SAND2015-8196PE

Used Fuel Disposition Campaign

Environmental Considerations for SCC Testing

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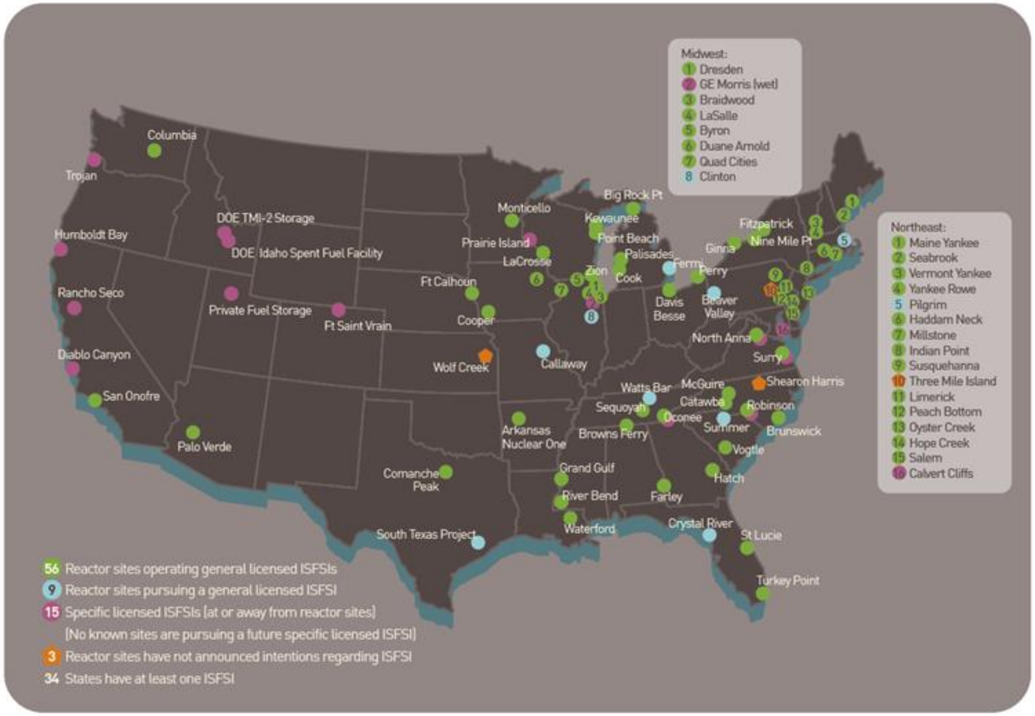
ISFSI locations

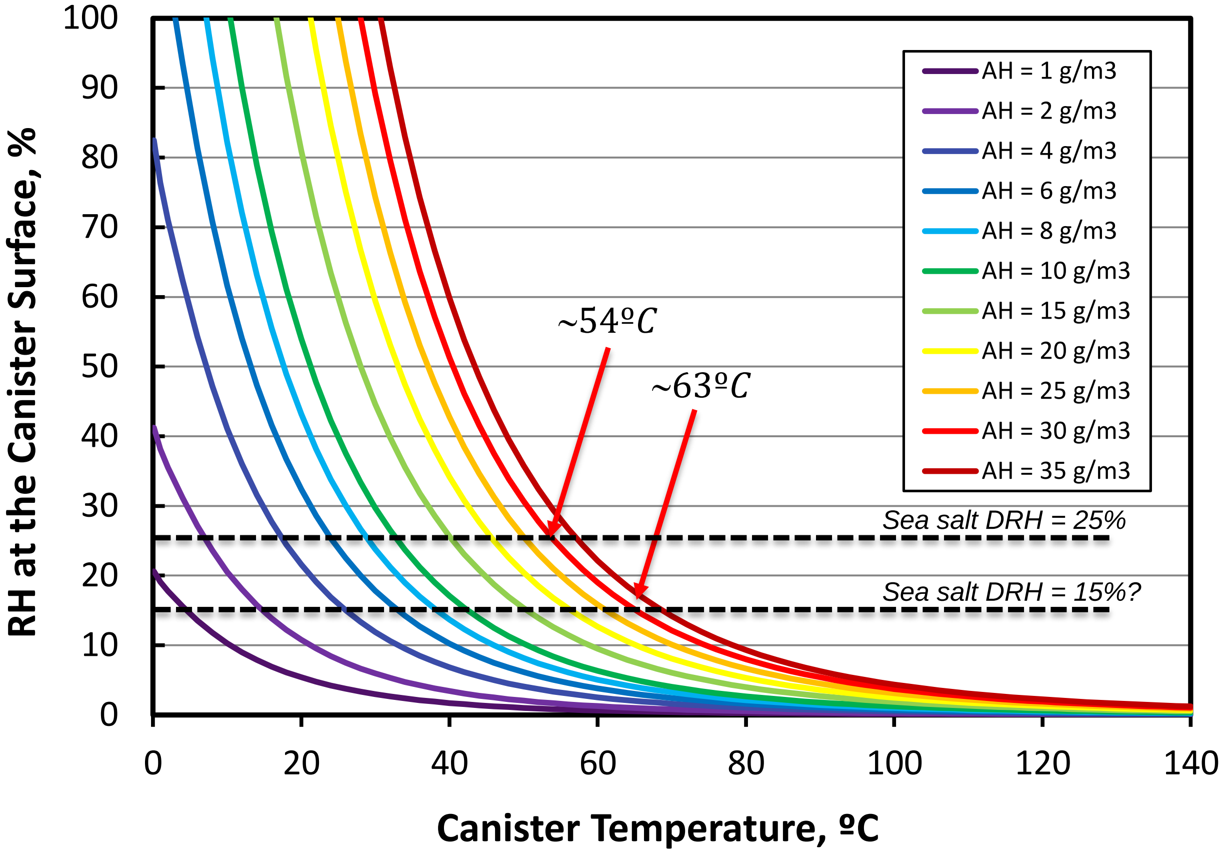
Different settings

- Varying salt assemblages
  - *Coastal (marine salt aerosols)*
  - *Inland (ammonium, sulfate, and nitrate-rich aerosols; possible road salts, cooling tower emissions)*
  - *Salt assemblages control DRH and RH_L*
- Range of weather conditions
  - *Dewpoints (absolute humidity (AH) values)*
  - *Ambient temperatures*
- Temperature range of interest
  - *Determined by RH_L and AH*



Temperature Range of Interest

The temperature range of interest for corrosion experimental work is a function of AH and RH_L.

