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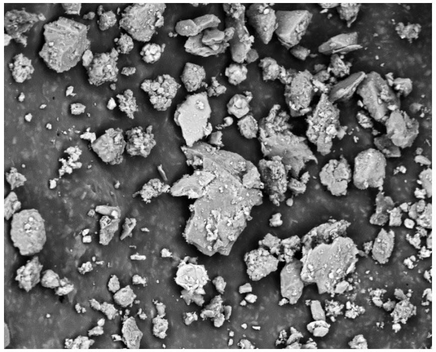

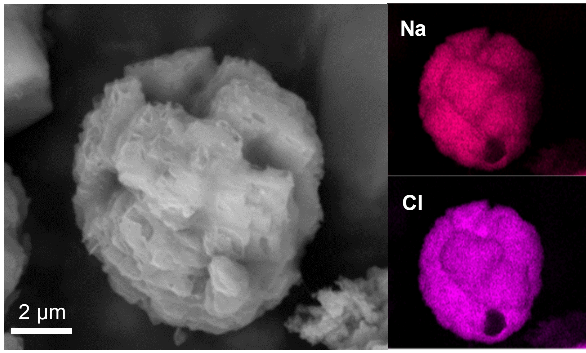

Understanding the Risk of Chloride Induced Stress Corrosion Cracking of Interim Storage Containers for the Dry Storage of Spent Nuclear Fuel: Evolution of Brine Chemistry on the Container Surface

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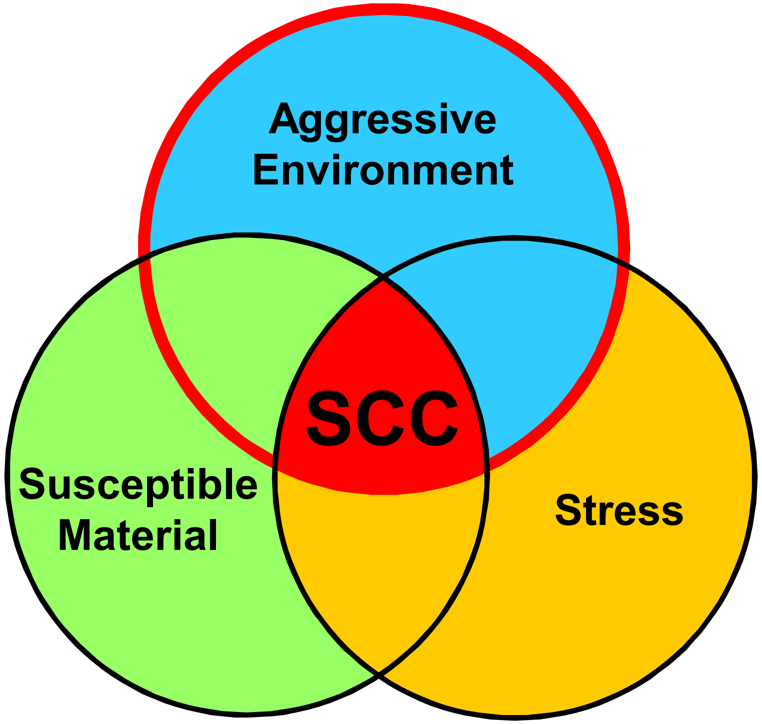
March 8th, 2016

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Degradation Mechanism of Concern: Stress Corrosion Cracking (SCC)

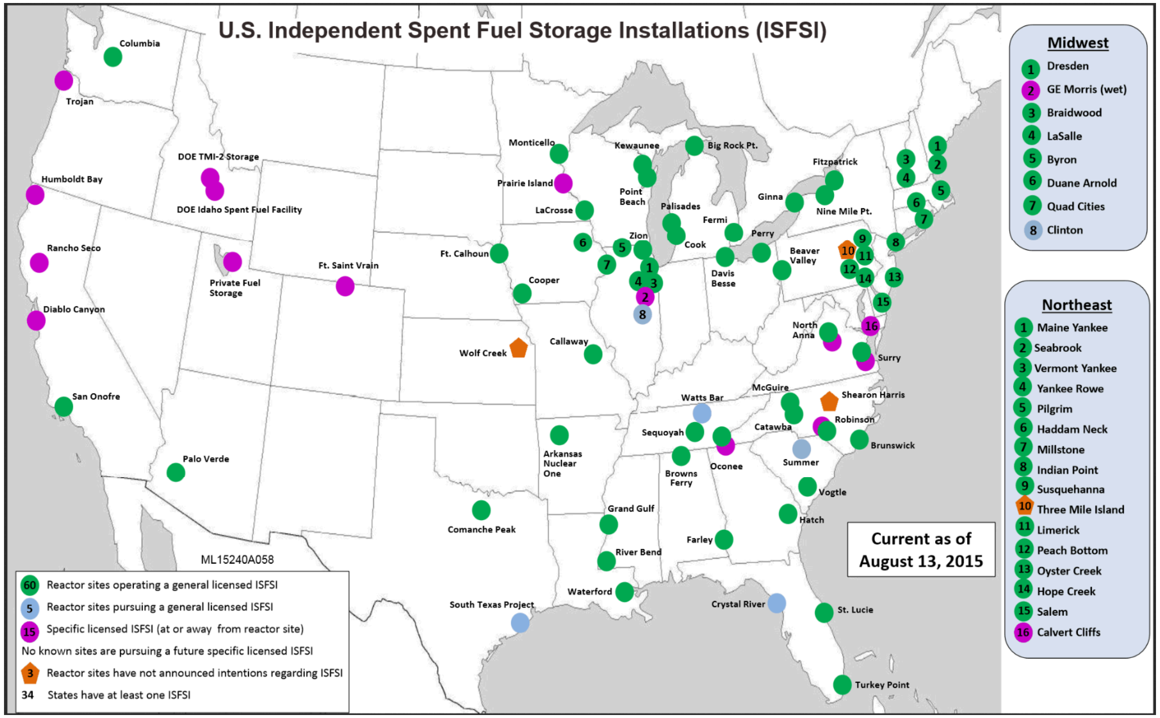


Goal: Establish environmental conditions that need to be considered for evaluation of the SCC risk for used nuclear fuel interim storage containers

ISFSI Locations

Different settings

- **Range of weather conditions**
  - Dewpoint
  - Temperature
- **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
- **Temperature range of interest**
  - Determined by RH_L and AH



