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Spent Fuel and Waste Science and Technology

Brine Stabilities on Hot SNF Storage Canister Surfaces

Charles Bryan and Eric Schindelholz
Sandia National Laboratories

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Canister SCC: Important Processes

Storage Time

Incubation | *Pit Growth*

Begin Storage — *Pit Initiation* — *C In*

What are relevant brine chemistries and deliquescence properties, and how do they evolve due to atmospheric reactions and corrosion?

SNL — Surface Environment, Brine Stability

SNL/OSU — Pitting initi
Pit-to crack transition (ex

CSM/SNL — Pitting initiation and growth (effect of stress)

CSM — Pit-to-Crack Transition (Modeling)

NCSU (SNL) — SCC growth rates

OSU (SNL) — SCC growth rates

SNL/LANL — mockup pitting/cracking

Importance of Brine Composition and Evolution

- **For near-marine sites, salts are assumed to be unmodified sea-salts**
  - Deliquescence controlled by $MgCl_2$
  - Brine properties (volume, conductivity)
  - These properties determine when corrosion initiates, maximum pit size, and timing of pit conversion to stress corrosion cracks. *These are critical parameters for estimating timing of canister SCC*
- **Salt/brine properties will change due to atmospheric reactions and corrosion reactions**
  - Understanding brine evolution is critical for accurately predicting the timing of canister SCC.

Are Sea-Salt Brines Really Present?

Effects of Atmospheric Exchange Reactions

- Predictive models for canister SCC always assume canister surface have sea-salt properties(deliquescence/chemistry). Is this correct?
- Atmospheric exchange reactions — acid gas (H_2SO_4, HNO_3, CO_2) absorption, coupled HCl degassing—are ignored:

$$NaCl(s, aq) + HNO_3(g) \leftrightarrow NaNO_3(s, aq) + HCl(g)$$

$$2NaCl(s, aq) + H_2O + ½O_2 + SO_2(g) \leftrightarrow Na_2SO_4(s) + 2HCl(g)$$

Similar reactions that occur with Ca, Mg. For instance:

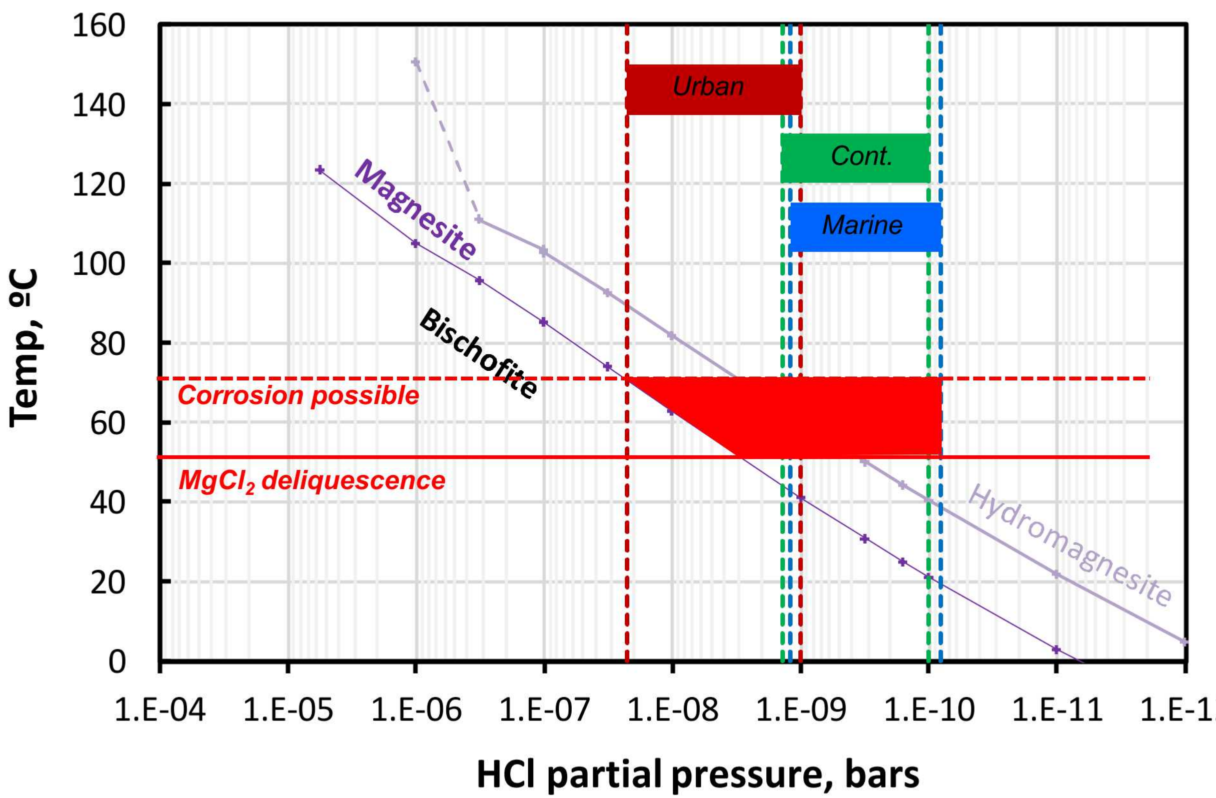
$$Mg^{+2}(aq) + 2Cl^{-}(aq) + H_2O + CO_2(g) \rightarrow MgCO_3(s) + 2HCl(g)$$

- In the field and especially the lab, the effects of these reactions must be considered.

$MgCl_2$ Brine Stability at Elevated Temperatures

$$Mg^{2+} + 2Cl^{-} + CO_2(g) + H_2O \leftrightarrow MgCO_3(s) + 2HCl(g)$$

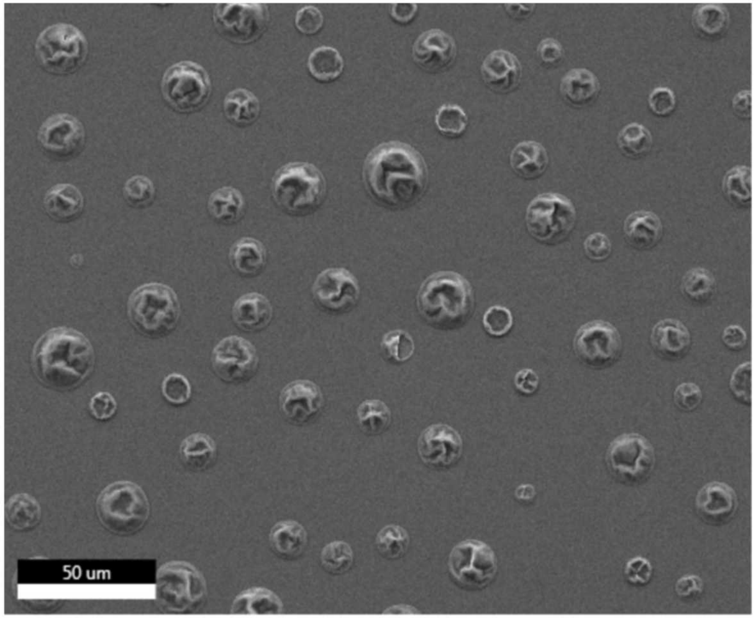
- **Brines may degas or absorb HCl, depending on background acid gas concentrations and temperature**
- **Elevated temperatures promote conversion to carbonate**
- **$MgCl_2$ brine stability experiments in progress**
  Difficult to run—carbonation is minimized in laboratory settings by low gas exchange rates

