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

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# Stability of Sea-Salt Deliquescent Brines on Heated Surfaces of SNF Dry Storage Canisters

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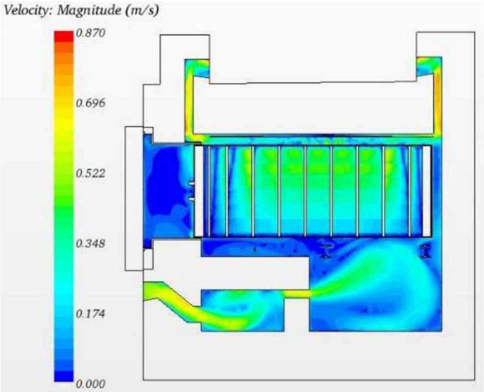
# Overview

- Background—SNF dry storage and possible canister SCC
- Expected salt aerosol and initial deliquescent brine compositions
- Effect of atmospheric exchange/degassing (acid degassing) reactions prior to corrosion
  - Chloride loss
  - Carbonation
  - Hydroxychloride formation
- Brine stability following corrosion
  - Cathodic reactions/precipitation
  - Incorporation of brine components into corrosion products.

# Background

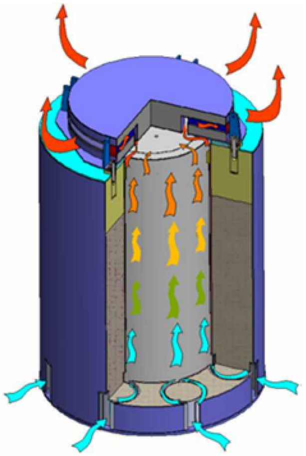
- United States currently has over 80,000 metric tons of Spent Nuclear Fuel (SNF), about 30% in dry storage systems. The dry storage systems are interim storage until a permanent disposal site is developed, which is likely to be many decades.
- Most dry storage systems utilize stainless steel (304 SS) canisters stored in passively-ventilated overpacks. Canisters accumulate surface dust over time.

Dry storage systems at the Diablo Canyon ISFSI



FCRD-UFD-2012-000114 Figure 7.3

Passive ventilation cools the canister within the overpack.

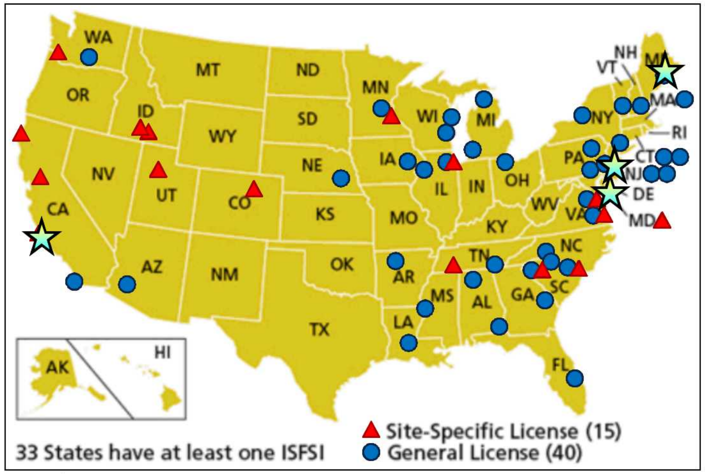


Dust on dry storage canister at Calvert Cliffs ISFSI

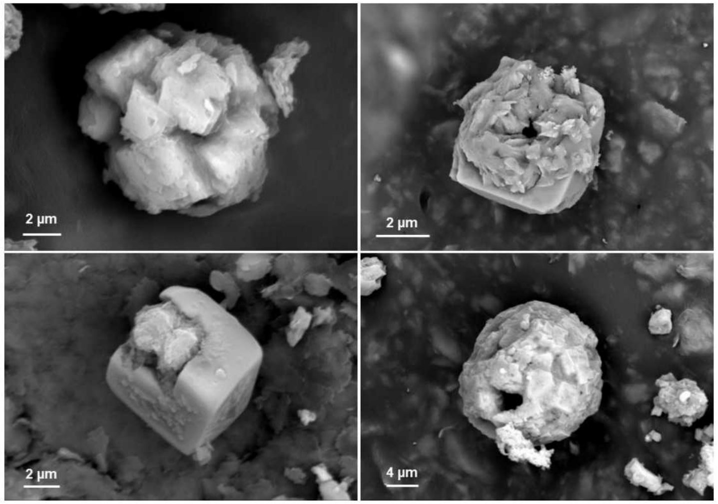
# Sea-Salt Aerosols

- **Many ISFSIs are at coastal sites. Anticipated deposition of chloride-rich sea-salts.**
- **EPRI-led sampling program confirmed that sea-salt aerosols are deposited on canisters at least at some sites.**
- **At near-marine sites, salt aggregates that form by evaporation of seawater can be deposited on canister surfaces, and will deliquesce to form chloride-rich brines.**

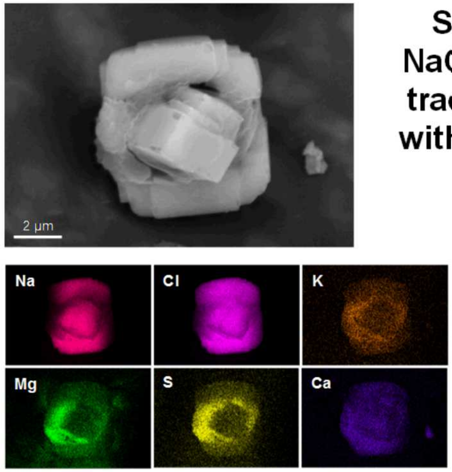
**Locations of U.S. Spent Nuclear Fuel Independent Storage Installations (ISFSIs)**



☆ ISFSI locations sampled.



Sea-salt aerosols recovered from the surface of SNF dry storage canisters at Diablo Canyon ISFSI

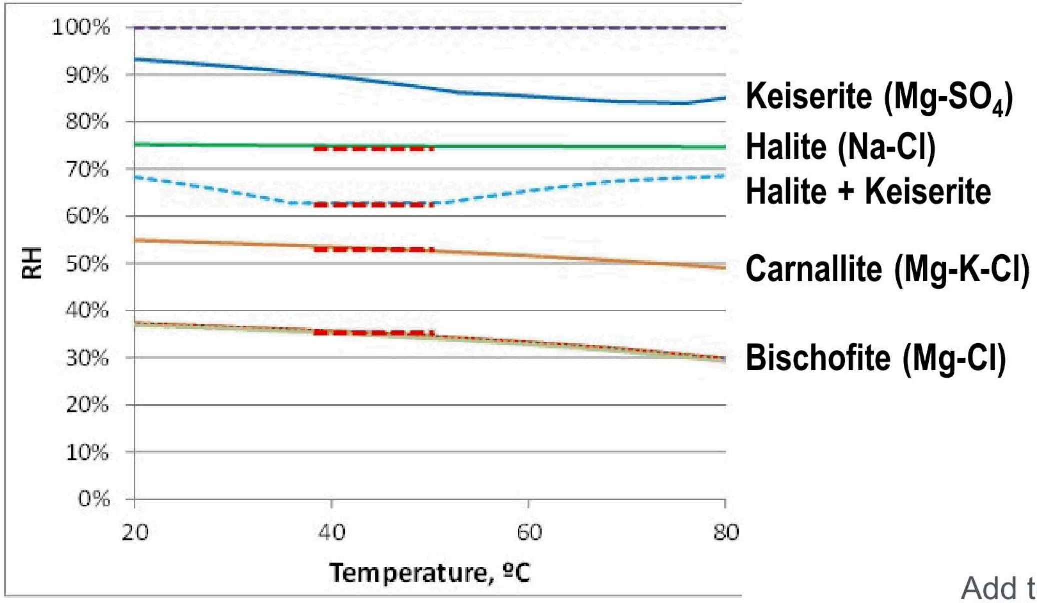


**Salt aggregates: dominantly NaCl with interstitial $MgSO_4$ and trace K, Ca phases. Consistent with seawater ion compositions.**

