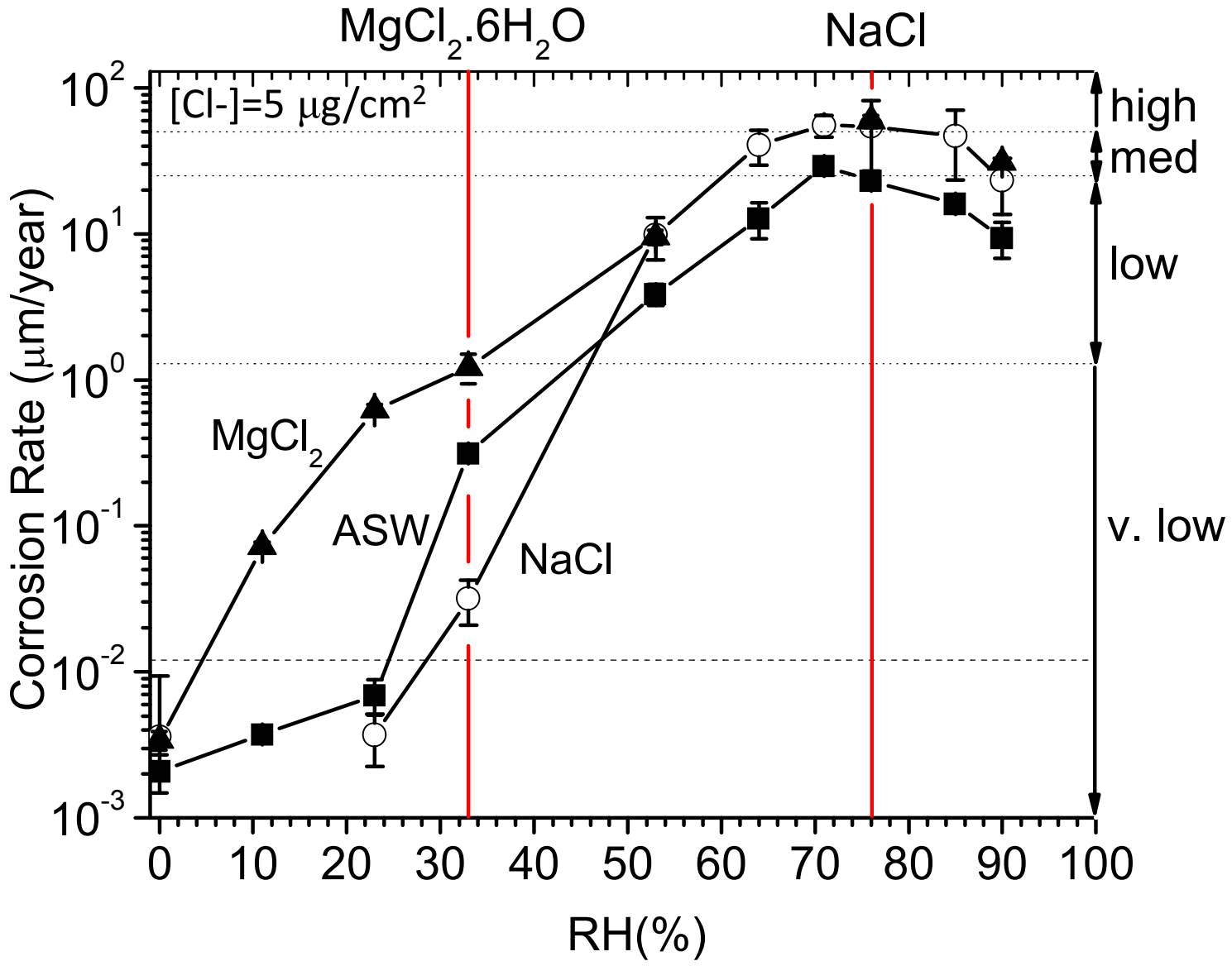
30 d Normalized Corrosion Rates



30 d Normalized Corrosion Rates

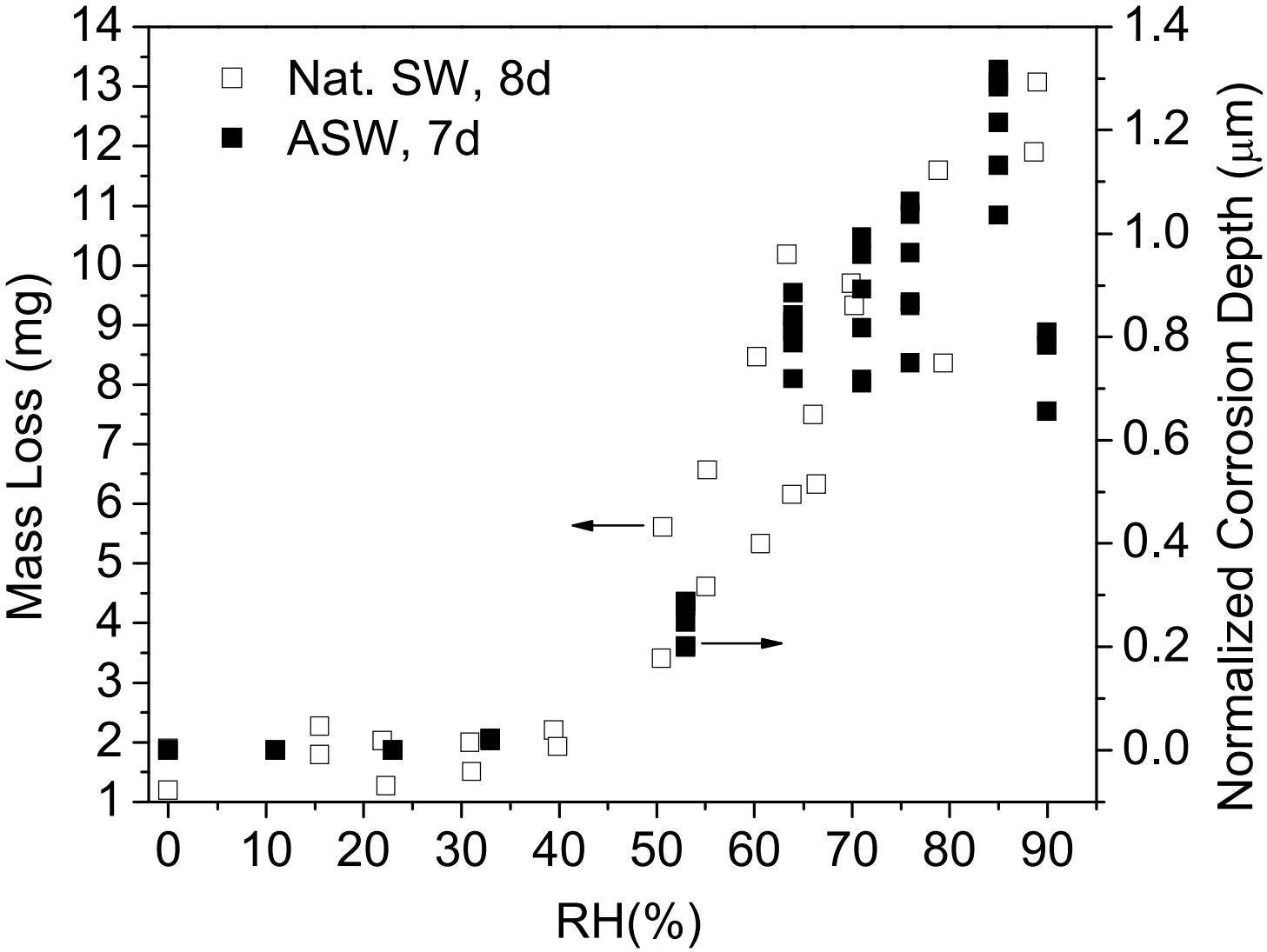


30 d Normalized Corrosion Rates



E. Schindelholz, et al. J. Electrochem. Soc. 2014. 161: C459-469

Comparison to Natural Contaminants



U.R. Evans and C.A. Taylor. 1974. Brit. Corr. J. 9: 26-28.

Conclusions

- Corrosion loss and attack morphology not directly reflective of liquid-solid phase transitions for NaCl, $MgCl_2$, or ASW

- Considerable corrosion and electrolyte below DRH
  - adsorbed water on salt crystals
  - non-equilibrium phases and fluid trapping
  - corrosion chemistry

- How do these results hold in natural enviroments, varying humidity?