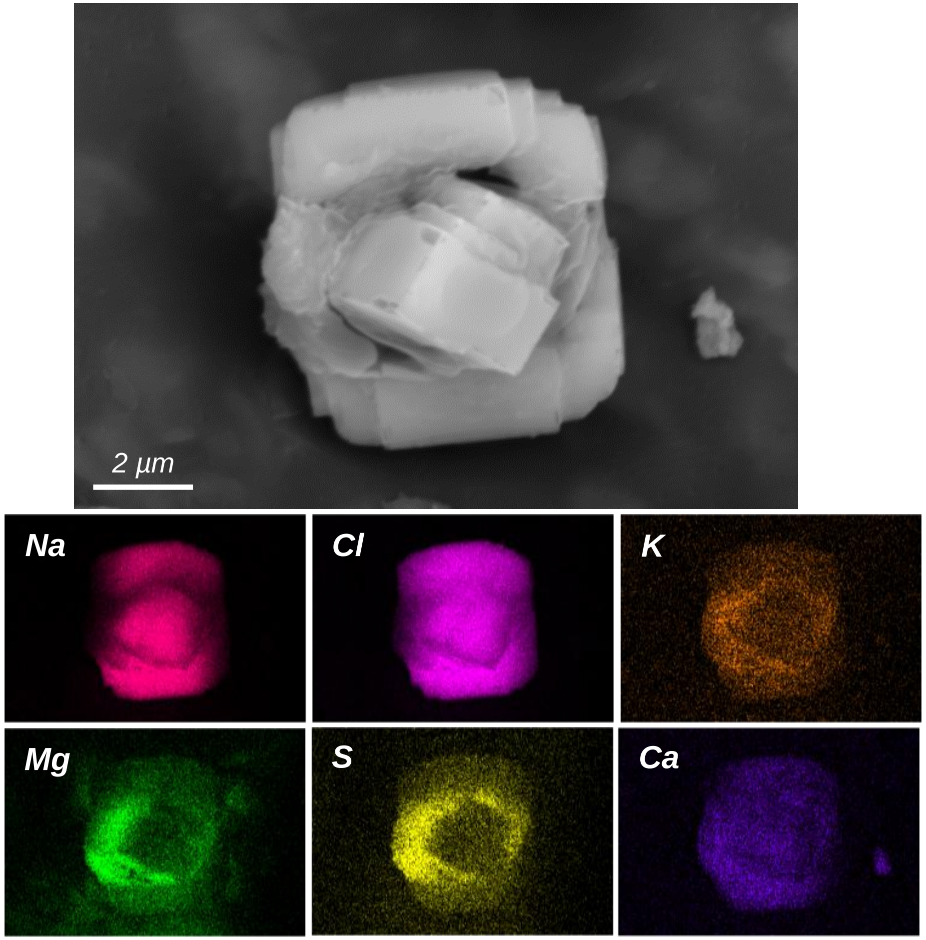


Marine aerosols—observed

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

Species	Conc., mg/L 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

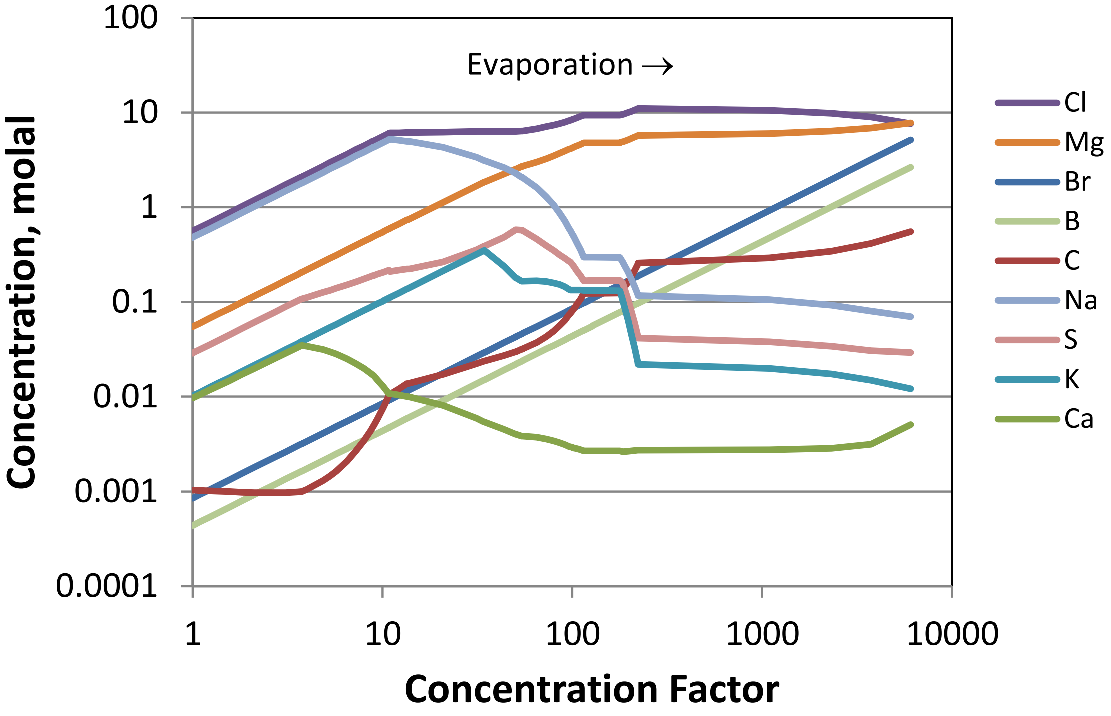
Sea-salt aggregate on Diablo Canyon ISFSI storage canister



Seawater evaporation

Brine composition:

- *Upon evaporation, salts precipitate and redissolve. Removed salts dictate the composition of remaining brine*
- *Seawater evolves towards concentrated Mg-Cl brine as NaCl precipitates*
- *Br and B conserved (but YMP Pitzer database is not qualified for B, and may not be accurate)*
- *Ca, K, S are mostly removed by minerals, and are very low in the remaining brine.*



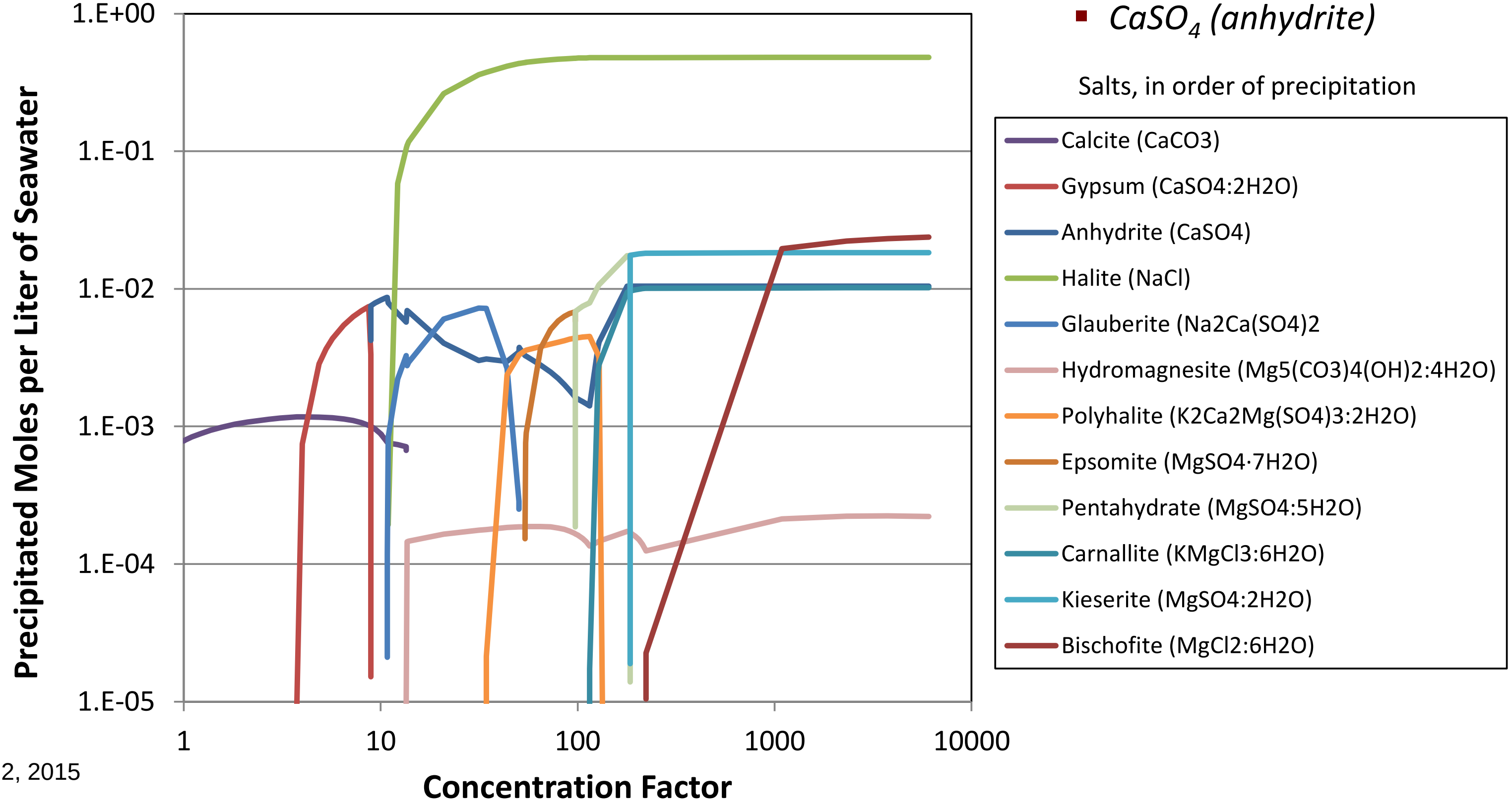
Seawater evaporation

Precipitated salts:

