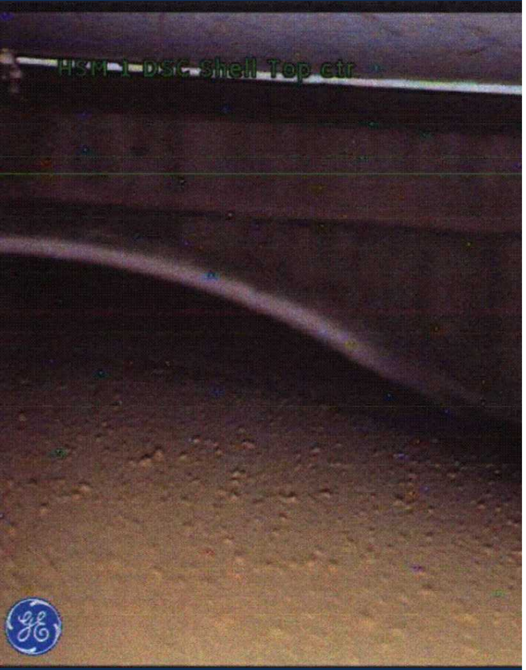
SAND2013-3519C

Interim Storage Environment: Considerations for Corrosion Testing of SNF Dry Storage Containers



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Presentation for IHLRWM, May 1, 2012

Albuquerque, NM

Sandia National Laboratories

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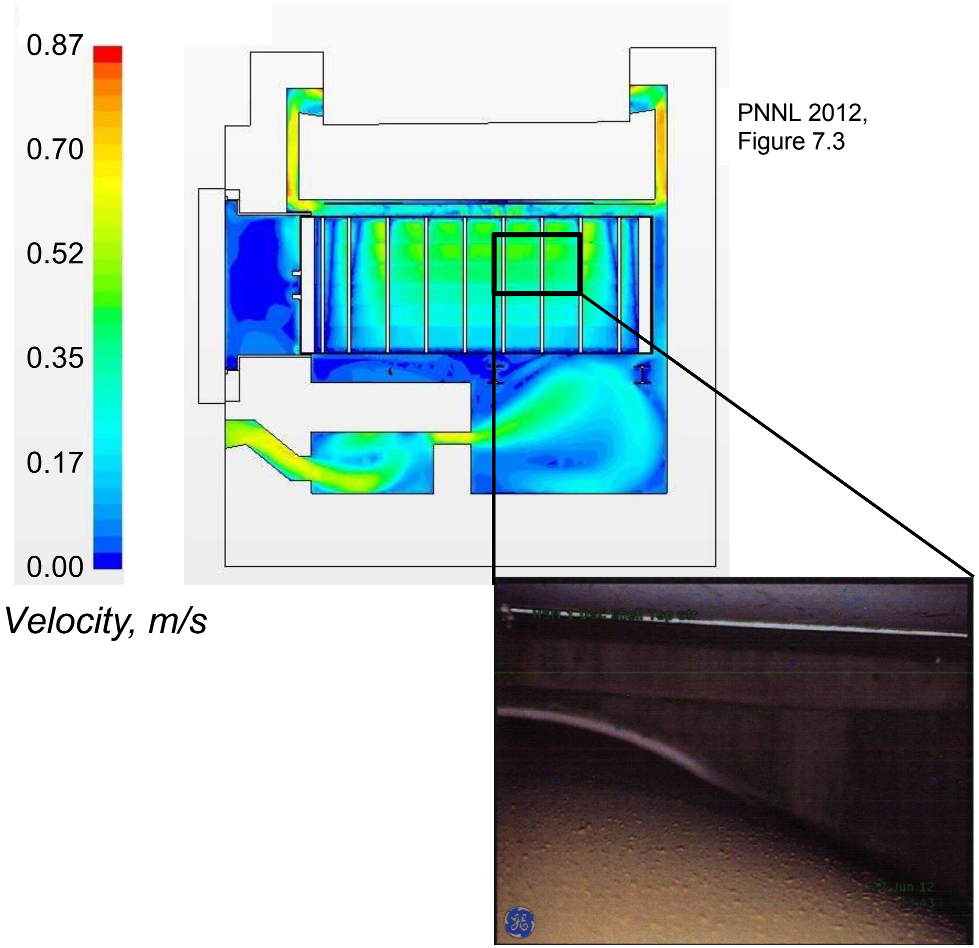
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Corrosion of SNF storage casks

Background: The United States currently does not have a disposal pathway for SNF. Dry storage casks currently in use may be required to perform their function for decades beyond their original design criteria. Localized corrosion, especially SCC, of welded stainless steel casks is considered most important potential failure mechanism.

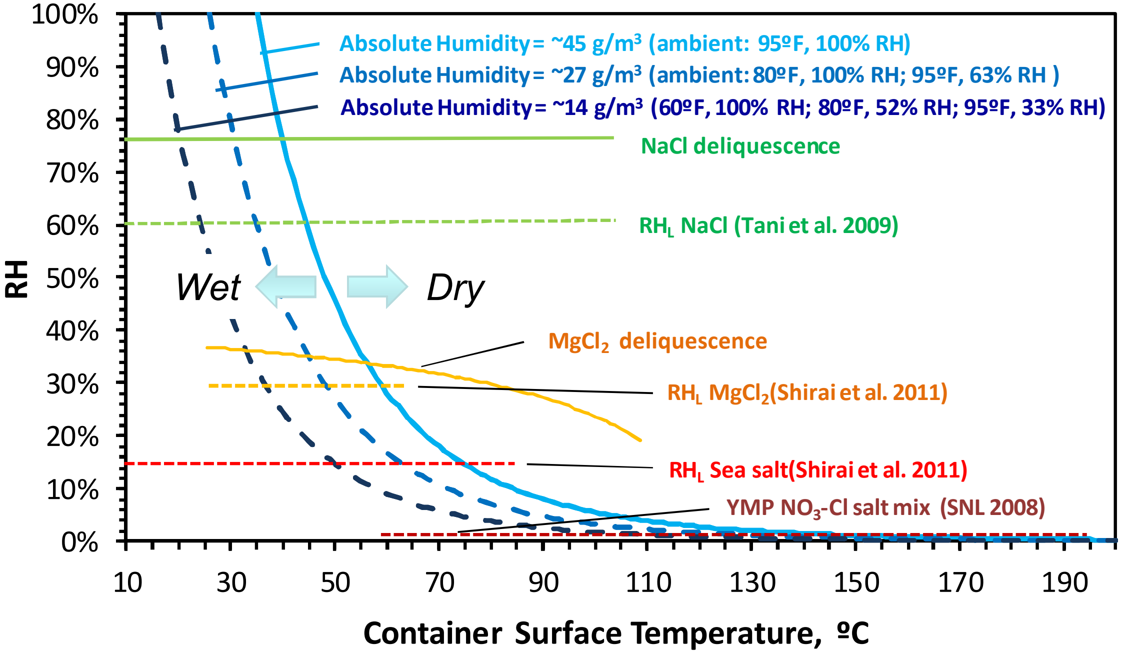
- SCC requires:
  - Presence of an aqueous solution
    - Immersed conditions unlikely — casks are protected from weather by overpacks
    - Deliquescence of salts in dust — passive ventilation draws large volumes of outside air through the overpacks, and dust and aerosols are deposited on the cask surfaces.
  - Chemically aggressive environment (e.g., chloride-rich)
- Salt deliquescence and brine composition are dependent on:
  - Temperature at the container surface
  - Relative humidity at the container surface
  - Composition of deposited salts