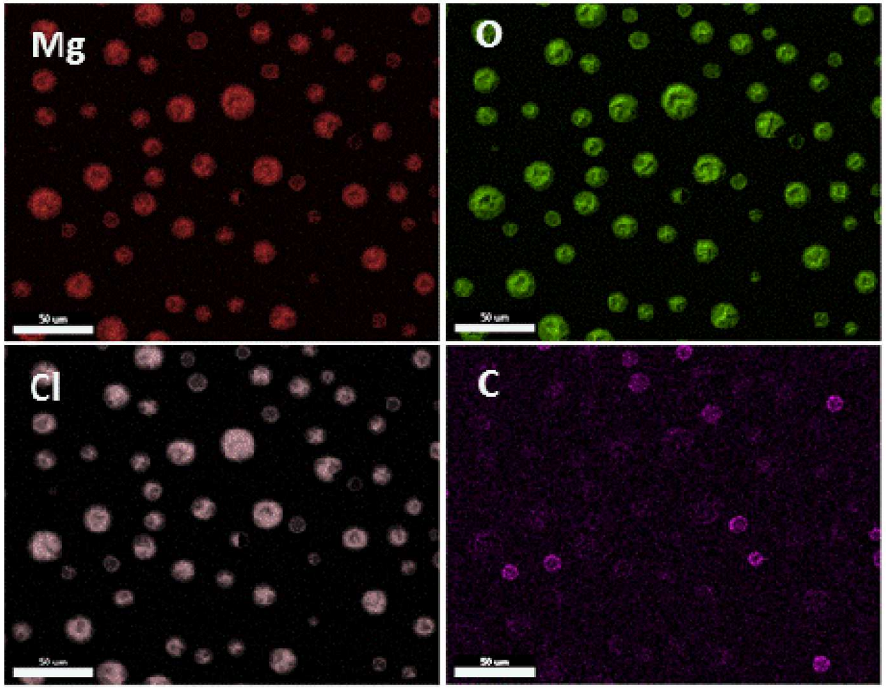


Experimental Results:

$MgCl_2$ brine at 48ºC, 40%RH, P_{HCl} = 0

- ***$MgCl_2$ brine, , deposited on silicon wafers***
- ***Experimental conditions 48ºC, 40% RH, 2 L/min air flow.***
- ***Experiment run for 6 weeks***

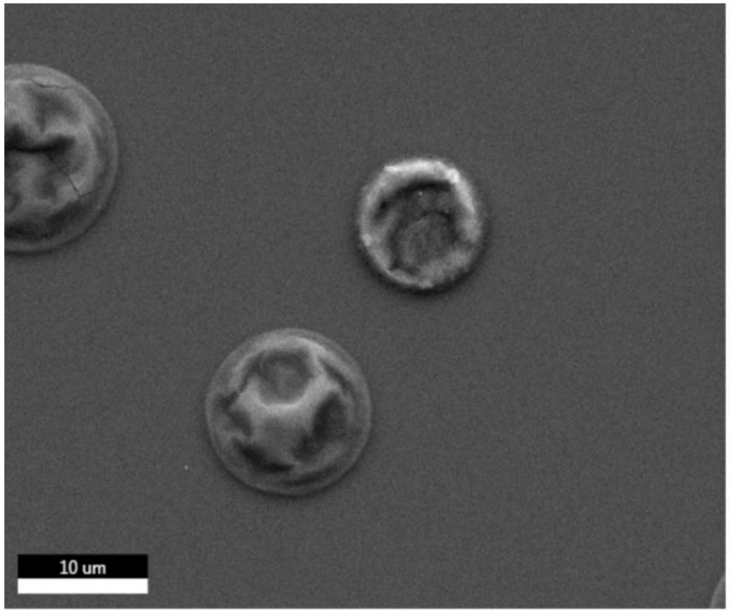


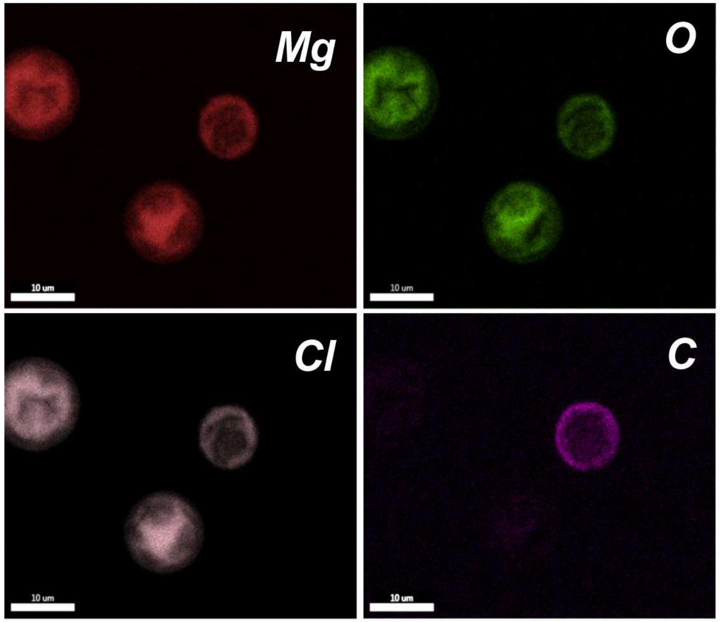


Experimental Results:

$MgCl_2$ brine at 48ºC, 40%RH, P_{HCl} = 0

- ***Effects very localized—only some smaller brine droplets affected.***
- ***Partial conversion to carbonate observed; later chemical analysis suggests <10% chloride lost.***
- ***Airflow too low to support complete conversion. At 48ºC, one m^3 of air can only remove 1.3 ug chloride (hydromagnesite) to 13 ug chloride (magnesite).***





Significance of Experimental Results

Are sea-salt brines really present on canisters? No exactly.
Are results from laboratory experiments relevant to field conditions? Not necessarily.