Upon evaporation, several salts precipitate and re-dissolve (order given below)

Final assemblage determines deliquescence RH (DRH)

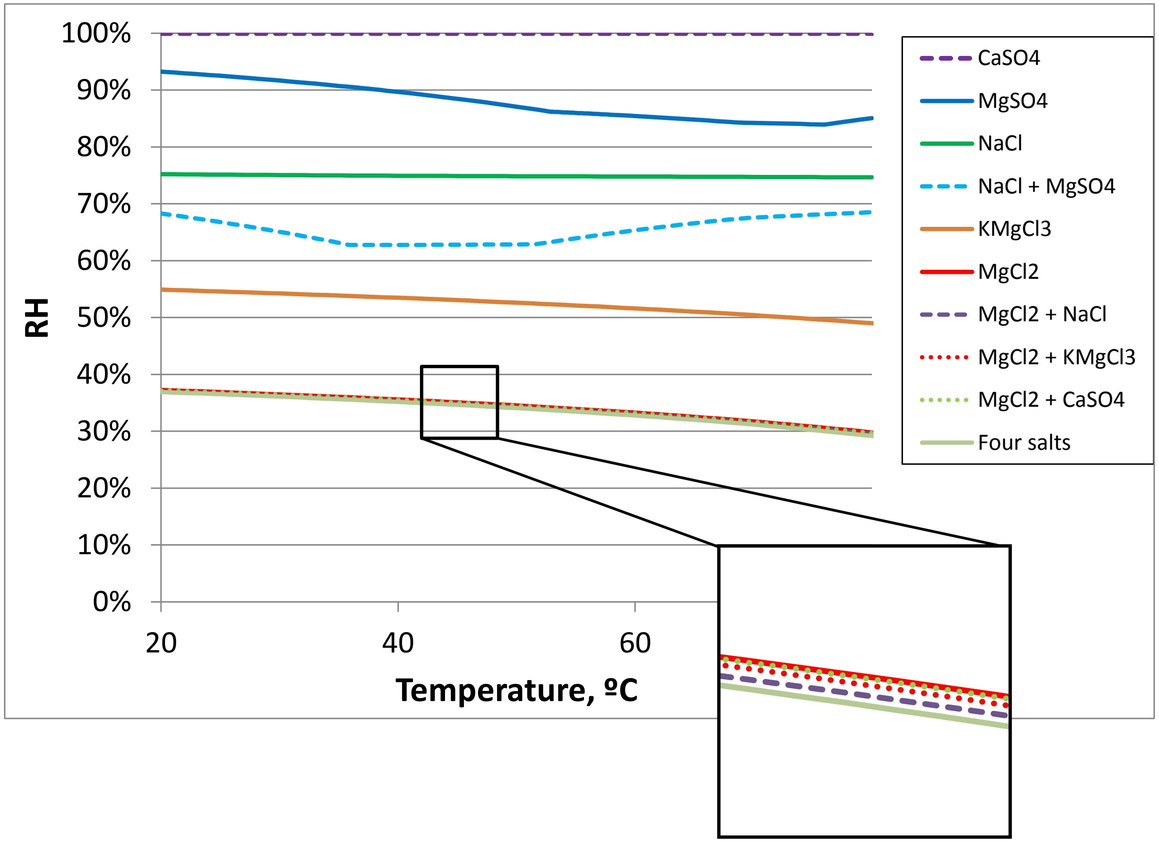
- *NaCl (halite)*
- *$MgCl_2$:6H_2O (bischofite)*
- *$MgSO_4$:2H_2O (kieserite)*
- *$KMgCl_3$:6H_2O (carnallite)*
- *$CaSO_4$ (anhydrite)*



Deliquescence RH Values for Sea Salts

Deliquescence points:

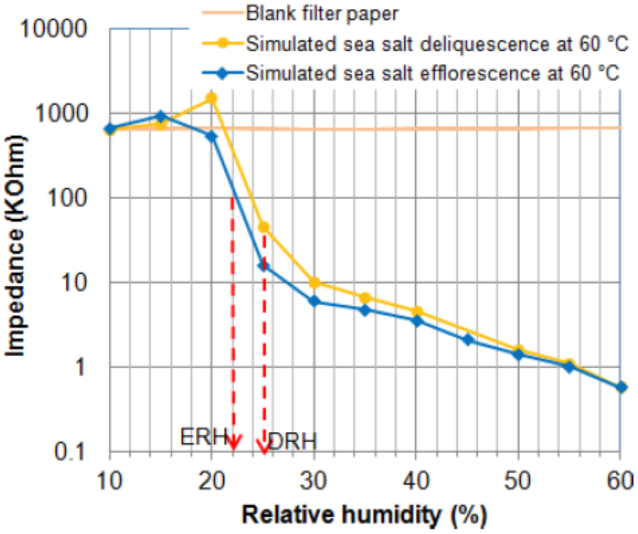
- $CaSO_4$ (gypsum or anhydrite): DRH >99%
- $MgSO_4$ (four different hydrates): DRH = 93-84%
- NaCl: DRH = ~77% at all temperatures
- $KMgCl_3{:}6H_2O$ (±sylvite): DRH = 55-49%
- $MgCl_2{:}6H_2O$: DRH = 36-29%
- $MgCl_2{:}6H_2O$ plus any or all other salts: DRH = ~Same as $MgCl_2{:}6H_2O$

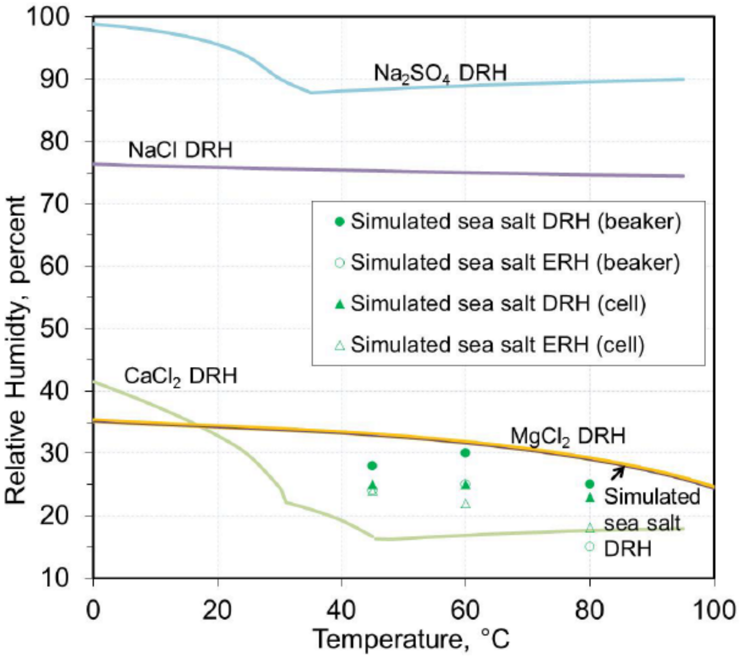


NRC/CNWRA Sea-Salt Deliquescence Experiments

Salts evaluated:

- $CaCl_2$
- $MgCl_2:6H_2O$
- NaCl
- Na_2SO_4
- Synthetic sea-salts





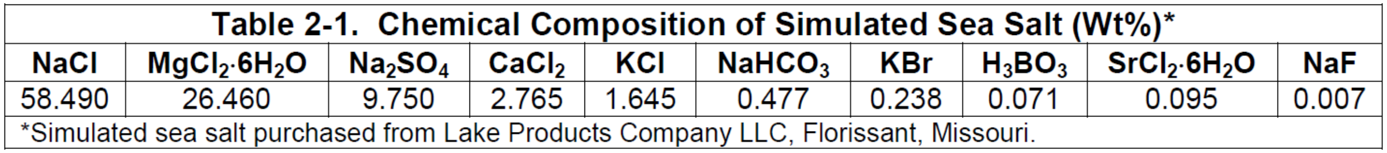


Table 2-1. Chemical Composition of Simulated Sea Salt (Wt%)*									
NaCl	$MgCl_2 \cdot 6H_2O$	Na_2SO_4	$CaCl_2$	KCl	$NaHCO_3$	KBr	H_3BO_3	$SrCl_2 \cdot 6H_2O$	NaF
58.490	26.460	9.750	2.765	1.645	0.477	0.238	0.071	0.095	0.007
*Simulated sea salt purchased from Lake Products Company LLC, Florissant, Missouri.									