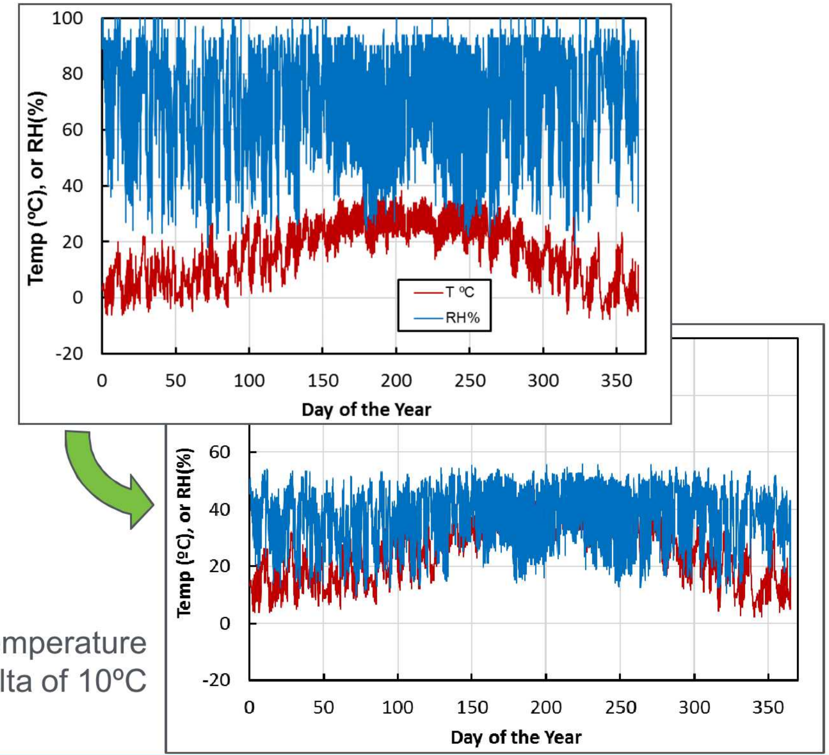
**At coastal sites, canister SCC due to deliquescence of chloride-rich salts is a potential failure mechanism.**

# Why Study $MgCl_2$ Brines?

- As temperatures drop and sea-salts deliquesce, $MgCl_2$ brines are the first to form—lowest deliquescence RH. If $MgCl_2$ brines are not stable, deliquescence RH is much higher, delaying corrosion until temperatures drop to much lower levels.
- Interpreting experimental studies, especially at elevated temperatures
  - Potential changes in brine volume, or even dryout.

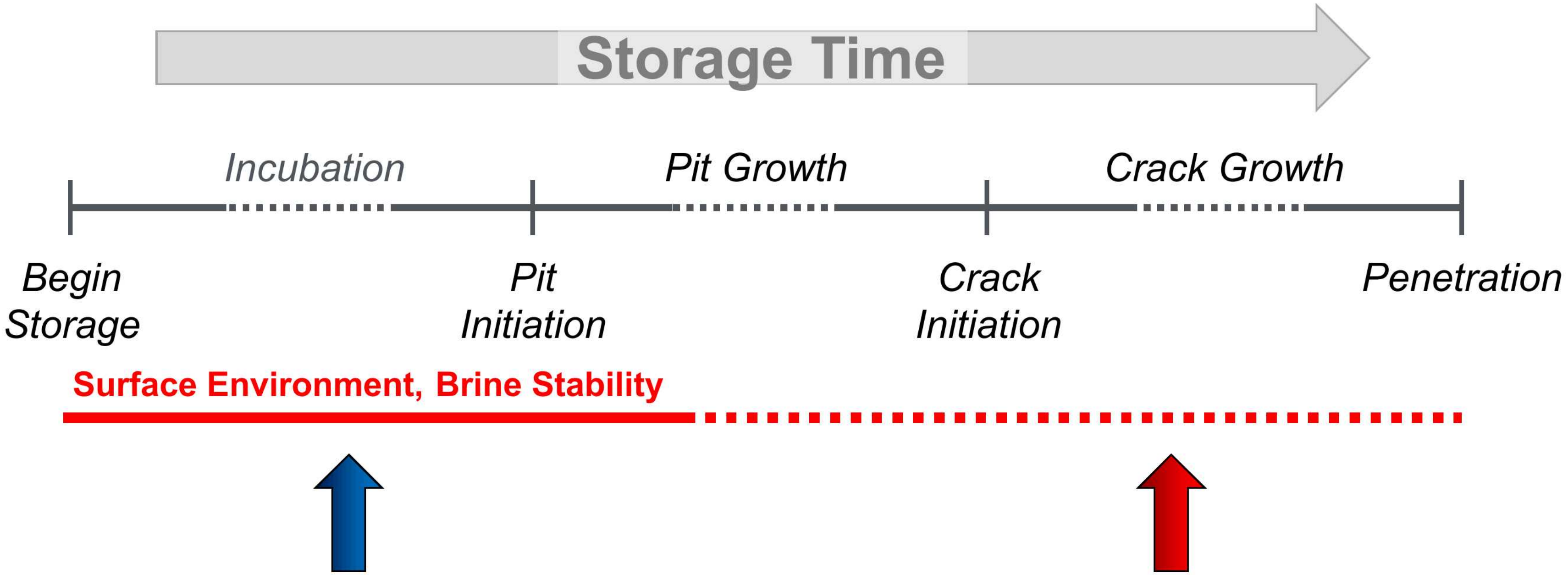


Weather near Arkansas Nuclear One



Add temperature delta of 10ºC

# Canister SCC: Surface Environment



Storage Time

*Incubation*

*Pit Growth*

*Crack Growth*

*Begin Storage*

*Pit Initiation*

*Crack Initiation*

*Penetration*

**Surface Environment, Brine Stability**

**Stability of salts and brines before…**

Impacts temperature and timing of deliquescence

**…and after initiation of corrosion**

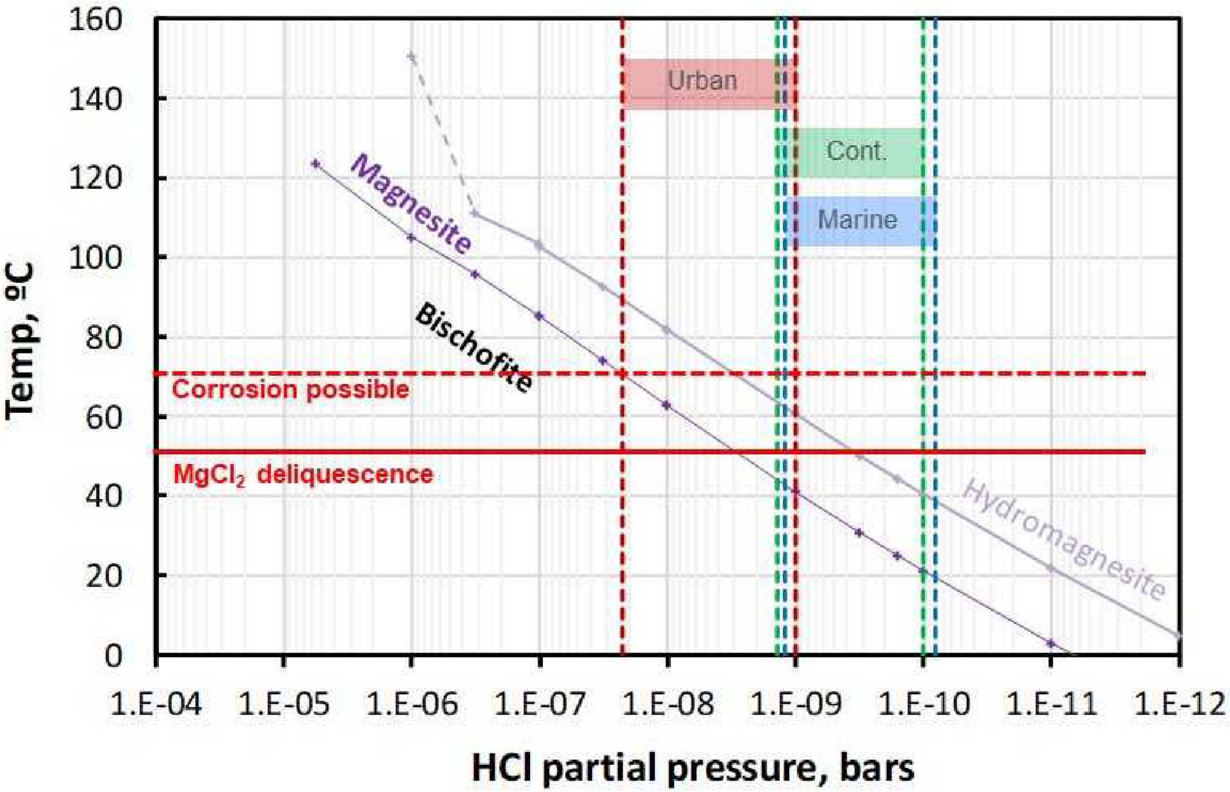
Impacts brine layer properties and cathode kinetics (brine layer composition, thickness); potentially brine dryout

