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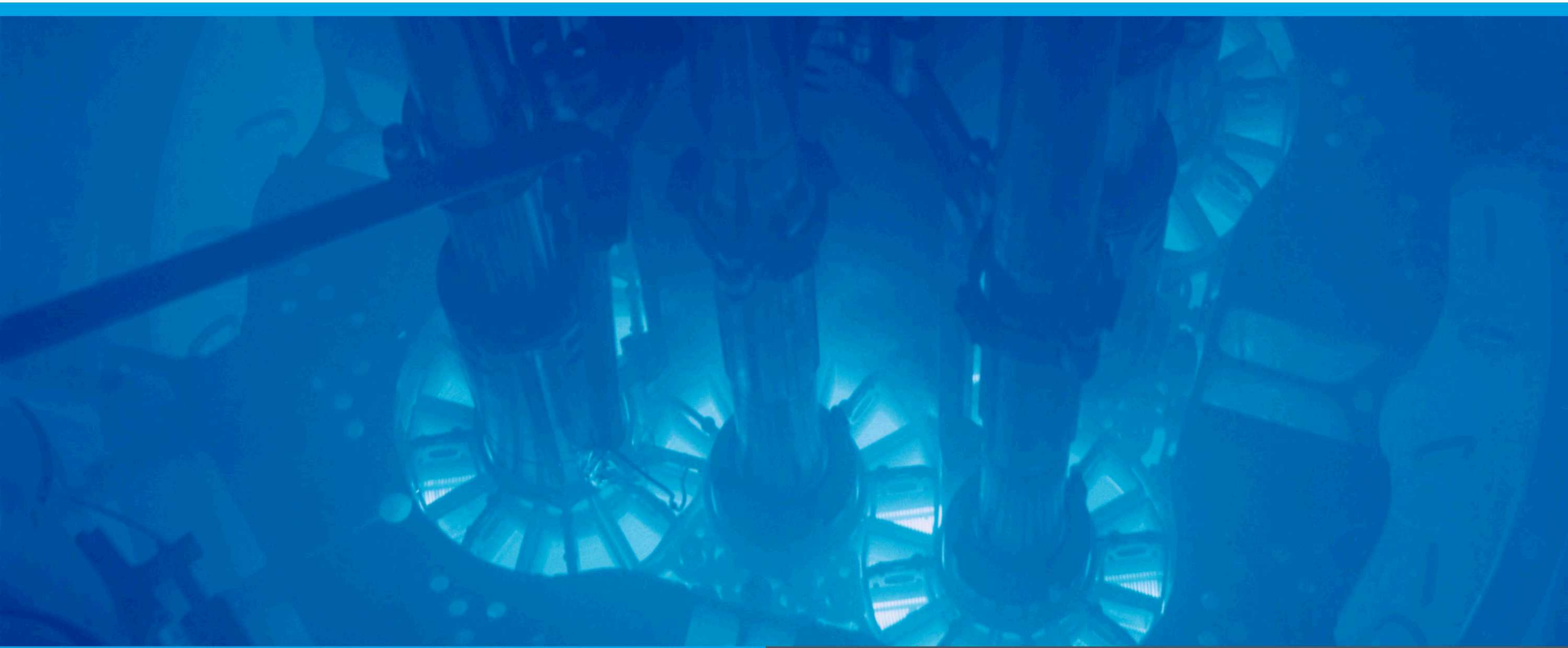

Composition and Evolution of Sea-Salt Deliquescent Brines on SNF Storage Canister Surfaces

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Sandia National Laboratories

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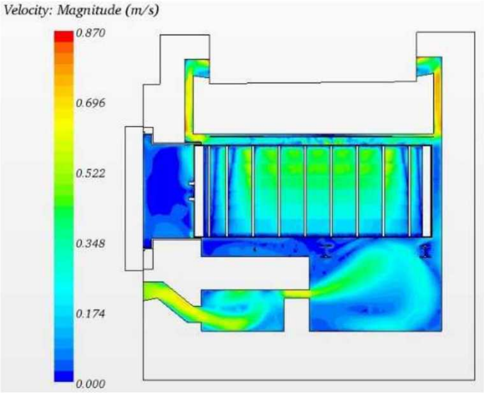
Overview

- Context: SNF dry storage and possible canister SCC
- Corrosion dependence on brine properties
  - Conditions and timing of corrosion
  - Extent of damage (e.g., Chen and Kelly, 2010 model).
- Brine properties as a function of relative humidity (RH) and temperature
- Effect of atmospheric exchange/degassing (acid degassing) reactions prior to corrosion
  - Chloride loss
  - Carbonation
  - Hydro-xychloride formation
- Brine stability after initiation of corrosion
  - Cathodic reactions/precipitation
  - Incorporation of brine components into corrosion products.

Background

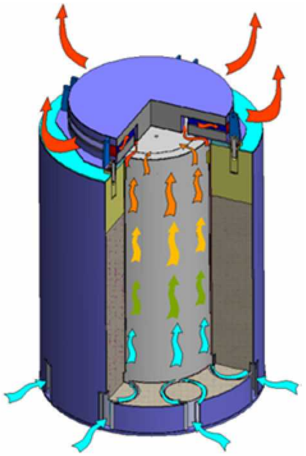
- United States currently has over 80,000 metric tons of Spent Nuclear Fuel (SNF), about 30% in dry storage systems. The dry storage systems are interim storage until a permanent disposal site is developed, which is likely to be many decades.
- Most dry storage systems utilize stainless steel (304 SS)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



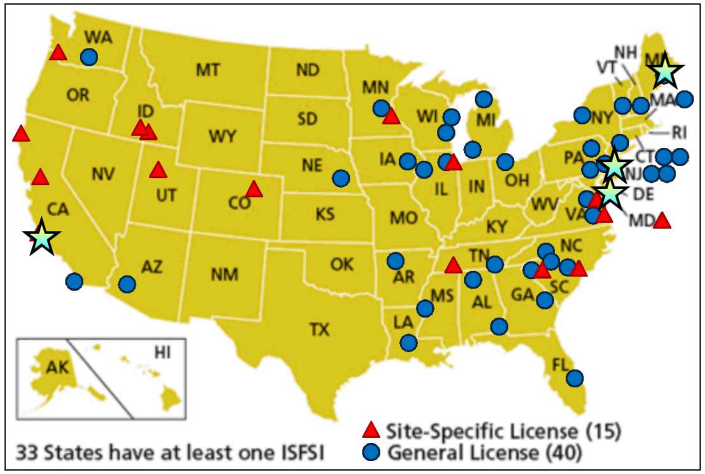
Dust on dry storage canister at Calvert Cliffs ISFSI

Salt Aerosol Compositions:

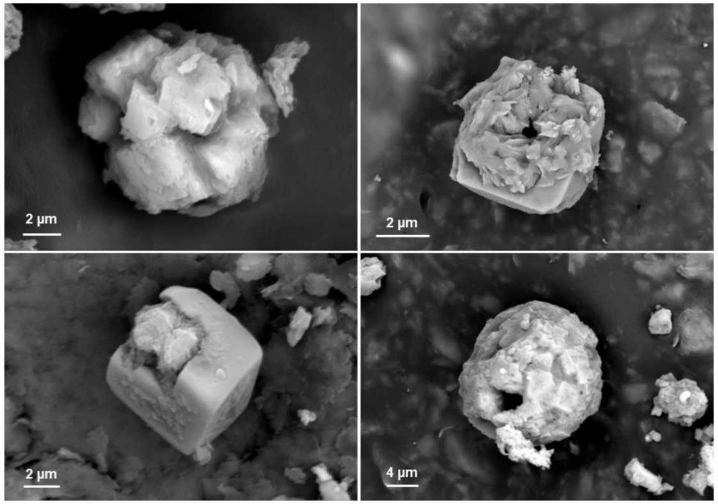
Primary concern is chloride-rich sea-salts, which could deliquesce and cause canister stress corrosion cracking (SCC)

- **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.**

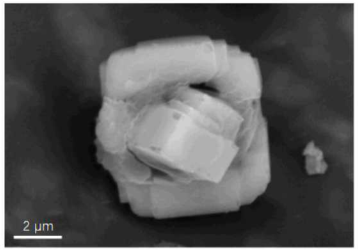
Locations of U.S. Spent Nuclear Fuel Independent Storage Installations (ISFSIs)

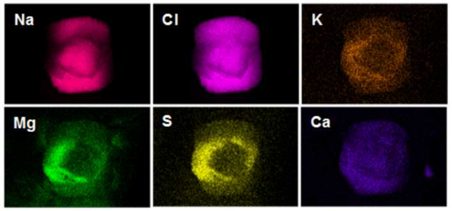


☆ ISFSI locations sampled.



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

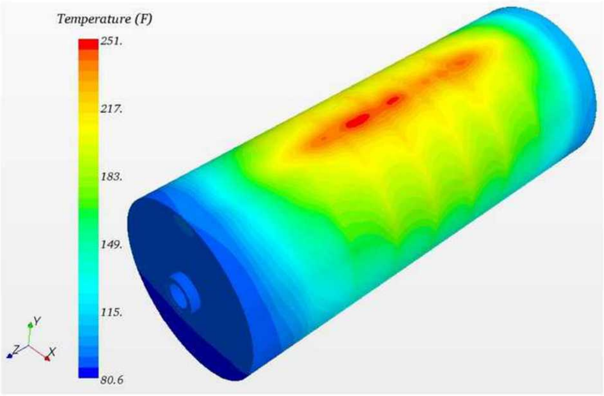


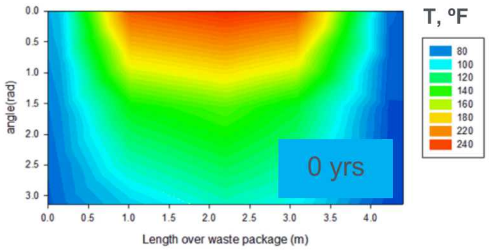


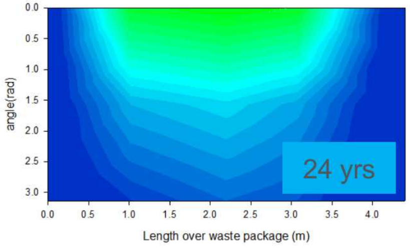
Salt aggregates: dominantly NaCl with interstitial $MgSO_4$ and trace K, Ca phases. Consistent with seawater ion compositions.

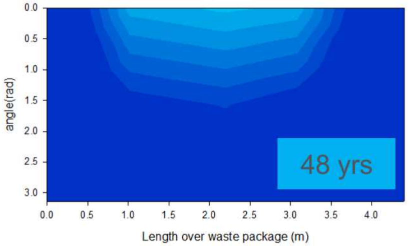
At coastal sites, canister SCC due to deliquescence of chloride-rich salts is a potential failure mechanism.

