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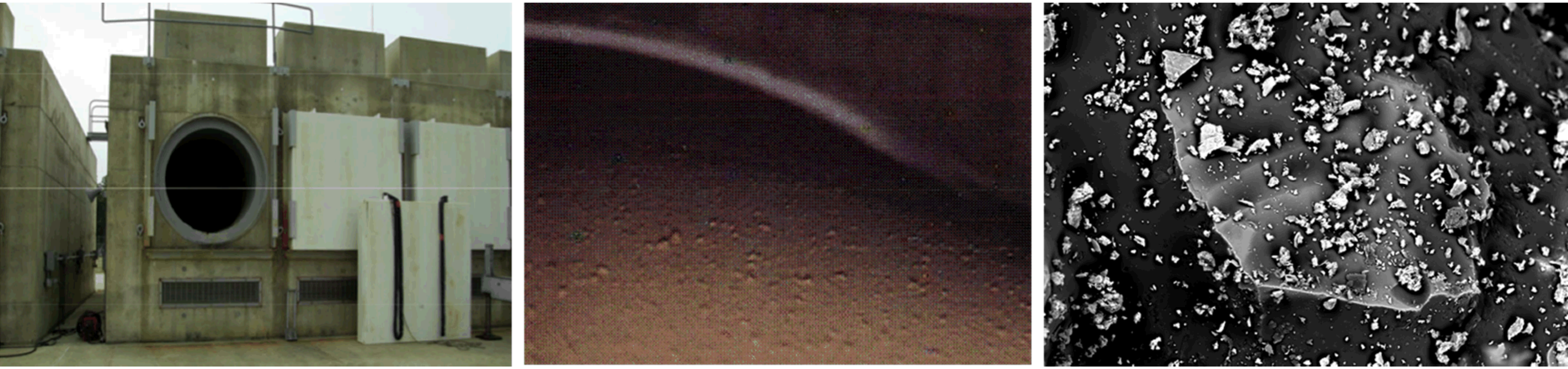

Understanding the Environment on the Surface of Spent Nuclear Fuel Interim Storage Containers

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PSAM 12 Conference, 24 June 2014, Honolulu

Overview

- Background: Corrosion of in-service SNF interim storage casks
- Describing the environment on the surface of in-service storage canisters.
  - Temperature
  - Relative Humidity
  - Salt compositions
  - Salt surface load and deposition/loss processes affecting it.
- Current state of knowledge. Field data from 3 ISFSI sites.

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 stress corrosion cracking (SCC), of welded stainless steel (304SS) canisters is considered the most important potential failure mechanism.
- Canisters are stored in passively ventilated overpacks, and accumulate dust on the surface over time. SCC of stainless steel due to deliquescence of chloride-rich salts on the metal surface is well-known, especially in near-marine environments.
- Directly inspecting in-service canisters for corrosion, or for dust composition, is difficult due to high radiation fields at the canister surfaces, and limited access through vents in the storage overpacks.
  - EPRI sampling program: Collect and analyze of dust on the surface of in-service storage canisters, with emphasis on the composition of the soluble salts that could deliquesce as the canisters cool. Three ISFSI locations sampled:
    - Calvert Cliffs: Transnuclear NUHOMS system, horizontal storage canister (June 2012)
    - Hope Creek: Holtec HI-STORM system, vertical canister (Dec 2013)
    - Diablo Canyon: Holtec HI-STORM system (Jan 2014)
- Accurate probabilistic assessment of canister performance would potentially reduce inspection requirements. It is critical to understand the environment on the surface of the canisters and its role in corrosion to develop such a model.

Criteria for Stress Corrosion Cracking

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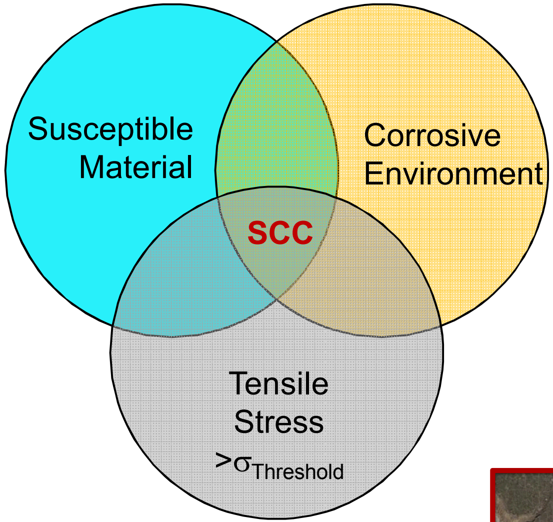


Susceptible Material

Corrosive Environment

SCC

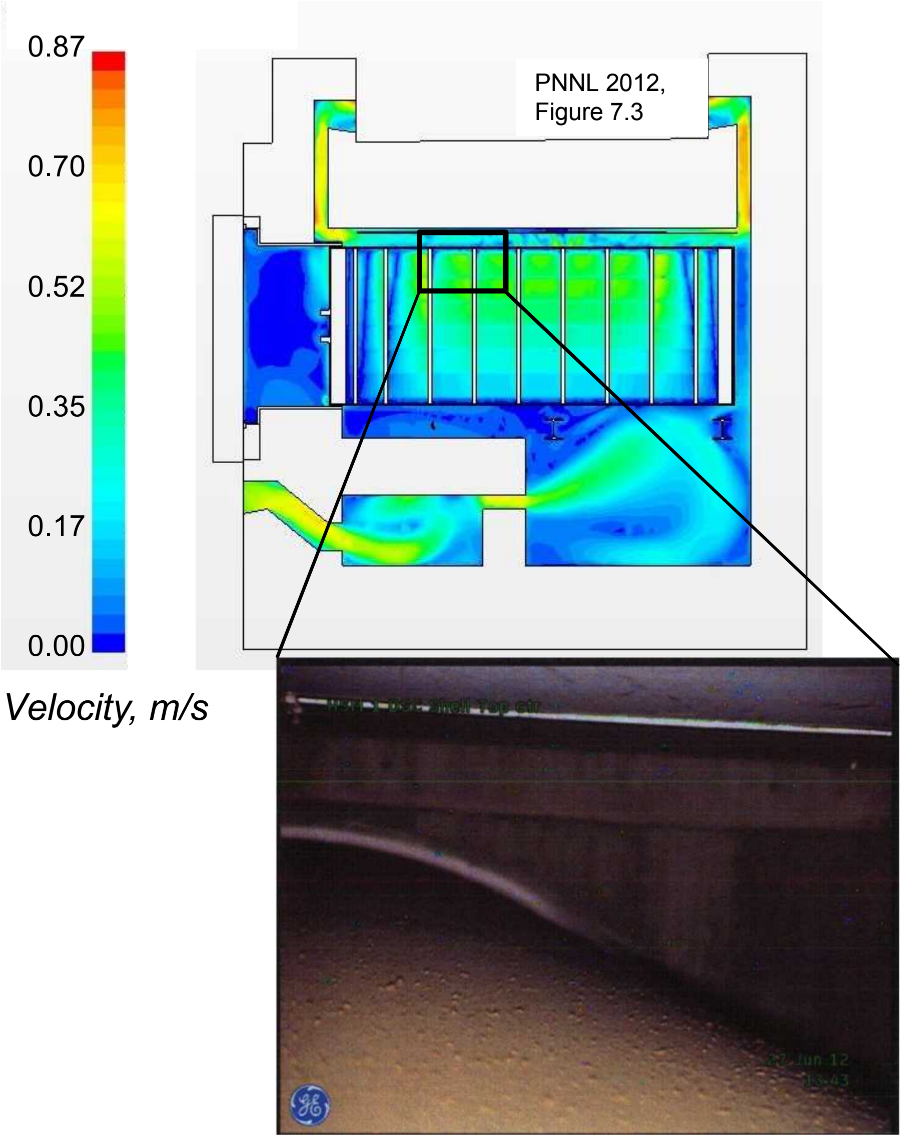
Tensile Stress

$>\sigma_{\text{Threshold}}$

Deposition of sea salts in near-marine environments. For example, Diablo Canyon Site: ISFSI is ~1/3 mile from the shoreline.