# Brine Stability at Elevated Temperatures:

## Carbonation Reaction: Absorption of atmospheric $CO_2$

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

- **Brines may degas or absorb HCl, depending on background acid gas concentrations and temperature**
- **Elevated temperatures promote conversion to carbonate**
- **Carbonation would result in brine dryout, eliminating corrosive environment.**
- **However, for SNF storage canisters, reaction could reverse itself as the canister cools.**



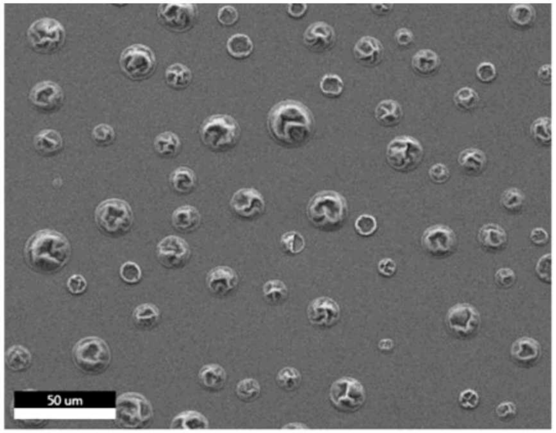
# Brine Stability In the Absence of Corrosion:

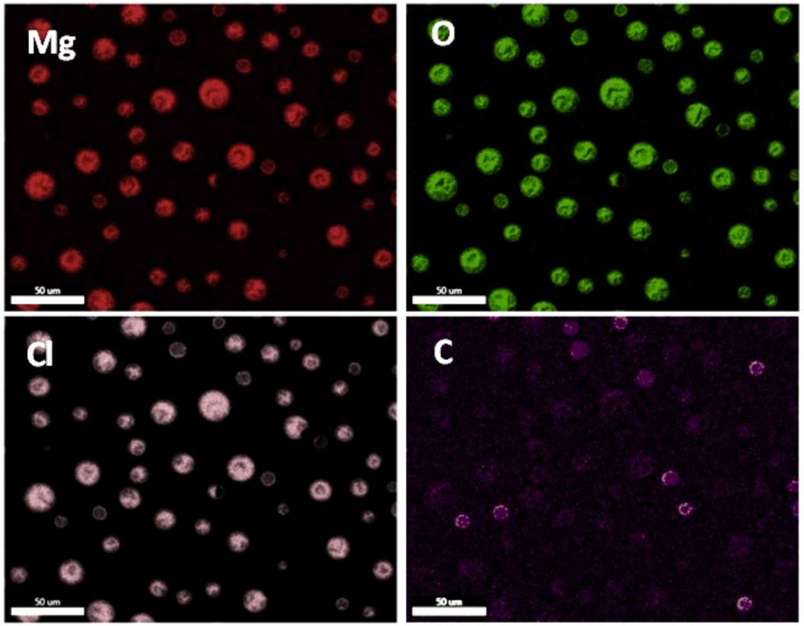
$MgCl_2$ brine stability near the max. temp. at which deliquescence can occur on a canister

## Experimental evaluation of degassing and carbonation

### Conditions:

- **$MgCl_2$ brine, deposited as droplets on an inert substrate**
- **48°C, 40% RH, flow rate 2 L/min “clean air” ($p_{HCl}$ = 0)**
- **Samples exposed for 2, 4, 8 weeks**





### Results:

- **Partial conversion to carbonate observed; later chemical analysis suggests 5-7% chloride lost.**
- **Airflow was too low to support complete conversion. At 48ºC, one $m^3$ of air can only remove 1.3 – 13 µg Cl (hydromagnesite/ magnesite). Under field conditions, airflow is enormous.**

# Significance of Experimental Results

**Are sea-salt brines really present on canisters? Not exactly.**
**Are results from laboratory experiments relevant to field conditions? Not necessarily.**

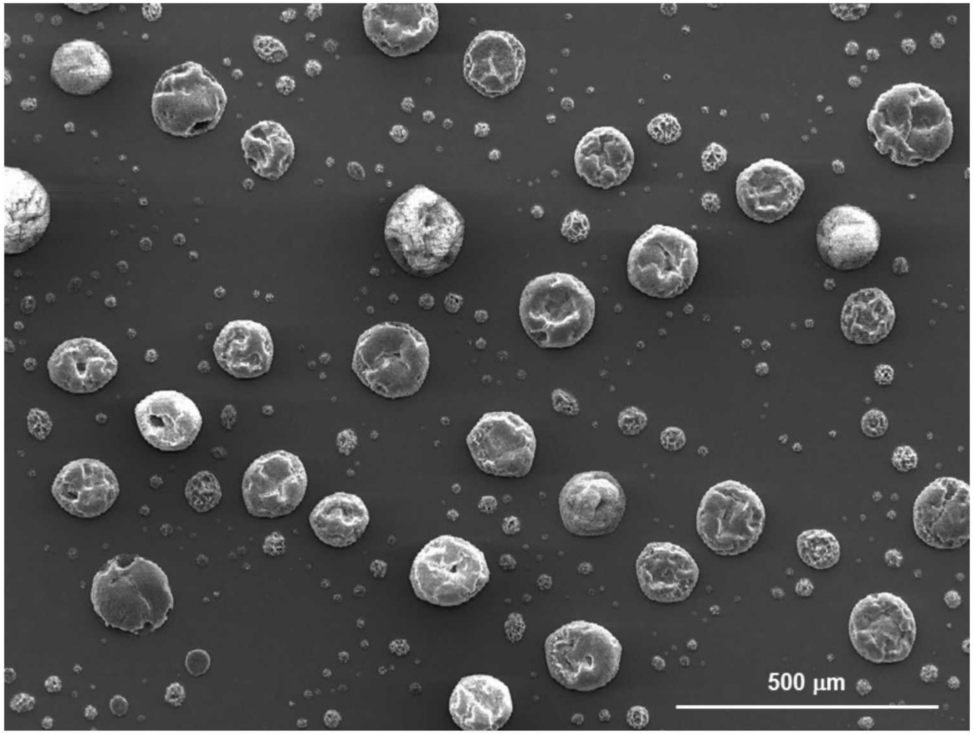
- **Reactions with atmospheric gases modify sea-salt brines (chemistry, $RH_d$).**
- **Effects artificially limited in laboratory experiments due to limited air flow.**
- **Experiment design may strongly affect test results. E.g.,**
  - RH chamber → high air flow, atmospheric exchange
  - RH controlled 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, H2SO4 or SO2, HNO3) may have a significant effect.
- **$MgCl_2$ carbonation may be especially important in accelerated (high temperature) tests, as HCl degassing is promoted at elevated temperatures.**
  - SNL is running an additional experiment at accelerated conditions (80°C and 35% RH) to evaluate potential for degassing and dry-out

# Brine Stability: $MgCl_2$ brine at 85°C and 35% RH

Experimental conditions:

- 85°C, 35% RH
- Inert substrate (Si wafer)
- 300 µg/cm$^2$ $MgCl_2$:$6H_2O$ (1520 µg/sample): 105 µg/cm$^2$ Cl (530 µg/sample)
- Deposited using inkjet printer (droplets ~10 to 150 µm in diameter)
- Airflow rate 2 liters/minute
- Sampled after 2/4/8 weeks.