Evolution of Canister Surface Environment





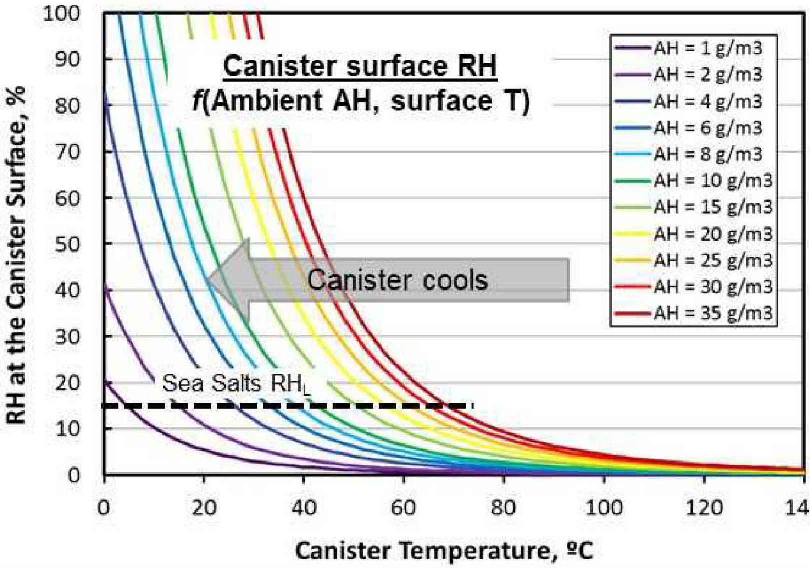




Flattened canister temperature maps (side view)

Over time, during storage:

- Canister dust load increases
- Canister cools
  - Salts eventually deliquesce, forming surface brines
  - Brine layer properties change as salt load and RH continue to increase



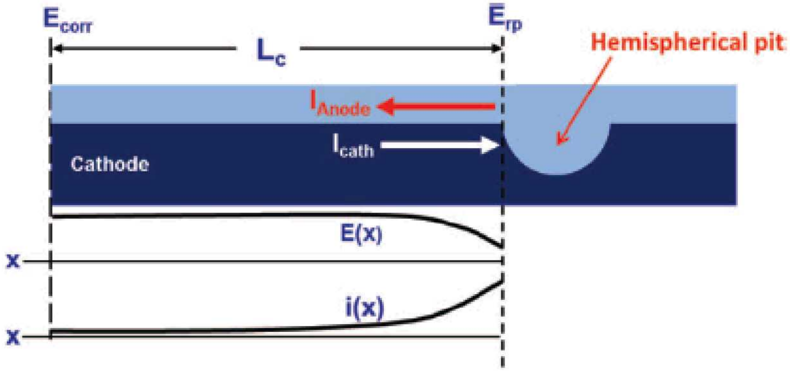
Brine layer properties change as a function of T, RH, and salt load

Why are brine compositions important?

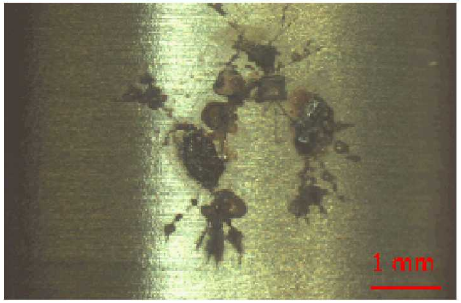
Temperature and timing of deliquescence (brine formation)

Brine corrosivity—brine composition affects extent of corrosion damage. For example, maximum pit size model of Chen and Kelly (2010)

- Metal oxidation occurs in the pit (anode), while the oxygen reduction (cathodic reaction) occurs on the surrounding surface.
- Cathode and anode must be connected by a conductive aqueous film: anode current demand must be met by cathode current
- Maximum possible anode current (maximum pit size) is determined by the maximum available cathode current.
- Maximum cathode current is function of brine layer *conductivity* and *thickness*, in turn functions of *temperature*, *RH*, and *salt load.*

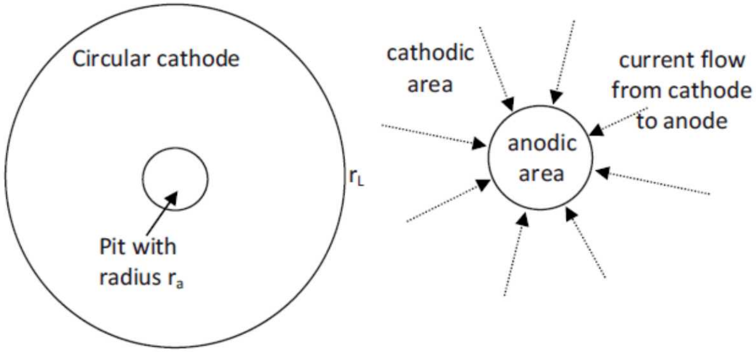


Chen et al., 2008



Maximum Pit Size

(Chen and Kelly 2010)



Max. cathode current

Brine conductivity

Brine layer thickness

Cathodic kinetics

$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p)dE}{\Delta E_{max}}\right]$$

Thermodynamic modeling of brines formed by sea-salt deliquescence

Thermodynamic modeling:

- Geochemical speciation and solubility code EQ3/6 (Wolery and Jarek, 2003).
- Yucca Mountain Program thermodynamic database for high ionic strength solutions, incorporating Pitzer (1991) activity model. Validated for solutions of individual salts and salt mixtures to 140ºC (SNL 2007).
- Deliquescence modeled as seawater evaporation: evaporation is the reverse of deliquescence, predicts the same brine compositions as a function of RH
- Starting seawater composition taken as that of ASTM D 1141-98.
- Assumes equilibrium with atmospheric CO_2 concentration of $10^{-3.4}$ bars. Does not consider other atmospheric exchange reactions.

Sea salt/spray — generally simulated with synthetic ocean water *(ASTM D1141-98)*

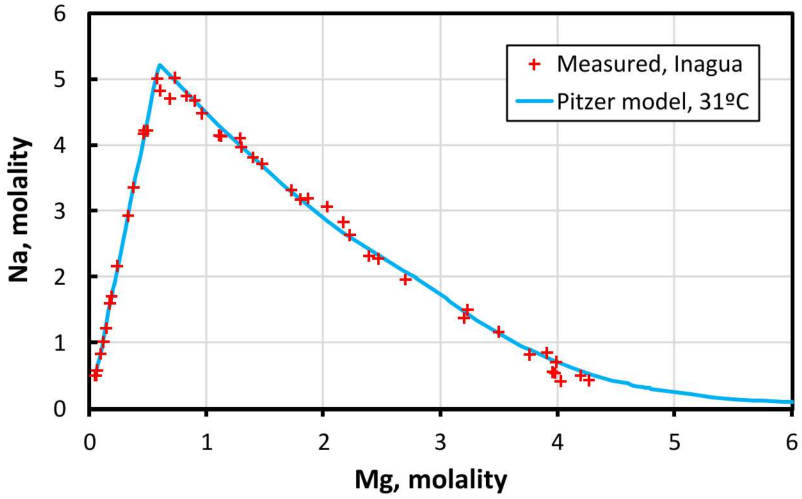
	Conc., mg/L	
Species	**ASTM D1141-98**	**McCaffrey et al. (1987)**
Na^+	11031	11731
K^+	398	436
Mg^{2+}	1328	1323
Ca^{2+}	419	405
Cl^-	19835	21176
Br^-	68	74
F^-	1	—
SO_4^{2-}	2766	2942
BO_3^{3-}	26	—
HCO_3^-	146	—
pH	8.2	8.2

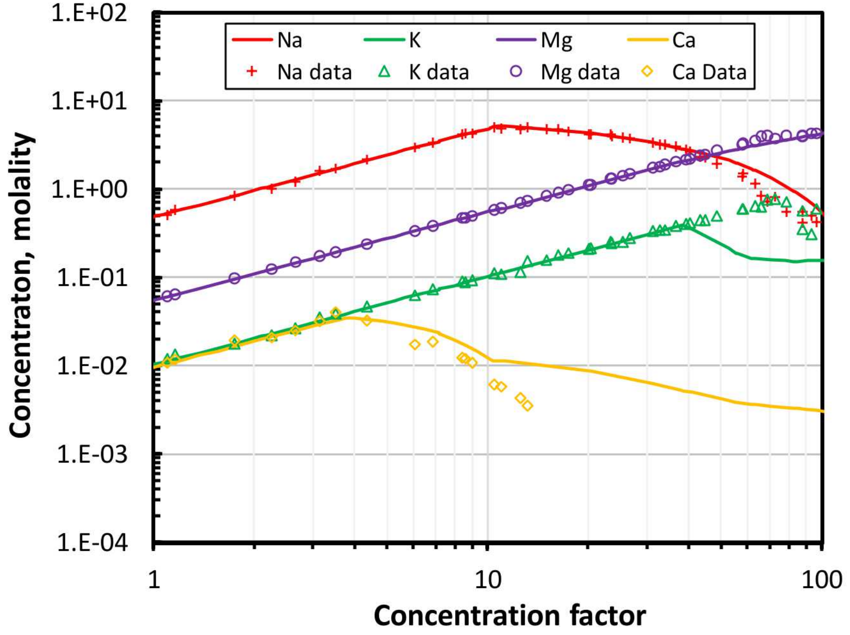
Thermodynamic model validation

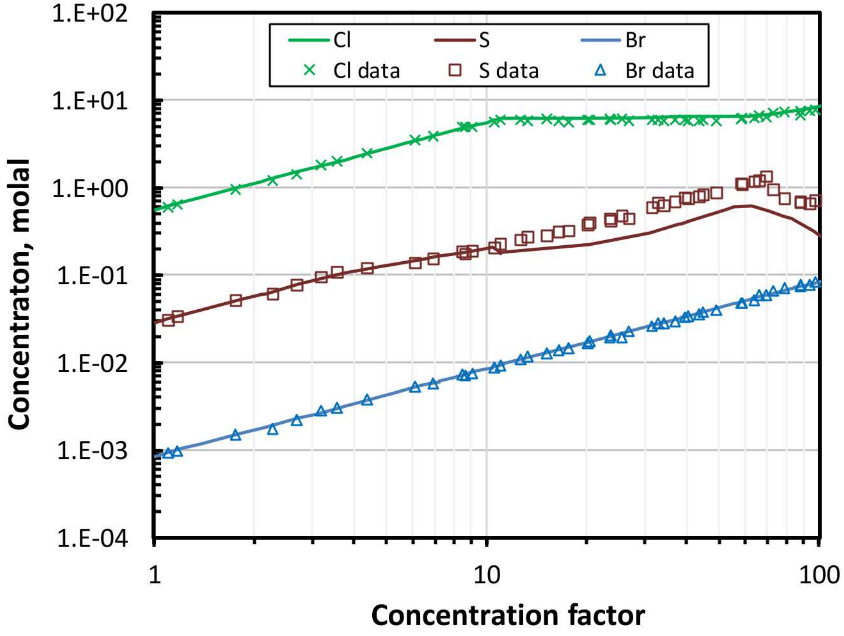
(example of seawater evaporation)