Corrosive Environment

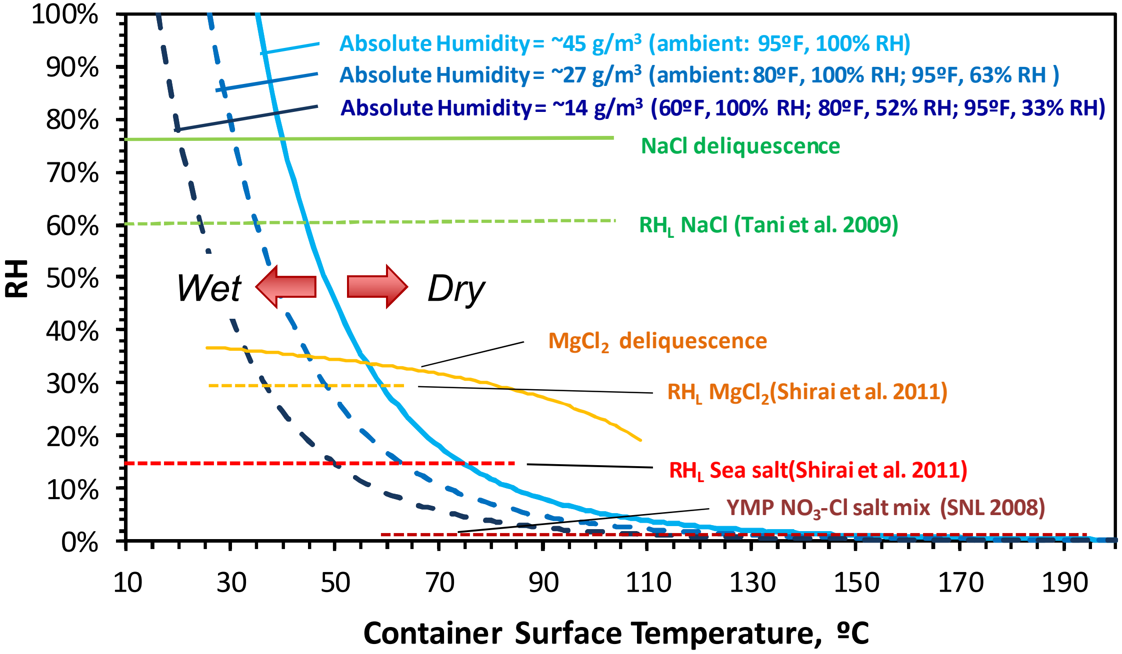
- SCC requires:
  - Presence of an aqueous solution
    - Immersed conditions unlikely — casks are protected from weather by overpacks
    - Deliquescence of salts in dust — passive ventilation draws large volumes of outside air through the overpacks, and dust and aerosols are deposited on the cask surfaces.
  - 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 canister corrosion (assuming RHL ≈ 15%) is ~80-85ºC.

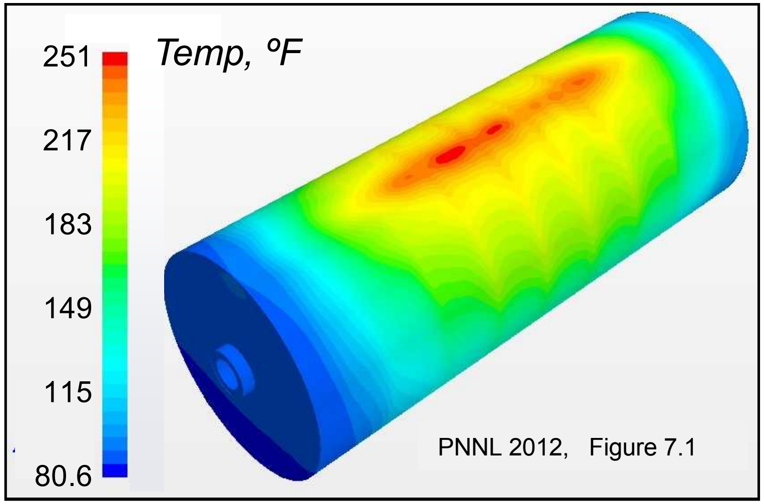


Does high heat generation protect the canister for an extended period after placement in dry storage? No…

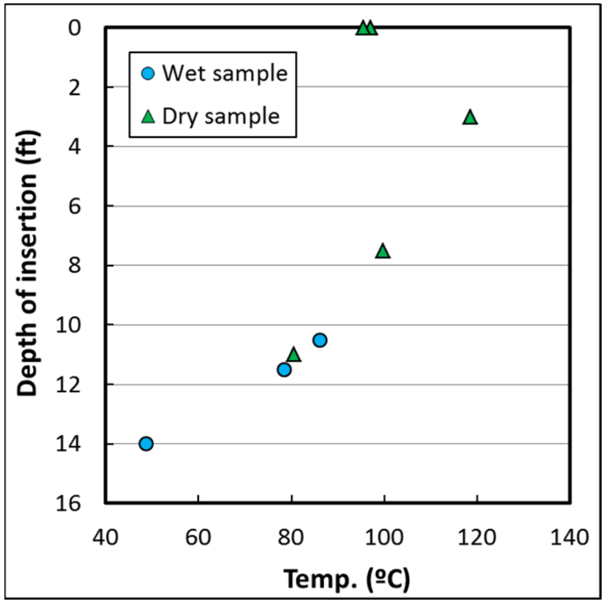
Temperature: Variation with Surface Location

- Changes in location-specific surface temperatures are important to determine:
  - Timing of deliquescence and potential corrosion initiation
  - Temperature-dependent corrosion parameters (e.g. crack growth rate)
- Thermal modeling (PNNL 2012)
  - Calvert Cliffs NUHOMS HSM-15 canister/storage module
  - Temperature map of canister surface, internals
    - Huge temperature range (>90ºC) on the surface
    - Seasonal temperature fluctuations correspond to similar-magnitude container surface temperature fluctuations
- Field measurements, Diablo Canyon
  - High burnup fuel, two years in dry storage
  - Measured temperatures varied from 49º to 119ºC, from canister bottom to top.

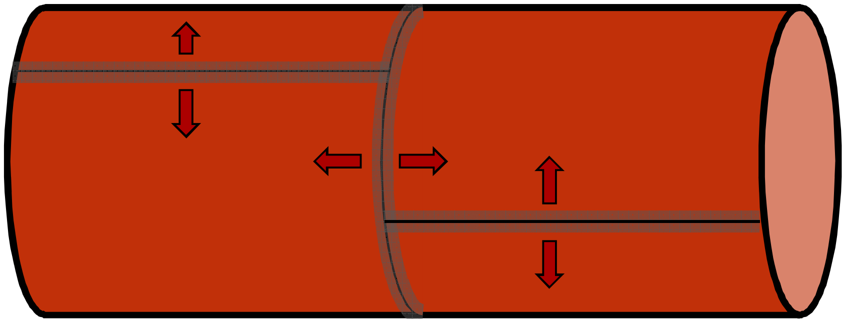
Timing of initial deliquescence and potential for SCC (<80-85ºC) will vary greatly over the container surface. Even for high burnup waste, conditions for corrosion can occur soon after emplacement on at least part of the package.



PNNL 2012, Figure 7.1



Temperature: Implementation in a probabilistic model

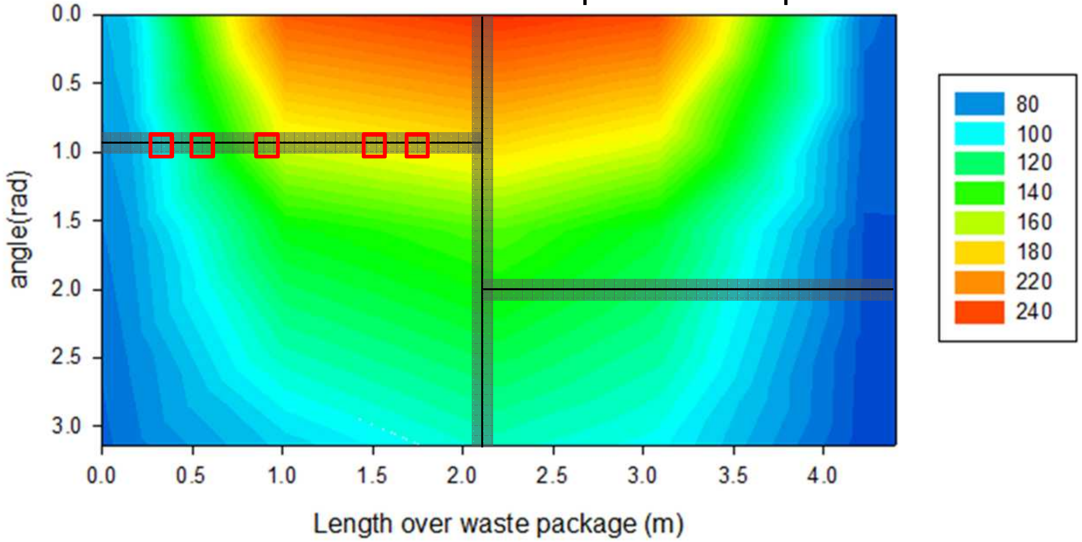


Welds (SCC occurs in weld heat-affected zones due to residual weld stresses):