- **Reactions with atmospheric gases modify sea-salt brines (chemistry, RH_d).**
- **Effects artificially limited in laboratory experiments due to limited air flow.**
- **Experiment design may strongly affect test results. E.g.,**
  - *RH chamber → high air flow, atmospheric exchange*
  - *RH controlled by saturated salt solution → no air flow, no atmospheric exchange*
  - *Results may be affected by total amount of chloride or number of samples present.*
  - *Background acid gas concentrations in lab (HCl, H_2SO_4 or SO_2, HNO_3) may have a significant effect.*

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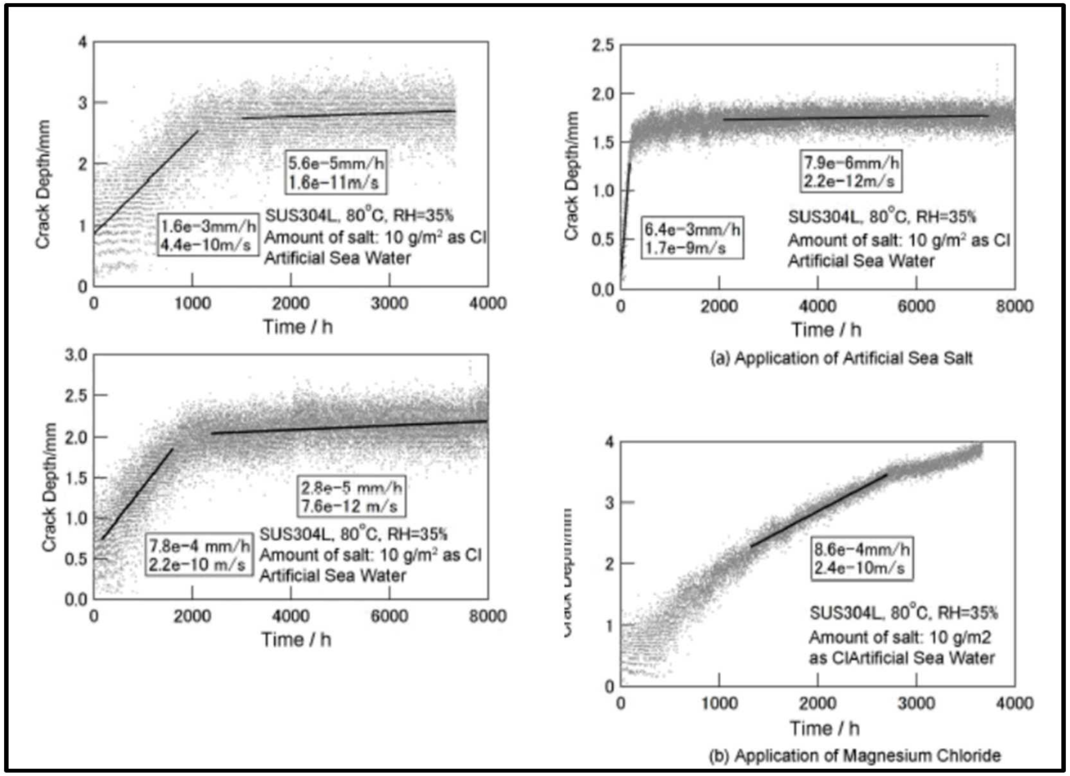
$MgCl_2$ Brine Stability

Other acid gas reactions (e.g., H_2SO_4) may be more important under field conditions. However, considering carbonation may be VERY important for interpreting laboratory experiments.

- *CRIEPI experiments: At 80ºC, 35% RH, air exchange of only a cubic meter is necessary to convert the small amount of $MgCl_2$ present in the sea-salts to carbonate, drying out the brine.*
- *Difficulties in initiating SCC in some tests?*

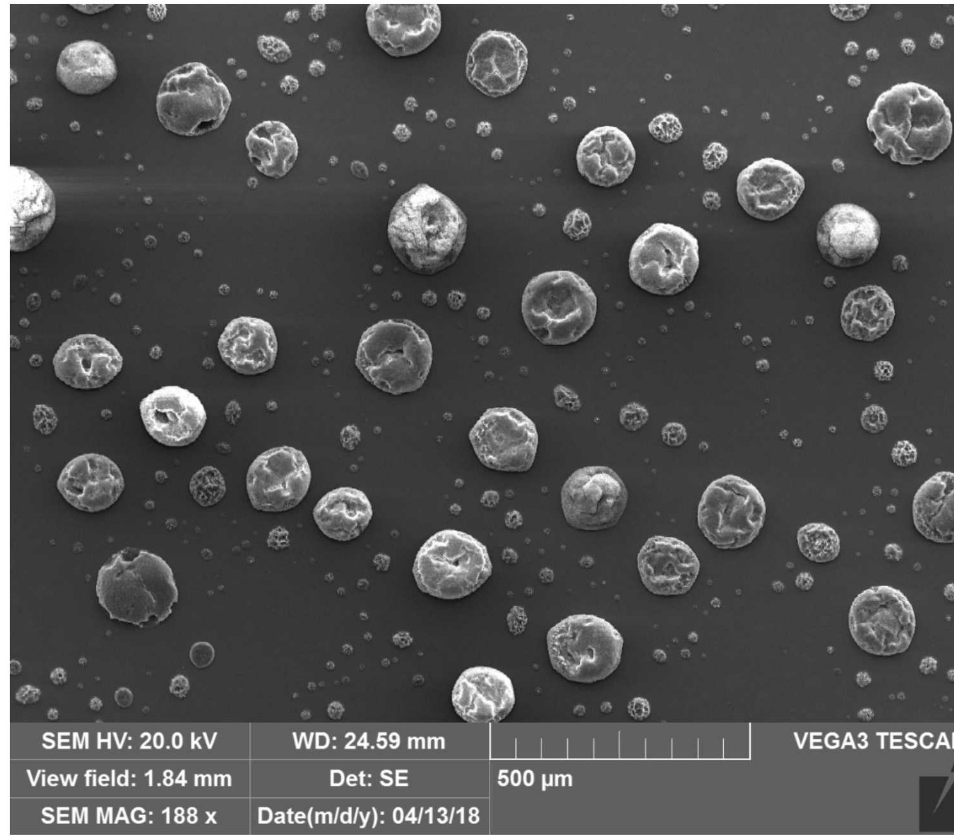
We are running $MgCl_2$ stability experiments under identical conditions to CRIEPI right now.