Model validation against seawater evaporation data from the Morton salt facility at Inagua Island, Bahamas

(data from McCaffrey et al., 1987)

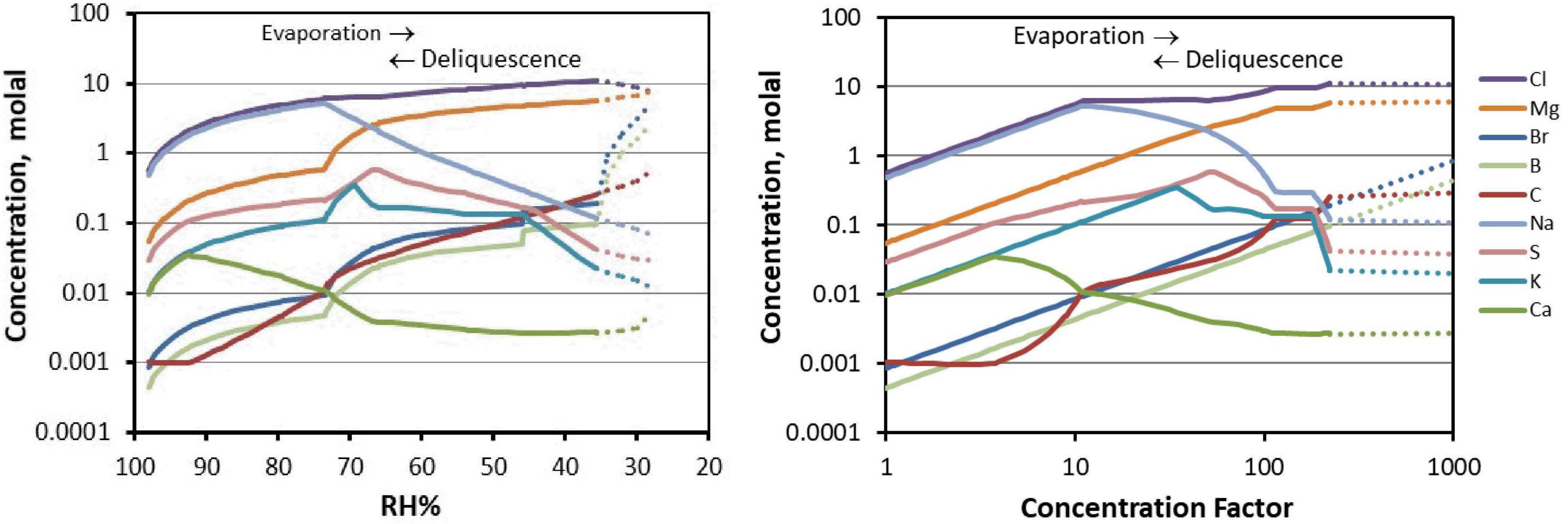






Sea-salt Deliquescent Brine Compositions

Seawater evaporation/deliquescence at 25ºC



Brine compositions:

- *Upon evaporation, salts precipitate and re-dissolve. Precipitated salts dictate the composition of remaining brine*
- *Seawater evolves towards concentrated Mg-Cl brine as NaCl precipitates*
- *Ca, K, S are mostly removed by minerals, and are very low in the final remaining brine*
- *Br and B are conserved (but the thermodynamic database is not qualified for B compounds)*
- *General trends vary little with temperature (10-80ºC)*

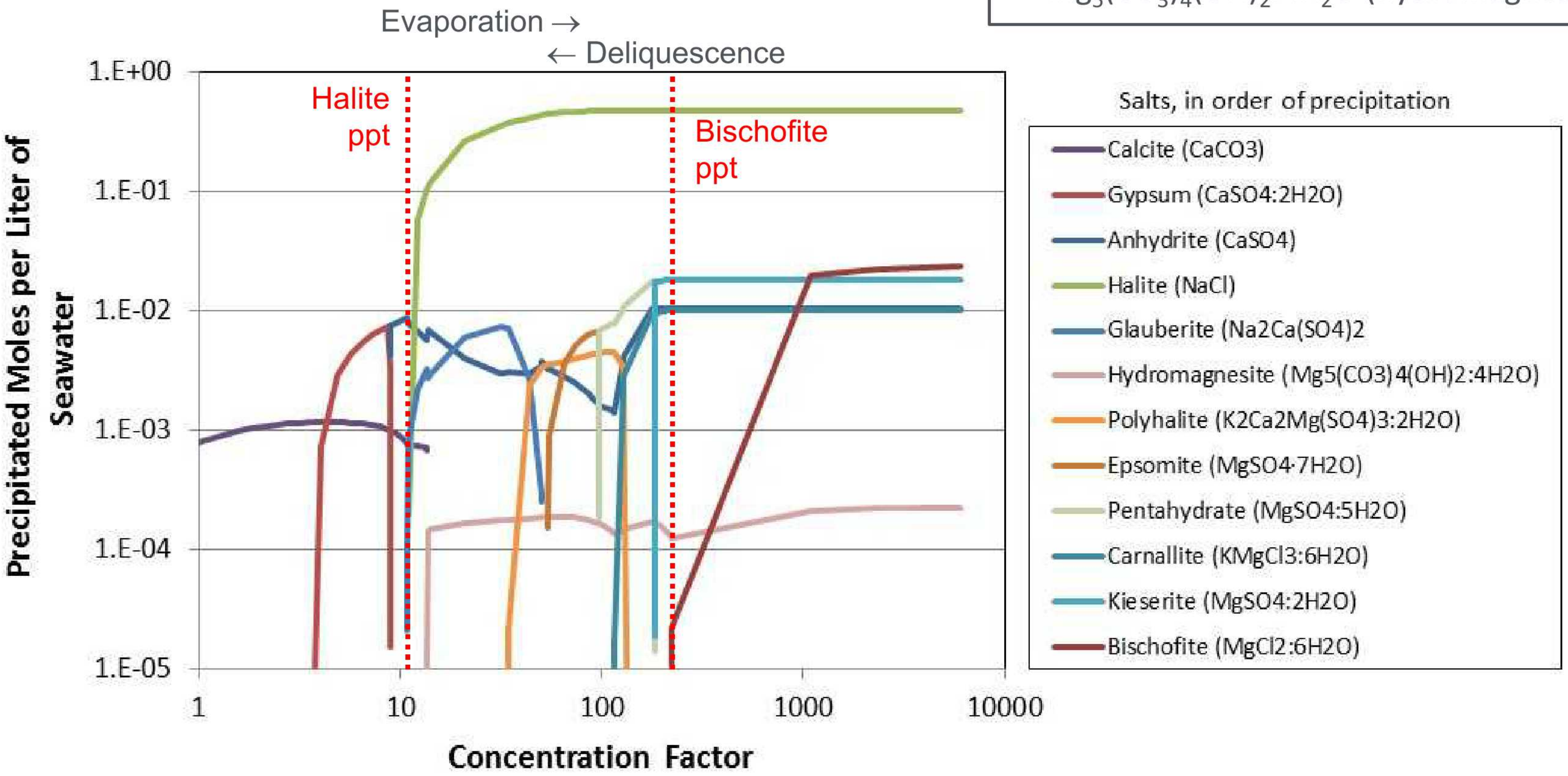
Seawater Evaporation: Precipitated Salts

Precipitated salts:

Upon evaporation, several salts precipitate and re-dissolve (order given below). The final assemblage determines the deliquescence RH.

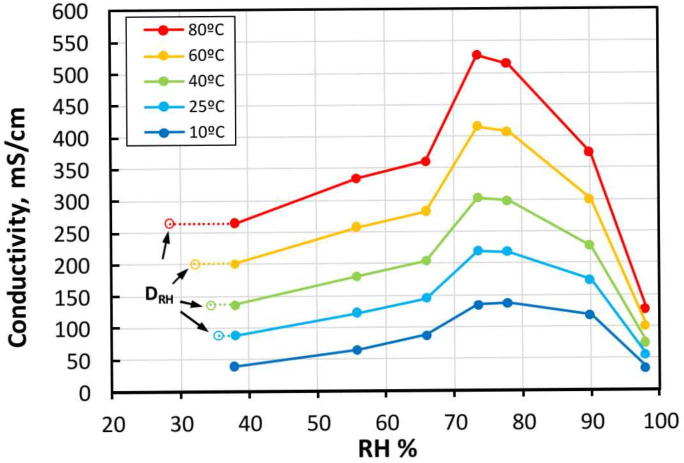
Final assemblage

- NaCl (halite)
- $MgCl_2$:6H_2O (bischofite)
- $MgSO_4$:2H_2O (kieserite)
- $KMgCl_3$:6H_2O (carnallite)
- $CaSO_4$ (anhydrite)
- $Mg_5(CO_3)_4(OH)_2$:4H_2O (hydromagnesite)



Experimental Measurement of Brine Properties

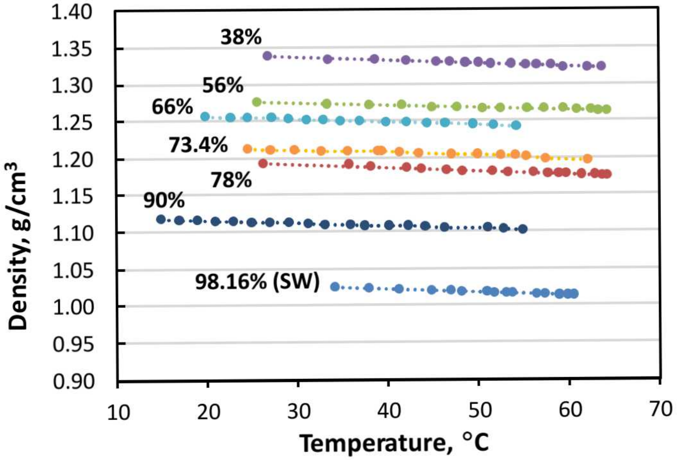
Selected brine compositions mixed, and brine properties measured *f*(T, RH)