PNNL 2012, Figure 7.3

Parameters Controlling Deliquescence: Temperature, RH, composition

- Salt assemblages have a minimum RH at which they deliquesce (RH_d)
- $RH = P_{water\ vapor}/P_{sat}$
- $P_{water\ vapor} = f(Abs.\ Humid_{outside\ air})$
- $P_{sat} = f(T_{WP\ surface})$
- During cooling, *T* decreases and $RH_{WP\ surface}$ increases until RH_d is reached, and deliquescence occurs.
- The limiting RH for corrosion, RH_L, is somewhat below RH_d, (adsorbed water films).



For seawater: The maximum temperature for salt deliquescence and cask corrosion (assuming $RH_L \approx 15\%$) is ~80-85^oC

Temperature: Canister Temperature Range Varies with Loading and with Cooling Time

- Maximum Temperatures
  - From Storage System SARs for large containers
    - Calculate only maximum surface temperatures
    - Commonly use bounding thermal loads
    - Generally, do not provide temperature histories
  - Smaller canisters may be within the temperature range allowing SCC immediately upon loading.
  - Over time, all canisters will cool into the critical temperature range.

Storage System	Container type	Heat load (kW)	Ambient temp., ºF	Max. shell T, ºC	Source
NAC UMS	24 PWR	23.0	76	177	A
			106	194	
	56 BWR	23.0	76	191	
			106	207	
NUHOMS HSM-H	24PTH-S(1)	40.8	0	186	B
			100	235	
			117	237	
	24PTH-L	31.2	117	203	
	24PTH-S-LC	24.0	117	176	
NUHOMS HSM-HD	32PTH(2)	34.8	115	208	C
	32PTH(3)	32.0	115	201	
	32PTH(4)	26.1	115	187	
HI-STORM	MPC-68	38.0	80	233	D
	MPC-32	38.0	80	242	

(1)Flat stainless steel heat shields

(2)Finned Al side shields

(3)Unfinned Al side shields

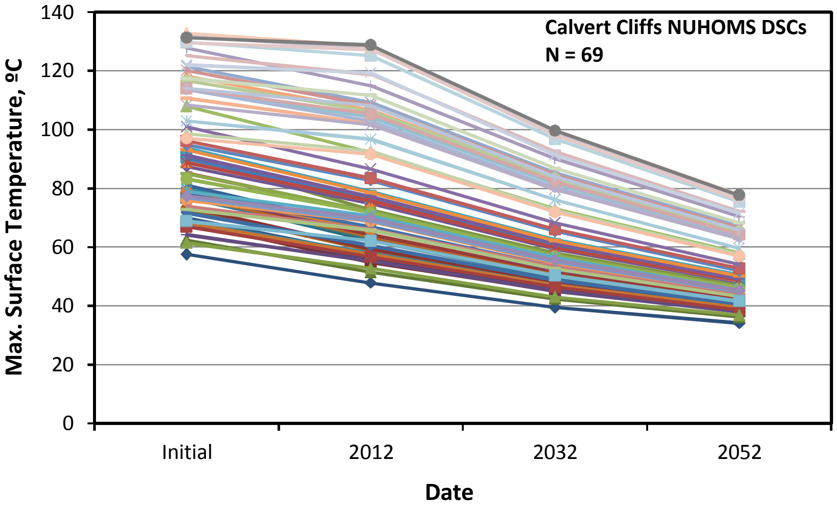
(4)galvanized steel side shields

ANAC-UMS FSAR, Revision 5 (2005)

BNUHOMS FSAR, Revision 10 (2008)

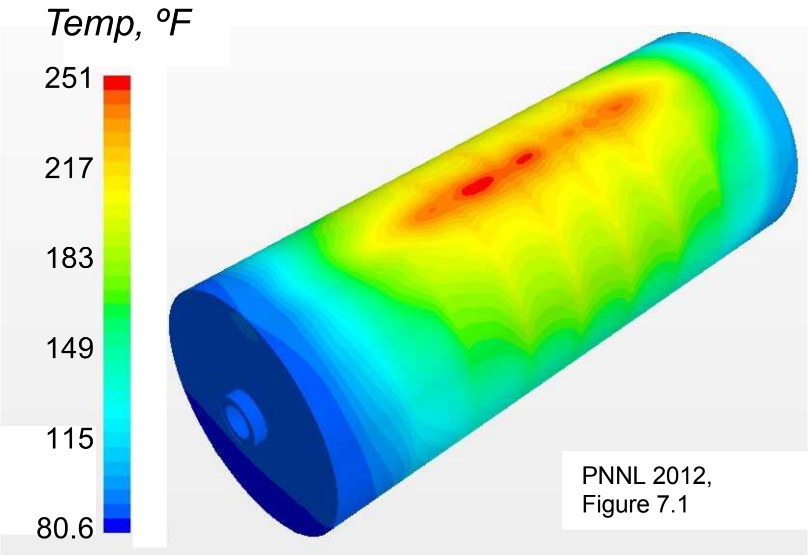
CNUHOMS-HD FSAR, Revision 0 (2007)

DHI-STORM FSAR, Revision 8 (2010)



Temperature: Variation with Surface Location

- Thermal modeling (PNNL 2012)
  - Calvert Cliffs NUHOMS HSM-15 canister and storage module
  - Temperature map of canister surface, internals; map of ventilation velocities through overpack
  - Results:
    - Huge temperature range (>90ºC) on the surface
    - Seasonal temperature fluctuations correspond to similar-magnitude container surface temperature fluctuations