$MgCl_2$ brine stability, 80°C, 35% RH

Experimental setup similar to previous experiment

- Silicon wafer substrates (chemically inert)
- $MgCl_2$ applied using inkjet printer
- Higher salt load to facilitate analysis: 300 μg/cm²
  - Resulted in much larger range of droplet sizes, from ~10 μm to ~150 μm)
- Sampled after 2 and 4 weeks (8 weeks too come)



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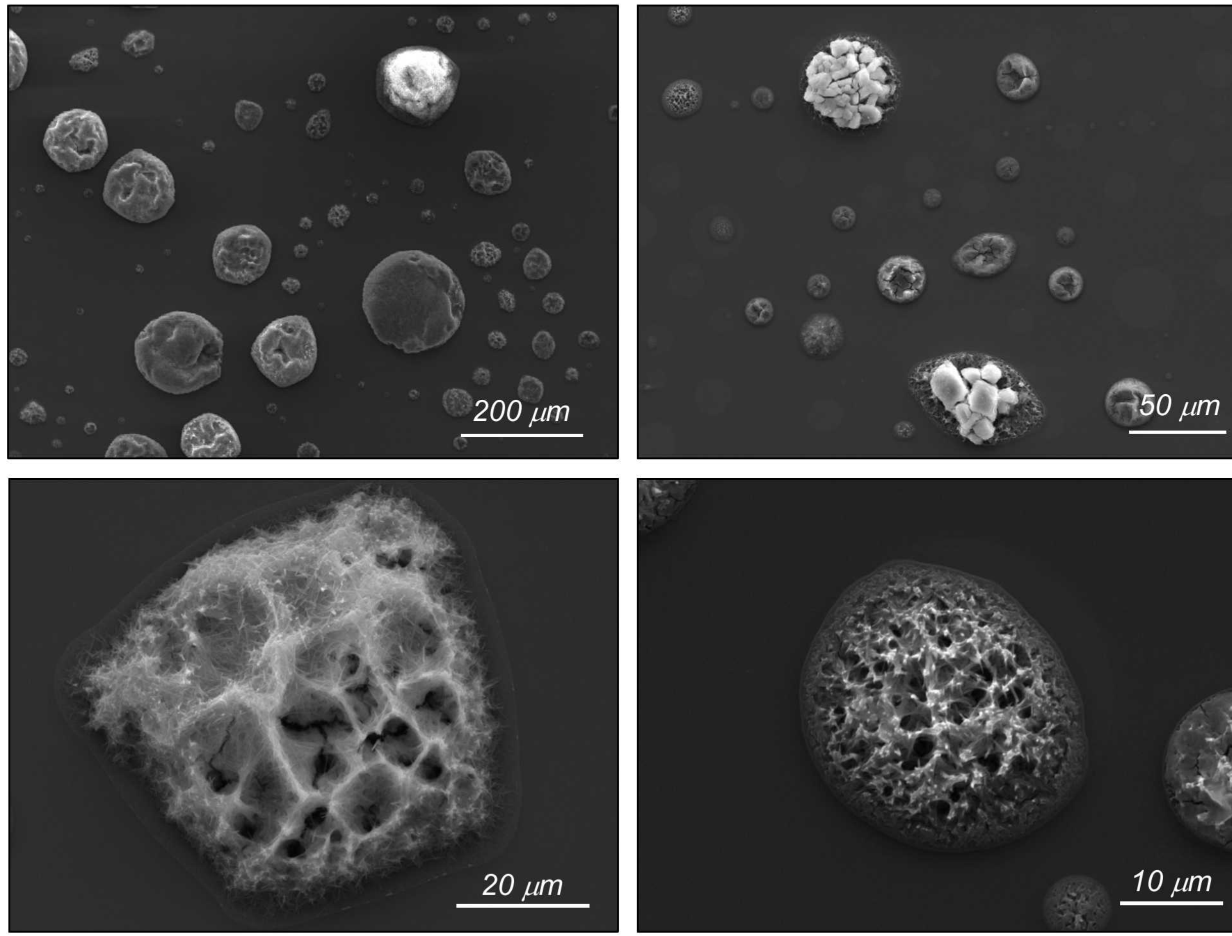
$MgCl_2$ brine stability, 80°C, 35% RH
(2 weeks, 4 weeks)

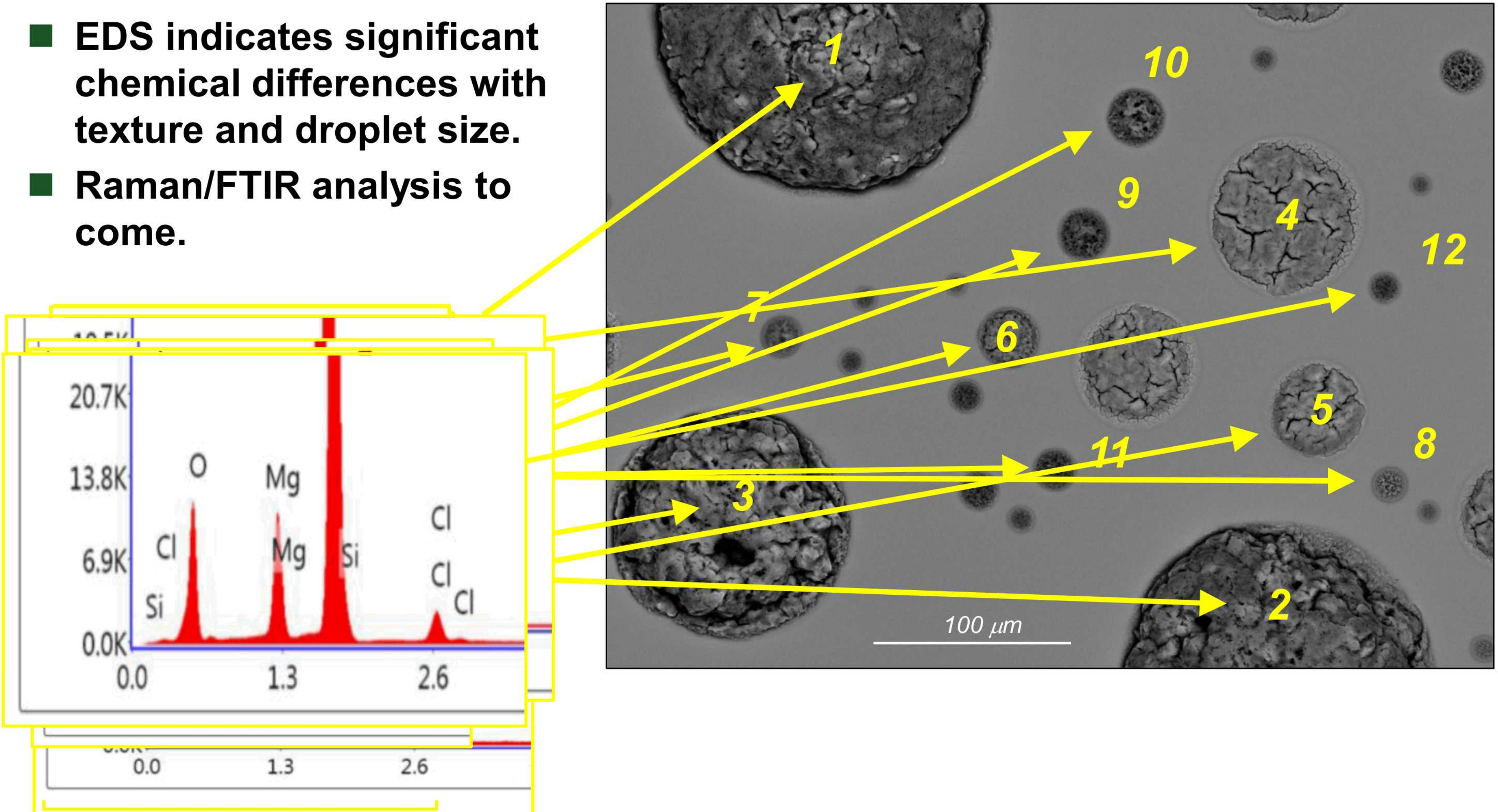
Textural variation with droplet size

- Large droplets smooth and rounded
- Mid-sized droplets sometimes crystalline, with selvages
- Smallest droplets partially or completely fibrous
- Difference in mineralogy or chemistry? X-ray diffraction of the wafers shows only bischofite



$MgCl_2$ brine stability, 80°C, 35% RH

- EDS indicates significant chemical differences with texture and droplet size.
- Raman/FTIR analysis to come.