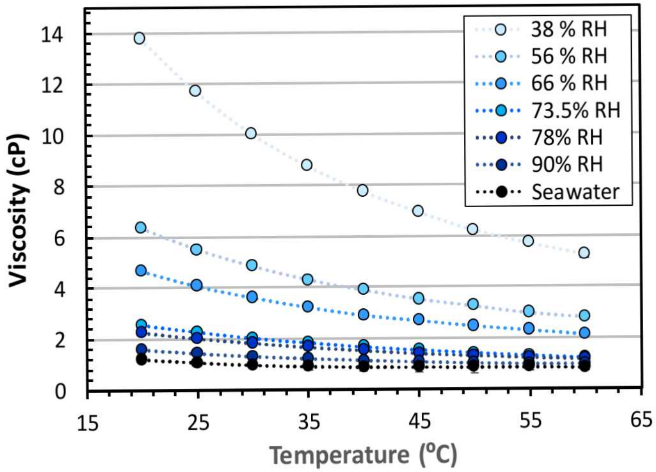
Conductivity

Density

(to calculate brine volume/layer thickness)



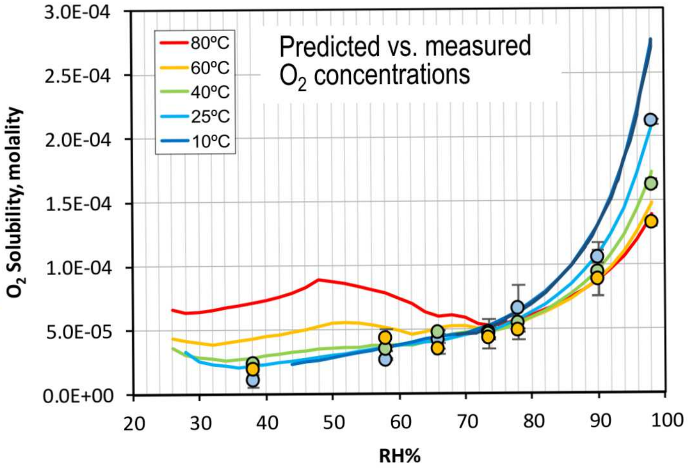
Parameters to estimate the limiting cathodic current density



Viscosity

(to estimate oxygen diffusivity)

Dissolved oxygen concentration



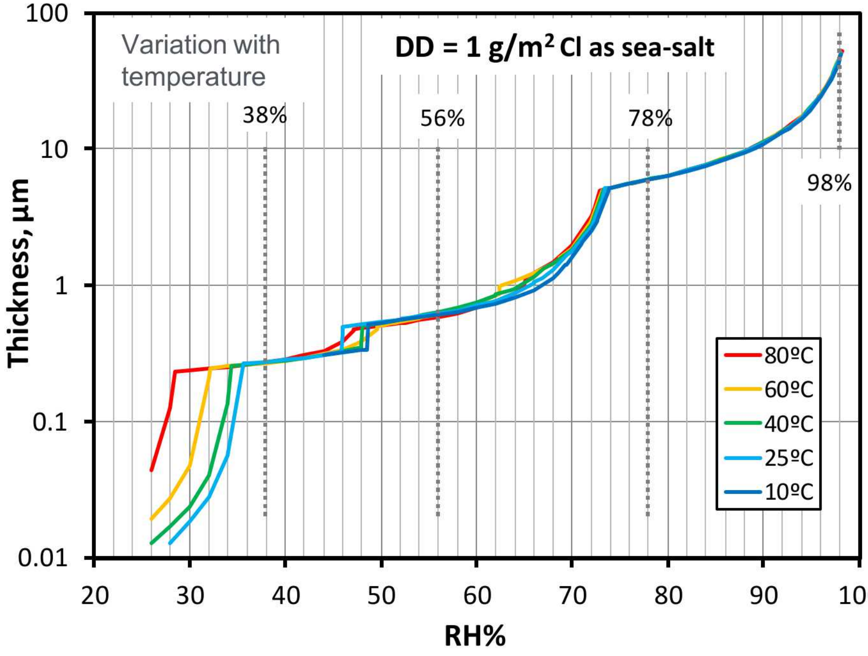
Cathodic polarization curves

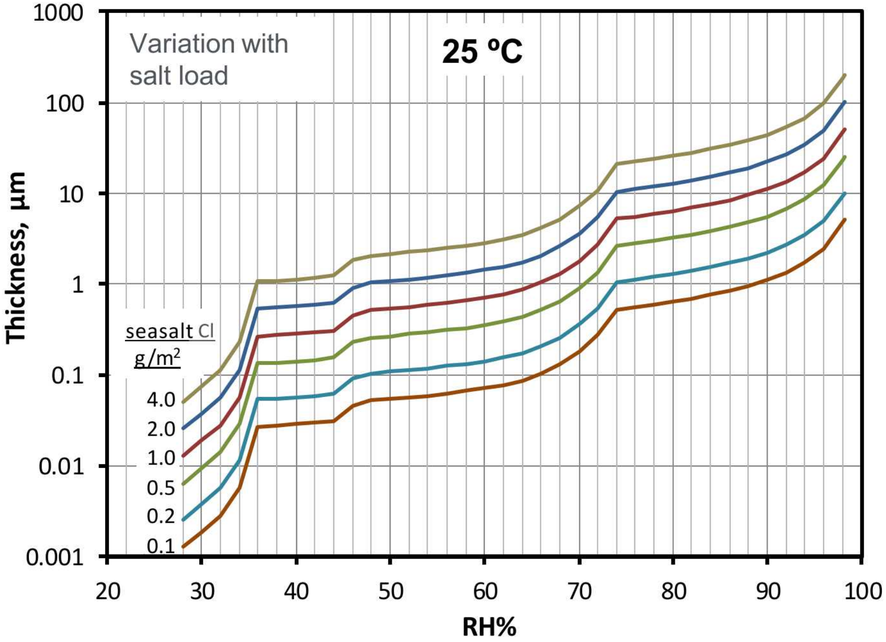
(not presented here)

Brine Layer Thicknesses

Brine volumes based on geochemical modeling (mass of water/solutes remaining) and measured brine density data. Brine is assumed to be uniformly distributed on surface.

- Brine layer thicknesses decrease by orders of magnitude as brines evaporate and salts precipitate
- For any given RH, temperature has little effect on brine volume
  - Slight shift due to changes in RH of precipitation of ternary salts at 50% RH
  - Change in RH at which bischofite precipitates
- Volume varies linearly with salt load



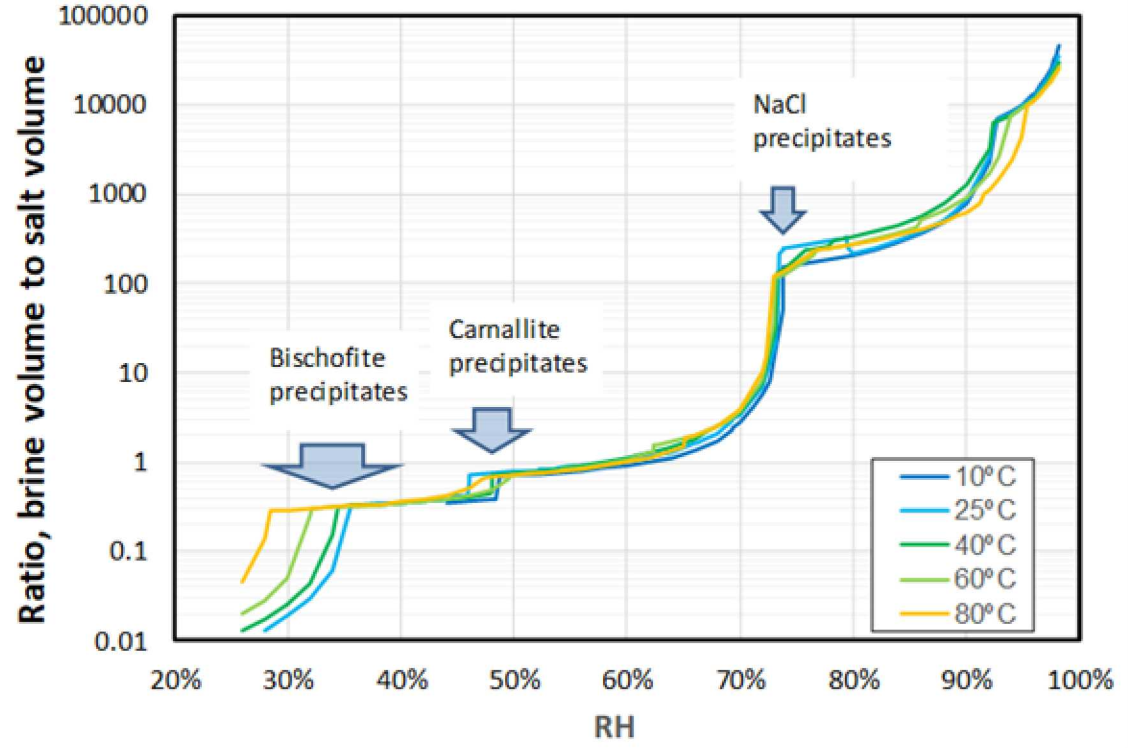


Brine Layer Properties

Sea-salt brines: ratio of brine volume to salt volume

Brine volume decreases rapidly with evaporation, while salts accumulate.

- ❑ Once NaCl precipitates (74% RH), brine/solid ratio drops rapidly.
- ❑ Below 60% RH, salt volume exceeds brine volume.
- ❑ Below 45%, brine volume is 0.3-0.4 of salt volume.
- ❑ At point of bischofite precipitation (deliquescence) brine volume is 0.3 salt volume.