- Location unknown
  - 1 circumferential
  - 2 longitudinal
- Circumferential end-plate welds

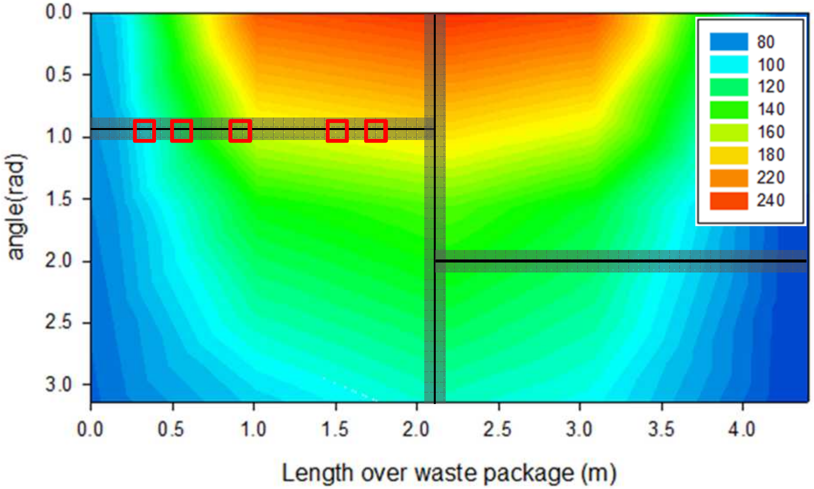
Thermal models provide surface temperature maps through time. Aleatory sampling of the weld locations on the package surface. Divide welds into segments and calculate a temperature history for each segment.

Flattened canister temperature map

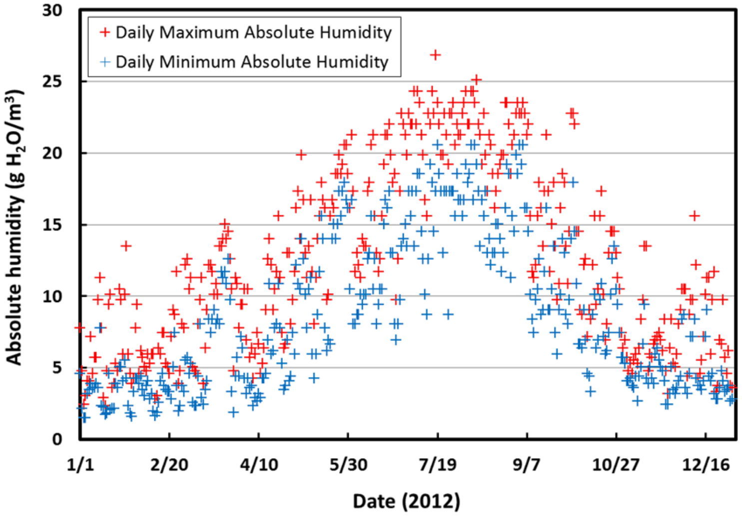


RH at the Canister Surface:

Time of initial occurrence of potentially corrosive conditions (RH_L), and total “time of wetness”



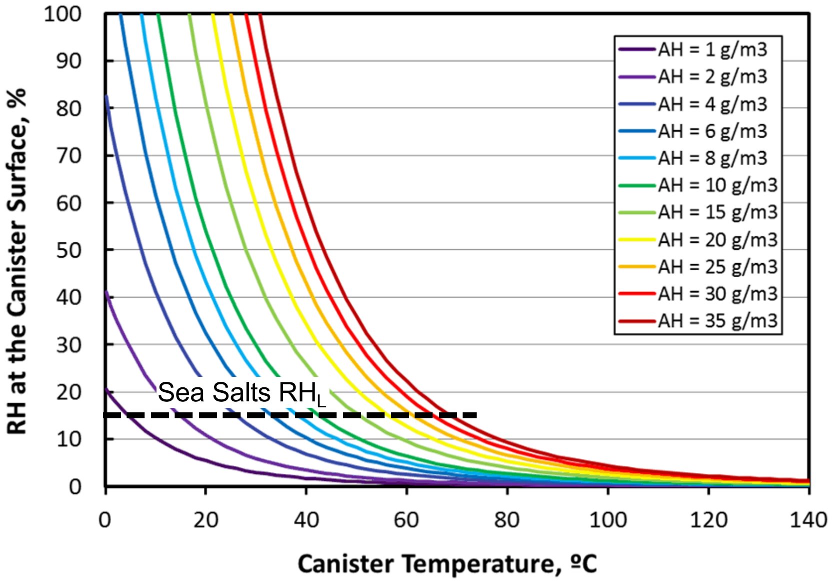
Surface temperature estimates



Site-specific National Weather Service data

Canister surface RH = *f*(Ambient AH; canister surface T)

Use weather data and predicted canister surface temperature to predict RH at any location and time.



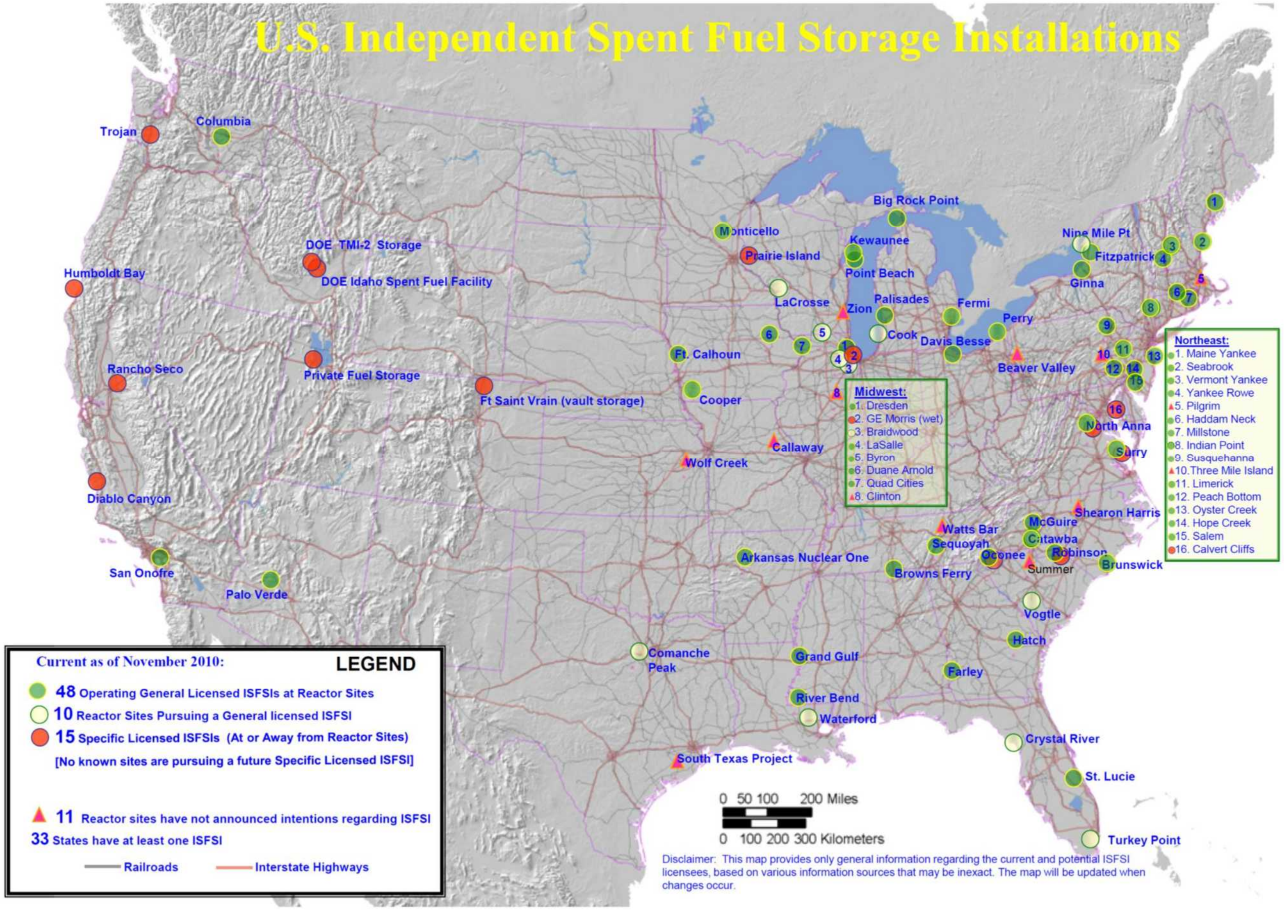
Timing of corrosion initiation—point in time at which RH_L is first reached.