$MgCl_2$ brine stability, 80°C, 35% RH

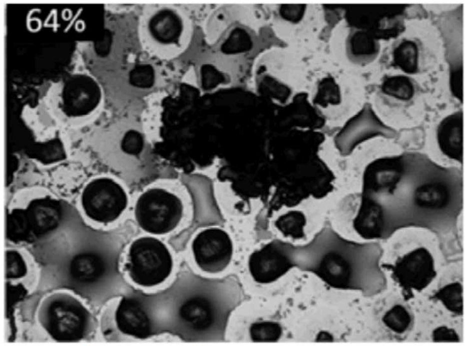
- At 80°C, $MgCl_2$ brine droplets lost Cl through degassing
- Smaller droplets (higher surface area to volume ratio) most affected
- Large droplet sizes (and low air flow?), led to slow conversion.
- Over time, complete conversion to magnesium hydroxychloride hydrate?

Possible brine dry-out must be considered when interpreting results of long-term corrosion testing under "accelerated" (high temperature) conditions

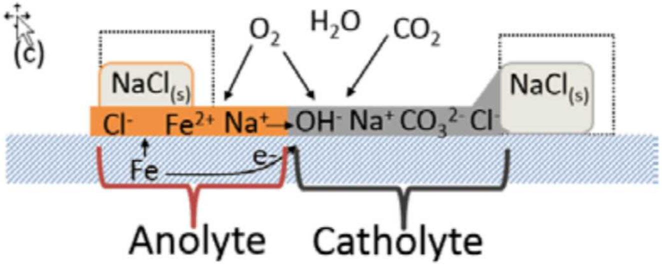
Effects of Corrosion: Cathodic Brine Chemistry

Corrosion reaction

NaCl on steel



Schindelholz, 2014



- **Metal oxidation at the anode (pit or SCC crack)**
- **Oxygen reduction at the cathodic region surrounding the anode produces hydroxide.**

$$\frac{1}{2}O_2 + H_2O \rightarrow 2(OH^-)$$

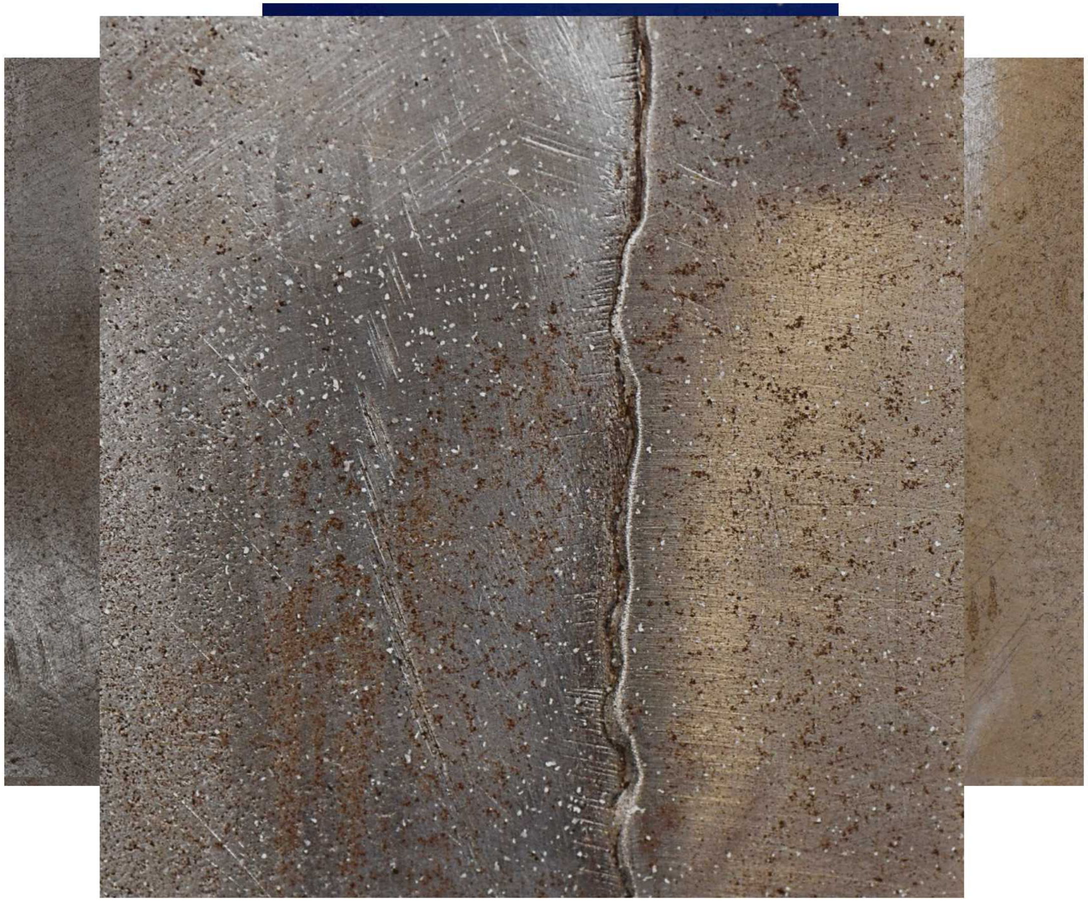
- **OH^- generated at the cathode (pH increases); in the atmosphere, carbonation occurs.**
- **Cathodic brine chemistry can result in brine dryout, changes in brine properties (thickness, composition)**

Corrosion of Mockup Weld Samples

- ***Test conditions: 80°C, 35% RH***
- ***Large mockup plates (18" x 20") to maintain most weld residual stresses near the center of the plates***
  - *Circumferential weld*
  - *Longitudinal weld*
  - *Weld intersection*
- ***Heavy salt load (nominally 3 g/m² $MgCl_2$)***
- ***Goal: Accelerated test to determine location and orientation of canister SCC cracks***