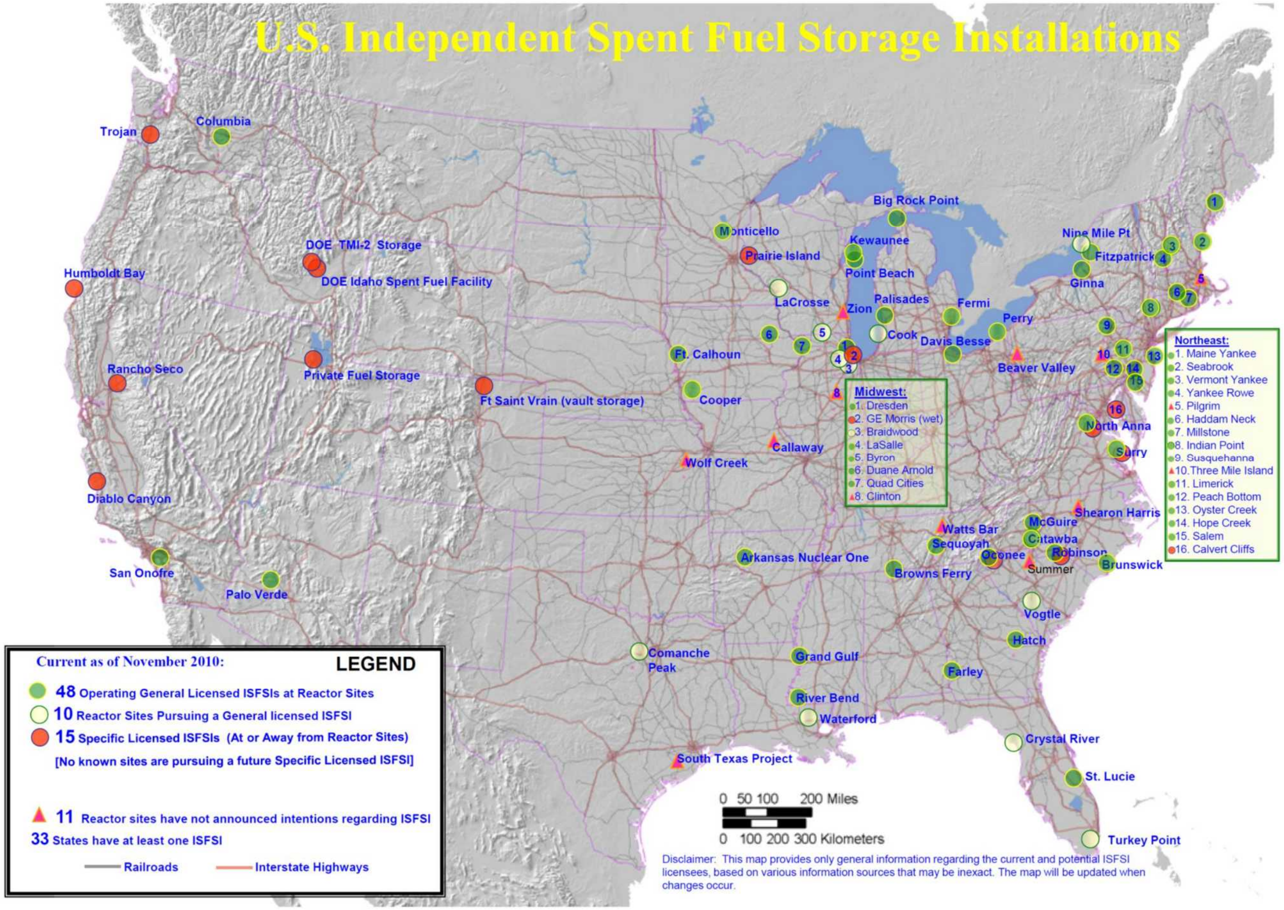
PNNL 2012, Figure 7.1

- Timing of initial deliquescence and potential for SCC (<80-85ºC) will vary greatly over the container surface
- Corrosion, SCC penetration models based on “time of wetness” would have to be location-specific on the storage container surface

Parameters Controlling Deliquescence: Salt Composition

Storage sites can be grouped into two general categories

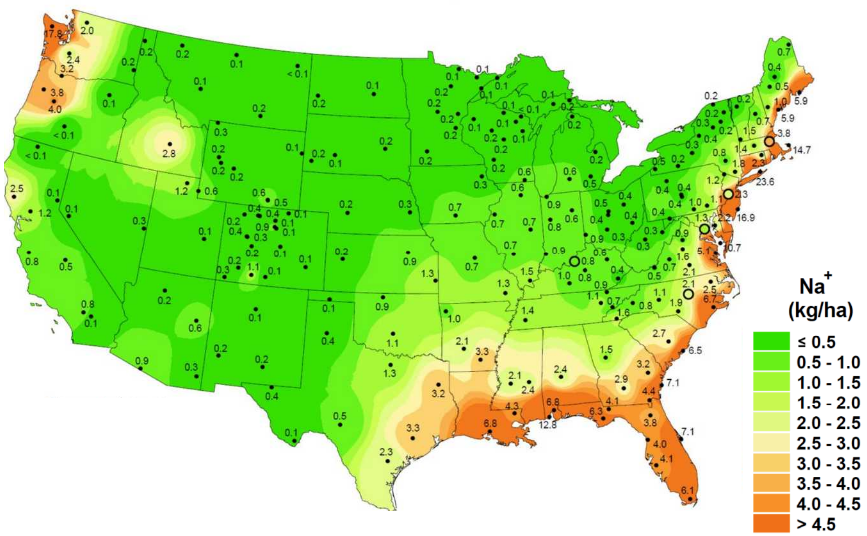
- *Near-marine*
  - A large component of sea salt in dust/aerosols
- *Inland*
  - Salts largely derived from anthropogenic activities, terrestrial sources, and atmospheric reactions with marine salts