Summing time when $RH > RH_L$ provides “time of wetness”

Salt Composition: Controls Brine Corrosivity and Timing of Deliquescence

Storage sites can be grouped into two general categories

- *Near-marine*
    - A large component of sea salt in dust/aerosols
    - Deliquescent brines anticipated to be chloride-rich, corrosive
- *Inland*
    - Salts largely derived from anthropogenic activities, terrestrial sources, and atmospheric reactions with marine salts
    - Brines anticipated to be nitrate and sulfate-rich



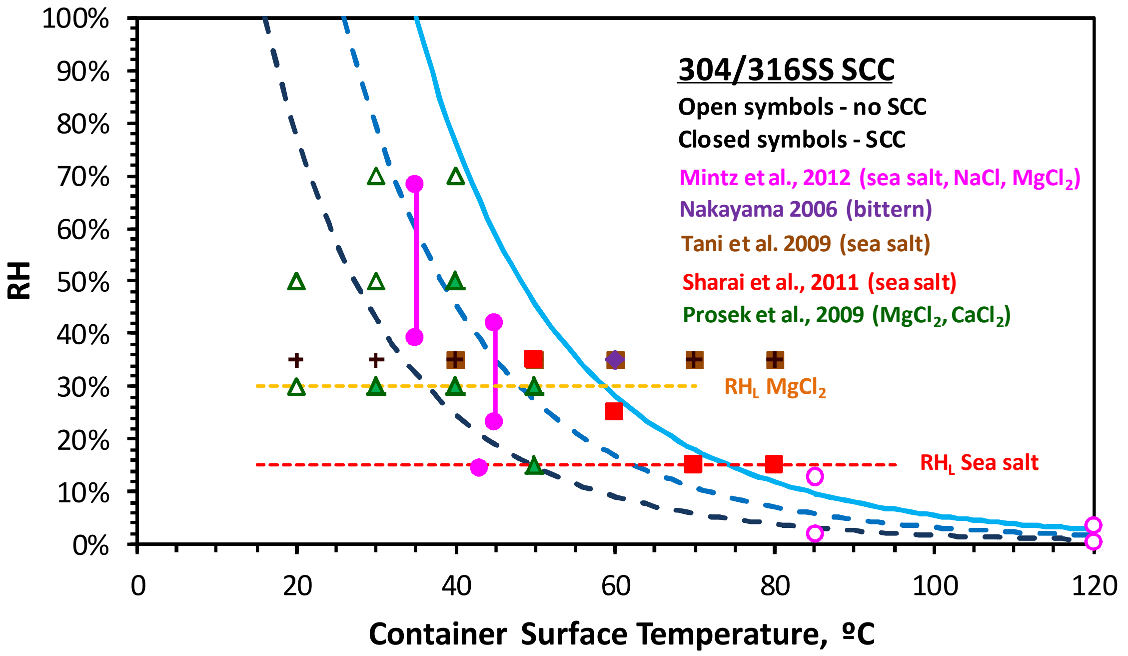
Source: U.S. NRC website, downloaded 5/10/2012

Near-Marine Settings

Sea salt/spray — Na-Mg-Cl-SO_4 major species. Chloride-rich and corrosive.

	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

Corrosion testing using synthetic seawater and sea salt components shows that SCC occurs under many environmentally relevant conditions



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

Do near-marine settings necessarily mean sea salts are deposited?

- 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
  - 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.

- Deposited salts or deliquesced brines may degas acid gases or undergo reactions with atmospheric gases
  - Acid degassing may raise the brine pH and result in chloride loss from the canister surface.
  - While carbonate may scavenge acid gases at low temperatures, the reaction is reversed at high temperatures. CO_2 absorption and Mg- or Ca-carbonate precipitation is coupled to acid degassing and potential loss of HCl to the gas phase.
  - Brine may evolve to lower chloride concentrations, and if conversion of Mg an Ca is complete, may dry out.

- Despite proximity to the ocean, deposited salts may be largely terrestrial in nature.
  - Sea salt aerosols are mostly coarse (>10µm), and settle rapidly from the air.
    - What is actual distance to the shoreline?
    - What is elevation?
    - What is dominant wind direction?

SCC Experiments with Inland salt compositions

Inland salts—for example, data from an Iowa NADP site

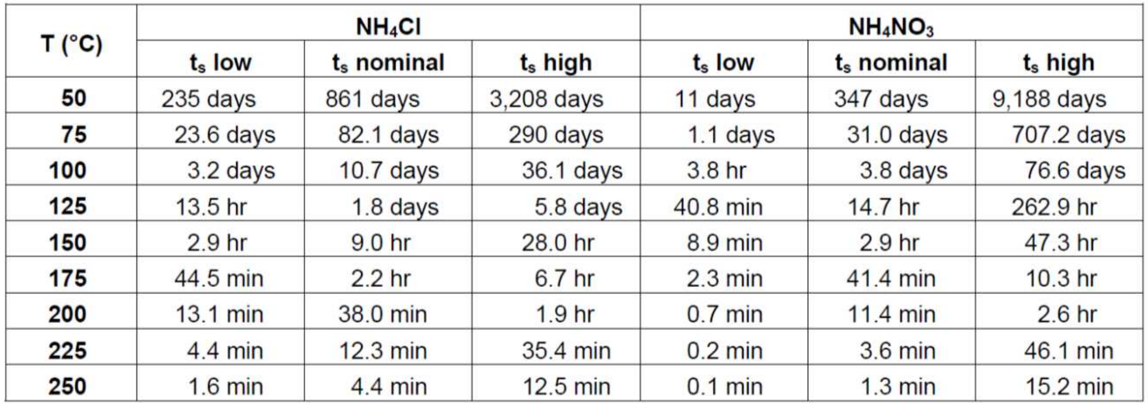
Species	Rain Conc., µeq/L
NH_4^+	29.217
Na^+	2.045
K^+	0.511
Mg^{2+}	3.208
Ca^{2+}	16.766
Cl^-	1.975
NO_3^-	15.565
SO_4^{2-}	17.685

- Inland salts are dominated by Ca and NH_4 sulfates and nitrates.

- Generally, these salts are benign with respect to SCC. However, the presence of incidental Cl (from road salt or cooling tower mists) cannot be ruled out. Can a stable Cl mineral be present on the hot canister surfaces?
- If Cl is deposited as an ammonium salt, no. Ammonium salts decompose readily into ammonia and an acid gas species, e.g.:

$$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$$

- Decomposition of NH_4Cl and NH_4NO_3 is rapid (SNL 2008)



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

- If the chloride is deposited as NaCl, it can persist stably as a mineral until deliquescence occurs

Can a chloride-containing brine persist stably on a canister surface?

After deposition: once deliquescence occurs:

- Salt deposition continues
- Ammonium-containing brines rapidly degas ammonium and acid gases. Components lost according to their acid gas partial pressures above the deliquesced brine. Chloride and nitrate degas more rapidly than sulfate. Brines evolve towards sulfate-rich compositions.
- Reactions with atmospheric gases
  - SO_2, nitric acid gas-to-particle conversion reactions result in preferential degassing of HCl.
  - Absorption of CO_2 with concomitant acid degassing, precipitation of chloride/hydroxides and carbonates (but at low temperatures, this reaction may reverse itself, resulting in acid gas absorption)

Is it important to know the amount of chloride on the surface over time?

- Necessary to determine when SCC can occur, *if there is a threshold chloride concentration for SCC* (e.g., Shirai et al., 2011). This is a point of contention.
- In some studies, rate of SCC initiation and/or corrosion rate is a function of the amount of chloride present (e.g., Cook et al., 2011. Implemented in some SCC models (Nakayama and Sakakibara, 2013).
- Chloride surface concentration will be a function of both chloride deposition rate and chloride loss reactions, both a potentially a function of temperature, RH, and location.
- EPRI is currently developing a chloride deposition model.

Field data: What has been observed?

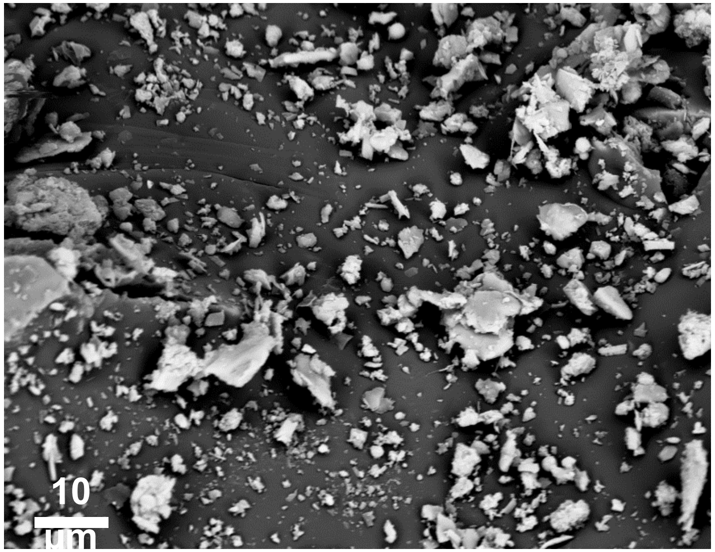
EPRI sampling program: Collect and analyze dust on the surface of in-service storage canisters, with emphasis on the composition of the soluble salts that could deliquesce as the canisters cool.