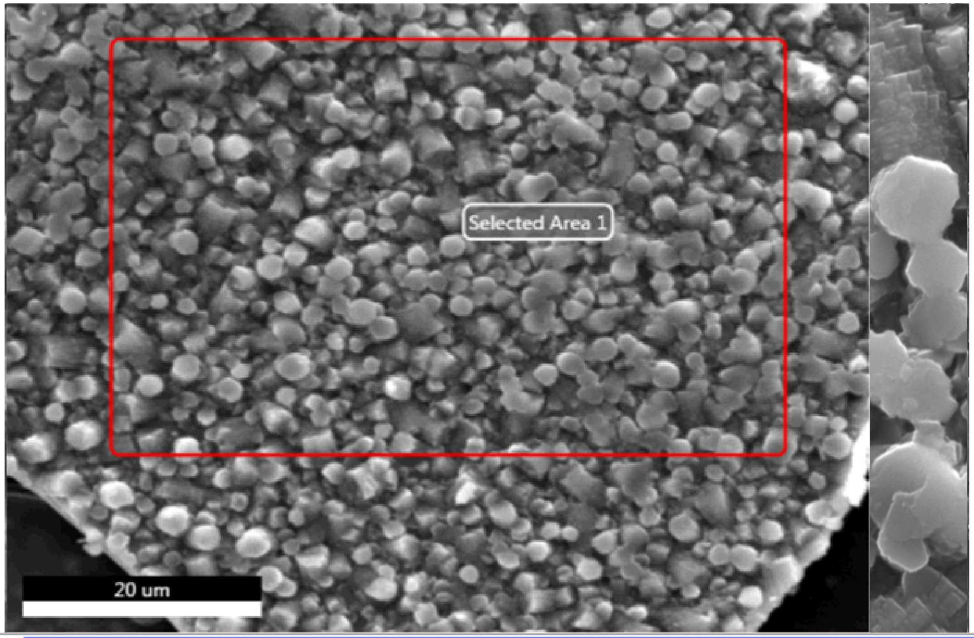
Corrosion of Mockup Weld Samples

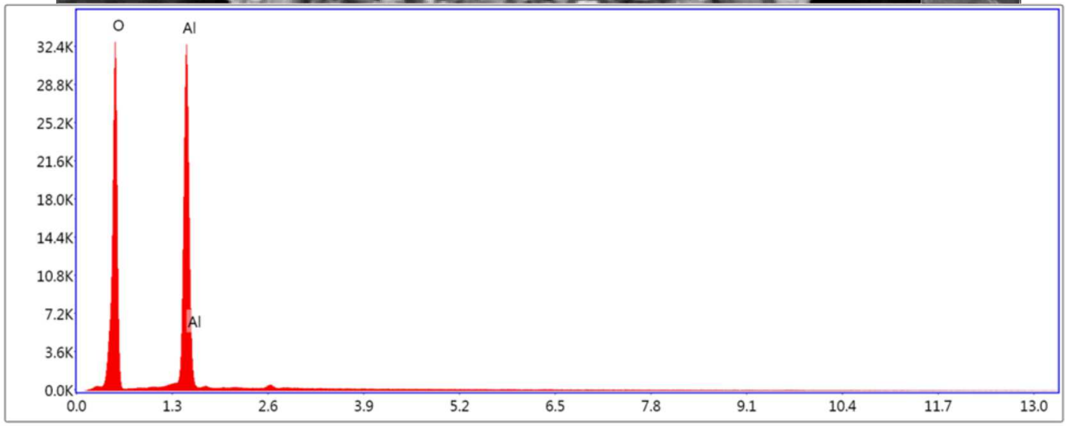
- ***After 2 months, pitting observed on all samples, both in weld and HAZ***
- ***Vibro-thermography of plates indicated no SCC formation***
- ***However, deposits observed on the metal plates… Contaminant pulled into the RH chamber? Salts? Mg-carbonate or other phase?***



Corrosion of Mockup Weld Samples
White particulates

- ***Particles are plates, thin and delicate, with one smooth surface and one textured surface (scale?)***
- *Higher magnification: textured surface consists of intergrown hexagonal or pseudo-hexagonal crystals*
- *Flakes are aluminum oxide/hydroxide!*