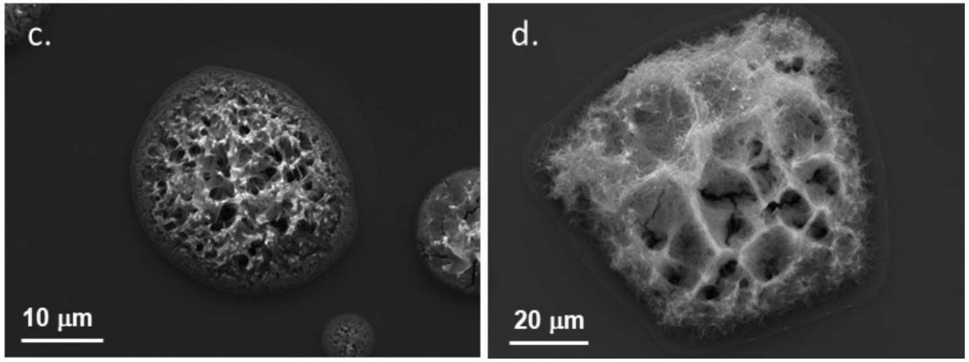
SEM photo: $MgCl_2$ brine droplets on silicon wafer

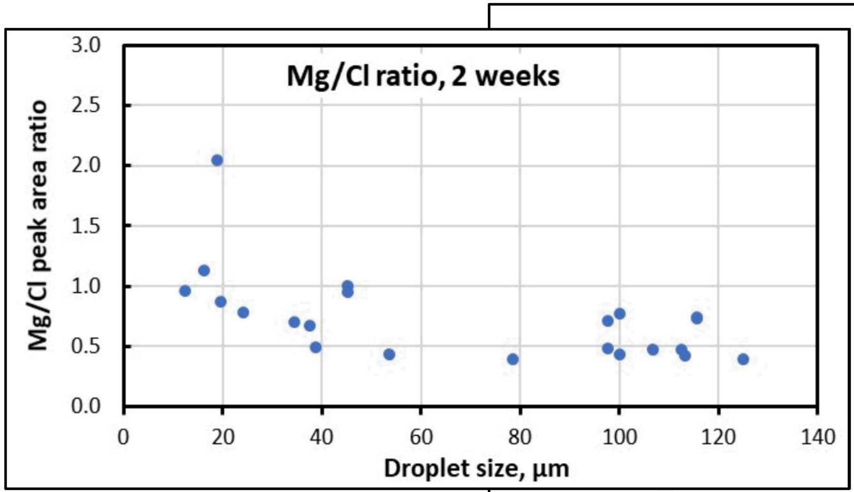


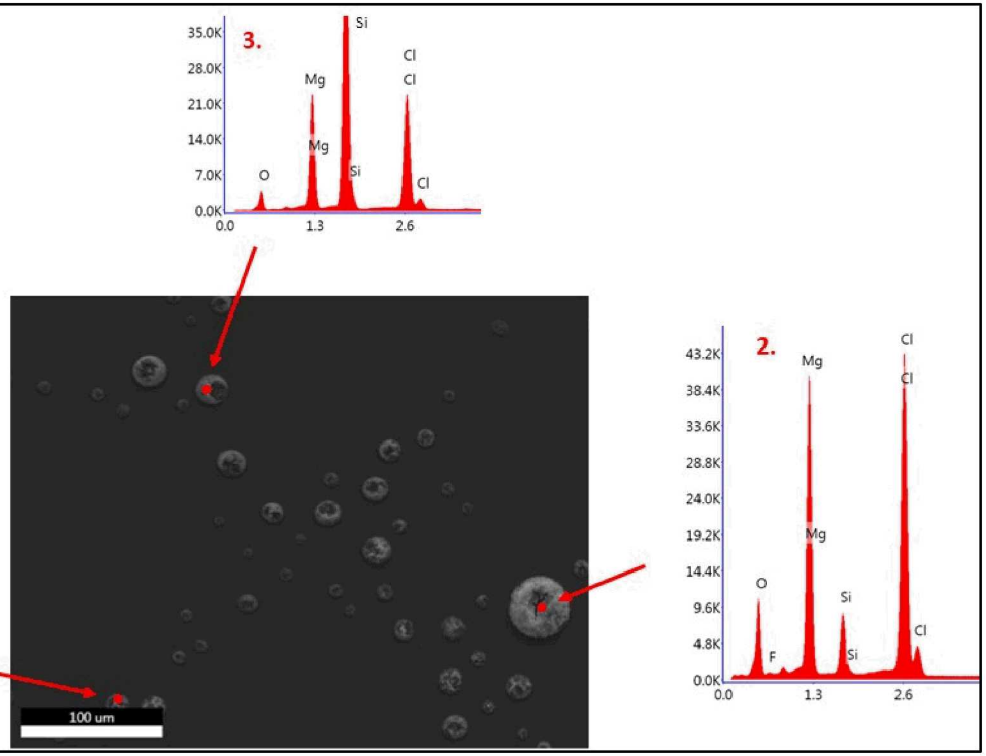
# Mg-Cl Brine Stability: 2-Week Samples

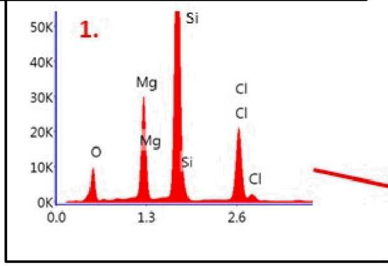
## Results

- Large droplets remain smooth, but smaller droplets change texture (fibrous).
- Possible slight increase in Mg-Cl peak area ratio in smaller droplets?