Example Coastal Site: Diablo Canyon

- Located on coast
- ISFSI 550m from water
- Elevated 120m from sea level

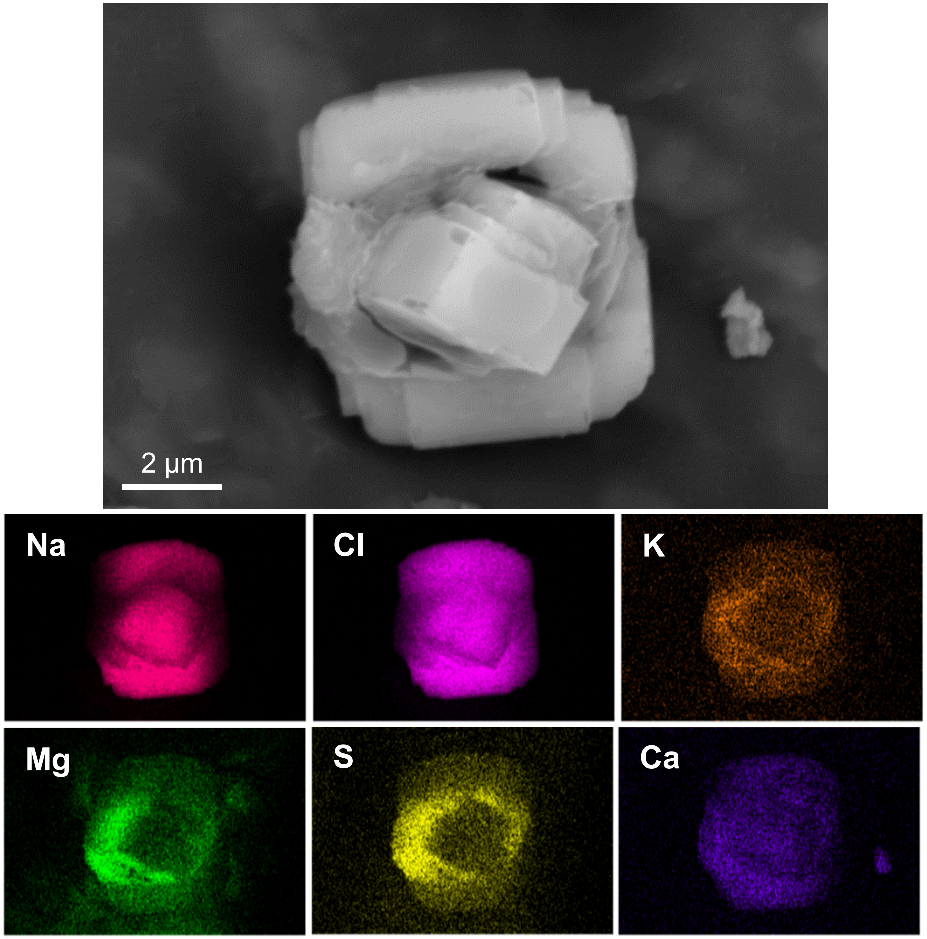
- EPRI coordinated inspection in 2014
  - Holtec HISTORM system
  - Wet and dry samples taken from two containers

Marine Aerosols—Observed

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

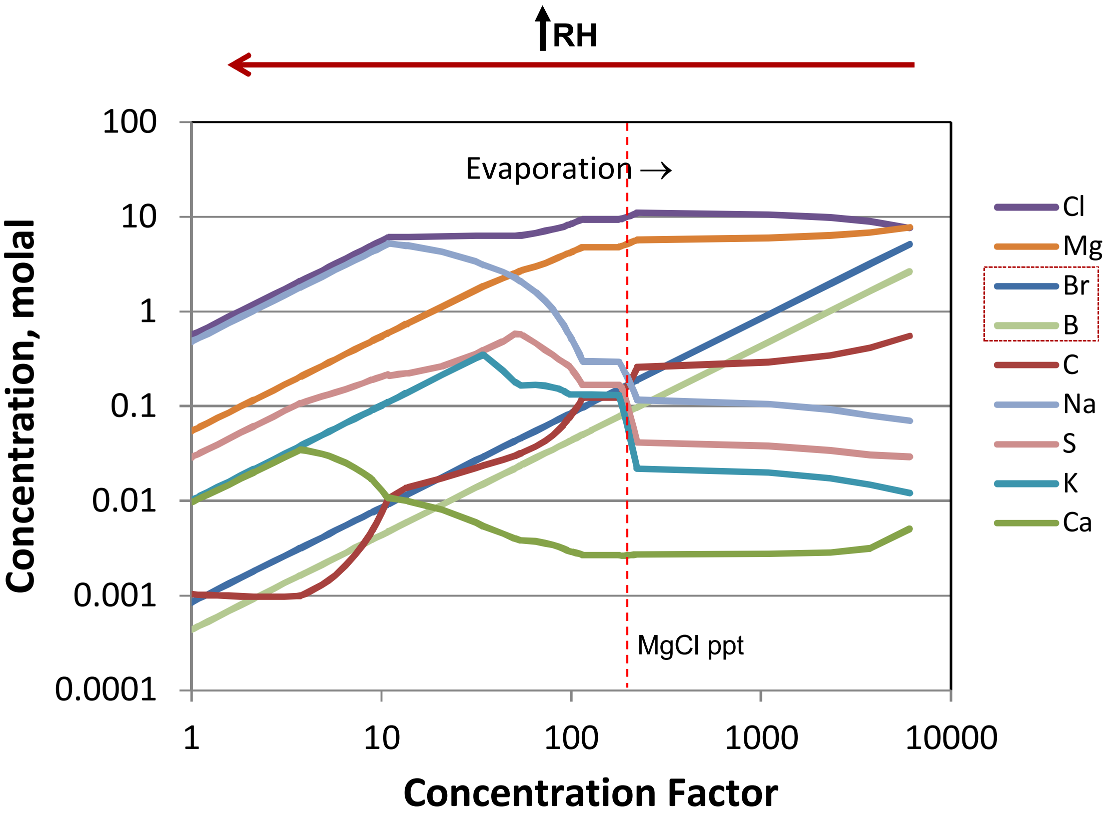
Sea-salt aggregate on Diablo Canyon ISFSI storage canister



Seawater Evaporation – Brine Composition

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*
- *Ca, K, S are mostly removed by minerals, and are very low in the remaining brine.*