NRC (2014)

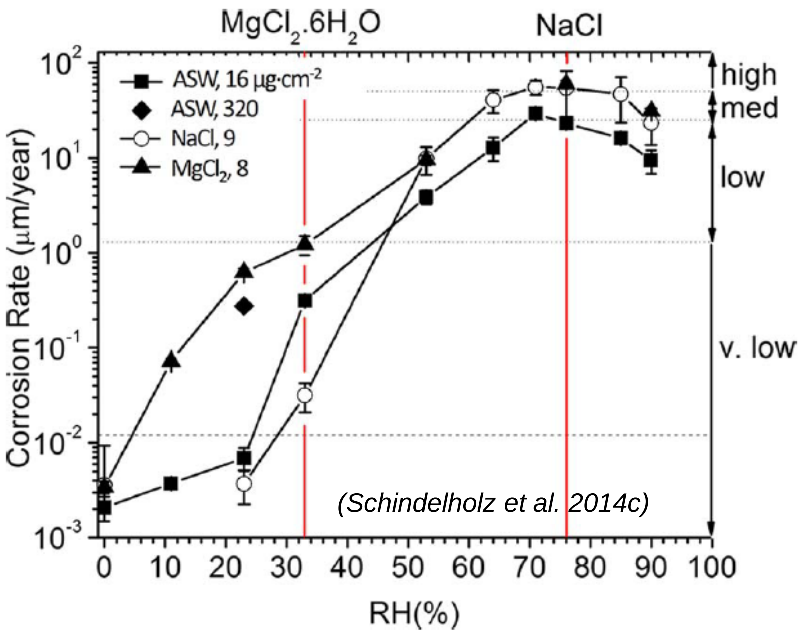
<u>NRC Conclusion</u>: Sea-salt deliquescence is controlled by $MgCl_2$ and $CaCl_2$, and a deliquescent brine could form at RH conditions between those two. This assumption seems incorrect. Ca is present as $Ca\text{-}SO_4$ in dried sea-salts, and is not present as $CaCl_2:XH_2O$.

- ***If $CaCl_2$ were present, then the deliquescence point would have to be equal to or lower than that of $CaCl_2$, as a brine mixture must deliquesce at a lower RH than any component salt***
- ***Would the correct salt assemblage have the same deliquescence behavior?***

DRH vs RH_L (RH Threshold for Corrosion)

Corrosion Below the Deliquescence RH

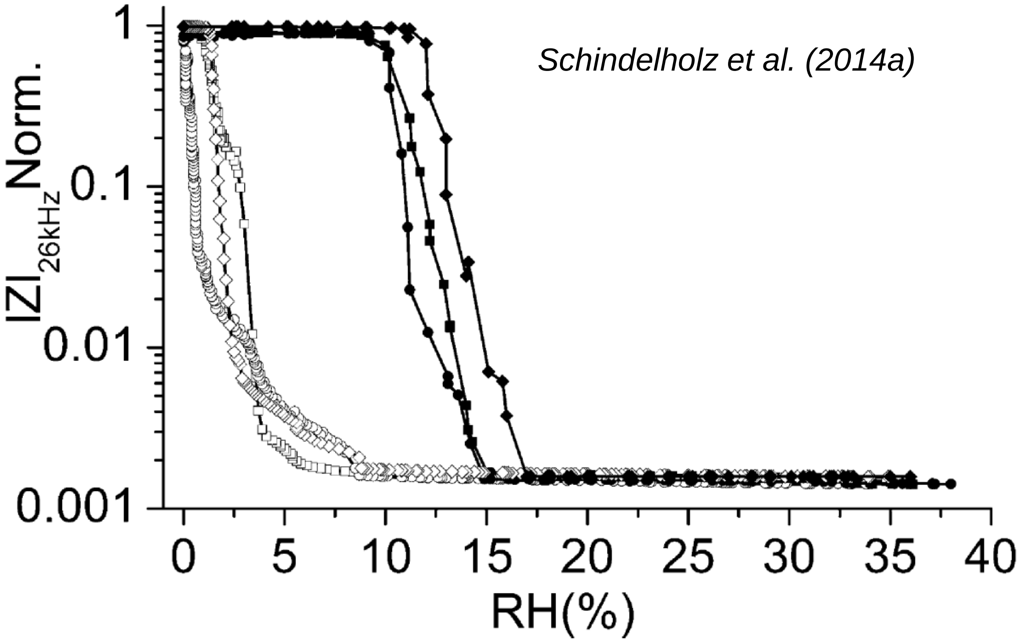
- *NaCl (DRH 77%)*
    - *Schindelholz et al. (2014b) summarizes several studies--corrosion of mild steel at RH values of 50-58% RH. Their own study showed corrosion as low as 33% RH.*
    - *Once corrosion starts, it can persist to lower RH (at least 27% RH) due to highly deliquescent iron chloride salts.*
- *$MgCl_2$ (DRH ~33%) (Schindelholz et al. 2014c)*
    - *observed corrosion (mild steel) as low as 11% RH (21ºC), at a loading of 8 µg/cm^2.*
- *Sea-salts (Schindelholz et al. 2014c)*
    - *Corrosion (mild steel) observed as low as 33% RH (21ºC), at a loading of 16 µg/cm^2.*
    - *Corrosion observed as low as 23% RH (21ºC), at a loading of 160 mg/m^2.*
    - *Inferred that at higher sea-salts loadings, results would match $MgCl_2$*
- *Sea-salts (NRC)*
    - *SCC (304SS) observed as between 20% and 30% RH (variable temperatures).*
- *Sea-salts (Mayuzumi et al. 2008)*
    - *SCC (304SS) observed at 15% RH and 80ºC.*



(Schindelholz et al. 2014c)

Why Corrosion Below the Deliquescence RH?

- **Salt surfaces have adsorbed water films well below the deliquescence**
  - NaCl has adsorbed water films on all surfaces down to 35% RH. Water adsorbs at surface steps (high energy sites) to even lower RH values. (Dai et al., 1997, "Adsorption of Water on NaCl (100) Surfaces: Role of Atomic Steps")
  - SNL experiments with ammonium salts. Salts absorb increasing amounts of water with increasing RH prior to deliquescence.
- *Metastable salt phases?*
  - *Schindelholz et al. (2014a) observed $MgCl_2:XH_2O$ deliquescence at ~15% RH in 3 replicate experiments (complete dissolution did not occur until 33%). Attributed to possible presence of metastable hydrate phase?*



What is a reasonable value for RH_L?