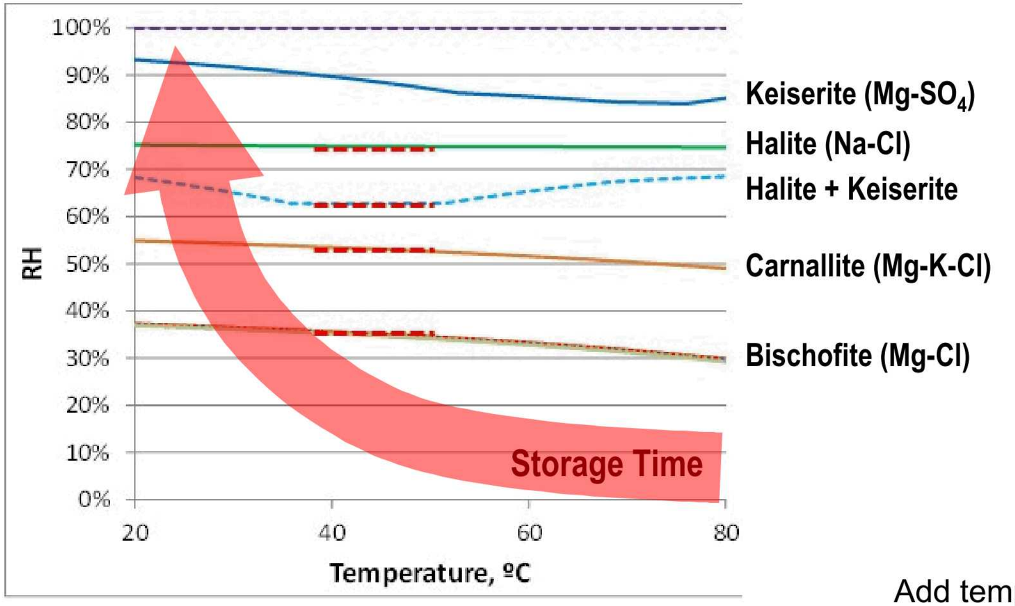


For sea-salts deposited as discrete salt aerosols, the assumption that brine forms a continuous layer may be unlikely, at low salt loads or low RH values.   *However:*

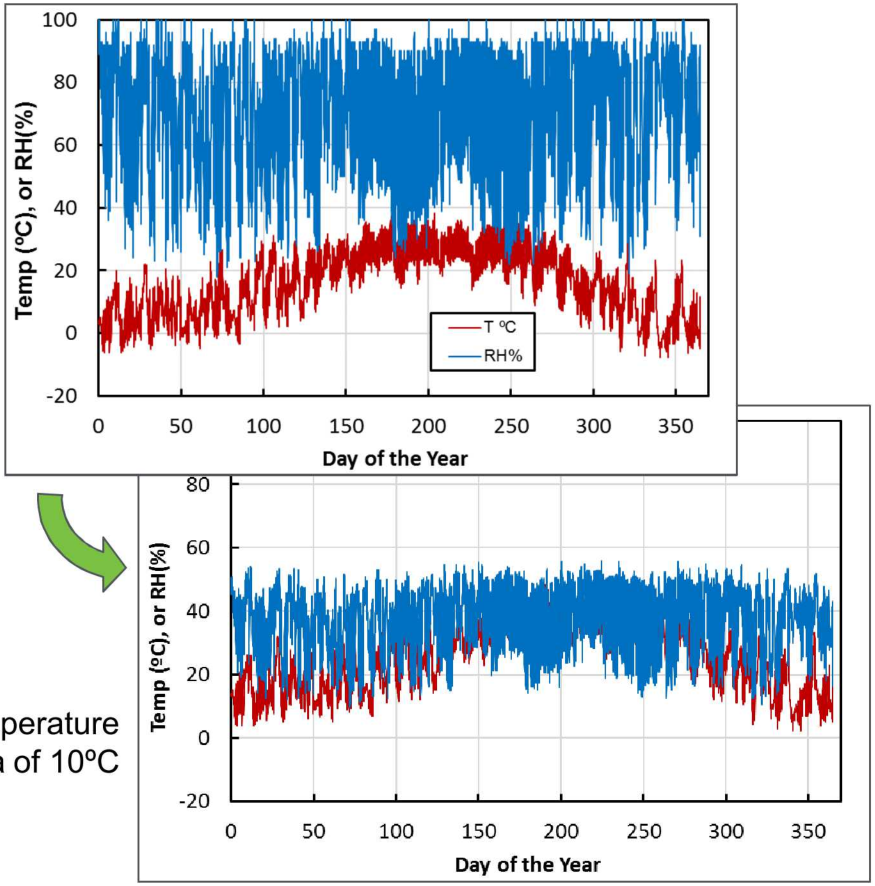
- Experimental data suggest that the cathode can extend well beyond the perimeter of salt grains (Schindelholz et al., 2016).
- Insoluble dust particles will increase brine film continuity via capillary effects.

For Sea-Salts, Bischofite ($MgCl_2{:}6H_2O$) Controls Timing/Temperature of Deliquescence

- 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 canister surface temperatures reach lower values. Canister surface RH is highly sensitive to temperature.



Weather near Arkansas Nuclear One



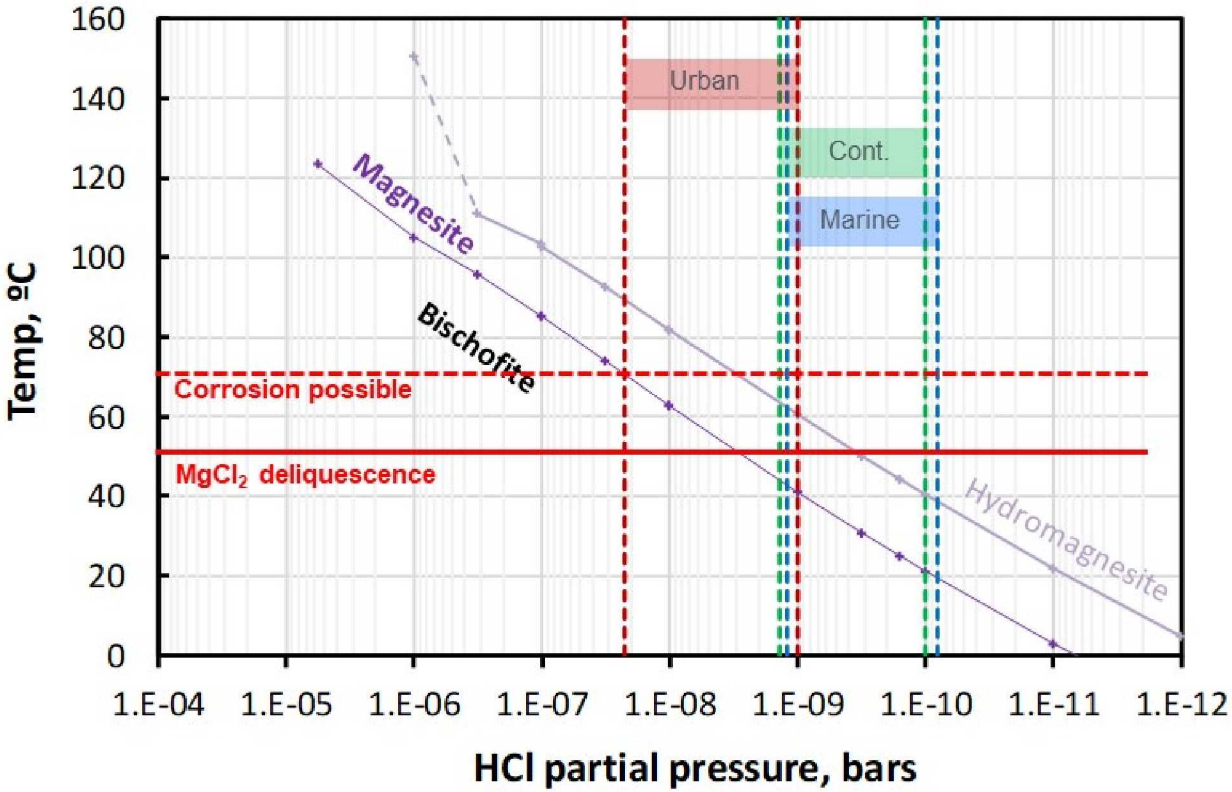
Add temperature delta of 10ºC

Mg-Cl Brine Stability at Elevated Temperatures:

Carbonation Reaction: Absorption of atmospheric CO_2

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

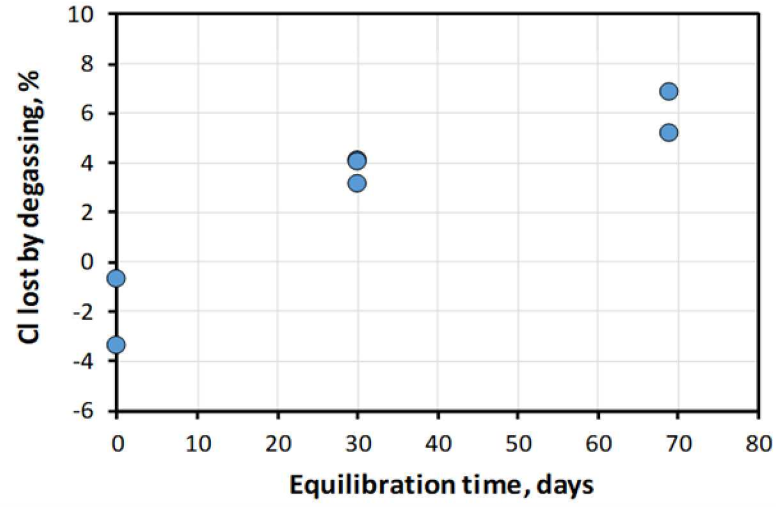
- Brines may degas or absorb HCl, depending on background acid gas concentrations and temperature
- Elevated temperatures promote conversion to carbonate
- Carbonation would result in brine dryout, eliminating corrosive environment.
- However, for SNF storage canisters, reaction could reverse itself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

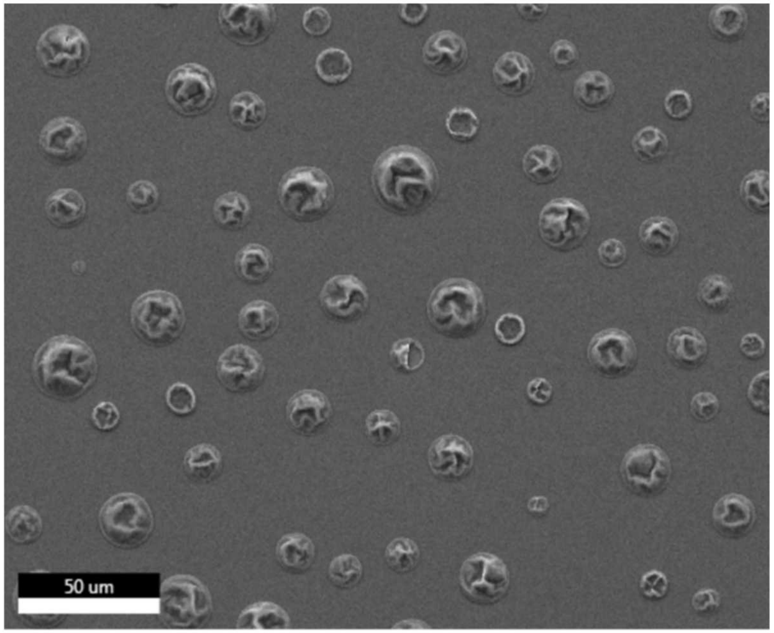


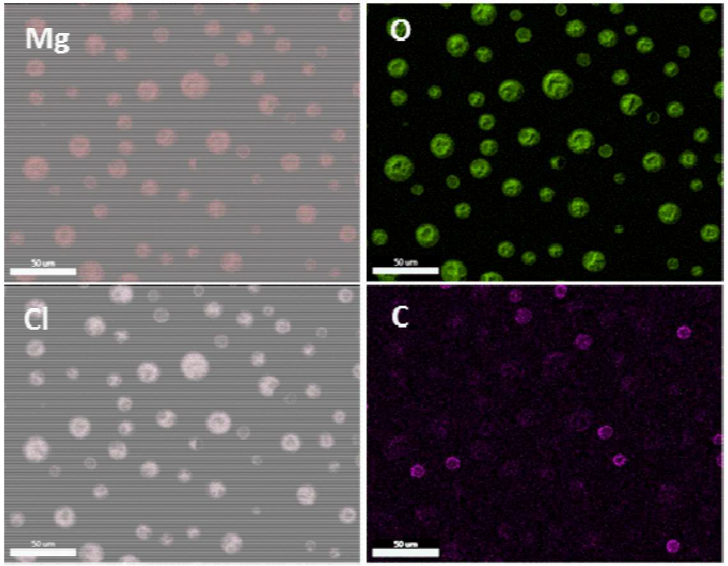
Experimental Evaluation of $MgCl_2$ Brine Stability:

$MgCl_2$ brine at 48ºC, 40%RH (~highest T/RH conditions for deliquescence on real canisters)

- $MgCl_2$ brine droplets on inert substrate (Si wafer), 48ºC, 40% RH, 2 L/min air flow ($P_{HCl} = 0$). Sampled after 2-4-8 weeks.
- Results: Partial conversion to carbonate observed; later chemical analysis suggests <10% chloride lost.
- Airflow was too low to support complete conversion. At 48ºC, one m^3 of air can only remove 1.3 – 13 µg chloride (hydromagnesite/magnesite). *Under field conditions, airflow is not limiting.*







Experimental evaluation of $MgCl_2$ Brine Stability:

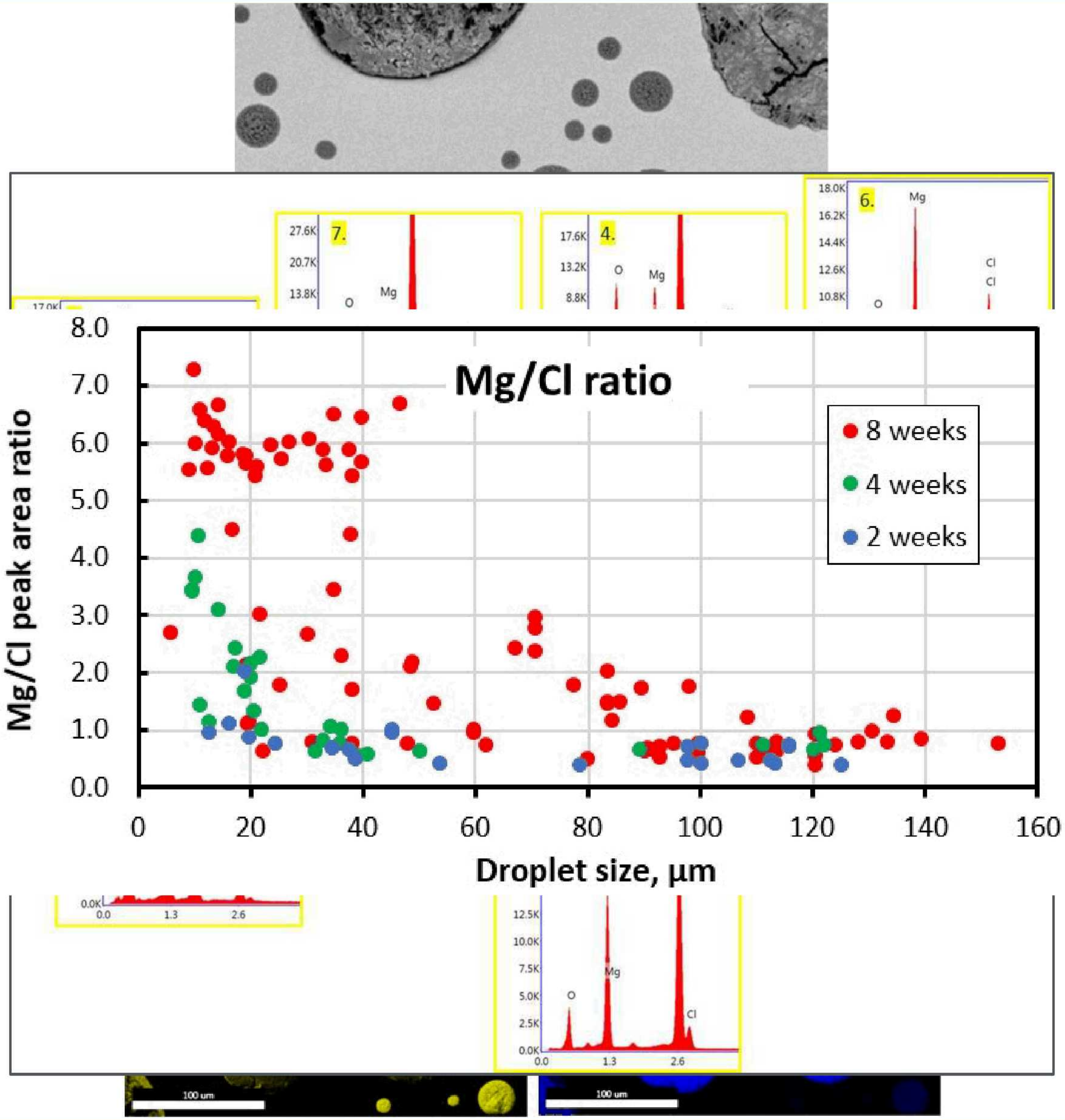
$MgCl_2$ brine at 80ºC, 35%RH (conditions used by SNL and others for accelerated testing)

Experimental conditions:

- ❑ $MgCl_2$ brine deposited on inert substrate (Si wafer), 80°C, 35% RH. Airflow rate 2 liters/minute (P_{HCl} = 0). Sampled after 2-4-8 weeks.

Results

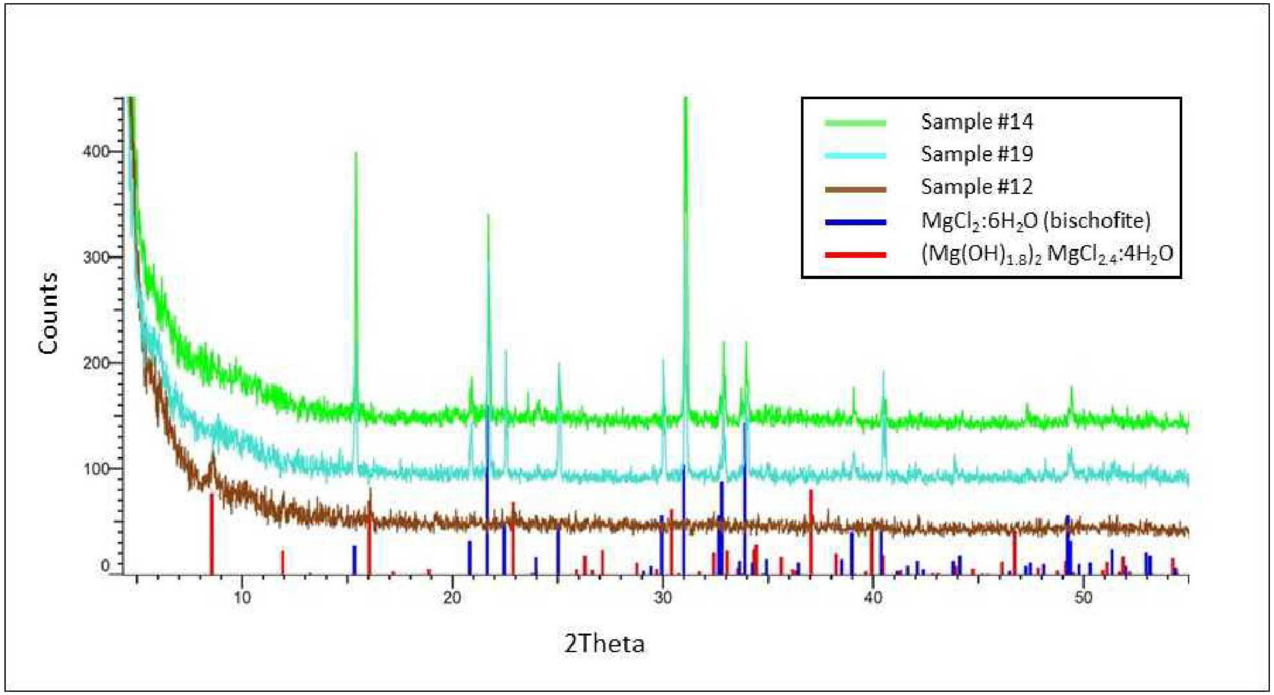
- ❑ After 8 weeks, in SEM BSE images, smaller droplets and some larger droplets appear darker, indicating lower average Z.
- ❑ SEM EDS maps indicate ***chloride loss***, oxygen gain, and minor carbon gain.
- ❑ Large increased in measured Mg/Cl peak area ratios in small and medium-sized droplets



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>***

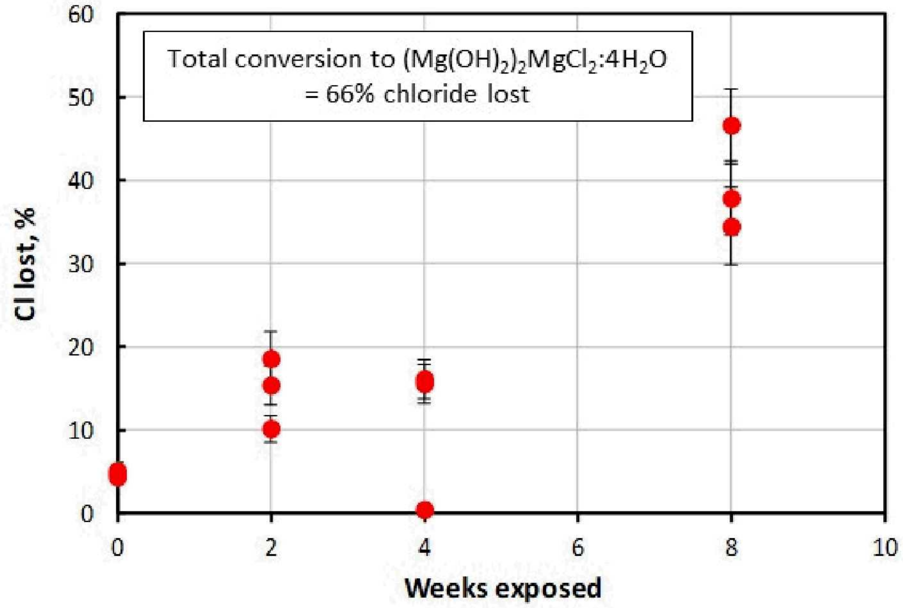
$(Mg(OH)_2)_2MgCl_2$:$4H_2O$ ***(Mg:Cl = 3:2)***

Chemical Analyses of Remaining Salts

Remaining salts depleted in chloride, showing that chloride loss via HCl degassing had occurred.