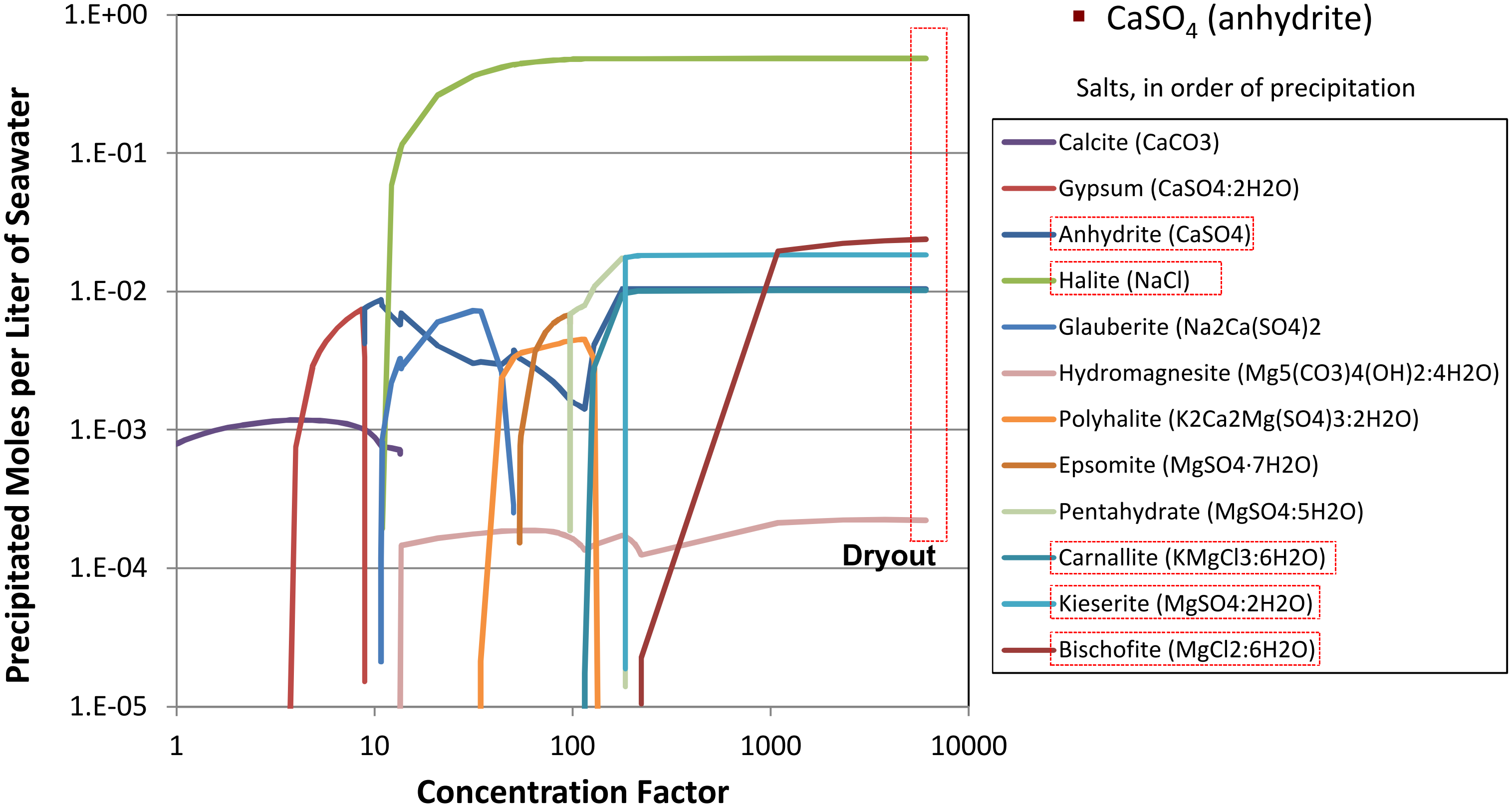
Seawater Evaporation – Precipitated Salts

Precipitated salts:

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

Final assemblage determines deliquescence RH (DRH)

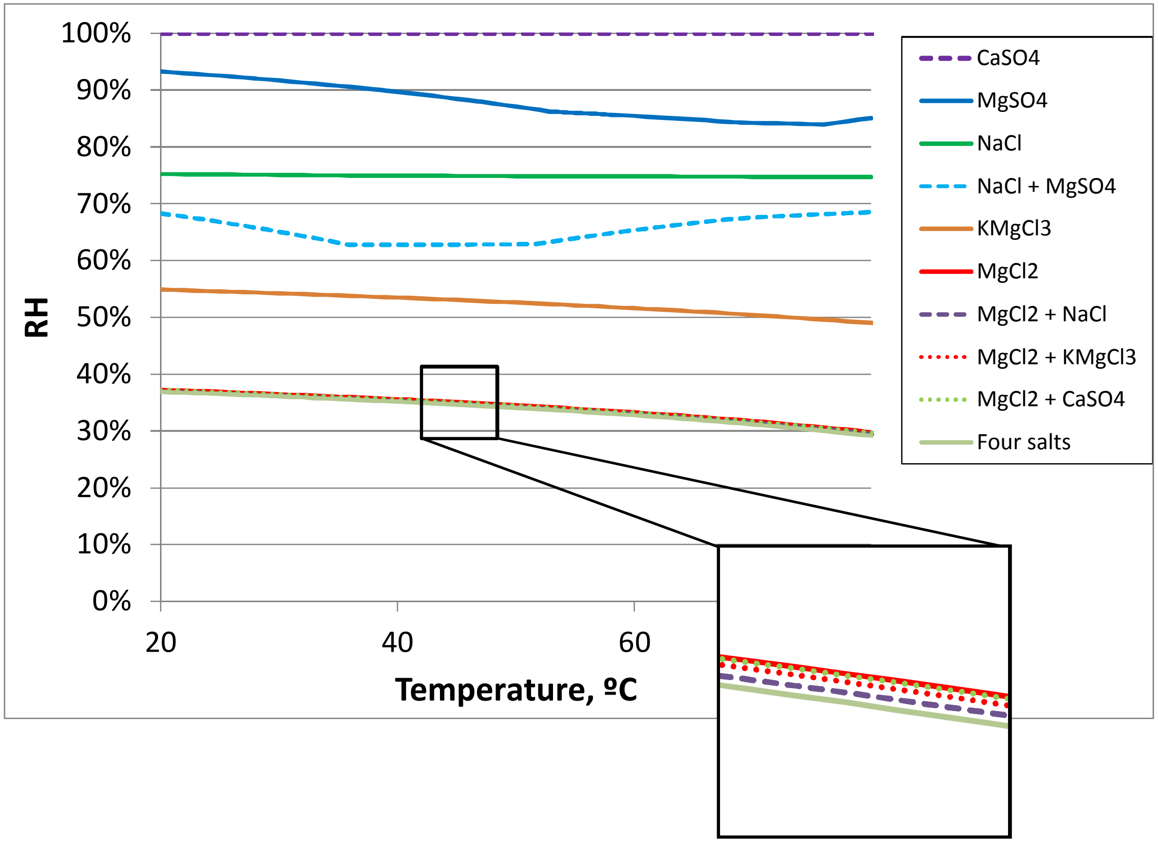
- NaCl (halite)
- $MgCl_2{:}6H_2O$ (bischofite)
- $MgSO_4{:}2H_2O$ (kieserite)
- $KMgCl_3{:}6H_2O$ (carnallite)
- $CaSO_4$ (anhydrite)



Deliquescence RH Values for Sea Salts

Deliquescence points:

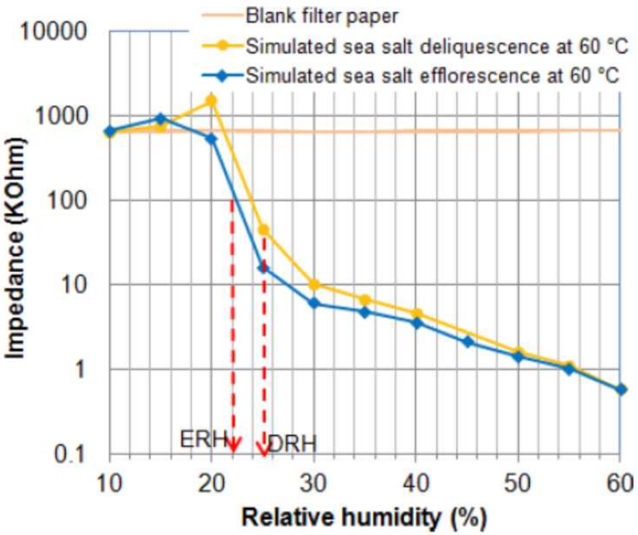
- Ca-SO_4 (gypsum or anhydrite):
  DRH >99%
- Mg-SO_4 (four different hydrates):
  DRH = 93-84%
- NaCl:
  DRH = ~77% at all temperatures
- $KMgCl_3{:}6H_2O$ (±KCl):
  DRH = 55-49%
- $MgCl_2{:}6H_2O$:
  DRH = 36-29%
- $MgCl_2{:}6H_2O$ plus any or all other salts:
  DRH = ~Same as $MgCl_2{:}6H_2O$