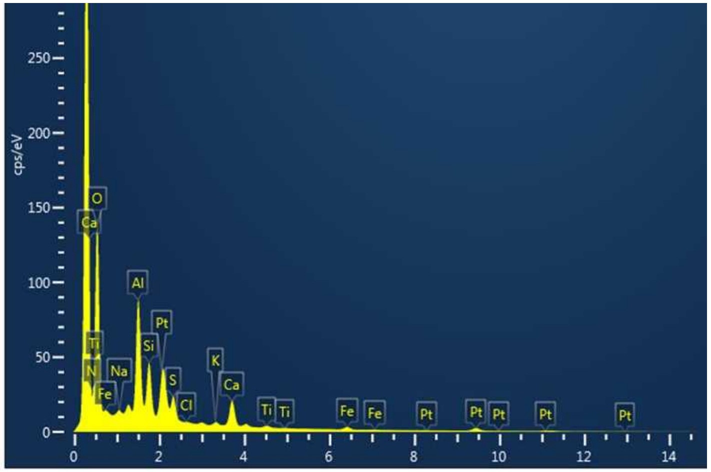
Three ISFSI locations sampled:

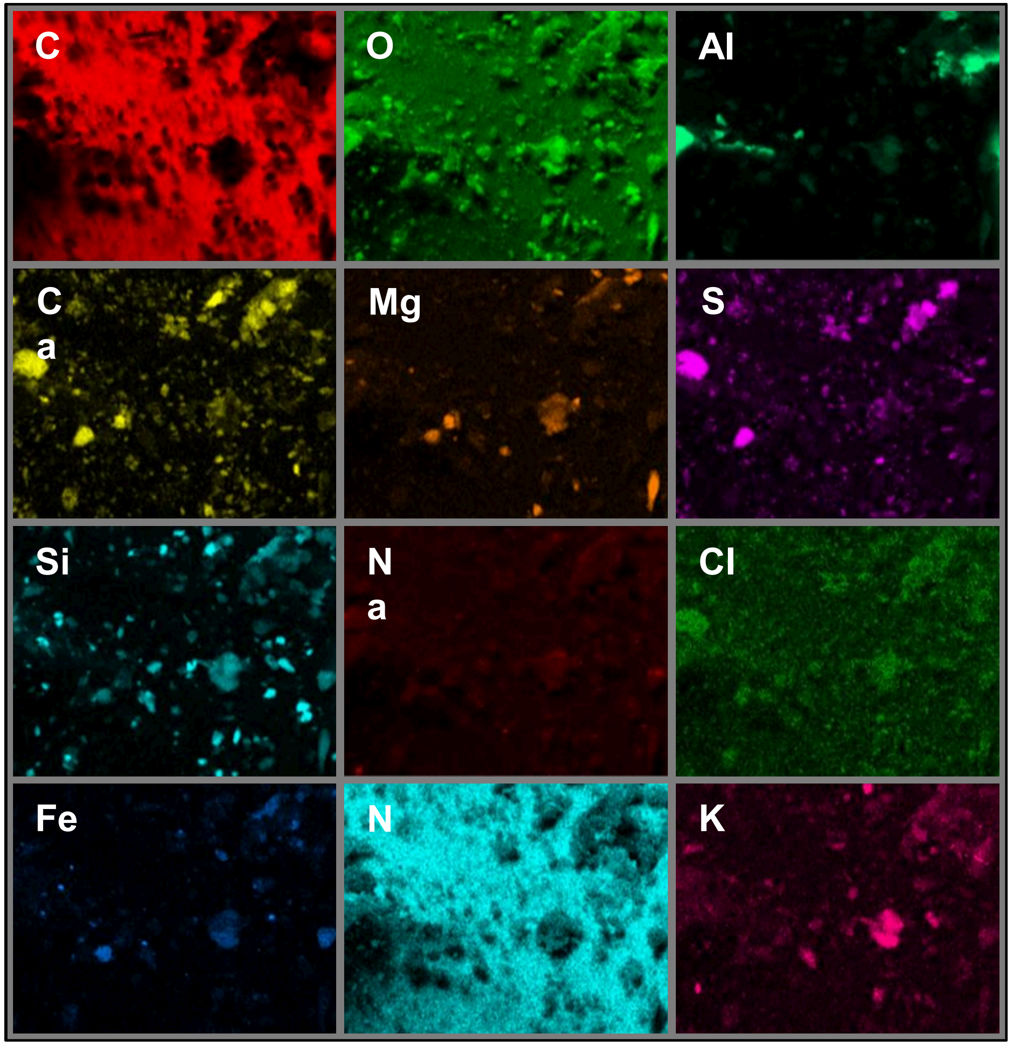
- **Calvert Cliffs Nuclear Plant, MD**
  - 0.5 miles from the Chesapeake Bay,
  - Transnuclear NUHOMS system, horizontal storage canister
  - Sampled June 2012
- **Hope Creek, NJ**
  - 0.2 miles from the Delaware River, 15 miles upstream from Delaware Bay
  - Holtec HI-STORM system, vertical canister
  - Sampled December 2013
- **Diablo Canyon**
  - 0.3 miles form the Pacific Ocean
  - Holtec HI-STORM system, vertical canister
  - Sampled January 2014

Calvert Cliffs Samples: SEM/EDS Analysis

Dust loads highest on the upper surface of the canister. Dust is dominantly aluminosilicate minerals of detrital origin. Soluble salts are largely Ca-sulfate. Trace amounts of chloride salts, dominantly NaCl. Salts are not sea salts.







Calvert Cliffs Chemical Analysis: Soluble Salts

Water soluble salts:

- 30 minute leach with deionized water
- Cations: Ca^{2+} >> $Na+$, Mg^{2+}, K^+
- Anions: SO_4^{2-} >> NO_3^- > Cl^-
- *Poor charge balances indicate analyses are deficient in anions* (CO_3 and OH not measured)

Salt phases observed by SEM:

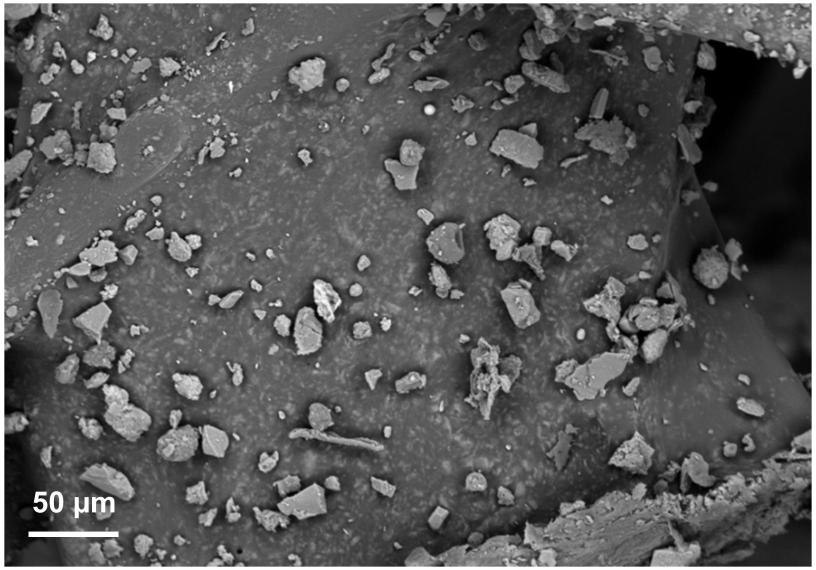
- Calcium sulfate (gypsum) — dominant salt phase present, especially in EPRI #4 sample.
- Chlorides rare
  - *Halite (NaCl) — sparse*
  - *Sylvite (KCl) — single grain*
  - *Ca, Mg chlorides not observed*
- Ca, Mg, and Ca/Mg carbonates or hydroxides common.