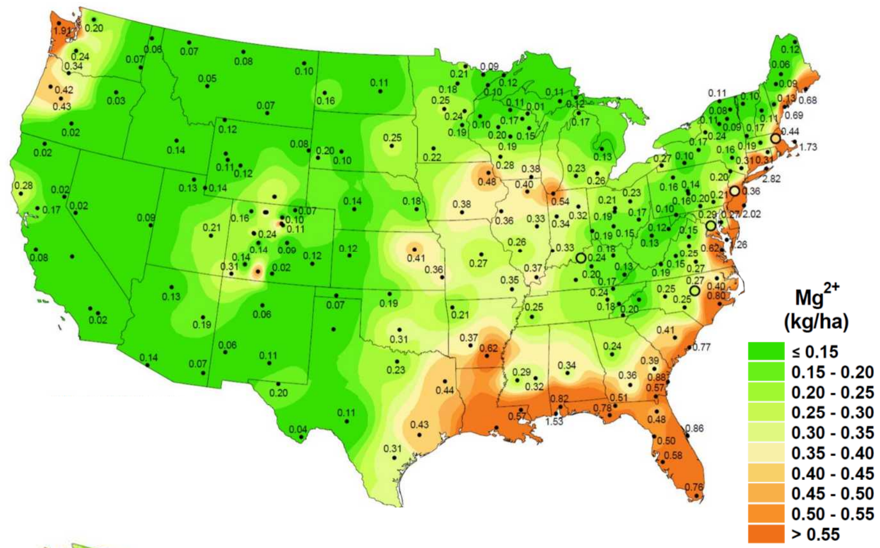


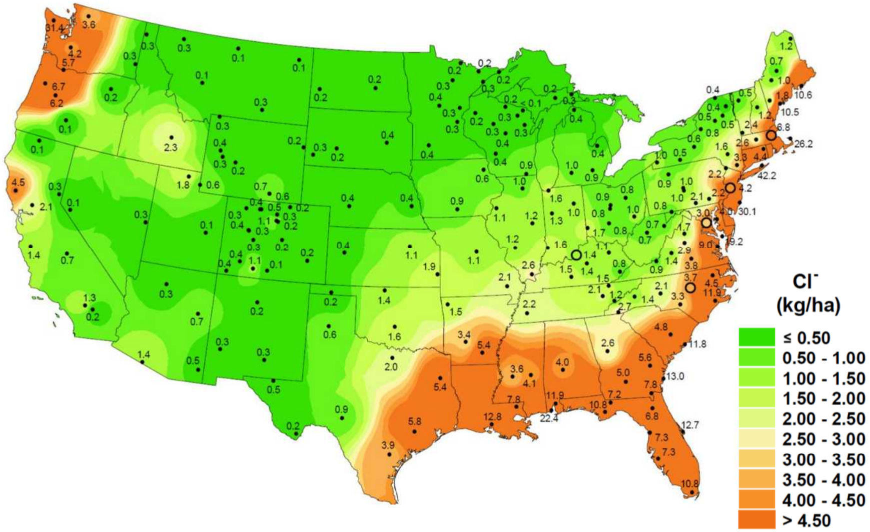
Source: U.S. NRC website, downloaded 5/10/2012

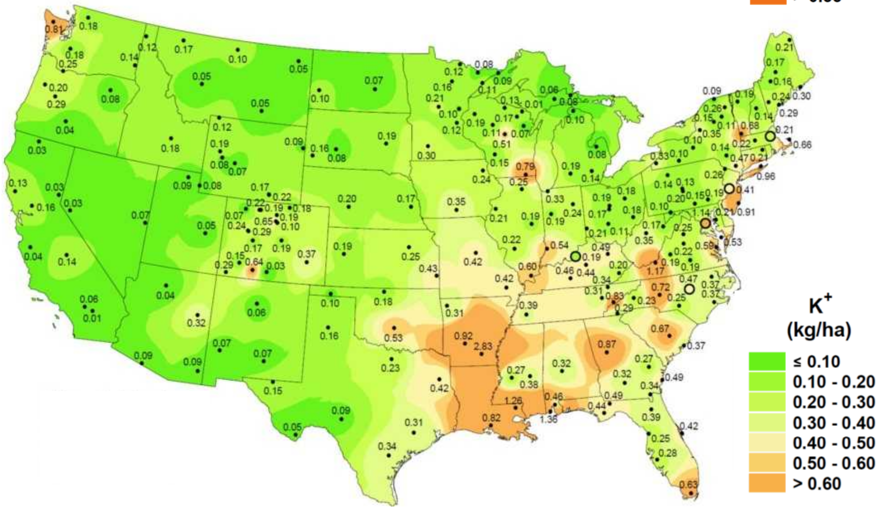
Salt compositions: Species enriched in near-marine areas