NRC/CNWRA Sea-Salt Deliquescence Experiments

Salts evaluated:

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



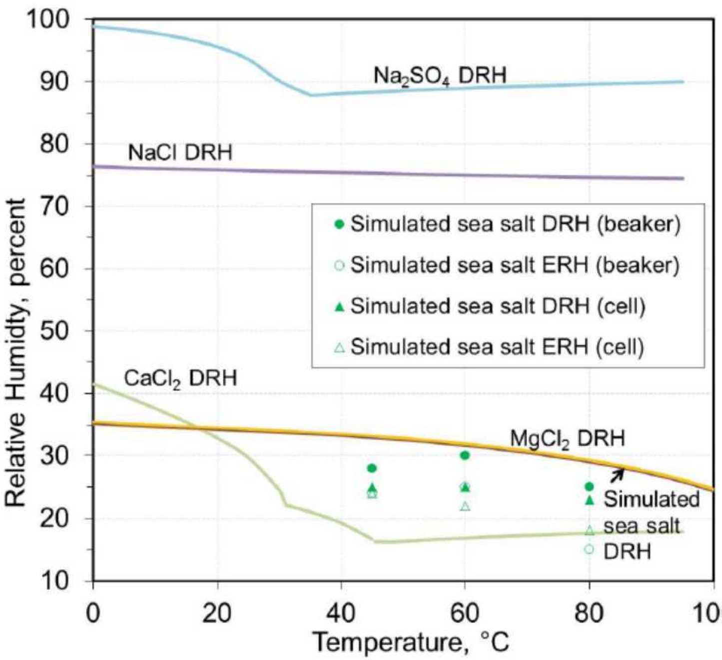


Table 2-1. Chemical Composition of Simulated Sea Salt (Wt%)*

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)

NRC Conclusion: 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-SO_4 in dried sea-salts, and is not present as $CaCl_2$:XH_2O.

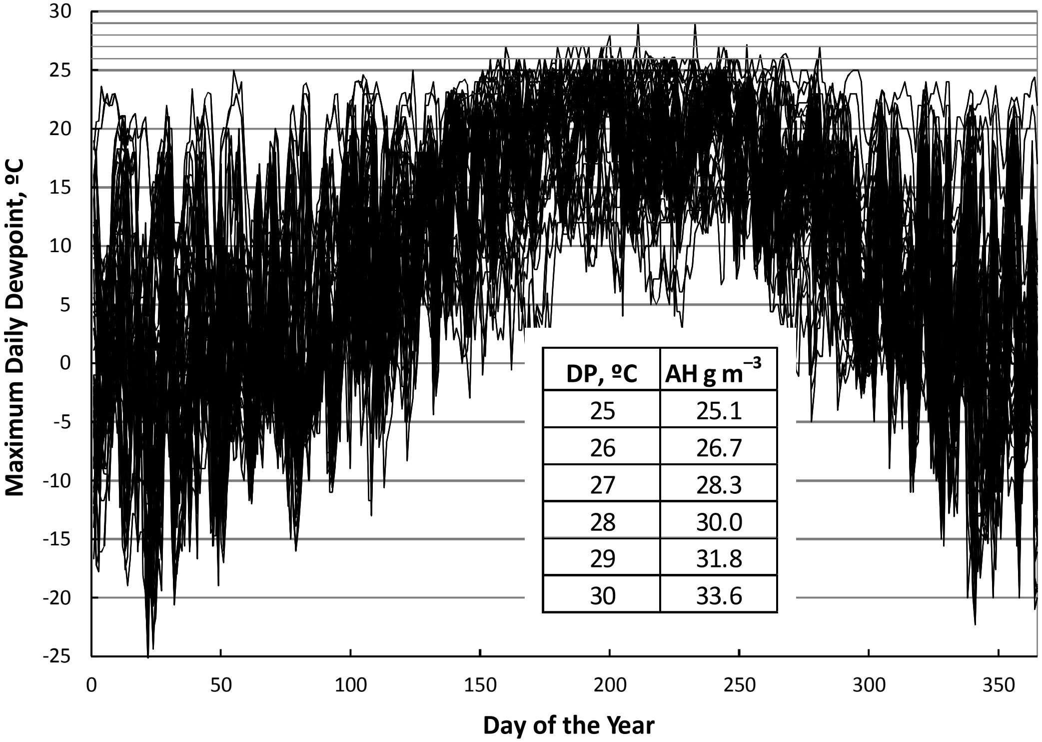
- **If $CaCl_2$ were present, then the deliquescence point would have to be equal to or lower than that of $CaCl_2$, as a brine mixture must deliquesce at a lower RH than any component salt**
- **Would the correct salt assemblage have the same deliquescence behavior?**

Salts used to make synthetic seawater are not the stable salts that form when you evaporate seawater

Possible Range of AH at ISFSI Sites

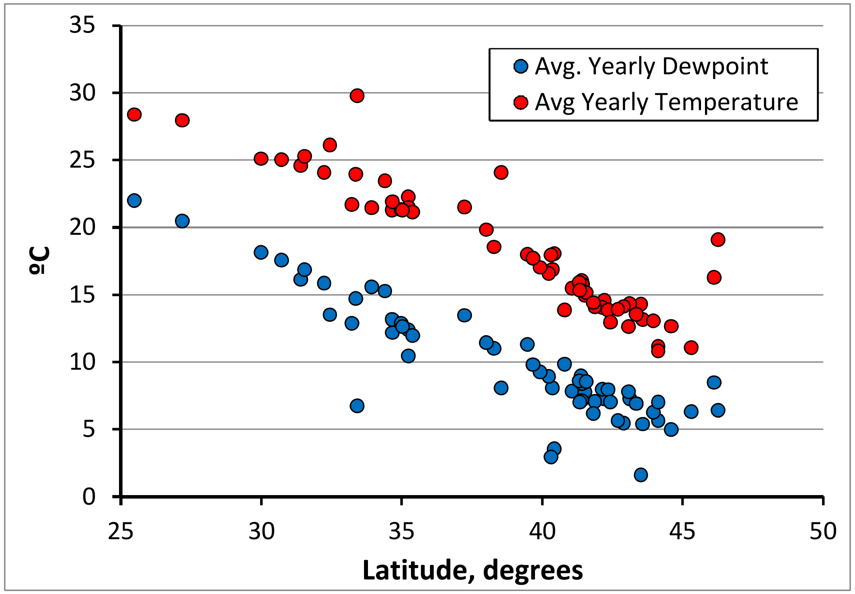
NRC/CNWRA (2014) suggested 30 g/m^3 was an upper limit for AH, “based on meteorological monitoring data”

Weather data from vicinity of 65 ISFSI sites confirm this is true.