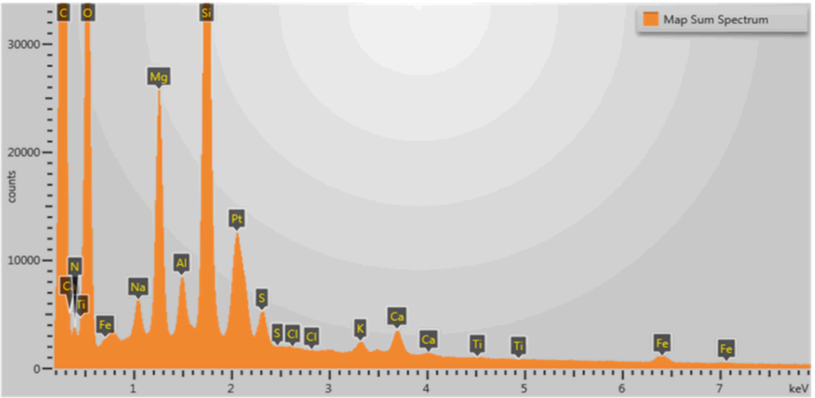
Soluble salts, µg/sample

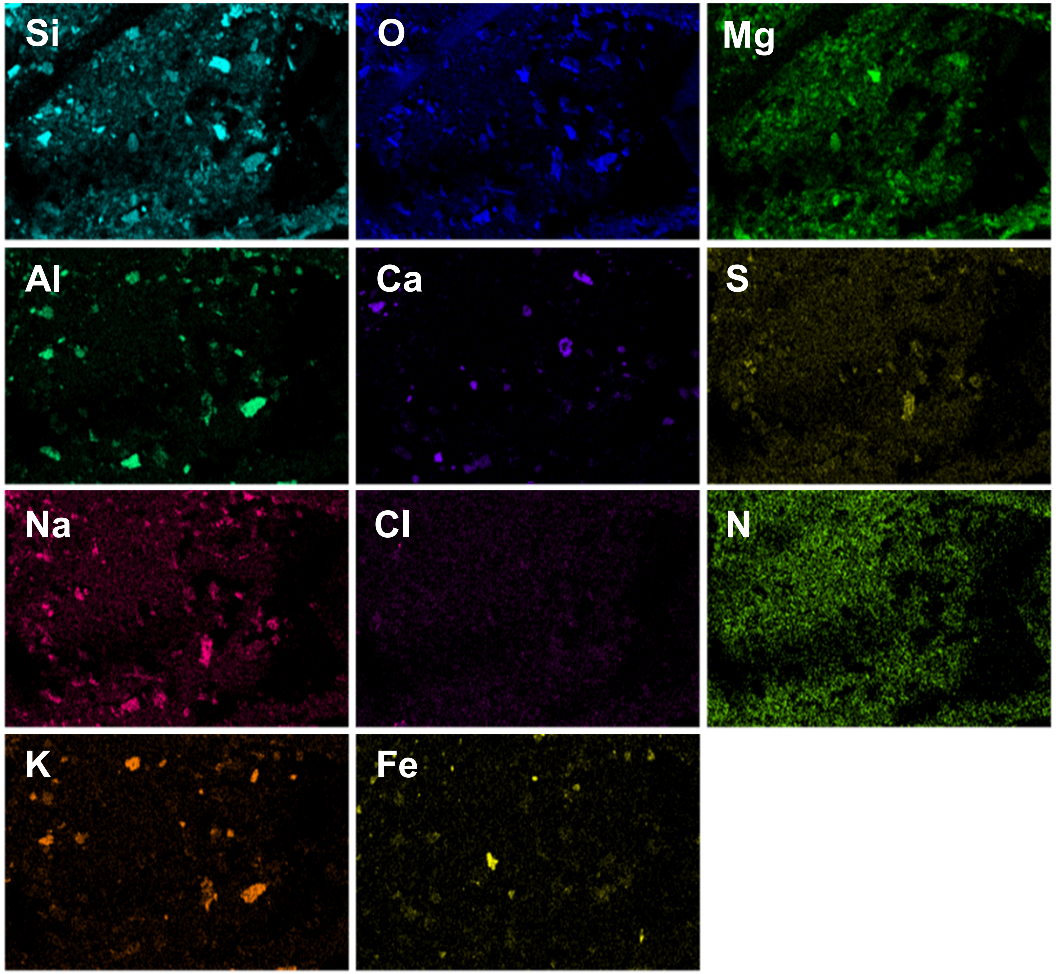
Ion	**Filter blank**	**Pad Blank**	**EPRI #1 filter**	**EPRI #1 pad**	**EPRI #4 filter**	**EPRI #4 pad**
Na^+	4.80	3.38	23.6	18.4	3.66	14.7
K^+	3.66	1.77	21.4	15.6	3.93	9.50
Ca^{+2}	0.92	0.46	**78.0**	**21.1**	**24.9**	**154**
Mg^{+2}	0.11	0.01	17.0	5.98	2.03	17.7
F^-	0.48	0.37	0.74	1.01	0.15	0.29
Cl^-	**3.13**	**2.23**	**8.52**	**2.08**	**1.60**	**5.32**
NO_3^-	1.37	n.d.	22.6	9.09	5.43	14.2
SO_4^{-2}	1.33	1.87	**90.9**	**53.5**	**49.0**	**292**
PO_4^{-3}	0.53	n.d.	7.17	2.05	0.87	n.d.
Total mass, µg	16	10	270	129	92	508
Mass, minus blanks, µg	—	—	255	118	80	498
Charge Balance, %			43.1	31.3	12.4	21.2

Hope Creek Samples: SEM/EDS Analysis

Dust load highest on the top of the canister. Dust is dominantly aluminosilicate minerals. Few salts were observed; chemistry indicates that Ca-sulfate should be most the abundant soluble salt, but it was only rarely observed. Trace amounts of chloride salts, dominantly NaCl. Salts are not sea salts.







Hope Creek Chemical Analysis: Soluble Salts

Soluble salts are dominated by Ca-sulfate. Only trace amounts of chloride in most samples.

Dominant ions

Sample	Loc.	Depth, ft	Temp, °F	Amount present, µg/sample										SUM
				K	Ca	Mg	Na	NH_4^+	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	
144-008	Side	13.0	93.2	*0.8*	3.4	0.6	*0.1*	2.7		0.9	2.7		4.1	15.4
144-009	Side	7.5	116.5	1.7	4.5	0.5	*0.1*	2.7		0.9	6.4	*1.1*	6.5	24.3
144-010	Side	1.0	133.9	1.4	4.2	0.4	*0.4*	2.4		1.2	5.0		4.4	19.4
144-013	Top	0.0	138	18	102	33	42	2.8	0.4	4.2	19	4.8	91	317
144-014	Top	0.0	141.2	6.4	29	8.0	13.4	2.7	0.4	18	7.3	*1.3*	55	142
144-003				*0.6*	2.2	0.4		1.4		*0.5*	3.3	1.2	2.1	11.6
144-004				*0.3*	3.2	0.6		2.9		0.8	1.8	*0.5*	1.7	11.8
145-006*	Side	13.0	70.6	2.2	4.4	0.6	*0.5*	2.3		2.2	8.1		4.7	25.1
145-007	Side	7.5	100.8	1.0	2.4	0.6	*0.7*	2.9		2.1	2.2	*0.7*	5.3	17.9
145-014	Side	1.0	130.3	*0.9*	3.2	0.8	*0.6*	3.2		1.2	2.5		9.1	21.5
145-013**	Top	0.0	174.1	15	91	30	32	2.8		2.2	15	3.5	82	273
145-011**				*0.2*	2.3	0.3		3.0		*0.7*	1.3		1.7	9.6
145-002				1.2	4.8	0.5		2.7		*0.7*	5.9	*0.8*	2.0	18.5
SS-Bl-8 min-1					1.3	0.2		1.1		*0.4*	1.6		*0.6*	5.1
SS-Bl-8 min-2					1.2	0.2		1.5		*0.7*	*0.9*	*0.5*	*0.2*	5.2
SS-Bl-15 min					1.5	0.5		5.7	0.2	*0.7*	1.1	1.6	1.7	12.9