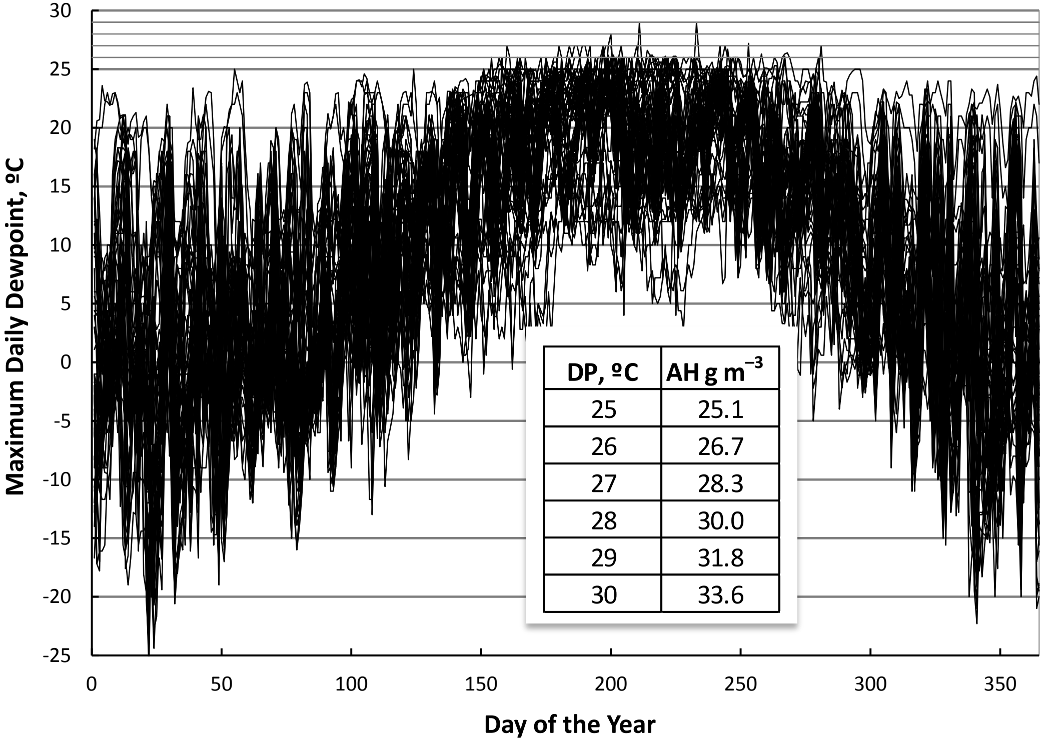
Note hysteresis in deliquescence/efflorescence. Schindelholz et al. suggest that Mg-Cl containing salt assemblages, once deliquesced, may never dry out. Time-of-wetness for periodic wetting/ drying may be much greater that current models calculate.

Possible Range of AH at ISFSI Sites

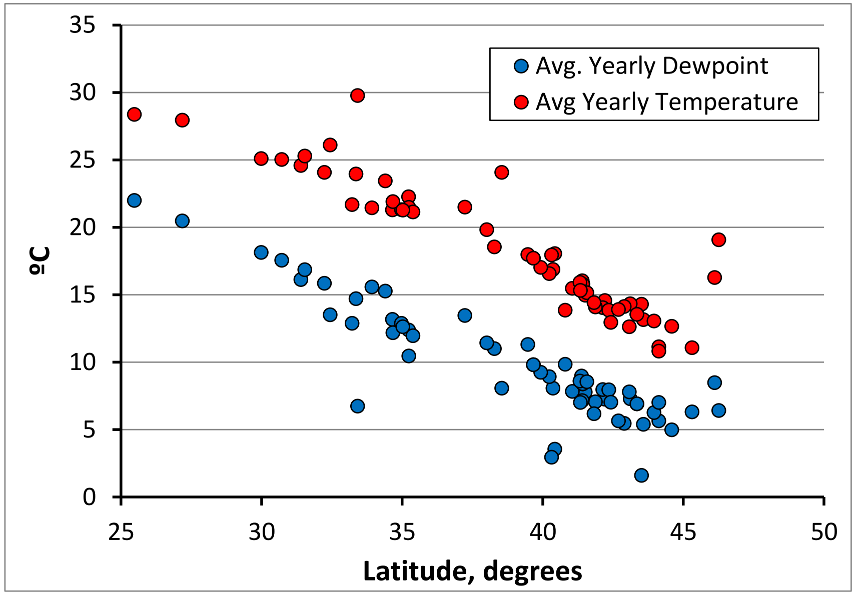
NRC/CNWRA (2014) suggested 30 g/m^3 was an upper limit for AH, "based on meteorological monitoring data"

Weather data from 65 ISFSI sites, collected for the probabilistic SCC model, confirm this is true.

Average yearly dewpoint may be a better indicator of time of wetness. Dominant control on average AH? Latitude.



DP, ºC	AH g m^{-3}
25	25.1
26	26.7
27	28.3
28	30.0
29	31.8
30	33.6



Inland salt compositions

Inland salts—ammonium, calcium, sulfate, and nitrate are the most abundant species. Chloride is present, but minor.

Inland site—continental salt aerosols. For example, data from an Iowa NADP site.

Species	Rain Conc., µeq/L
NH_4^+	29.217
Na^+	2.045
K^+	0.511
Mg^{2+}	3.208
Ca^{2+}	16.766
Cl^-	1.975
NO_3^-	15.565
SO_4^{2-}	17.685

Data from 5 selected IMPROVE Monitoring sites, showing relative abundances of nitrate, chloride, and sulfate (NRC 2014 NUREG/CR-7170).

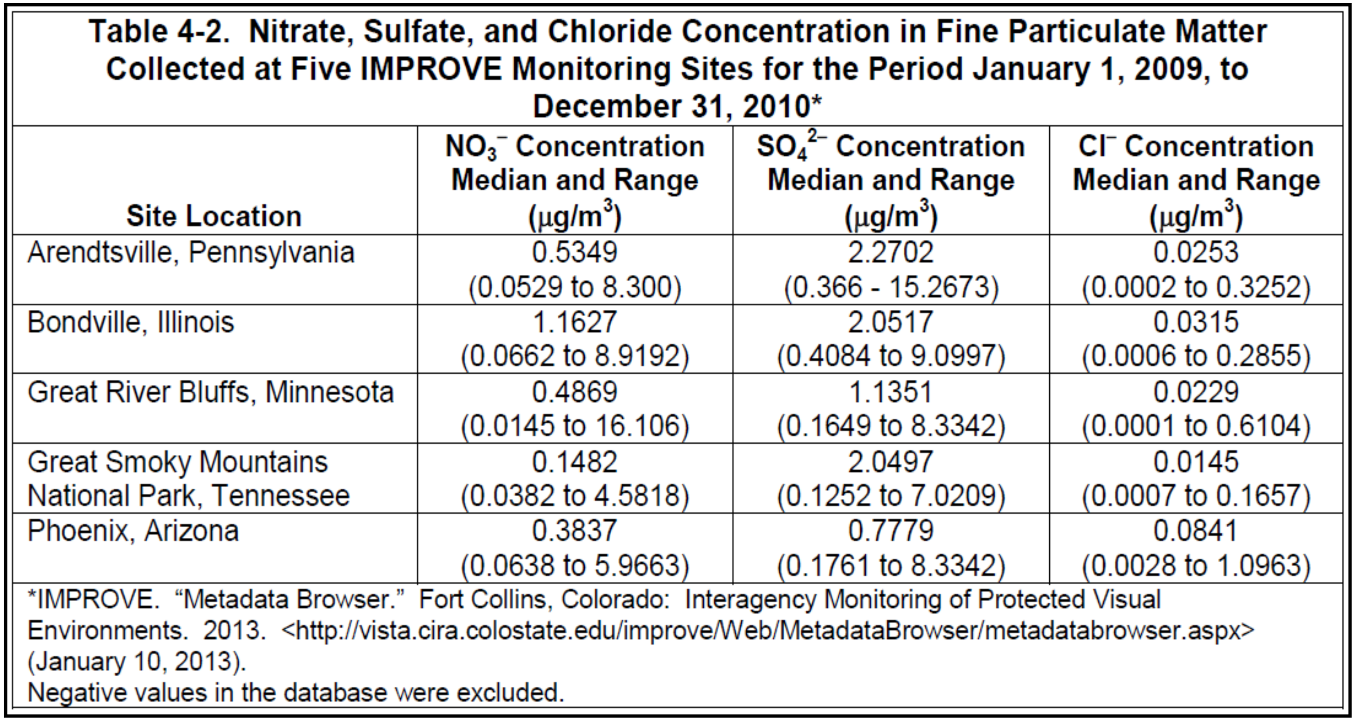


Table 4-2. Nitrate, Sulfate, and Chloride Concentration in Fine Particulate Matter Collected at Five IMPROVE Monitoring Sites for the Period January 1, 2009, to December 31, 2010*