Overall reaction:

$$3Mg^{2+}_{(aq)} + 6Cl^{-}_{(aq)} + 8H_2O \rightarrow (Mg(OH)_2)_2MgCl_2{:}4H_2O_{(s)} + 4HCl_{(g)}$$



Conclusion:

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

Effect of Corrosion Reactions on Brine Stability?

Corrosion cell

pH rises

Cathode

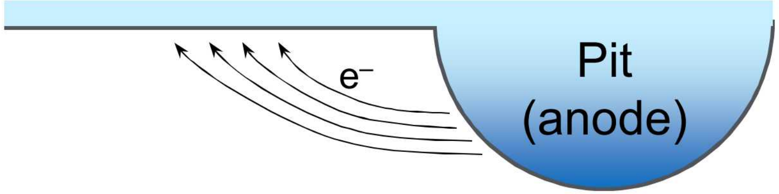
$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

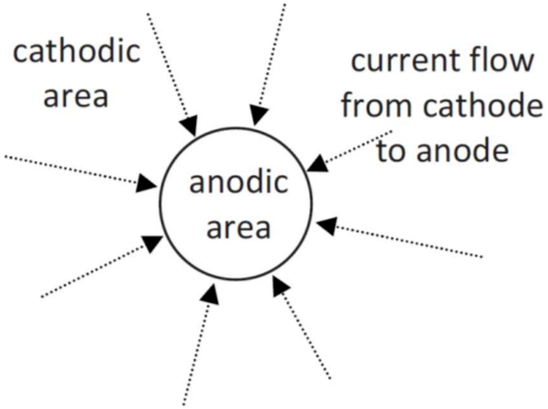
Anode

pH drops

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

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





Corrosion reactions

Cathode:

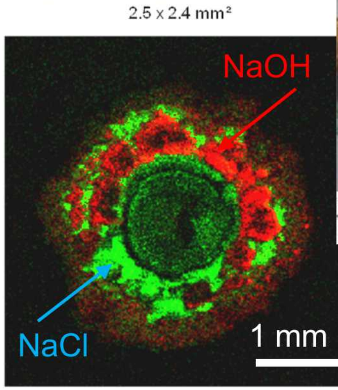
- Changes in brine chemistry may affect cathode kinetics by changing brine composition and volume
- Elevated pH may result in hydroxyl or carbonate precipitation. E.g., Al corrosion: high pH promotes CO_2 absorption, precipitation of carbonates and dryout (Schaller et al., 2017).

Anode:

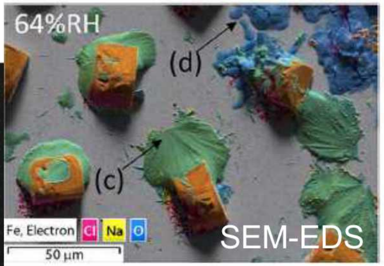
- Low pH promotes acid degassing?

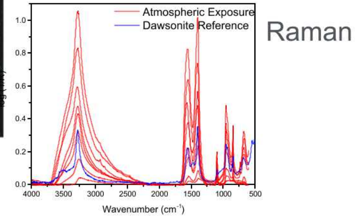
Example: Aluminum corrosion

TOF-SIMS



Schaller et al., 2017)





Effects of Corrosion on Brine Stability:

4-point bend test at 80ºC, 35% RH

4-Point bend test

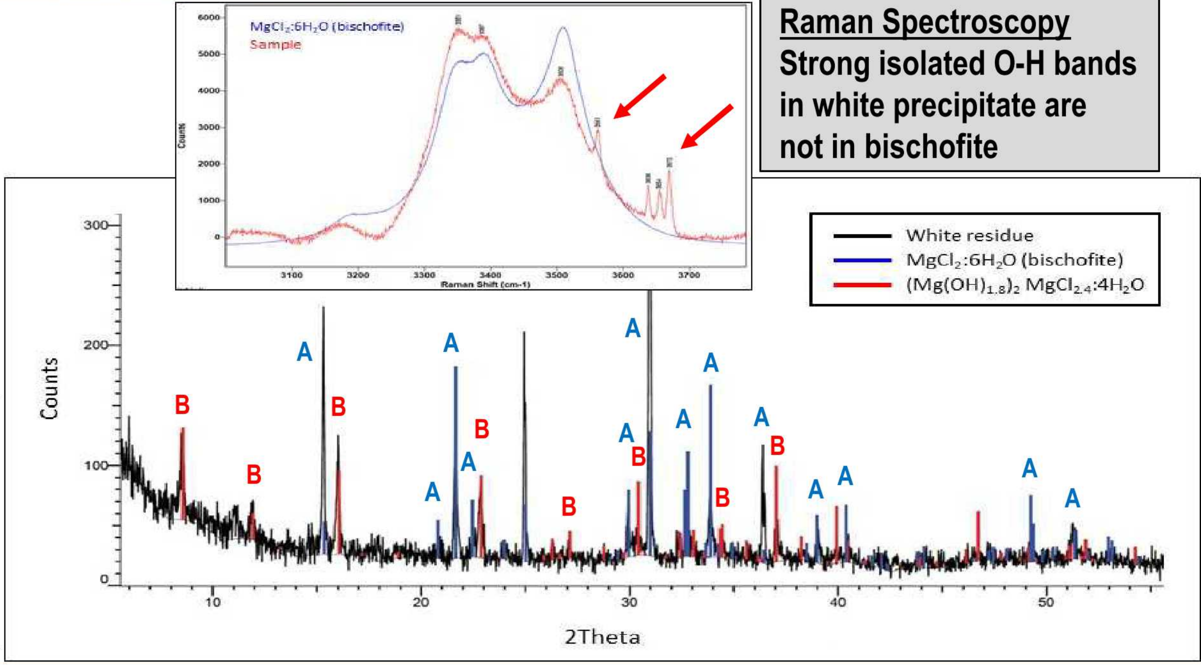
- $MgCl_2$ brine deposited as droplets
- 80°C, 35% RH

Results

- Heavy corrosion around brine droplets
- White precipitate observed around corroded areas
- Precipitate less deliquescent than bischofite (which still deliquesced). Identified by XRD as same Mg-hydroxychloride

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), ~ $2Mg(OH)_2{:}MgCl_2{:}4H_2O$
Same phase as seen previously in the $MgCl_2$ brine stability test at this temperature.



Effects of Corrosion on Brine Stability:

Sandia “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 and 8 months.
- By 8 months, surface was dry.

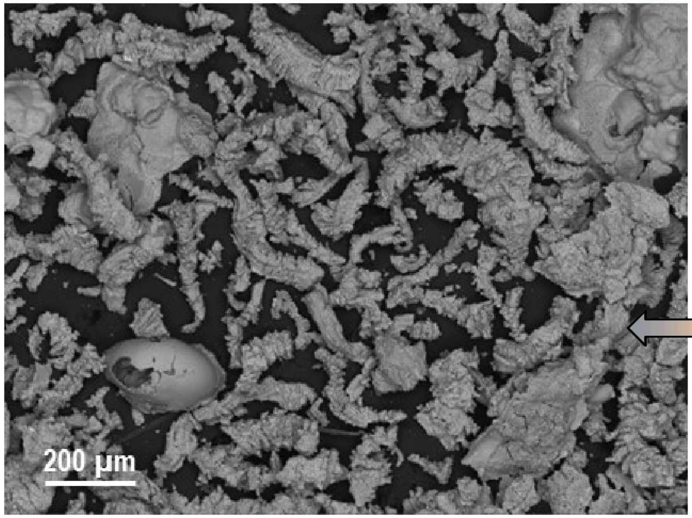
Dry-out had occurred. What happened to the brine?

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

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

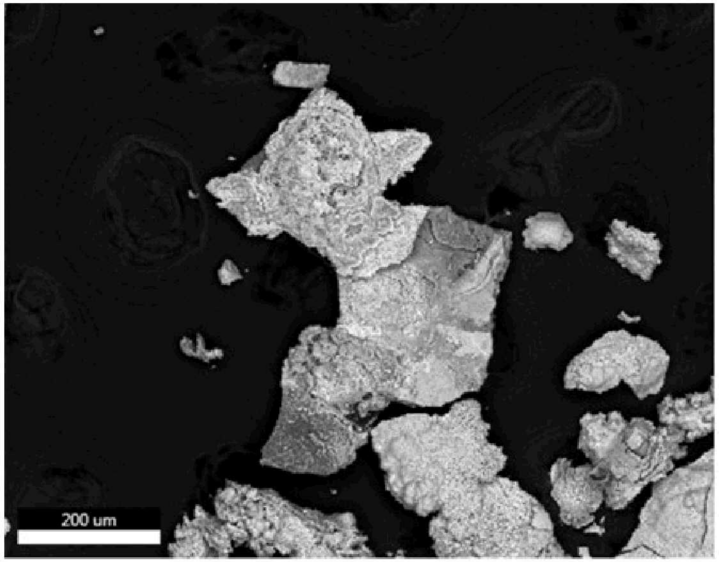
8 months: Surface completely dry, covered with loose corrosion products.