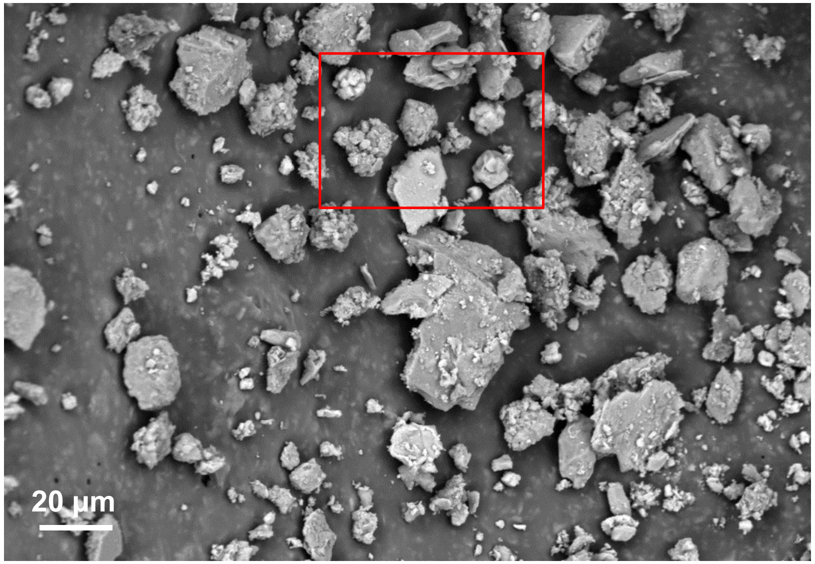
* Pad only damp

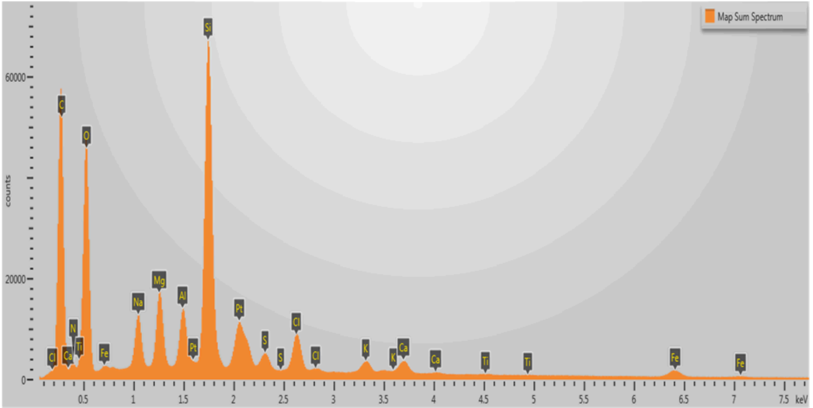
** Pad only partially saturated

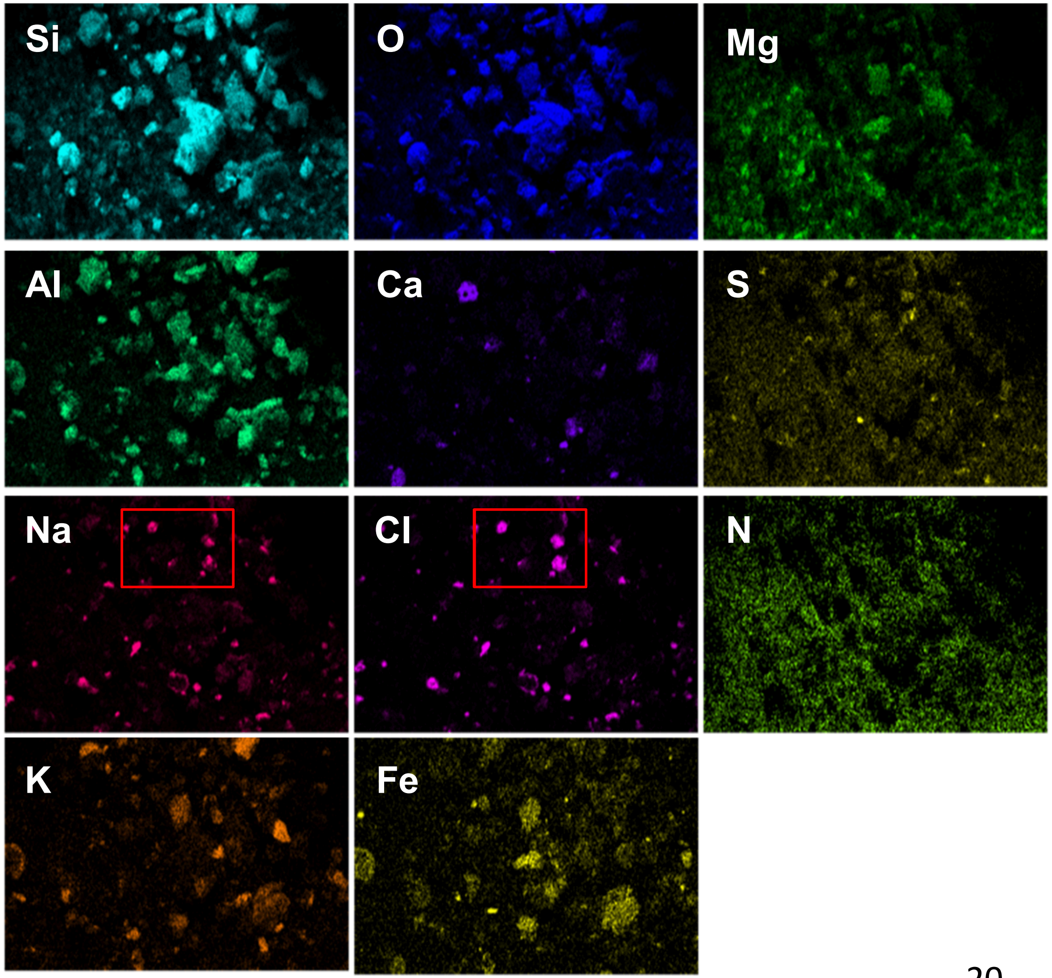
🟨 >10 µg/sample

Diablo Canyon Samples: SEM/EDS Analysis

Dust load highest on the top of the canister. While aluminosilicates are abundant in the dust, aggregates of sea salts are very common (see Na and Cl element maps).