NADP wet deposition maps



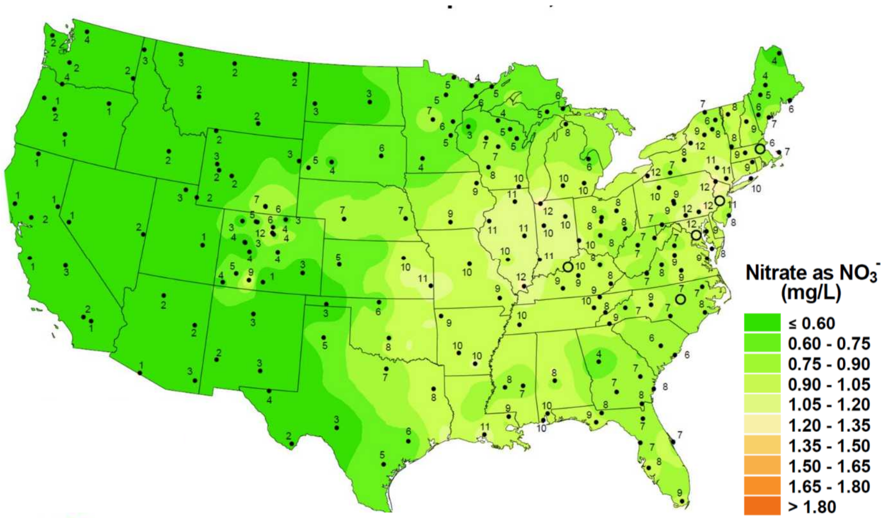


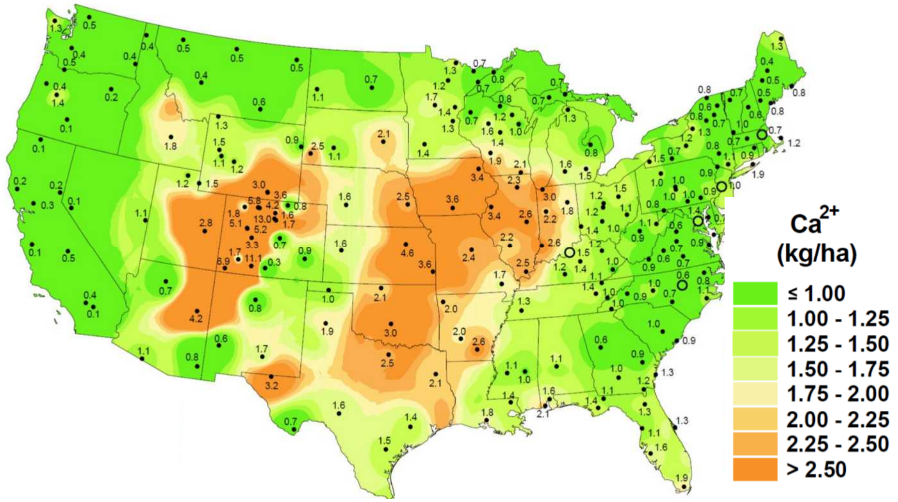


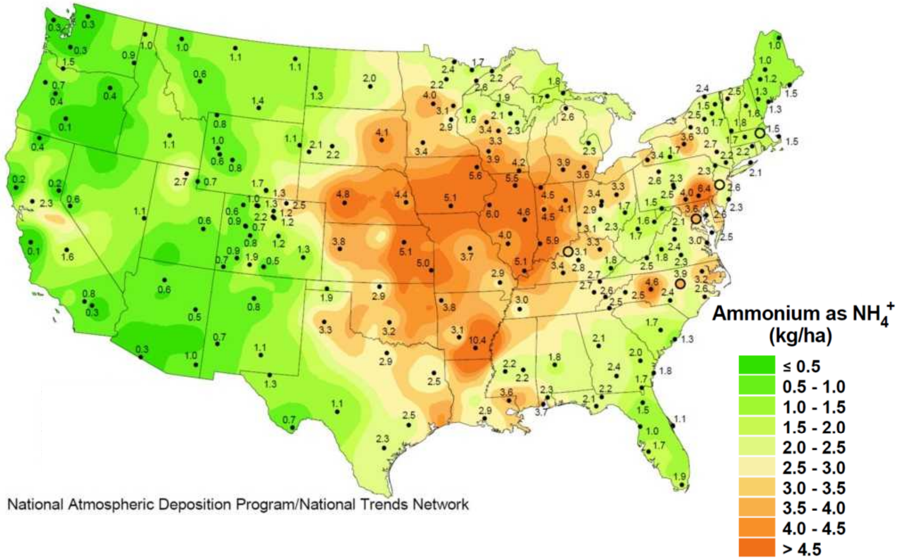


Salt compositions: Species enriched at inland sites

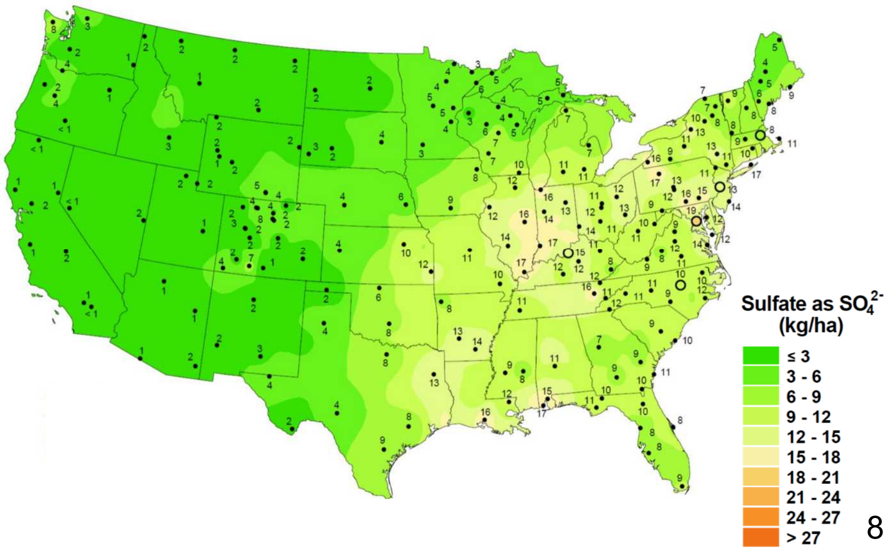
NADP wet deposition maps







National Atmospheric Deposition Program/National Trends Network

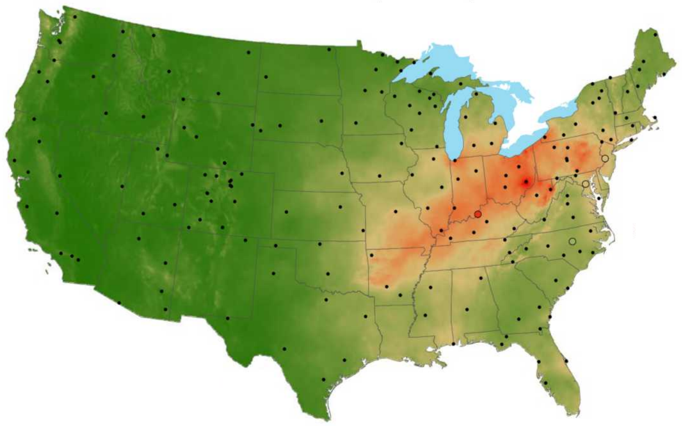


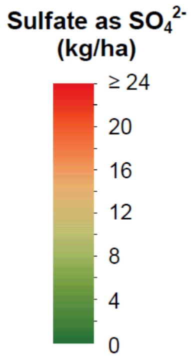
Salt compositions: Species enriched at inland sites

Sulfate concentrations

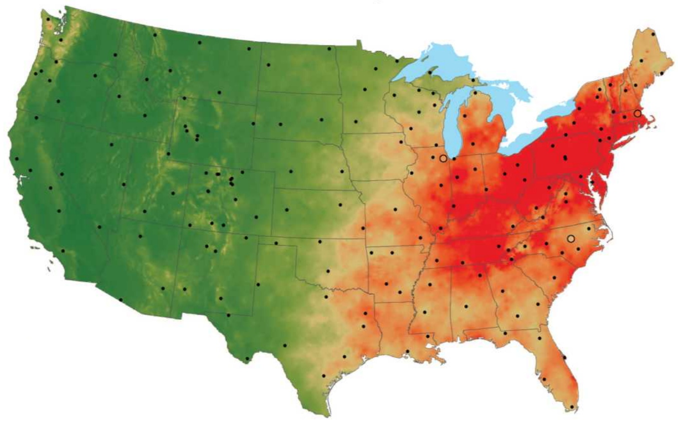
- Highest in the east and midwest.
- Largely due to SO_2 emissions by power plants; subsequent oxidation produces acid rain.
- Decreasing over time (EPA air pollution standards)
- May be difficult to estimate from past data.