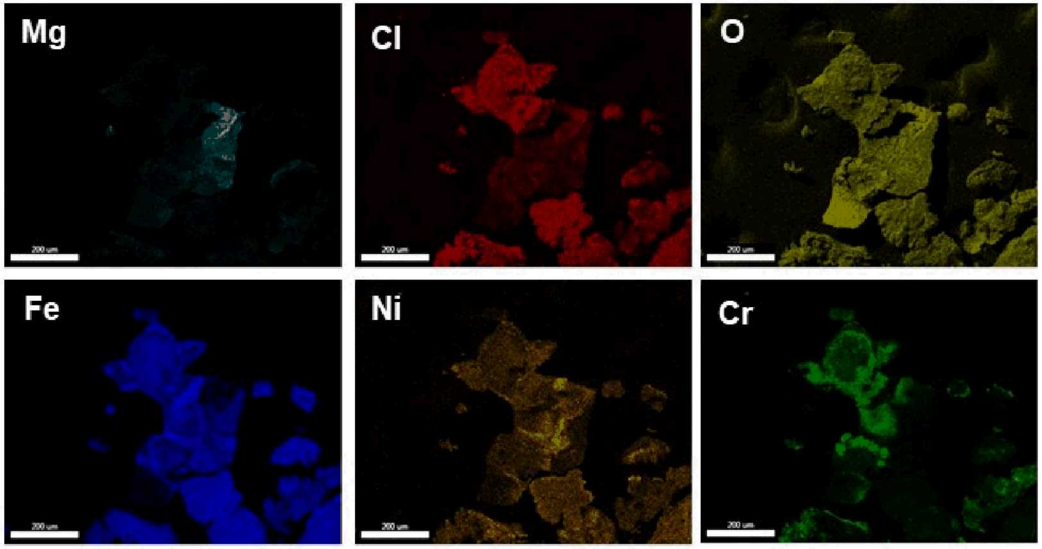
Corrosion products: loose “whiskers” and adhering “blisters”

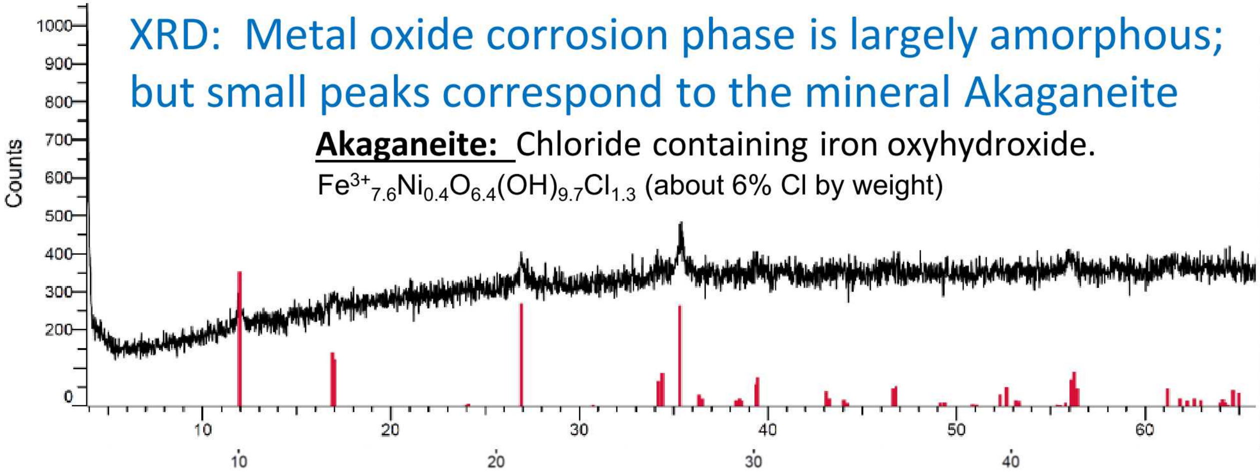


Corrosion residues from “Big Plate” Test

SEM/EDS Element Maps of Big Plate Corrosion Residues



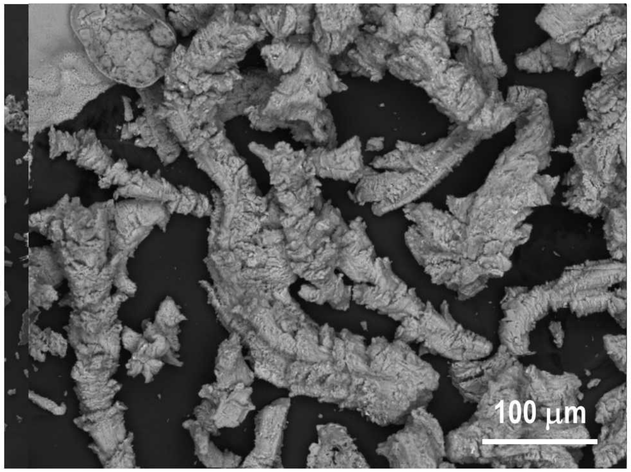




XRD: Metal oxide corrosion phase is largely amorphous; but small peaks correspond to the mineral Akaganeite

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 is several experiments to date

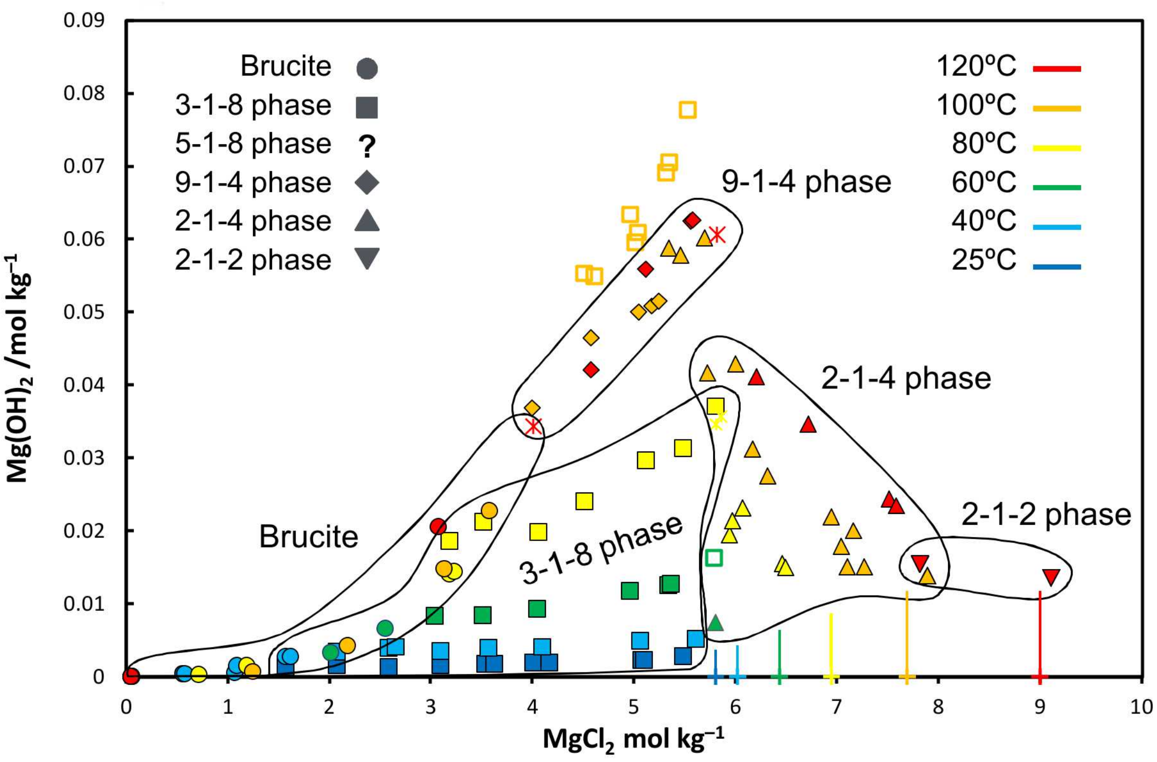
System $Mg(OH)_2$-$MgCl_2$-H_2O

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, and 2-1-4 observed
- Deliquescence properties? (less deliquescent than bischofite)
- Kinetic limitations? (e.g., carbonate vs hydroxychloride?)
- Thermodynamic data? (limited or entirely unavailable; working to develop data)

Conclusions: Sea-Salt Deliquescent Brines and Brine Properties

Atmospheric SCC of SNF dry storage canisters due to deposition and deliquescence of sea-salt aerosols is viewed as a possible risk to long-term interim storage of SNF.

- ☐ Deliquescent brine composition/properties will affect the extent of damage, and vary with temperature and RH, evolving over time as the SNF dry storage canisters cool.
  - Initial brines $MgCl_2$-rich, deliquesce at 25-36% RH.
  - 6M NaCl (minor other components) at 74% RH
  - Seawater at 98.6% RH
  - Brine layer properties vary widely with RH and salt load.
    - Volume (thickness) controlled primarily by RH and salt load on the metal surface; unlikely to result in development of continuous films below 70% RH
    - Conductivity varies with RH, peaking at about 75% RH (most concentrated NaCl brine). Increases with temperature, for any given brine by a factor of 3 to 5 from 10ºC to 80ºC.
    - Viscosity increases with ionic strength (as equilibrium RH decreases); decreases with temperature
    - Oxygen content decreases with increasing ionic strength (as RH decreases); temperature dependence more complex.

Conclusions: $MgCl_2$ Brine Stability at Elevated Temperatures

Understanding brine stability is critical to predicting corrosion behavior under field conditions, and to interpreting laboratory results.

- ☐ As canister surface temperatures drop, deposited sea-salt aerosols deliquesce to form Mg-Cl 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.
    - Acid gas reactions HCl degassing coupled with:
        - Nothing → conversion to Mg-hydroxychlorides
        - CO_2 absorption → conversion to carbonate
        - SO_x, NO_x absorption→ conversion to sulfates, nitrates (future work)
- ☐ Once corrosion initiates, the oxygen reduction reaction (ORR) produces hydroxides, resulting in precipitation of hydroxide-containing phases in the cathode.
- ☐ Precipitation removes brine components, reducing brine volume at a given RH and eventually leading to dry-out.
- ☐ Brine occurrence delayed until lower temperatures and higher RH conditions, delaying corrosion

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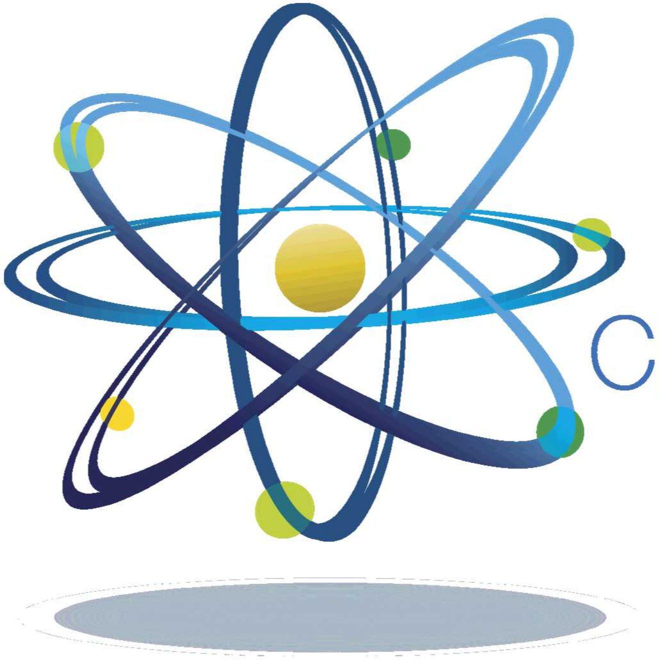
Questions?



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