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

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



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).

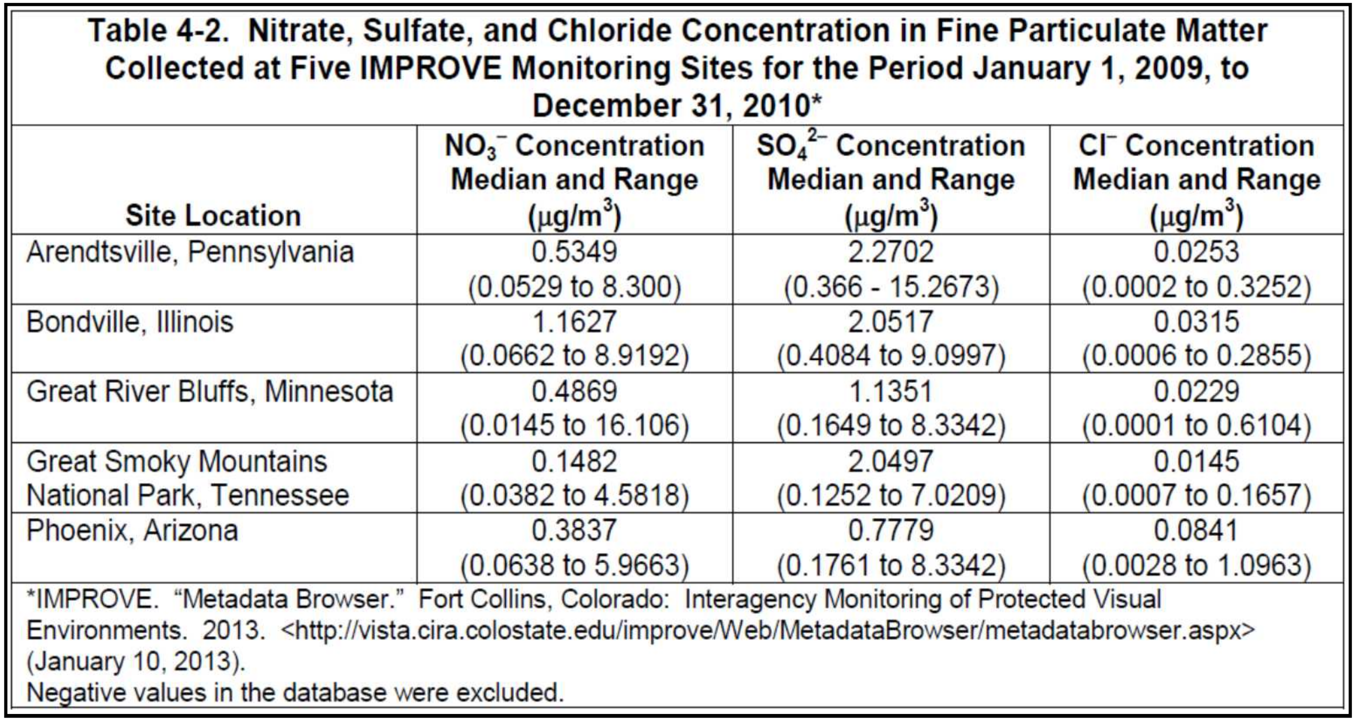


Table 4-2. Nitrate, Sulfate, and Chloride Concentration in Fine Particulate Matter Collected at Five IMPROVE Monitoring Sites for the Period January 1, 2009, to December 31, 2010*

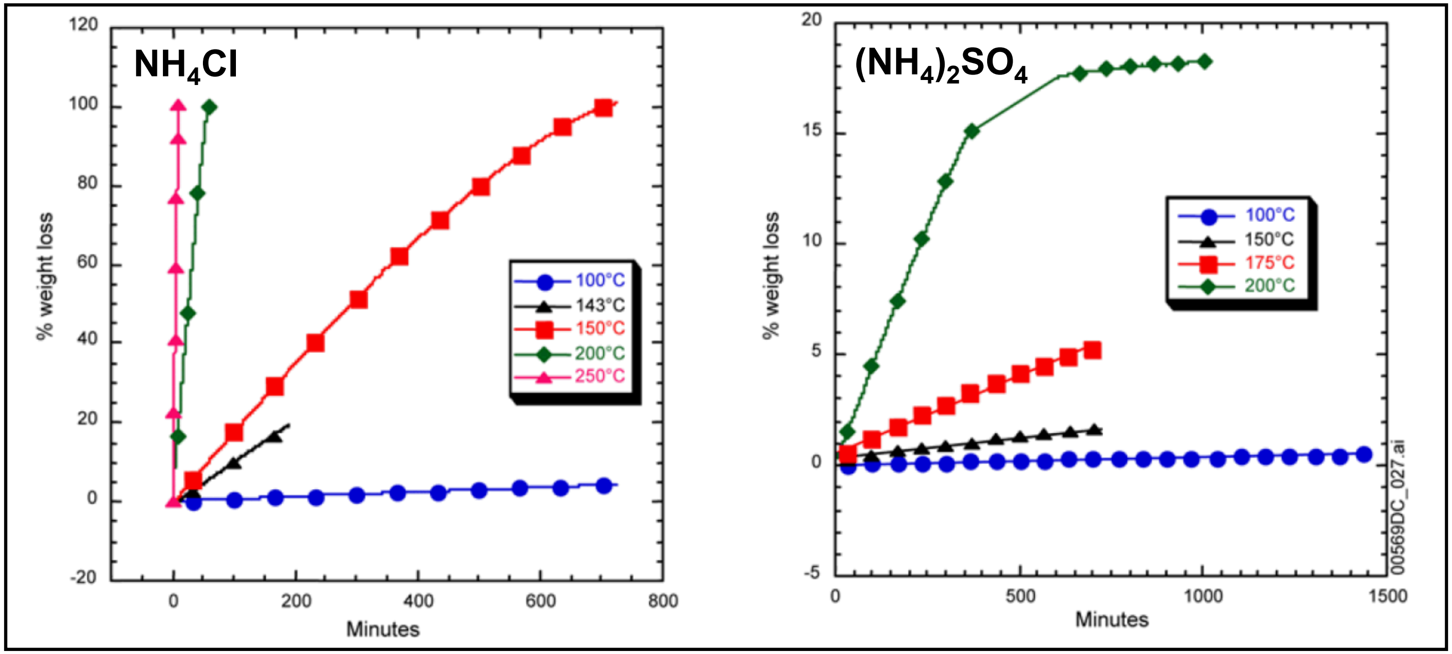
Site Location	NO_3^- Concentration Median and Range ($\mu g/m^3$)	SO_4^{2-} Concentration Median and Range ($\mu g/m^3$)	Cl^- Concentration Median and Range ($\mu g/m^3$)
Arendtsville, Pennsylvania	0.5349 (0.0529 to 8.300)	2.2702 (0.366 - 15.2673)	0.0253 (0.0002 to 0.3252)
Bondville, Illinois	1.1627 (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:

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



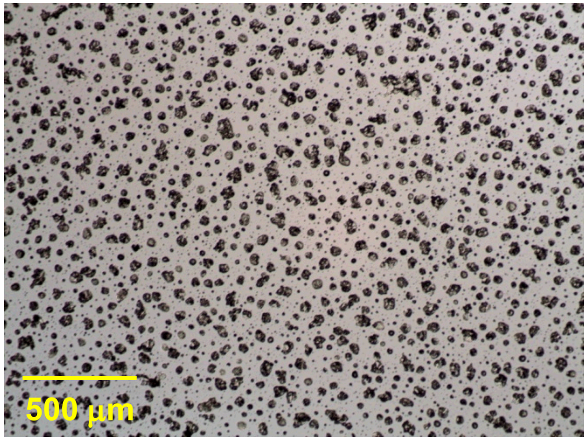
SNL 2008, Figure 6.1-2

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…

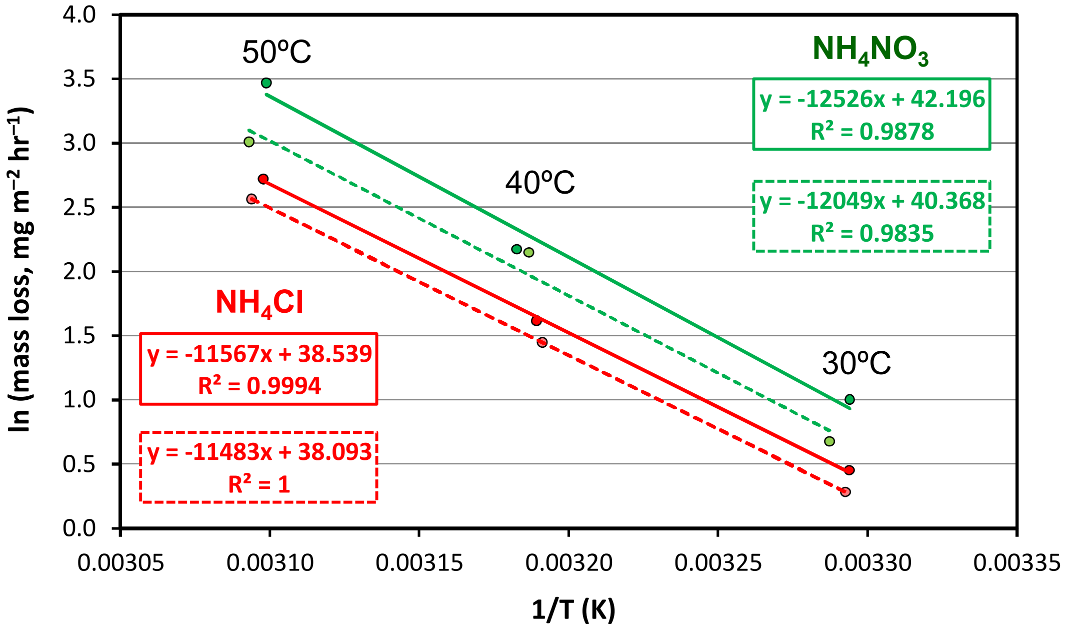
NH_4NO_3 and NH_4Cl degassing rates

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

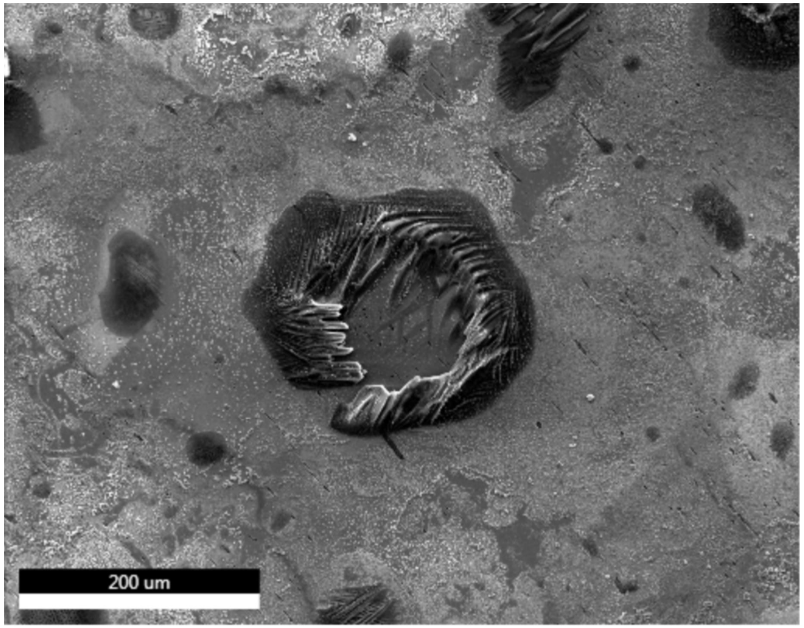


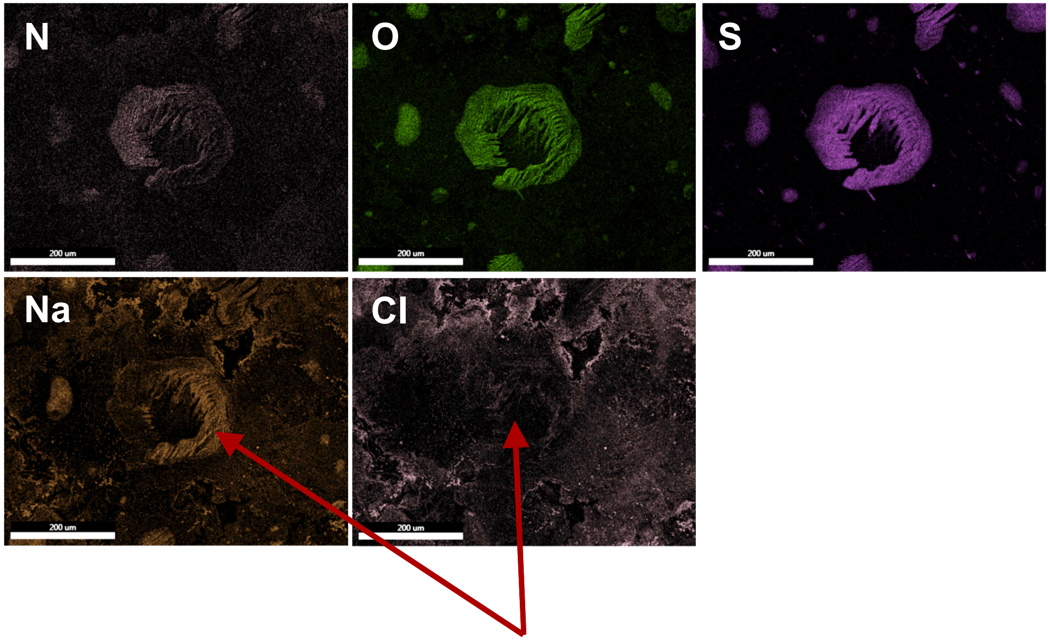
Salt	E_a, kJ/mol
NH_4NO_3, dry	104.1
NH_4NO_3, deliquesced	100.2
NH_4Cl, dry	96.2
NH_4Cl, deliquesced	95.5