Sulfate ion wet deposition, 2011

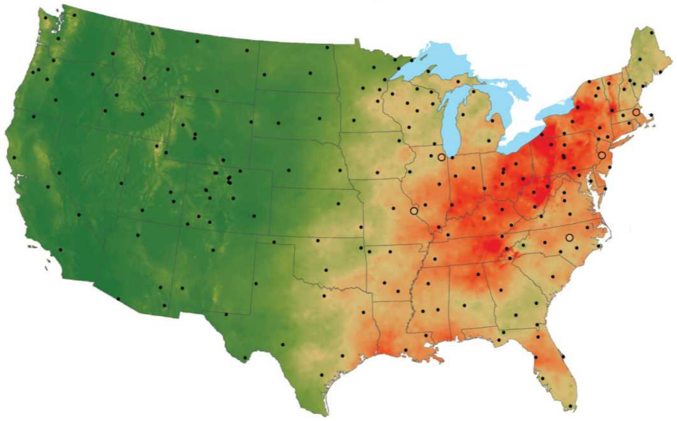




Sulfate ion wet deposition, 1994



Sulfate ion wet deposition, 2001



SCC Experiments with Sea Salt and Sea Salt Components

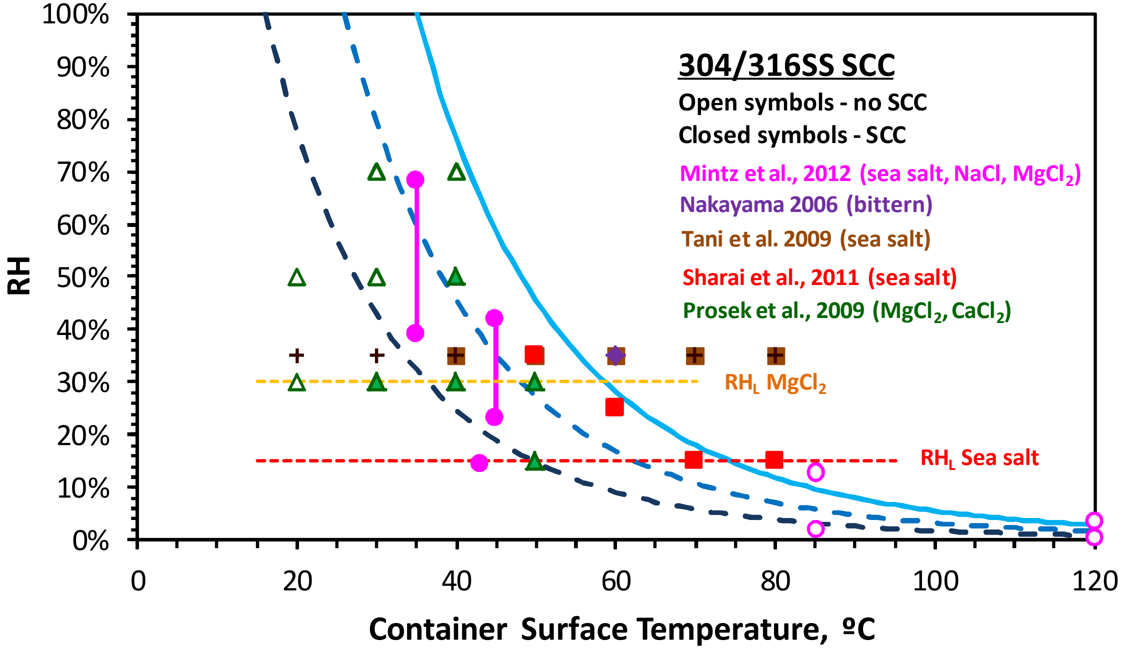
Sea salt/spray—generally simulated with synthetic ocean water (ASTM D1141-98)

	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

SCC occurs under many environmentally relevant conditions (and some not)

- No SCC under dry (high T, low RH) conditions
- No SCC under cool, high RH conditions

Localized corrosion, "rusting", including pitting, was observed under almost all conditions



Does this mean SCC of SNF storage casks in near-marine settings is likely to occur?

SCC Experiments with Inland salt compositions

Inland salts—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

Very little experimental data—salt assemblages anticipated to be nitrate-rich and chloride deficient, and benign (nitrate inhibits corrosion of passive metals such as stainless steels and Alloy 22)

- Recent NRC/CNWRA scoping study assessed corrosion by NH_4NO_3, NH_4HSO_4, $(NH_4)_2SO_4$, and $[NH_4NO_3 + (NH_4)_2SO_4]$ mixtures (He et al., 2013)
  - U-bend samples of as-received, sensitized, and welded 304SS
  - Tests at 35ºC, 72% RH; 45ºC, 44% RH
  - Samples exposed to NH_4HSO_4 (very acidic solution; pH = -0.79) had extensive general corrosion; welded samples also showed grain boundary attack.
  - $(NH_4)_2SO_4 + NH_4NO_3$
    - SO_4:NO_3 = 0.5: minor pitting observed
    - SO_4:NO_3 = 1.0, 3.0: no corrosion observed
    - Possible degassing of NH_3NO_3?
  - For this limited experimental matrix, no SCC was observed.

Are the relevant environmental conditions and salt assemblages correctly defined? Possibly not.

Sea salts may not be representative of salts on the cask surface, either initially or after deliquescence.

- Deposited salts will not be pure sea salts
  - Gas-to-particle conversion reactions change chlorides to sulfates and nitrates (e.g., Gibson et al., 2006):

$$NaCl(s,aq) + HNO_3(g) \xrightarrow{RH\%} NaNO_3(s,aq) + HCl(g)$$

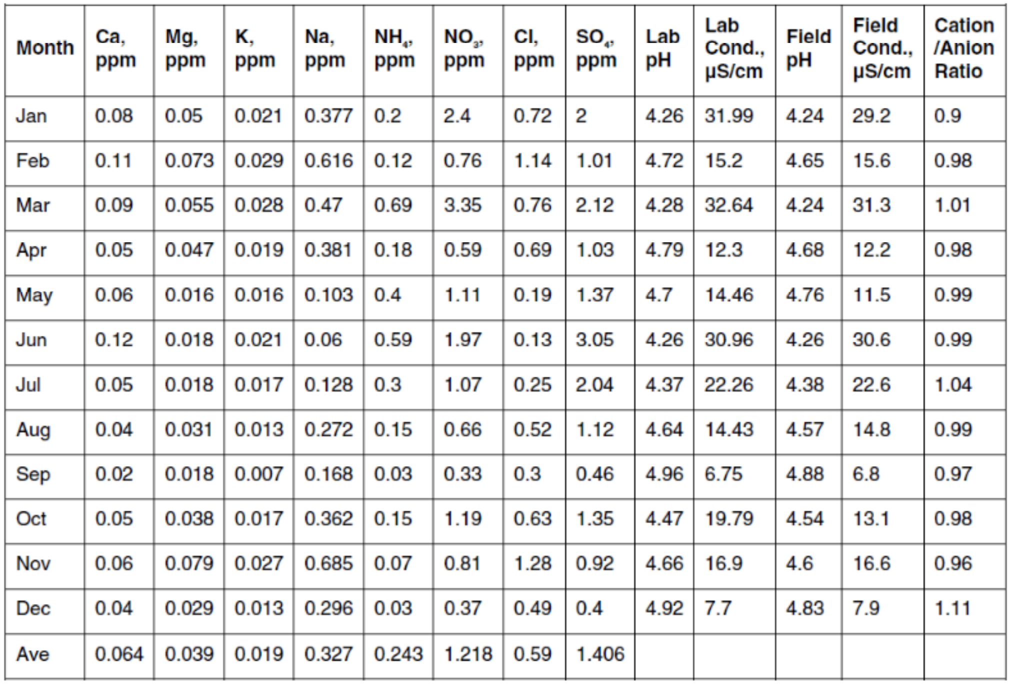
$$MgCl_2(s,aq) + 2HNO_3(g) \xrightarrow{RH\%} Mg(NO_3)_2(s,aq) + 2HCl(g)$$