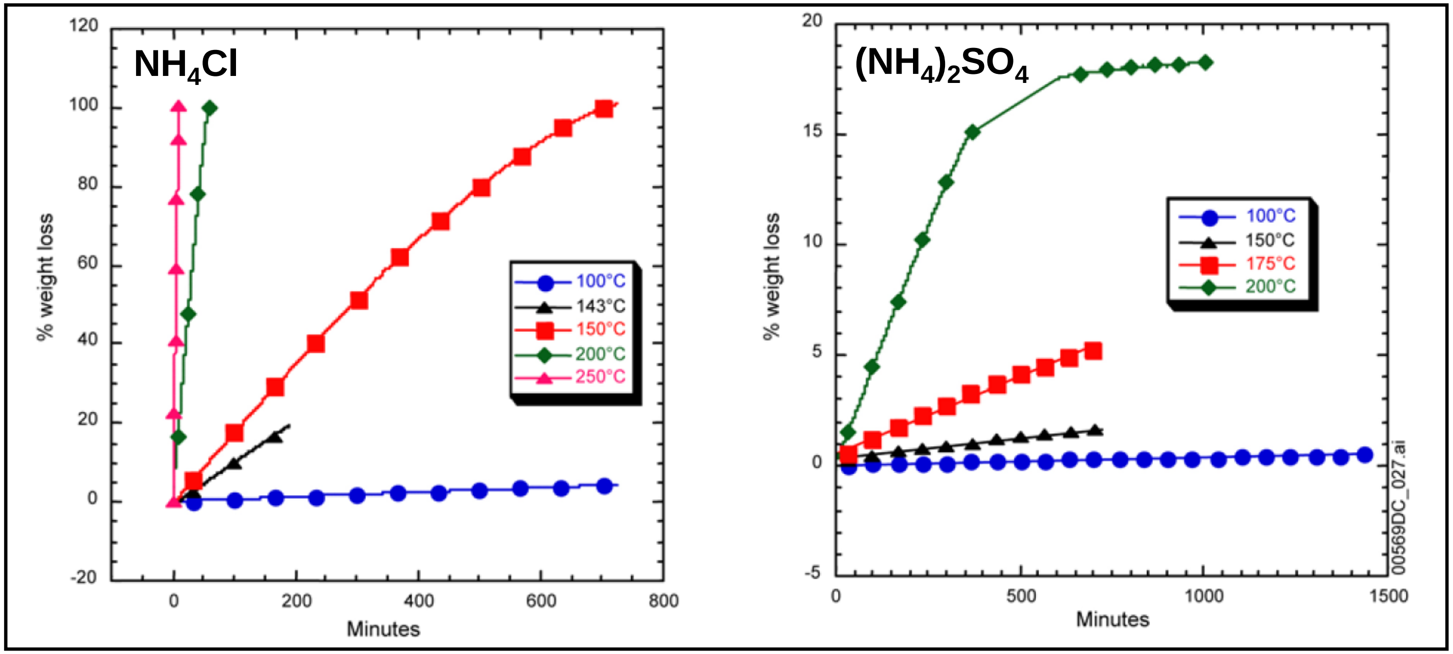
Site Location	NO_3^- Concentration Median and Range (µg/m^3)	SO_4^{2-} Concentration Median and Range (µg/m^3)	Cl^- Concentration Median and Range (µg/m^3)
Arendtsville, Pennsylvania	0.5349 (0.0529 to 8.300)	2.2702 (0.366 - 15.2673)	0.0253 (0.0002 to 0.3252)
Bondville, Illinois	1.1627 (0.0662 to 8.9192)	2.0517 (0.4084 to 9.0997)	0.0315 (0.0006 to 0.2855)
Great River Bluffs, Minnesota	0.4869 (0.0145 to 16.106)	1.1351 (0.1649 to 8.3342)	0.0229 (0.0001 to 0.6104)
Great Smoky Mountains National Park, Tennessee	0.1482 (0.0382 to 4.5818)	2.0497 (0.1252 to 7.0209)	0.0145 (0.0007 to 0.1657)
Phoenix, Arizona	0.3837 (0.0638 to 5.9663)	0.7779 (0.1761 to 8.3342)	0.0841 (0.0028 to 1.0963)

*IMPROVE. "Metadata Browser." Fort Collins, Colorado: Interagency Monitoring of Protected Visual Environments. 2013. <http://vista.cira.colostate.edu/improve/Web/MetadataBrowser/metadatabrowser.aspx> (January 10, 2013).
Negative values in the database were excluded.

Evaluating inland salts—ammonium mineral stability

- **Ammonium salts decompose in the solid state to release NH_3 and acid gas:**

$NH_4Cl \rightarrow NH_3 + HCl$ $NH_4NO_3 \rightarrow NH_3 + HNO_3$ $(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2SO_4$



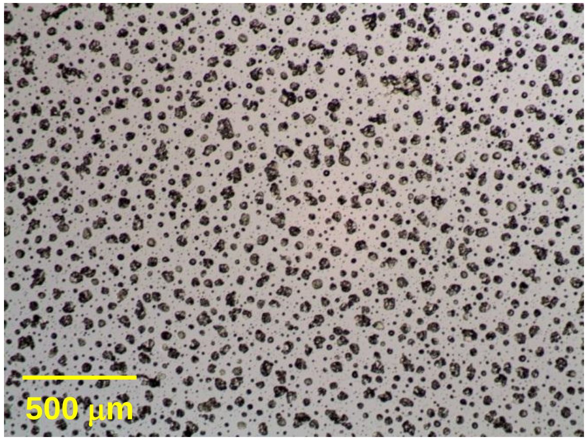
SNL 2008, Figure 6.1-2

Evaluating Ammonium Mineral Stability

Deposition of soluble salts using an airbrush

- *Aqueous solutions—for individual salts (0.1M)*
- *Deposited mass monitored using a QCM*
- *25-50 multiscan passes = 100 ± 2 µg/cm^2 (1 g/m^2)*
- *Each pass is ~20 mg/m^2 (2 µg/cm^2)*
- *Lower surface loads, down to perhaps a few mg/m^2, can be achieved using a more dilute starting solution*