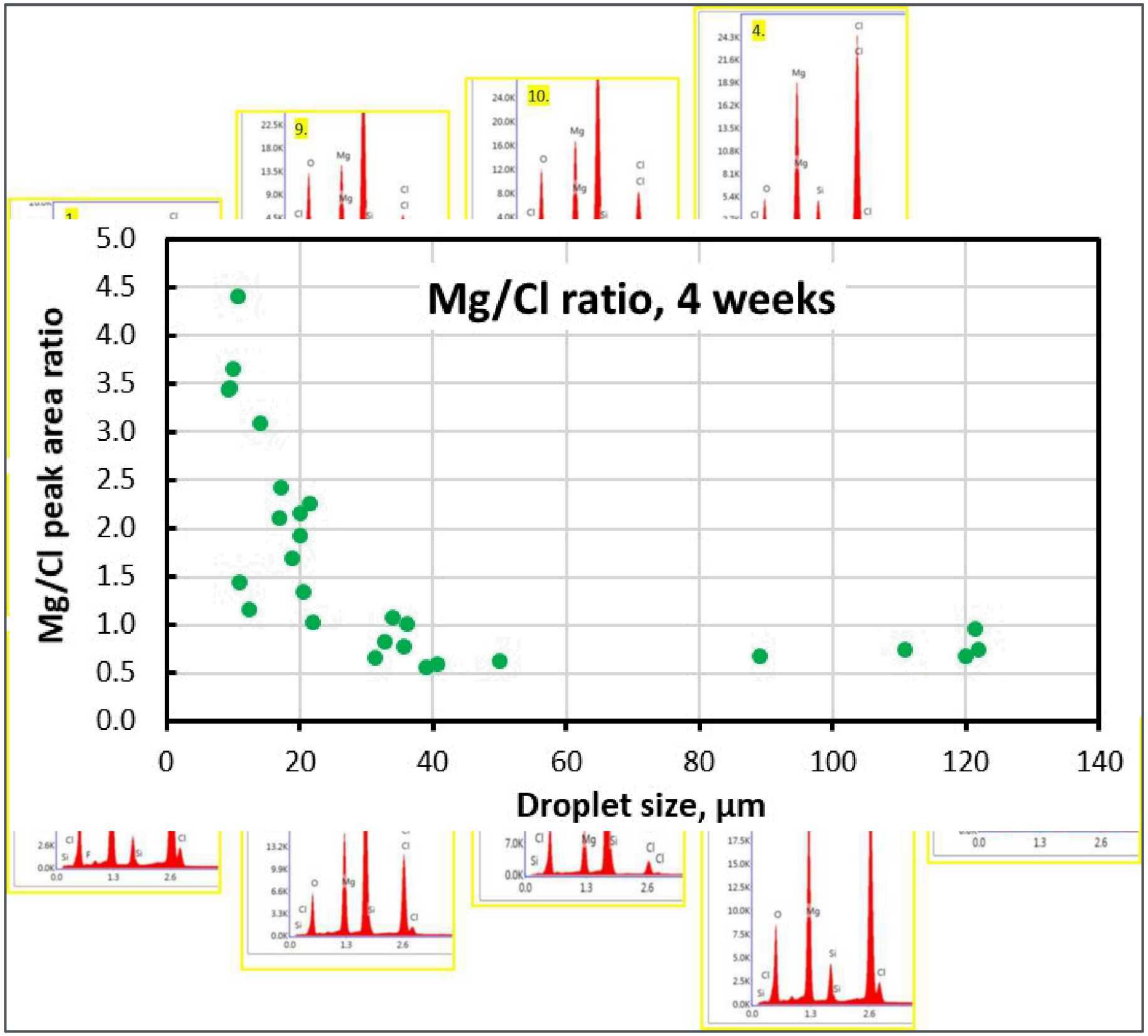




# Mg-Cl Brine Stability: 4-Week Samples

<u>Results</u>

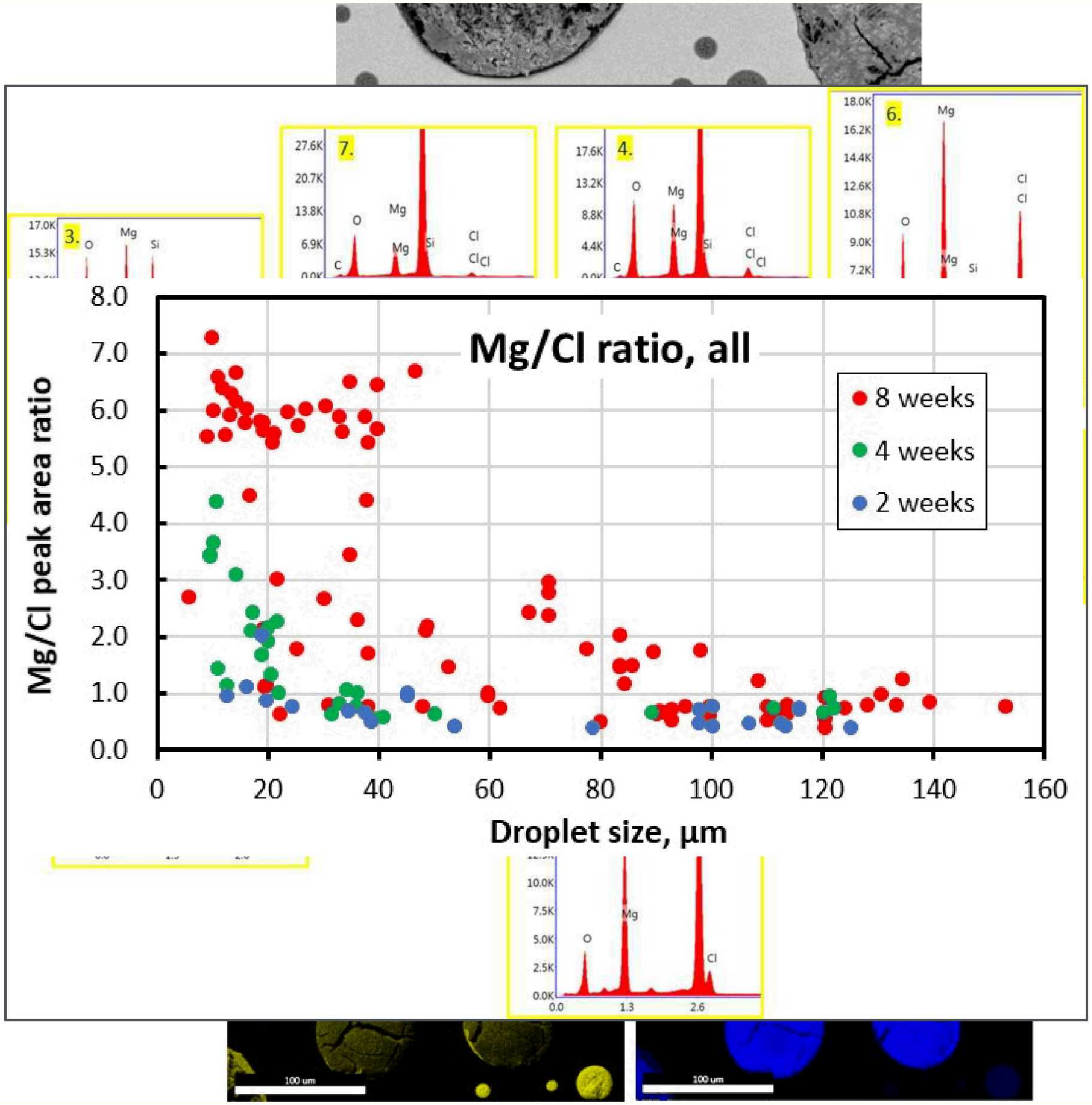
- In SEM BSE images, smaller droplets now appear darker—lower average atomic number (suggests chloride loss)
- Significant increase in measured Mg/Cl peak area ratios in smaller droplets



# Mg-Cl Brine Stability: 8-Week Samples

Results

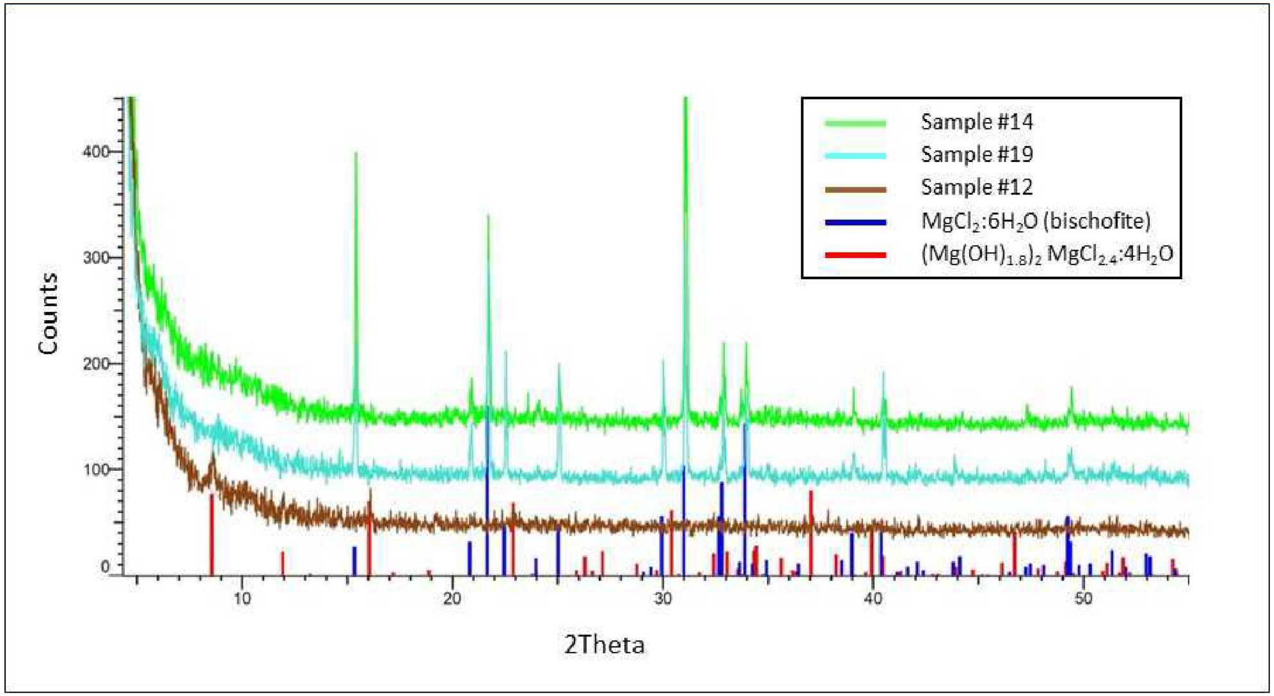
- In SEM BSE images, smaller droplets and some larger droplets appear darker. SEM EDS maps indicate chloride loss, oxygen gain, and minor carbon gain.
- Significant increase in measured Mg/Cl peak area ratios in small and medium-sized droplets



# Mg-Cl Brine Stability: What Formed?

X-Ray diffraction (XRD) of 8-week samples

- Rapid scan to avoid deliquescence
- Samples 14,19: only bischofite observed
- Sample 12: Inadvertently allowed to deliquesce. A crystalline phase remained.
- Identified as “phase 2” Mg-hydroxychloride.