(and reactions with nitrous oxides)

$$SO_2(g) + H_2O + ½O_2 + 2NaCl \rightarrow 2HCl(g) + Na_2SO_4$$

  - These reactions can be very efficient at converting chlorides to nitrates and sulfates
    - Even over oceans, atmospheric aerosols are deficient in chloride relative to sea salt (Hitchcock et al. 1980)
    - Coastal aerosols in Spain lose 24% (coarse particles) to 67% (fine particles) of their chloride prior to reaching the shoreline, ~11% per hour thereafter. (Pio and Lopes, 1998).
  - Carbonate mineral grains also react with NO_x and HCl/HNO_3 to form Ca, Mg nitrates/chlorides
  - Even in near-coastal regions, ammonium can be a significant component of aerosols.

NADP precipitation weighted mean concentrations, Casco Bay, ME (near Maine Yankee) for 2004.



Month	Ca, ppm	Mg, ppm	K, ppm	Na, ppm	NH_4, ppm	NO_3, ppm	Cl, ppm	SO_4, ppm	Lab pH	Lab Cond., µS/cm	Field pH	Field Cond., µS/cm	Cation /Anion Ratio
Jan	0.08	0.05	0.021	0.377	0.2	2.4	0.72	2	4.26	31.99	4.24	29.2	0.9
Feb	0.11	0.073	0.029	0.616	0.12	0.76	1.14	1.01	4.72	15.2	4.65	15.6	0.98
Mar	0.09	0.055	0.028	0.47	0.69	3.35	0.76	2.12	4.28	32.64	4.24	31.3	1.01
Apr	0.05	0.047	0.019	0.381	0.18	0.59	0.69	1.03	4.79	12.3	4.68	12.2	0.98
May	0.06	0.016	0.016	0.103	0.4	1.11	0.19	1.37	4.7	14.46	4.76	11.5	0.99
Jun	0.12	0.018	0.021	0.06	0.59	1.97	0.13	3.05	4.26	30.96	4.26	30.6	0.99
Jul	0.05	0.018	0.017	0.128	0.3	1.07	0.25	2.04	4.37	22.26	4.38	22.6	1.04
Aug	0.04	0.031	0.013	0.272	0.15	0.66	0.52	1.12	4.64	14.43	4.57	14.8	0.99
Sep	0.02	0.018	0.007	0.168	0.03	0.33	0.3	0.46	4.96	6.75	4.88	6.8	0.97
Oct	0.05	0.038	0.017	0.362	0.15	1.19	0.63	1.35	4.47	19.79	4.54	13.1	0.98
Nov	0.06	0.079	0.027	0.685	0.07	0.81	1.28	0.92	4.66	16.9	4.6	16.6	0.96
Dec	0.04	0.029	0.013	0.296	0.03	0.37	0.49	0.4	4.92	7.7	4.83	7.9	1.11
Ave	0.064	0.039	0.019	0.327	0.243	1.218	0.59	1.406					

(EPRI 2006)

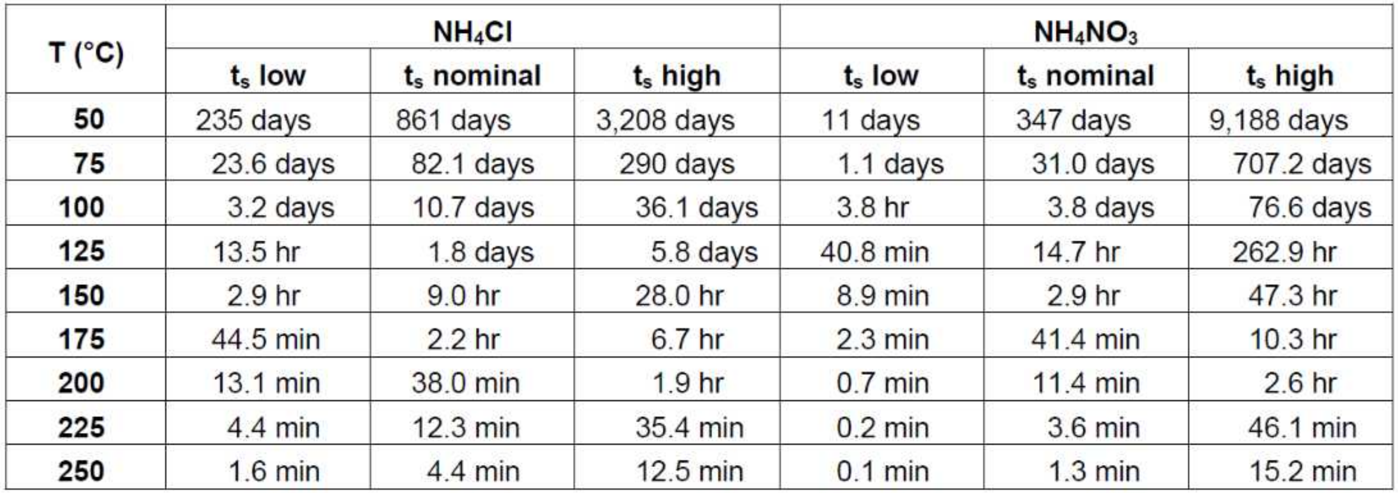
Are the relevant environmental conditions and salt assemblages correctly defined? Possibly not.

After deposition: prior to deliquescence, gas-to-particle conversion reactions are minimal, but deposited salts will be modified by decomposition reactions.