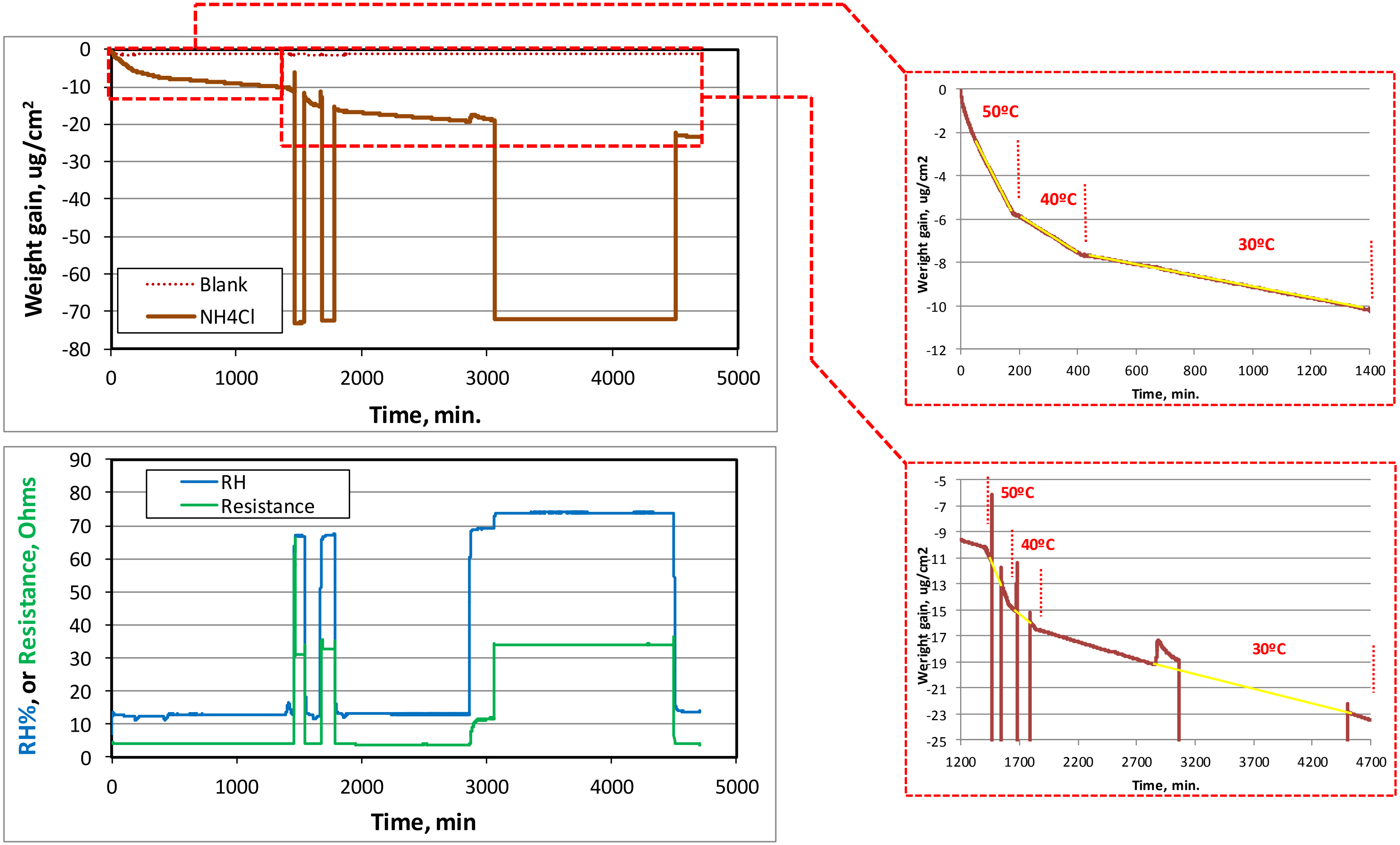
NH_4NO_3



Quartz Crystal Microbalance (QCM)

Tiny mass changes are measured by a change in the vibrational frequency of the piezoelectrically stimulated quartz wafer. The active area is the area of overlap between the two electrodes (38 mm^2). Mass sensitivity is on the order of 1/10 of a monolayer of salt…

NH_4Cl experiment



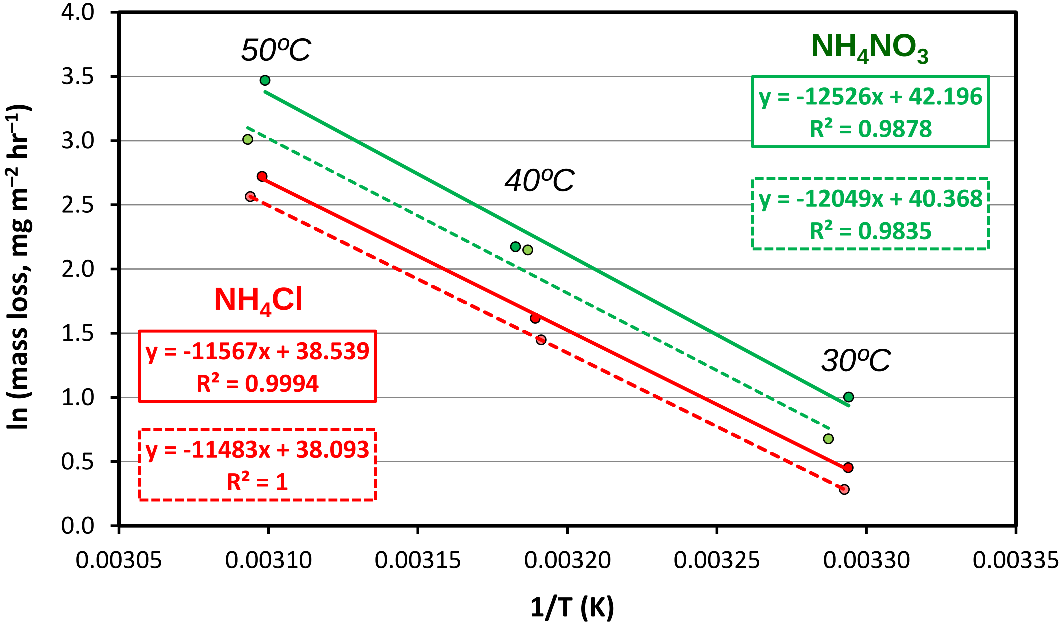
NH_4NO_3 and NH_4Cl degassing rates

NH_4Cl

T, ºC	RH	Rate, mg/m^{-2} hr^{-1}	Days to degas 1 g/m^{-2}
Dry			
49.8	12.6	-15.20	2.7
40.6	12.5	-5.03	8.3
30.6	13.0	-1.57	26.5
Deliquesced			
50.2	63.9	-12.98	3.2
40.4	62.1	-4.26	9.8
30.7	72.9	-1.33	31.4

NH_4NO_3

T, ºC	RH	Rate, mg/m^{-2} hr^{-1}	Days to degas 1 g/m^{-2}
Dry			
49.7	13.2	-32.10	1.3
41.2	13.2	-8.78	4.7
30.6	13.0	-2.72	15.3
Deliquesced			
50.3	41.2	-20.28	2.1
40.8	41.0	-8.56	4.9
31.2	50.3	-1.97	21.2



Salt	E$_a$, kJ/mol
NH_4NO_3, dry	104.1
NH_4NO_3, deliquesced	100.2
NH_4Cl, dry	96.2
NH_4Cl, deliquesced	95.5

Degassing is faster here that in the YMP experiments because particles sizes are smaller (higher surface area). Real dust aerosols much smaller, and will degas even more rapidly.

Relevant Inland Salt Assemblages

- **Dry salts of NH_4NO_3 or NH_4Cl cannot persist on the canister surface at even low temperatures.**
- **Dry $(NH_4)_2SO_4$ can persist on the canister surface for long periods.**
- **Deliquesced brines containing NH_4 and either NO_3^- or Cl^- cannot exist on the canister at above ambient temperatures.**
- **Incidentally deposited chloride salts (e.g. road salts or cooling tower salts) will only form persistent chloride-rich brines *if the chloride deposition rate is greater than the ammonium deposition rate*.**