Rate of degassing is a strong function of particle size – as the surface area to volume ratio increases, so does the degassing rate

$(NH_4)_2SO_4$ does not degas as a single salt

Deliquescence of a $(NH_4)_2SO_4$ and NaCl Salt Mixture

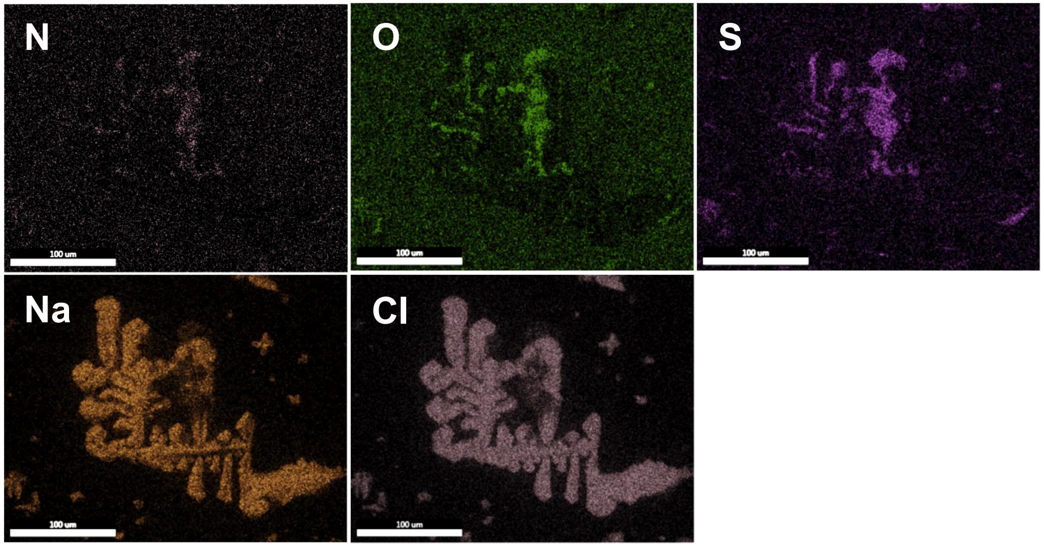




Sodium present, but no chloride

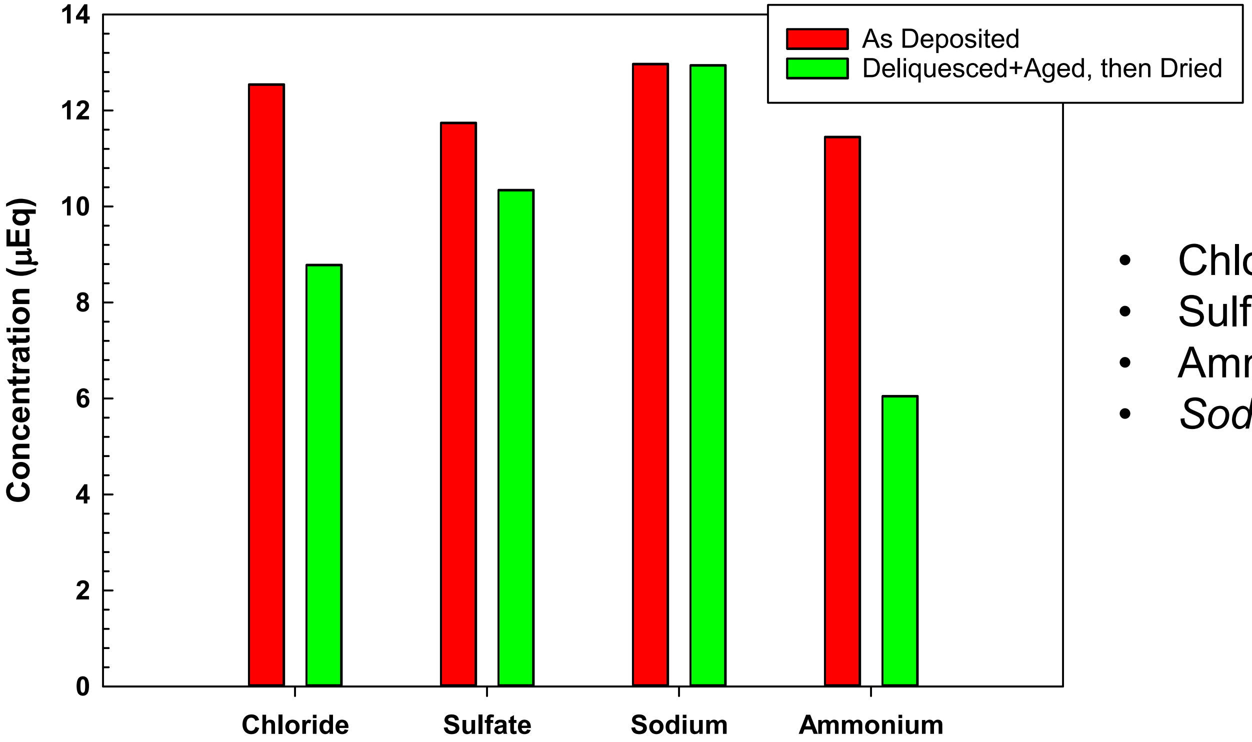
- Salts deposited on 303SS surface using an airbrush
- Ammonium sulfate deposited as an aqueous solution
- Sodium chloride deposited using a methanol carrier (to prevent dissolution and mixing with ammonium sulfate)
- Some reaction in the as-deposited state

Deliquescence of a $(NH_4)_2SO_4$ and NaCl Salt Mixture



- Salt mixture dried at 50^{o}C, 10% RH for 4 days, then deliquesced at 50^{o}C, 75% RH and held for 24 hours, after which it was re-dried at 10% RH
- Brine coalesced into larger droplets, as evidenced by large NaCl precipitates on surface
- Partial conversion to Na_2SO_4 (short time relative to time anticipated to go to completion)

Deliquescence of a $(NH_4)_2SO_4$ and NaCl Salt Mixture



- Chloride loss
- Sulfate loss
- Ammonium loss
- *Sodium unchanged*

- Salts extracted from surface of control sample and deliquesced sample
- Degassing took place, as evidenced by reduction in chloride and ammonium (ammonium loss = chloride loss plus sulfate loss)
- 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 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 + ammonium free sulfates ± nitrates?