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

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

- Decomposition of ammonium salts is rapid (SNL 2008, Table 6.1-1)



T (°C)	NH_4Cl			NH_4NO_3		
	t_s low	t_s nominal	t_s high	t_s low	t_s nominal	t_s high
50	235 days	861 days	3,208 days	11 days	347 days	9,188 days
75	23.6 days	82.1 days	290 days	1.1 days	31.0 days	707.2 days
100	3.2 days	10.7 days	36.1 days	3.8 hr	3.8 days	76.6 days
125	13.5 hr	1.8 days	5.8 days	40.8 min	14.7 hr	262.9 hr
150	2.9 hr	9.0 hr	28.0 hr	8.9 min	2.9 hr	47.3 hr
175	44.5 min	2.2 hr	6.7 hr	2.3 min	41.4 min	10.3 hr
200	13.1 min	38.0 min	1.9 hr	0.7 min	11.4 min	2.6 hr
225	4.4 min	12.3 min	35.4 min	0.2 min	3.6 min	46.1 min
250	1.6 min	4.4 min	12.5 min	0.1 min	1.3 min	15.2 min

- Ammonium/acid gas loss by solid phase decomposition is stoichiometric. Mineralogy of ammonium species is important.
- Especially important for ammonium-rich inland salt assemblages.

Are the relevant environmental conditions and salt assemblages correctly defined? Possibly not.

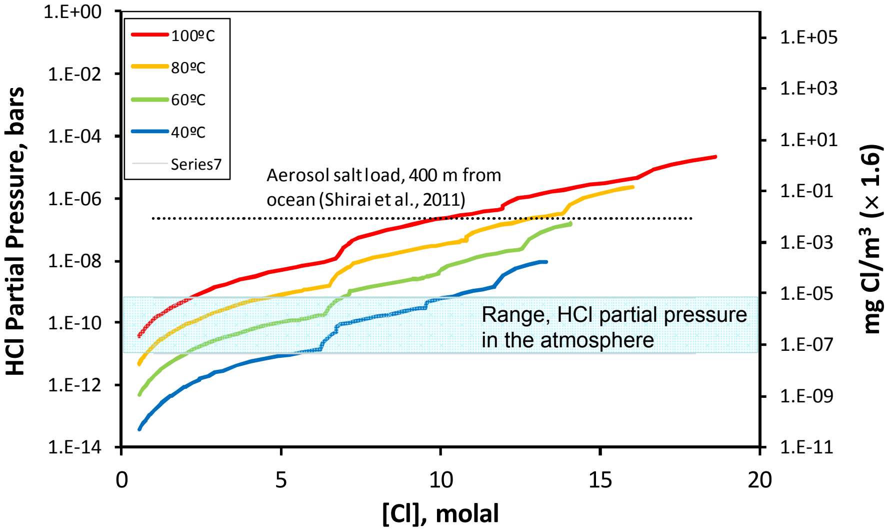
After deposition: once temperatures drop and deliquescence occurs:

- Salt deposition continues
- Ammonium salts
  - Ammonia/anion loss in no longer stochiometric
  - Components lost according to their acid gas partial pressures above the deliquesced brine. E.g., ammonium sulfate deposition results in preferential loss of ammonia/chloride/nitrate.
- Reactions with atmospheric gases
  - SO_2, nitric acid gas-to-particle conversion reactions resume
  - Acid degassing and adsorption of CO_2, precipitation of chloride/hydroxides and carbonates
- Reactions with other dust components
  - Organics—reactions consume nitrate (Yucca Mountain dusts; Peterman 2008, 2009)
  - Mineral phases (e.g., silicates)—reactions buffer pH to near neutral values (SNL 2008)

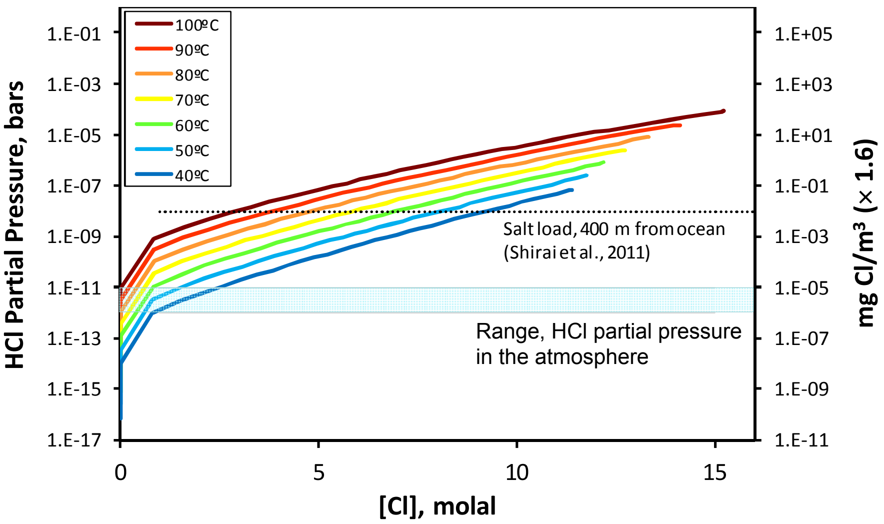
Acid degassing

Simulated evaporation of ASTM synthetic sea water and $MgCl_2$ brine

Acid gas partial pressures in equilibrium with evaporated seawater



Acid gas partial pressures in equilibrium with $MgCl_2$ solution



Degassing raises pH, but is self-limiting—as pH rises, acid gas partial pressures decrease, until a buffering reaction (e.g., carbonate precipitation) occurs.

Conclusions

- For near-marine environments, experimental work with sea salts suggests that SCC will likely occur. However, experimental conditions may not have been representative:
  - Use of synthetic sea salts to simulate near-marine environments may be unrealistic
    - Deposited salts will not be sea salts.
    - Salts deposited on the cask surface will be modified by reactions with atmospheric gases and degassing
    - Reactions with other dust components may mitigate/enhance corrosivity of deliquesced brines.
- For inland locations, corrosion studies with relevant salt assemblages are limited
  - Effects of ammonium mineral decomposition and ammonia/acid degassing are not well constrained
  - Reactions with organics, a large component of most dusts, may consume nitrates
- For both cases, limited air flow and use of clean air streams in experiments may minimize important atmospheric exchange reactions.

There are insufficient data to assess the environment produced by deliquescence on the SNF dry storage casks, or the corrosivity of that environment. There is a critical need for a field sampling program to evaluate dust and salt compositions on storage canister surfaces. Such a program has recently been initiated by EPRI.