Lsec: 30.0 0 Cnts 0.000 keV Det: Element-C2 Det

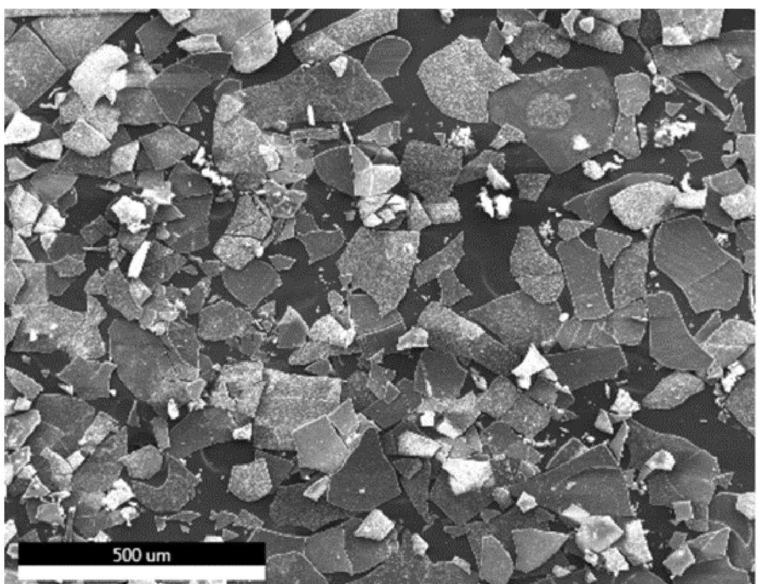
Corrosion of Mockup Weld Samples

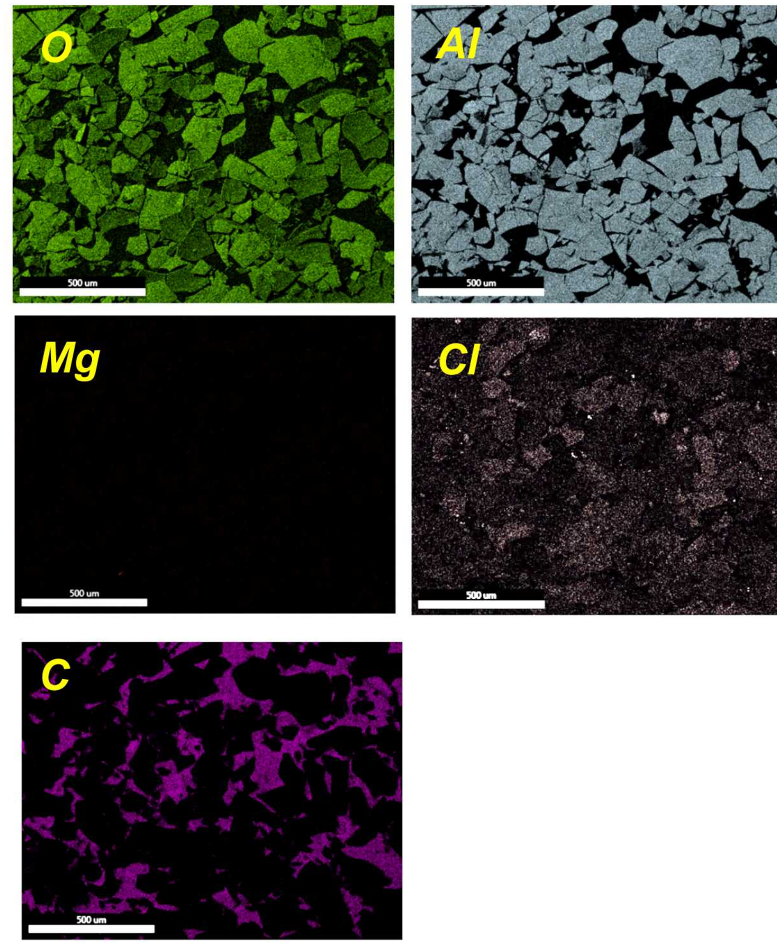
White particulates

<u>EDS element maps of flakes</u>

Aluminum hydroxide (trace Cl), generated by corrosion of aluminum plates in the RH chamber heating baffles.

<u>Conclusion:</u> Baffle corrosion due to HCl degassing from $MgCl_2$ on the plates. Under these conditions, $MgCl_2$ is not stable.

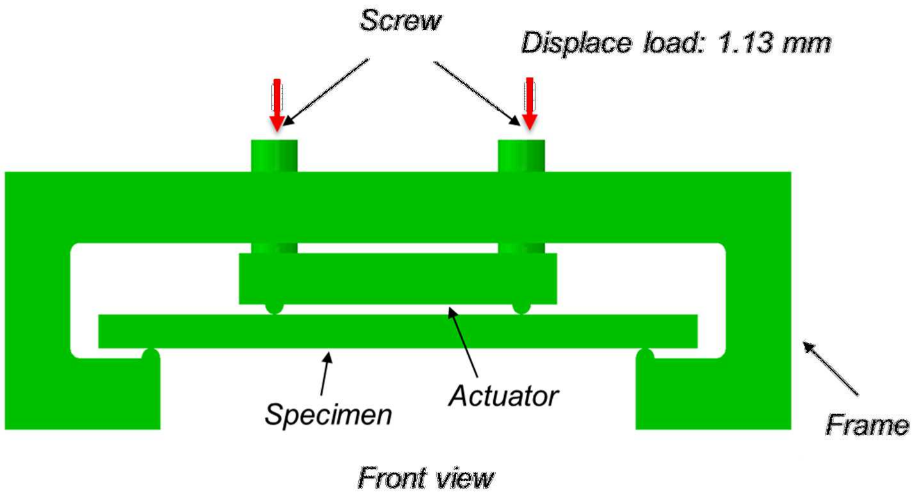


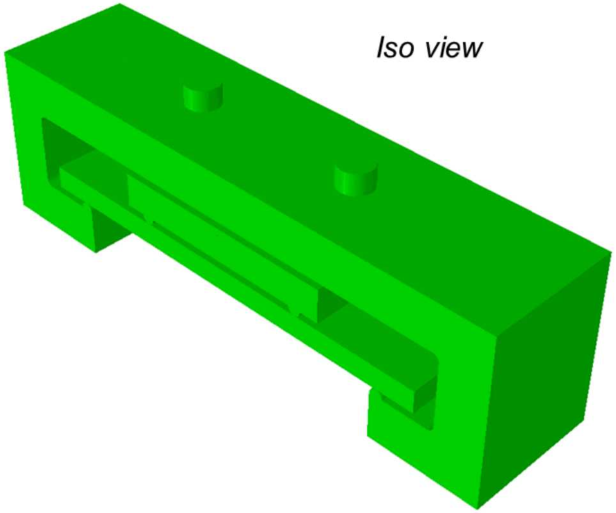


Corrosion of 4-point Bend Samples
Cathodic reactions

Experimental setup:

- ***4-inch wide 4-pt bend apparatus (CSM design)***
- ***Sample 12" x 4" x 5/8" 304L***
- ***Loaded to 200 MPa***



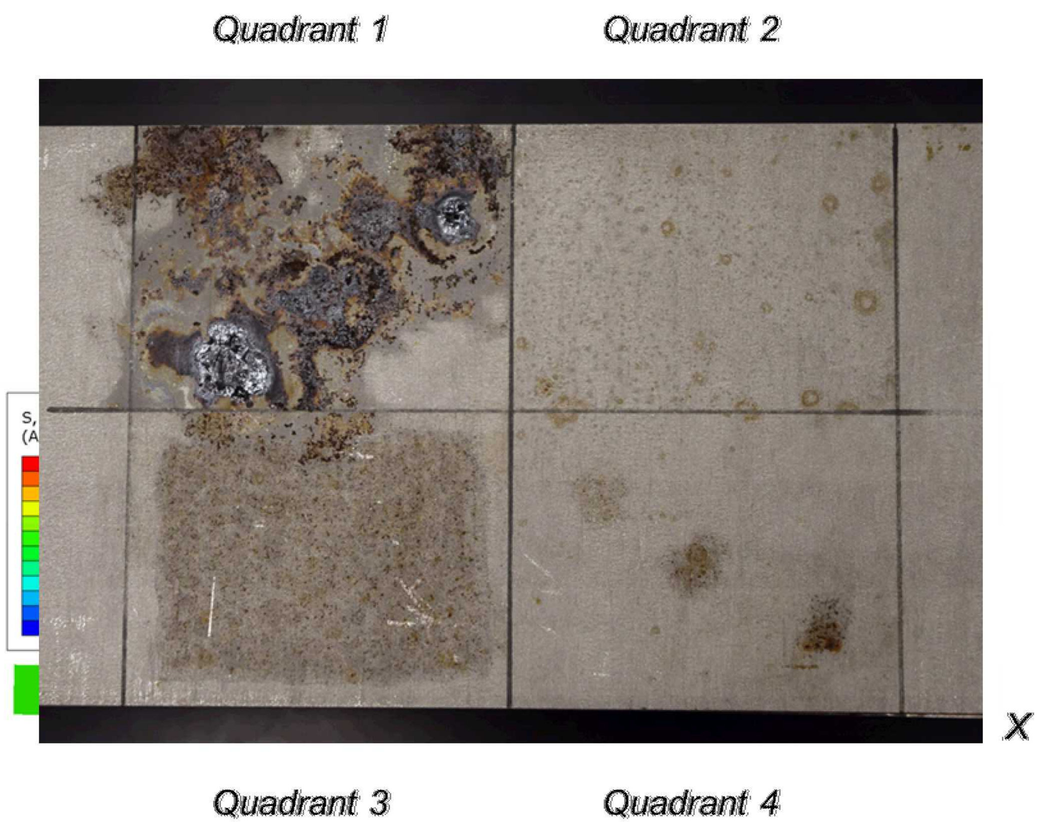


Corrosion of 4-point Bend Samples

Cathodic reactions

Uniform stress field over ~ 6" in the center of the sample. Divided into 4 sections and coated with salts.