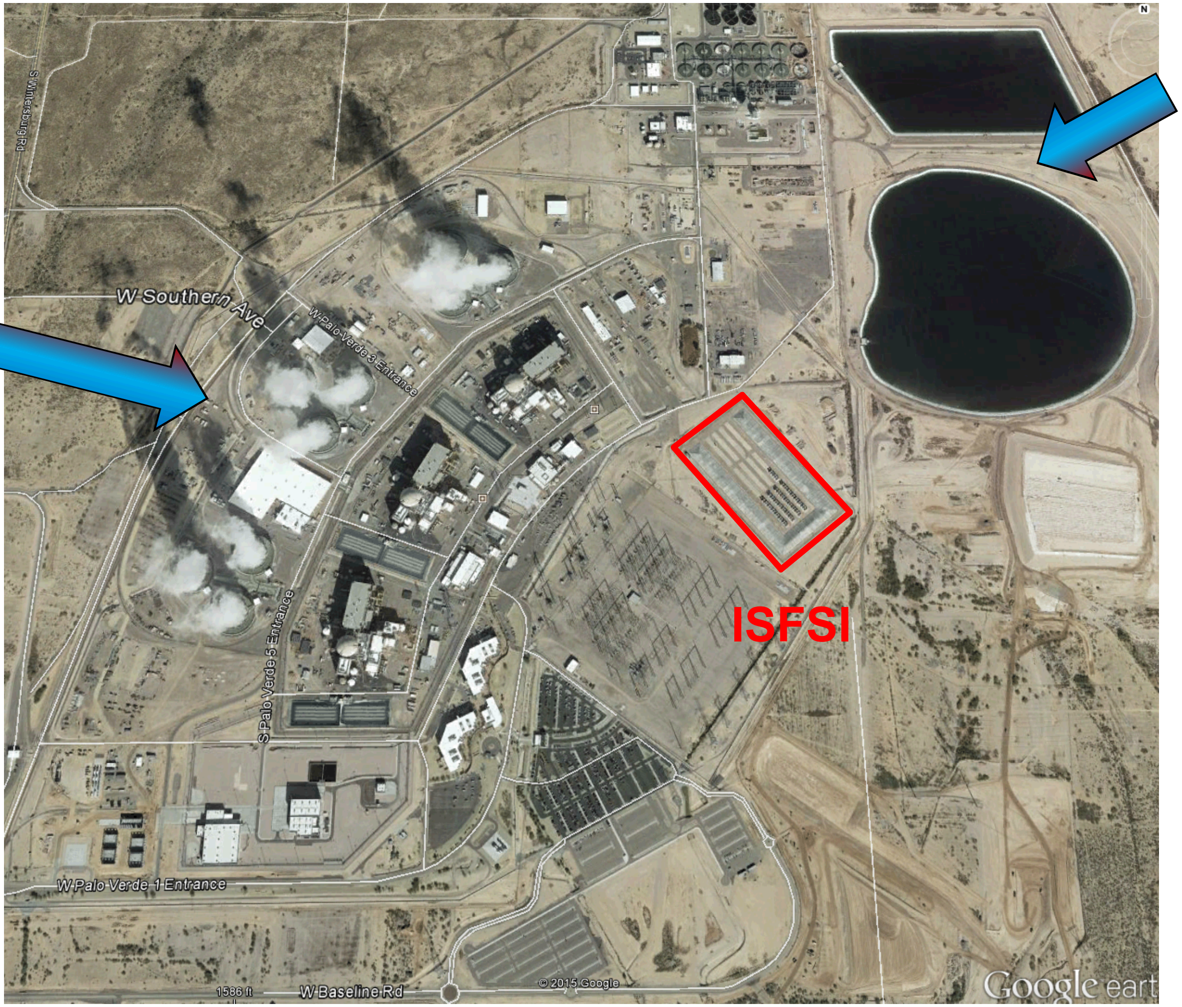
Does this mean that SCC is unlikely at inland sites? Maybe, but each site would have to be evaluated independently. For instance….

Environment: We know what we know, but do we know what we don't know?

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.
- Cooling towers are an added risk factor for SCC (EPRI, 2015)

We knew this….

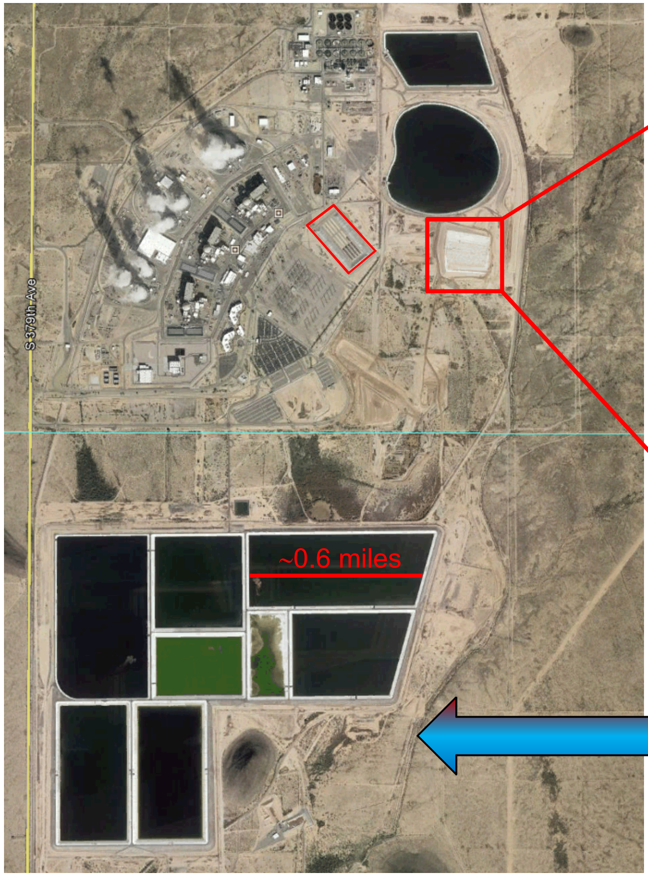


Cooling towers

Water treatment plant and storage ponds
(1 billion gallons, 14 day supply for cooling towers)

But we didn’t know this.

What about the evaporation ponds, or the landfill for salts from the water treatment plant? Do these affect our evaluation of risk? To adequately assess site risk, do we need to collect site-specific aerosol data?



Landfill for salts (composition?) from the water treatment plant.

Evaporation ponds – used cooling water is evaporated in these ponds, eliminating site releases (Palo Verde is a zero-release site).

Summary

Environmental conditions for corrosion testing

- Maximum AH 30 g/m^3
- Salts used to make synthetic seawater are not the stable salts that form when you evaporate seawater
  - $NaCl$ (halite), $MgCl_2{:}6H_2O$ (bischofite), $MgSO_4{:}2H_2O$ (kieserite), $KMgCl_3{:}6H_2O$ (carnallite), $CaSO_4$ (anhydrite)
- RH_d and AH define the upper temperature limit that should be considered. Data suggests at least 65ºC.
- Salt compositions:
  - Marine sites: Evaporated Seawater
  - Inland salts: Uncertain, but no NH_4Cl, NH_4NO_3, or combinations that would produce brines containing ($NH_4^+ + Cl^-$), or ($NH_4^+ + NO_3^-$)
  - Do we need site-specific data?