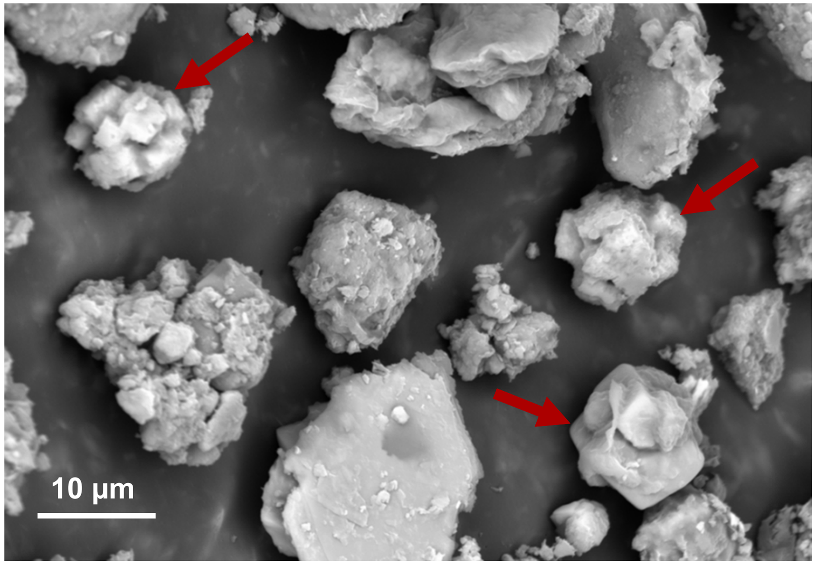


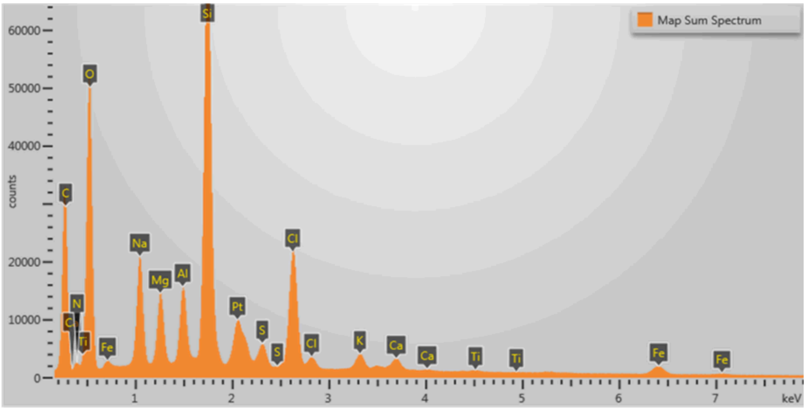


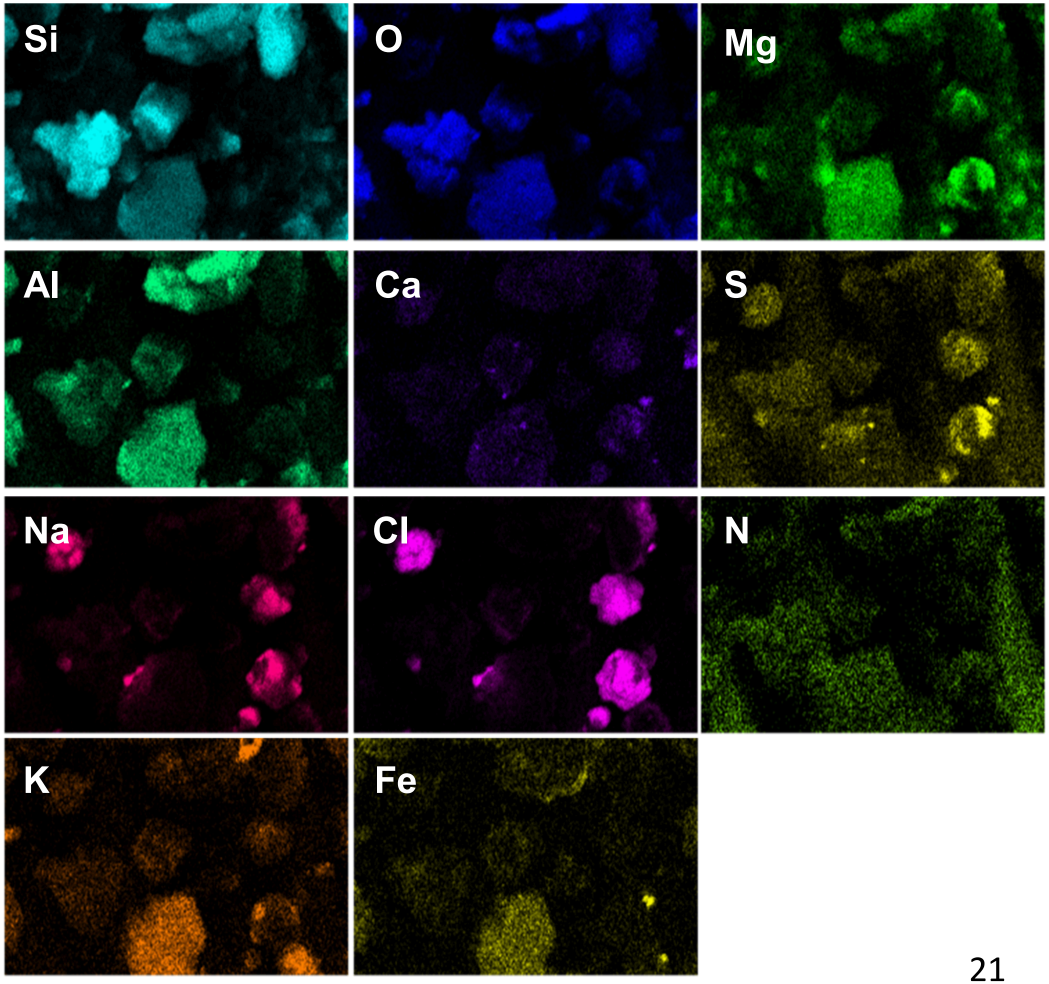


Diablo Canyon Samples: SEM/EDS Analysis

Sea-salt grains are spherical aggregates or crystals of NaCl and Mg-sulfate. They formed as sea-spray droplets dried while entrained in the atmosphere, possibly after being drawn into the heated environment within the overpack.







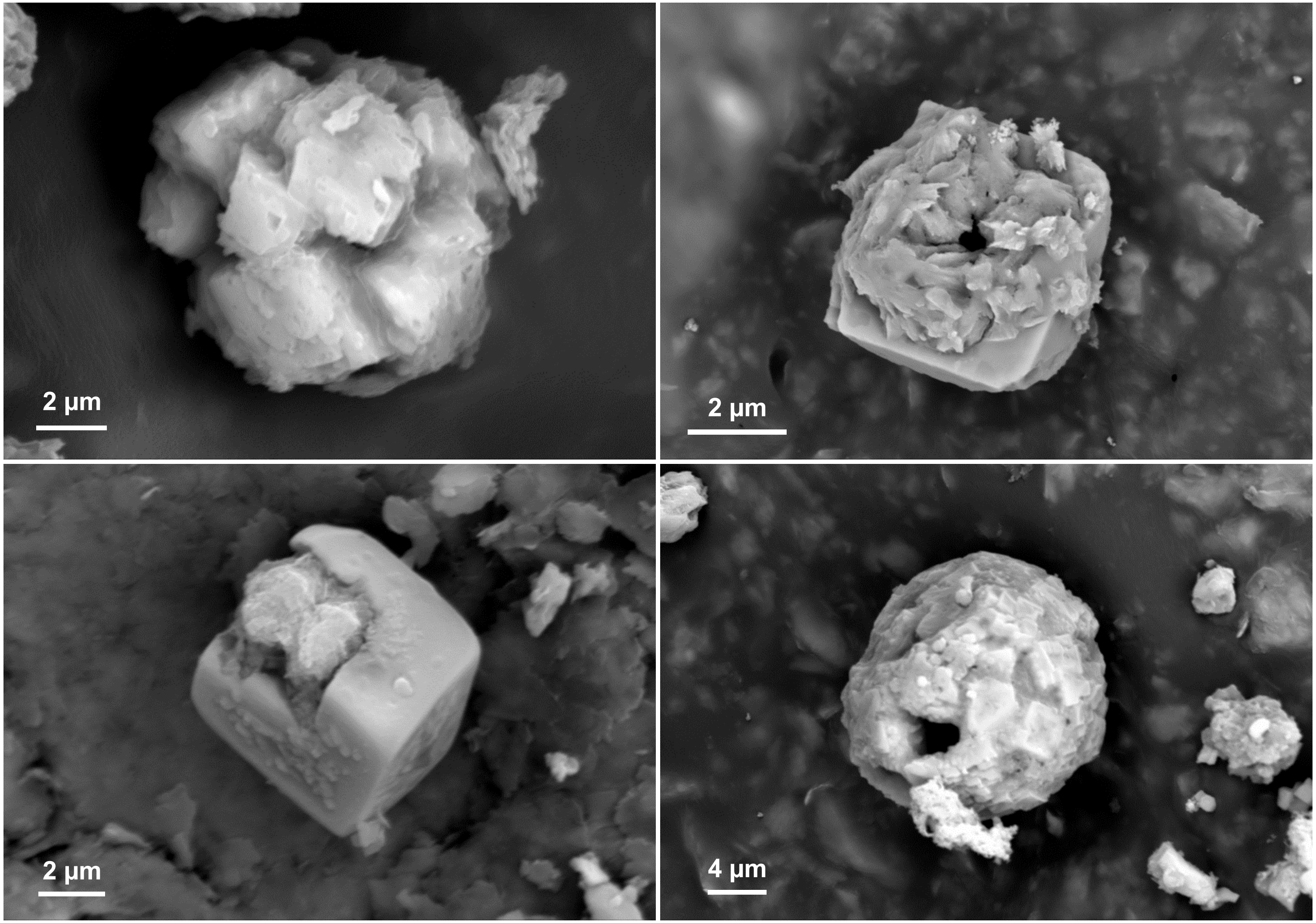
Diablo Canyon Samples: SEM/EDS Analysis

Sea salt aggregates. Dominant minerals are sodium chloride (cubic crystals), and Mg-sulfate (sheaf-like crystals and masses between cubes)

Common morphologies:

- ***Spherical aggregates (hollow)***
- ***Euhedral crystals***
- ***Skeletal and hopper crystals***

- ***Size range—aggregates are generally coarse (PM10 fraction or larger), but many finer (PM2.5) particles are present as well.***



Conclusions

- SCC of 304SS interim storage canisters for SNF requires a corrosive environment to develop on the canister surface:
  - Aqueous conditions via deliquescence
  - A corrosive (Cl-rich) salt assemblage/brine
  - Concentrations exceeding a chloride threshold?
- Accurate prediction of the occurrence of these conditions requires:
  - Temperature maps of the canister surface through time.

    Function of loading, fuel burnup, time out of reactor, ambient temperature, and other parameters.
  - ISFSI site-specific ambient absolute humidity data
  - Site-specific aerosol composition data

    Proximity to the ocean may not be a good discriminant. At two of three "near-marine" ISFSIs tested, salts were dominantly inland salts, not sea salts.
  - Chloride deposition model. Requires:
    - Aerosol particle deposition model that captures overpack/canister geometry and ventilation flow patterns, range in particle sizes, change in aerosol aerodynamic and sticking properties deliquesced droplet dries to salt minerals.
    - Thermodynamic/kinetic model that captures reactions with atmospheric components leading to chloride gain/loss.
- Limited field data indicate that in at least some near-marine ISFSI locations, sea salts are comprise a large fraction of dusts deposited on canister surfaces. Once deliquescence occurs, SCC will be possible.

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