**Mg-Cl brine *(Mg:Cl = 1:2)* converts to *<u>less deliquescent</u>***

**$(Mg(OH)_2)_2MgCl_2$:$4H_2O$ *(Mg:Cl = 3:2)***

## Conclusion:

**Elevated temperatures promote HCl degassing, resulting in pH rise and Mg-hydroxychloride precipitation, which would eventually lead to brine dryout.**

# Effects of Corrosion Reactions on Brine Stability?

## Corrosion cell

**pH rises**

Cathode

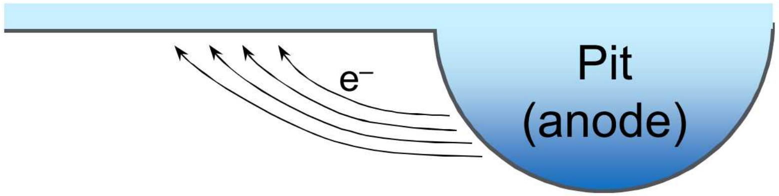
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

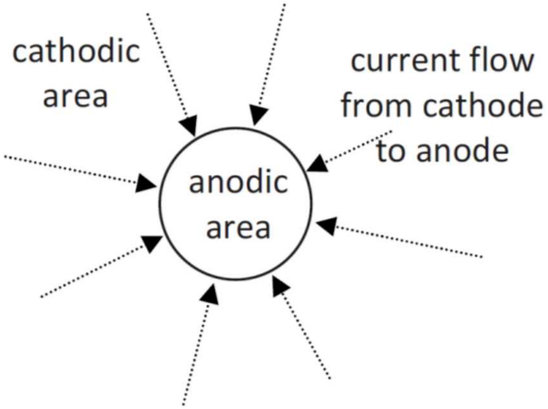
Anode

**pH drops**

$Fe \rightarrow Fe^{+2} + 2e^-$

$Fe^{+2} + 2\,H_2O \rightarrow Fe(OH)_2 + 2\,H^+$





## Corrosion reactions

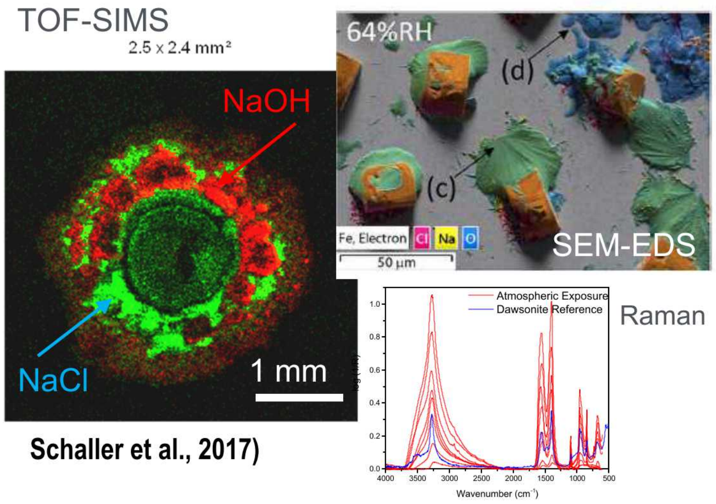
Cathode:

- Changes in brine chemistry may affect cathode kinetics by changing brine composition and volume
- Elevated pH may result in hydroxyl or carbonate precipitation. E.g., Al corrosion: high pH promotes $CO_2$ absorption, precipitation of carbonates and dryout (Schaller et al., 2017).

Anode:

- Low pH promotes acid degassing?

Example: Aluminum corrosion



**Schaller et al., 2017)**

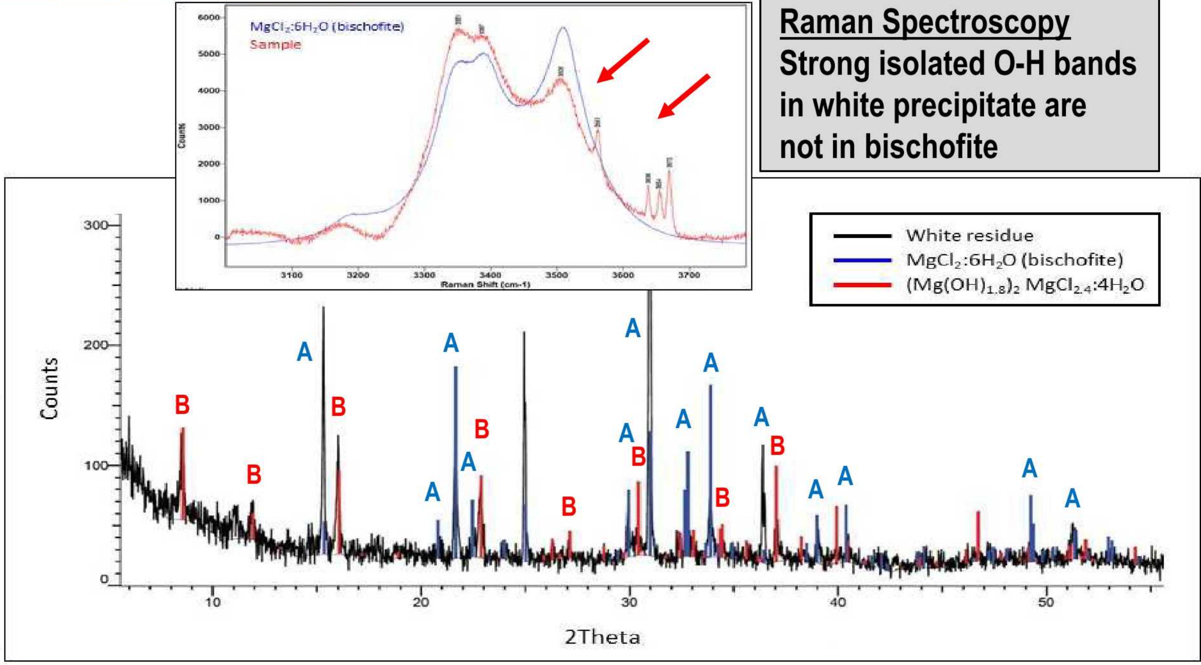
# Effects of Corrosion on Brine Stability:

## 4-point bend test

4-Point bend test with 4” wide test beam

80°C, 35% RH

- Different deposited salts, with salt loads and distributions
- Heavy corrosion around Mg-Cl brine droplets
- White precipitate observed around corroded areas
- Precipitate less deliquescent than bischofite (which is still deliquesced).



**Raman Spectroscopy**
**Strong isolated O-H bands in white precipitate are not in bischofite**

**X-ray Diffraction**

**Collected sample consists of bischofite (A) and Mg-hydroxychloride (B), ~ 2Mg(OH)$_2$:MgCl$_2$:4H$_2$O**

**Same phase as seen previously in the MgCl$_2$ brine stability test at this temperature.**

# Effects of Corrosion on Brine Stability:

## “big plate” test

- **Large weld samples from Sandia canister mockup.**
- **80ºC, 35% RH, salt load 8 g/m$^2$ $MgCl_2$ deposited as salt fog**
- **Samples examined after 2 months and 8 months.**
- **By 8 months, surface was dry.**

**Dry-out had occurred. What happened to the brine?**

**Initial condition: surface coated with brine droplets, rapidly corroding.**

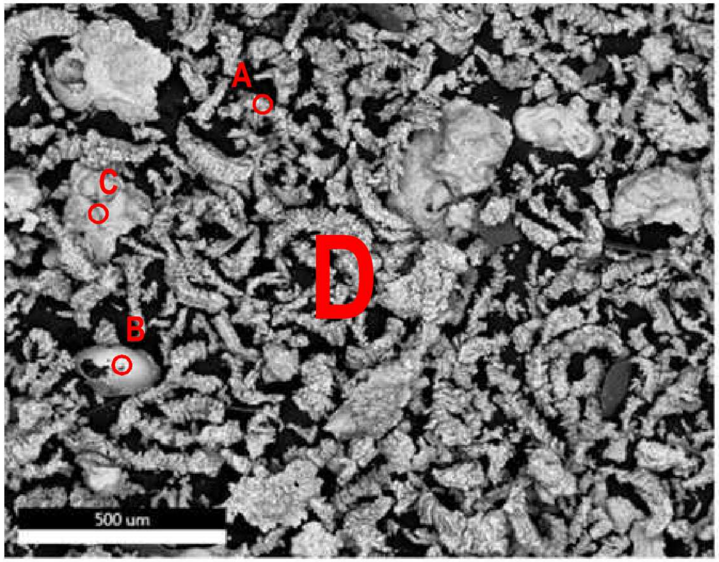
**2 months: surface heavily corroded, covered with moist corrosion products.**