- **Relevant chloride-rich inland assemblages? NaCl + sulfates ± nitrates?**

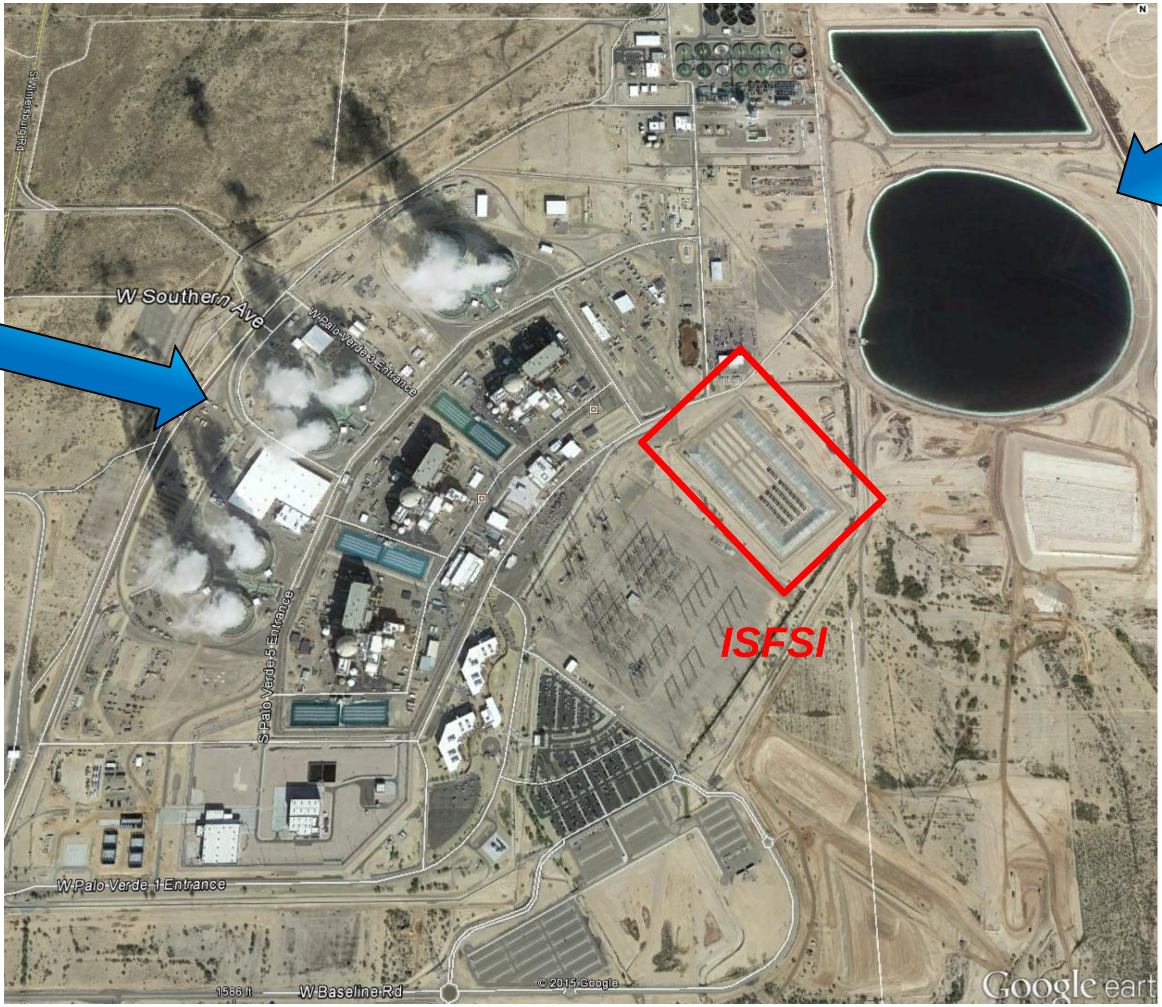
Does this mean that SCC is unlikely at inland sites? Maybe, but each site would have to be evaluated independently. For instance….

Palo Verde

- *Far from ocean; desert location with low AH (based on weather data from Buckeye).*
- *But there are cooling towers, using 40,000-50,000 gallons of water per minute.*
- *Towers use 20 billion gallons of recycled grey water from Phoenix each year.*

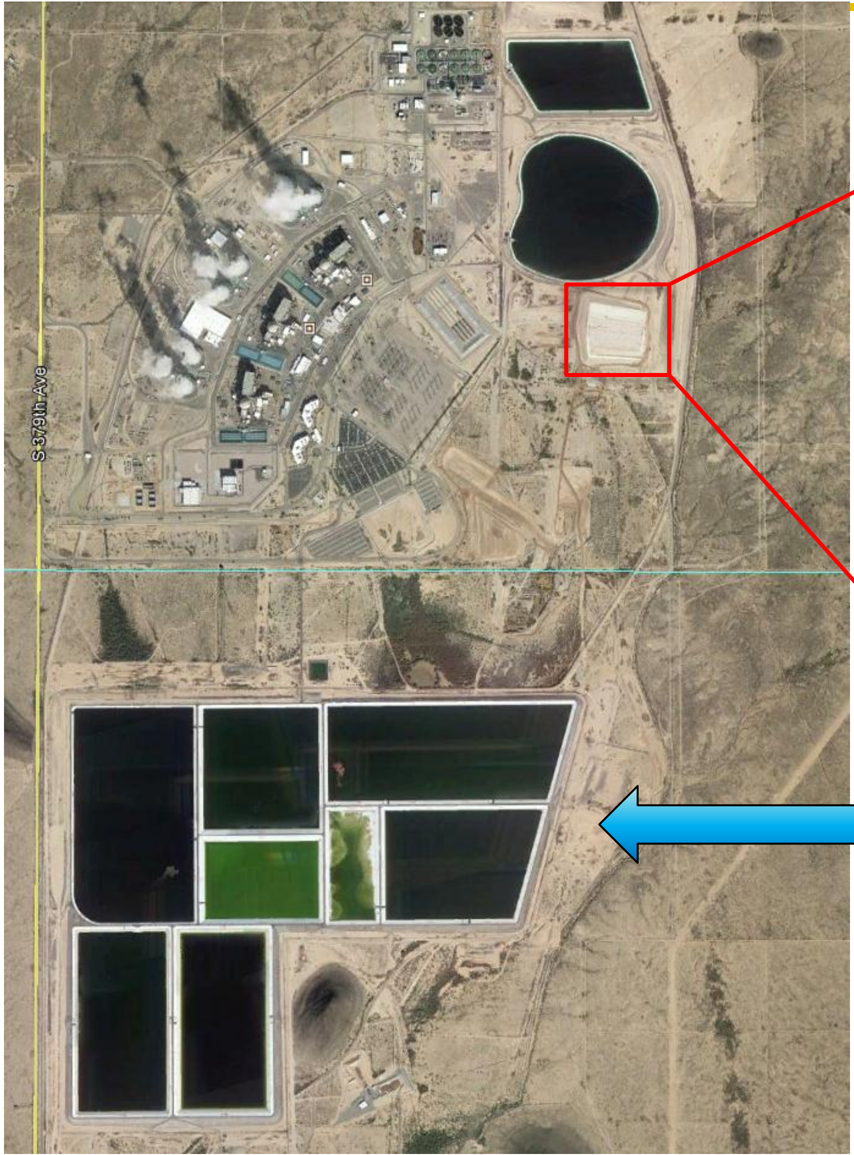
Palo Verde

Cooling towers



Storage ponds (1 billion gallons), 14 day supply

Palo Verde



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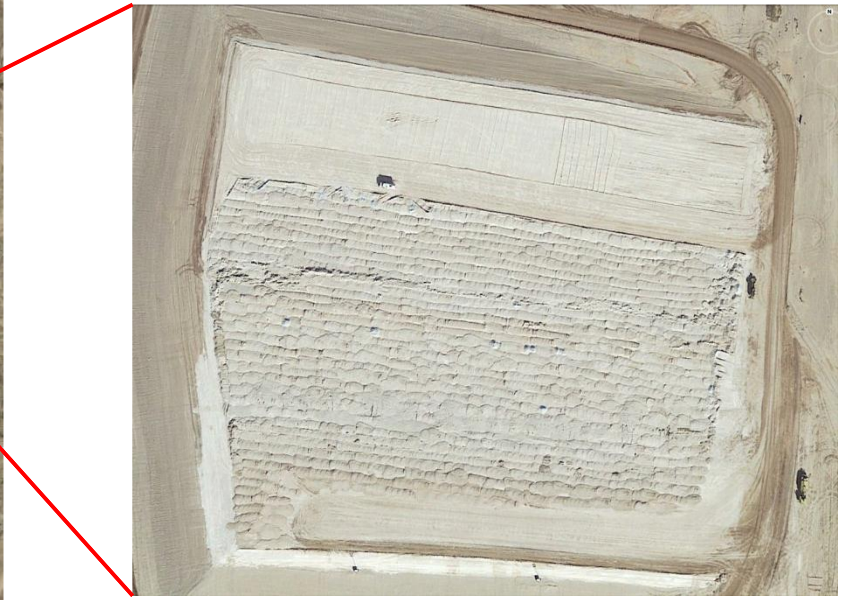

Evaporation ponds

Summary

Environmental conditions for corrosion testing

- **Maximum AH 30 g/m^3**
- **RH$_L$? For sea-salts, may be a function of salt load (minimum brine volume required). MgCl$_2$ data suggest it may be may be as low as 10-15%, if sufficient sea-salt present.**
- **Maximum temperature to consider? At least 65ºC (RH$_L$ =15%)?**
- **Salt compositions:**
  - Sea-salts
  - Inland salts. Uncertain, but no NH_4Cl, NH_4NO_3, or combinations that would produce brines containing (NH_4^+ + $Cl^–$), or (NH_4^+ + $NO_3^–$)