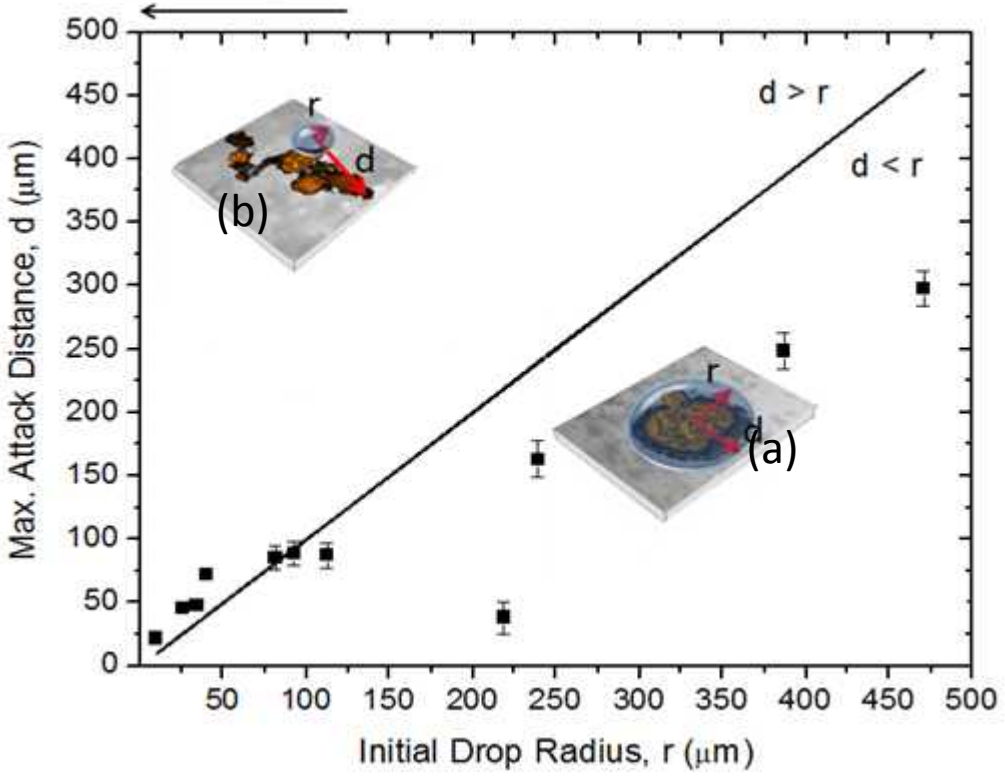
Acknowledgements

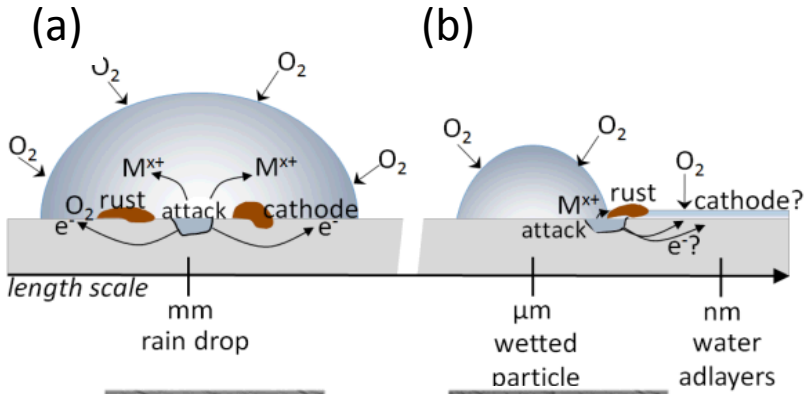
SERDP/ESTCP Program, W912HQ-09-C-0042, Accelerated Dynamic Corrosion Test Method Development

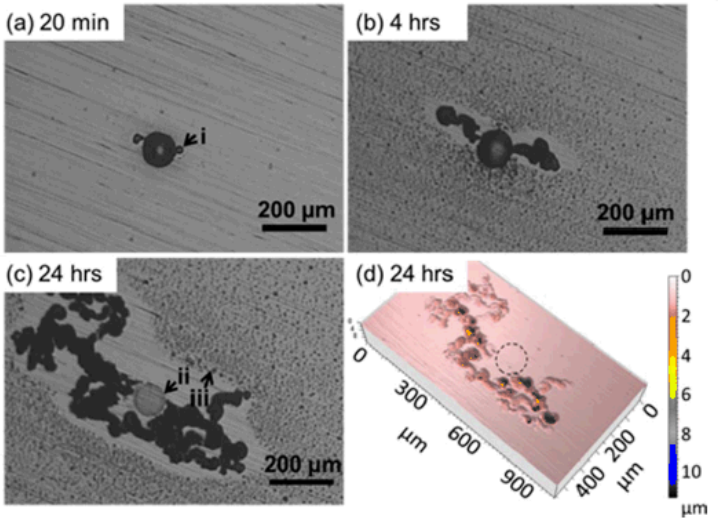
USAF, FA8501-UVA-002, DOD Corrosion Policy and Oversight, OUSD (AT&L)

Evolution and Influence of Electrolyte Geometry and Chemistry on Rate

Atmospheric Particles
Contaminants







Risteen, Schindelholz 2014