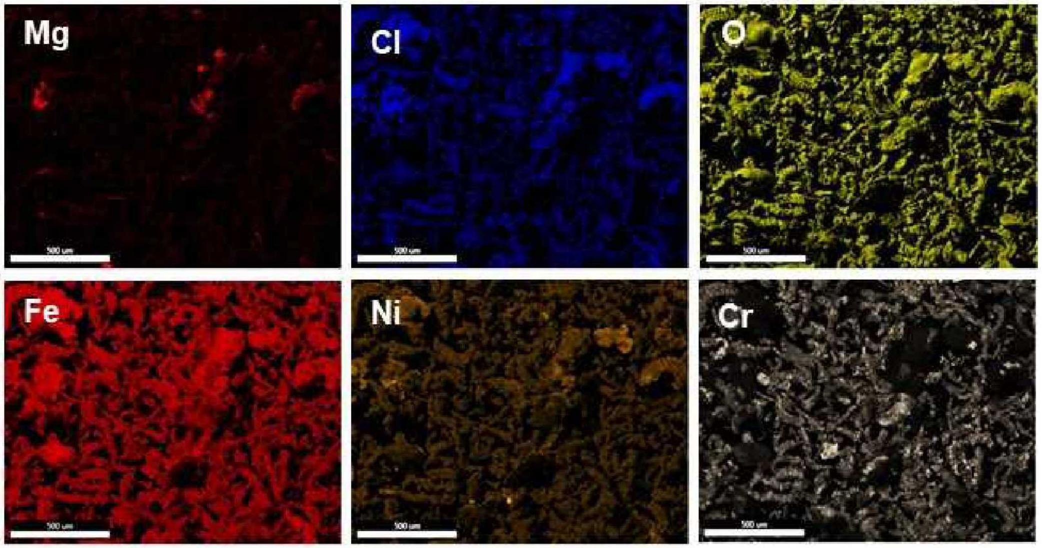
**8 months: Surface completely dry, covered with loose corrosion products.**

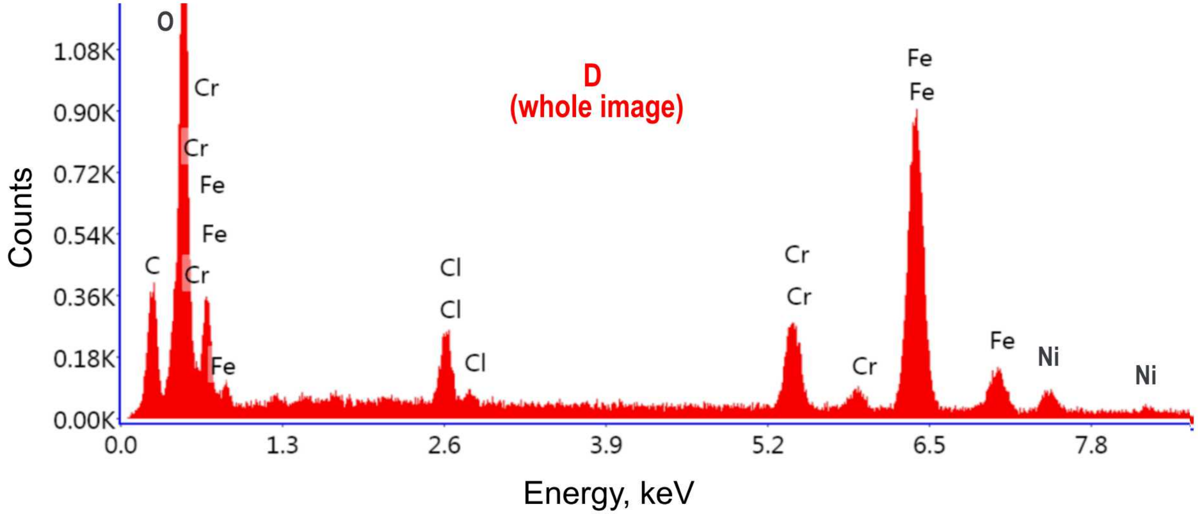
**Corrosion products: loose “whiskers” and adhering “blisters”**

# Corrosion residues from “Big Plate” Test

## SEM/EDS Element Maps of Big Plate Corrosion Residues







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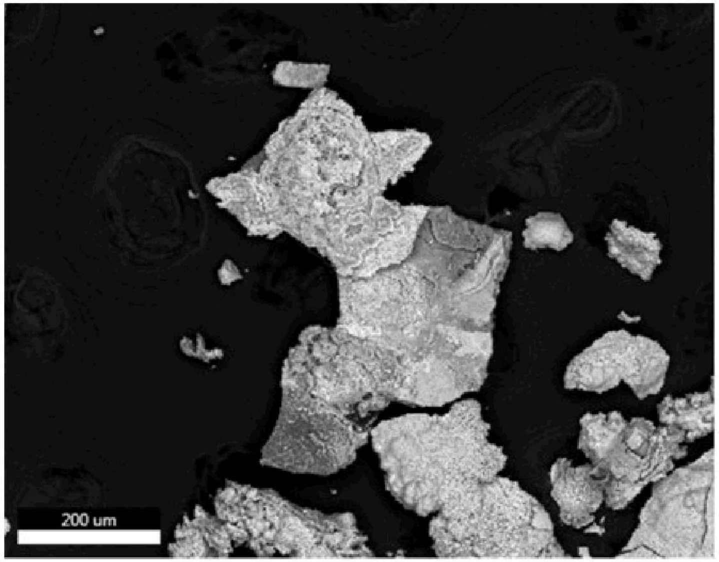
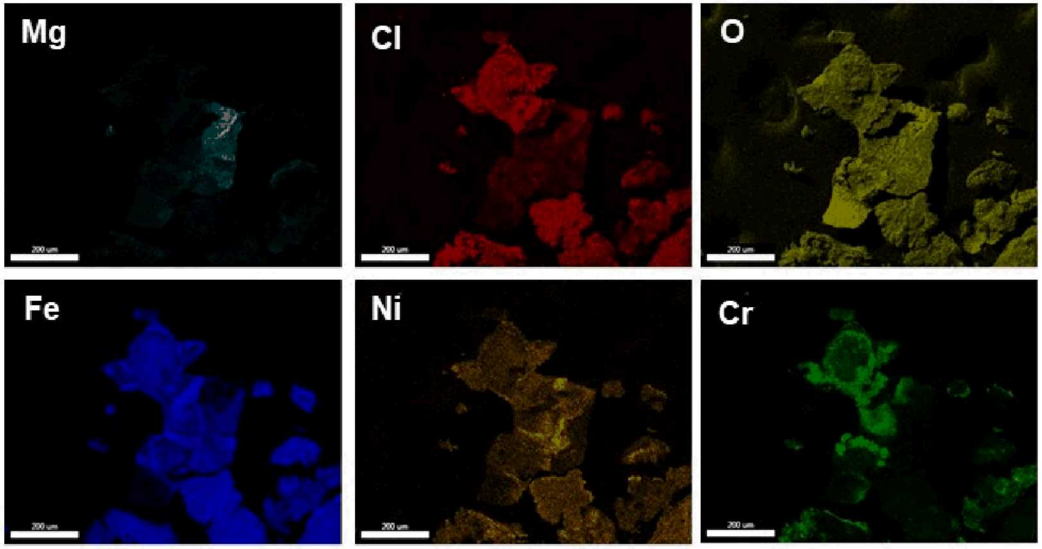
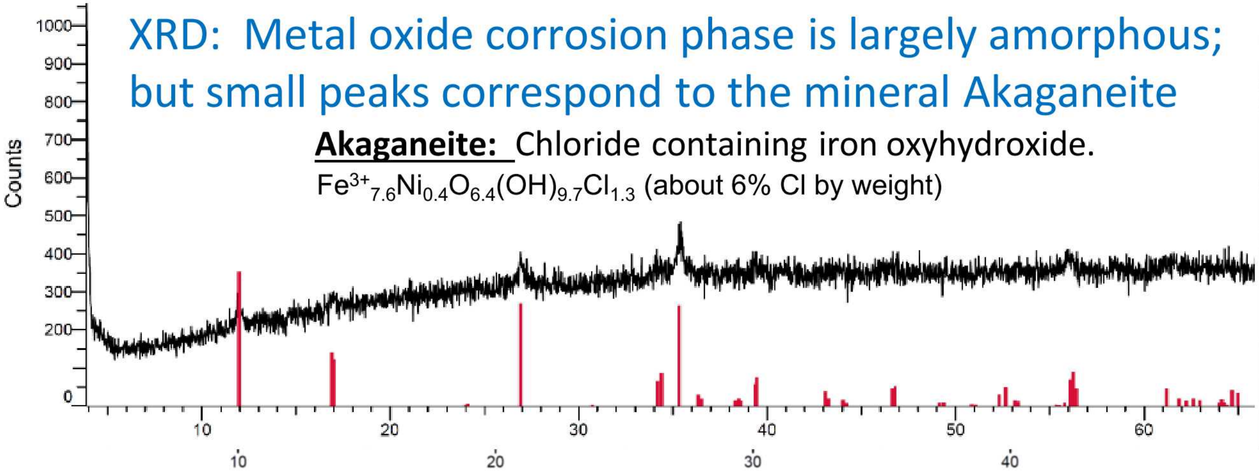