- ***Quadrant 1: Saturated $MgCl_2$ solution, 5, 10, 20 μL***
- ***Quadrant 2: NaCl aerosol, ~ 200 μg/cm2***
- ***Quadrant 3: Syn. seawater, same chloride load as Quadrant 2***
- ***Quadrant 4: Syn. Seawater, 5, 10, 20 μL***

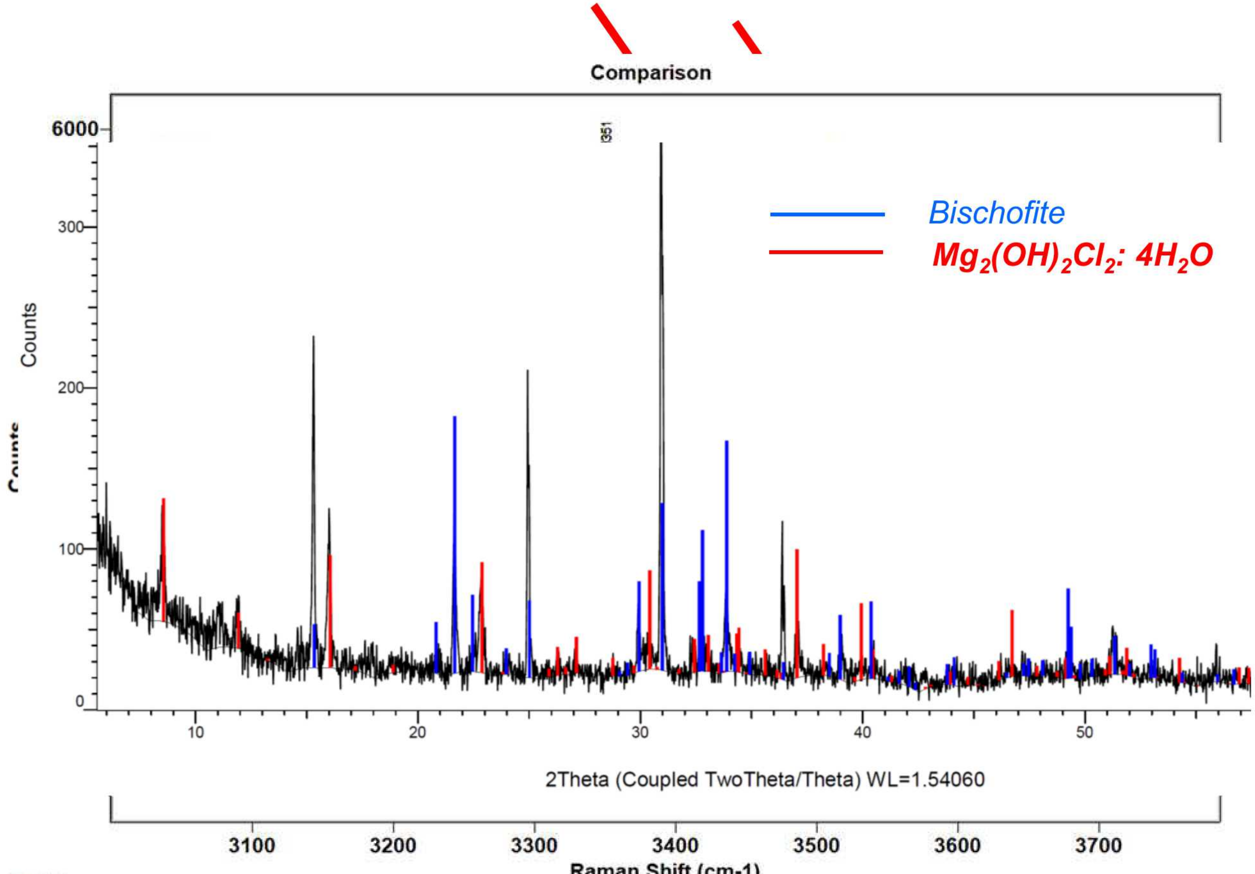


Corrosion of 4-point Bend Samples

Cathodic Reactions

Quadrant 1 – $MgCl_2$ droplets

- **Extensive corrosion**
- **White precipitate forms as halo around corroded areas (in the cathode).**
- ***Forms in the RH chamber.***
- ***SEM indicates it consists of Mg, Cl, O (H)***
- ***Raman/FTIR analysis indicates hydroxyls***
- ***X-ray diffraction indicates mixture of bischofite ($MgCl_2$:6H_2O), and Mg hydroxychloride hydrate ($Mg_2(OH)_2Cl_2$: 4H_2O)***



Corrosion of 4-point Bend Samples

Cathodic Reactions

Formation of Magnesium hydroxychloride hydrate

- **Formed in RH chamber at test conditions—less deliquescent than bischofite.**
  - *Brine volume reduced—reduced cathode region and smaller maximum pit size.*
  - *If goes to completion, no cathode, pitting stifles (Caveat—continued salt deposition will occur under natural conditions)*
- **Why did magnesium hydroxychloride form?**
  - *Oxygen reduction raises pH in cathode — likely*
  - *Degassing of HCl — possibly. Chemical analysis suggests degasing occurred…*

Sample	Salt	F^-	Cl^-	Br^-	NO_3^-	SO_4^{-2}	Na^+	K^+	Mg^{+2}	Ca^{+2}	Est. Cl lost %
Q1	$MgCl_2$	⍰	125.1	⍰	⍰	⍰	1.38	□	130.4	□	5
Q1	$MgCl_2$	□	125.3	□	□	□	1.34	□	130.4	□	5
Q2	NaCl	□	38.9	□	□	□	39.7	0.25	0.47	0.68	2-5?
Q2	NaCl	□	38.9	□	□	□	39.8	0.07	0.48	0.67	2-5?
Q3	SW	□	48.3	0.02	□	4.55	49.6	0.79	5.44	2.69	16
Q3	SW	□	48.3	0.04	□	4.51	49.0	0.61	5.49	2.54	16
Q4	SW	□	14.4	0.01	□	1.10	14.2	0.34	1.33	1.25	13
Q4	SW	□	14.5	□	□	1.13	14.0	0.21	1.25	1.11	12

Conclusions

Prior to and during corrosion

- Atmospheric exchange reactions (e.g., carbonation and HCl degassing) will affect the stability of Mg-chloride brines
- Reactions are highly temperature-dependent; HCl loss enhanced at higher temperatures
- May result in brine volume decreases (affecting max. pit size), or in extreme conditions, brine dry-out

During corrosion

- Oxygen reduction at the cathode can result in changes in brine composition
- Precipitation of hydroxides or carbonates may cause brine dryout
- Enhanced degassing from acidified pits??

Both processes affect brine composition and properties, potentially affecting timing of deliquescence and corrosion, and extent of corrosion (maximum pit size)