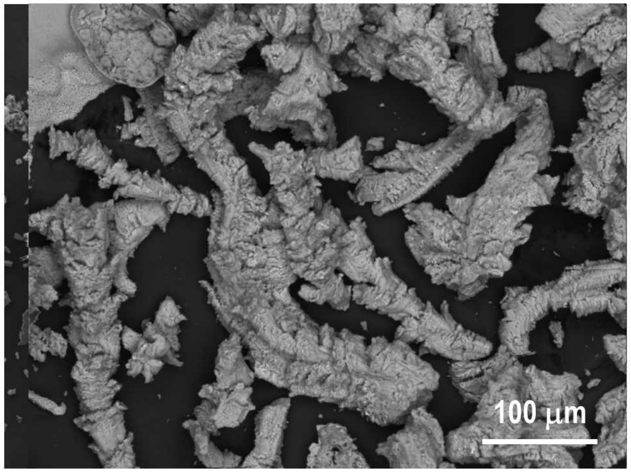




XRD: Metal oxide corrosion phase is largely amorphous; but small peaks correspond to the mineral Akaganeite

**Akaganeite:** Chloride containing iron oxyhydroxide.

$Fe^{3+}_{7.6}Ni_{0.4}O_{6.4}(OH)_{9.7}Cl_{1.3}$ (about 6% Cl by weight)



# Mg-hydroxychlorides

## Observed to form due to HCl degassing, and possibly cathodic reactions

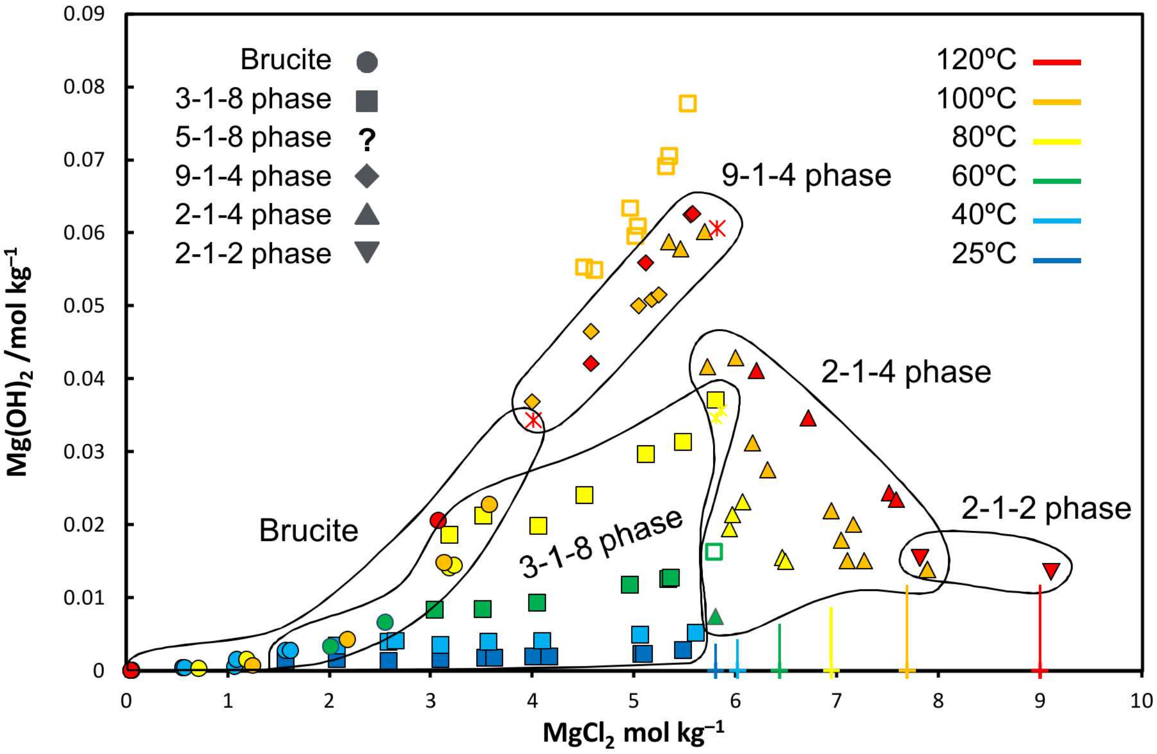
**System $Mg(OH)_2$-$MgCl_2$-$H_2O$**

Many species:

- (OH):Cl ratios 1:1. 2:1, 3:1, 5:1, 9:1.
- Variable # of waters of hydration

Species that form are controlled by environment:

- Brine concentration
- Temperature



**Questions:**

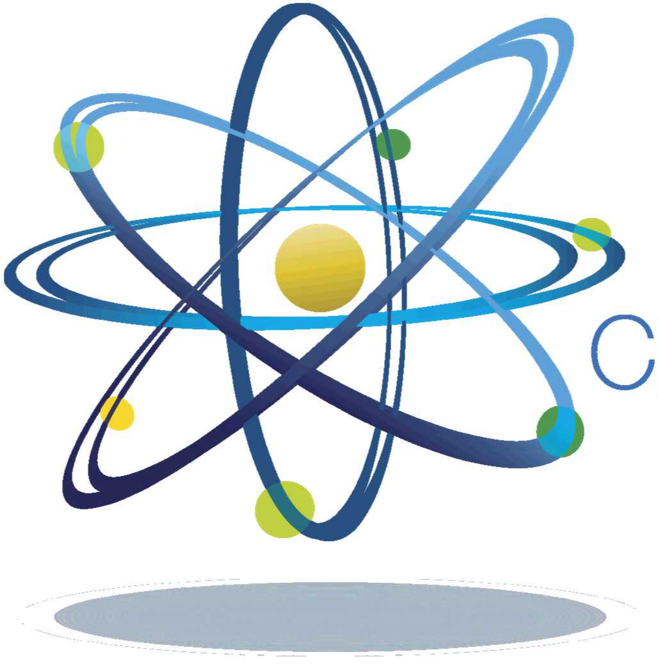
- Which phases form under conditions of interest? — brucite, 3-1-8, 5-1-8(?), and 2-1-4 (observed)
- Deliquescence properties  (less deliquescent than bischofite)
- Kinetic effects?  (e.g., carbonate vs hydroxychloride?)
- Thermodynamic data limited or entirely unavailable (working to develop data).

# Conclusions

As canister surface temperature drop, deposited sea-salt aerosols will deliquesce, initially forming magnesium chloride-rich brines.

- Concentrated Mg-Cl brines are unstable at elevated temperatures, degassing HCl.
  - Concomitant precipitation of a carbonate- or hydroxide-containing phase buffers the pH, allowing continued degassing.
- Once corrosion initiates:
  - The oxygen reduction reaction (ORR) produces hydroxides, and may promote precipitation of hydroxide-containing phases.
  - Corrosion products may sequester significant amounts of Cl from the brine.
- In both cases, precipitation removes brine components, reducing brine volume at a given RH and eventually leading to dryout.
- Understanding brine stability is critical to predicting corrosion behavior under field conditions, and to interpreting laboratory results.

# Questions?



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