

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

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Presentation for the 5th International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems

Asahikawa, Hokkaido, Japan



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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:

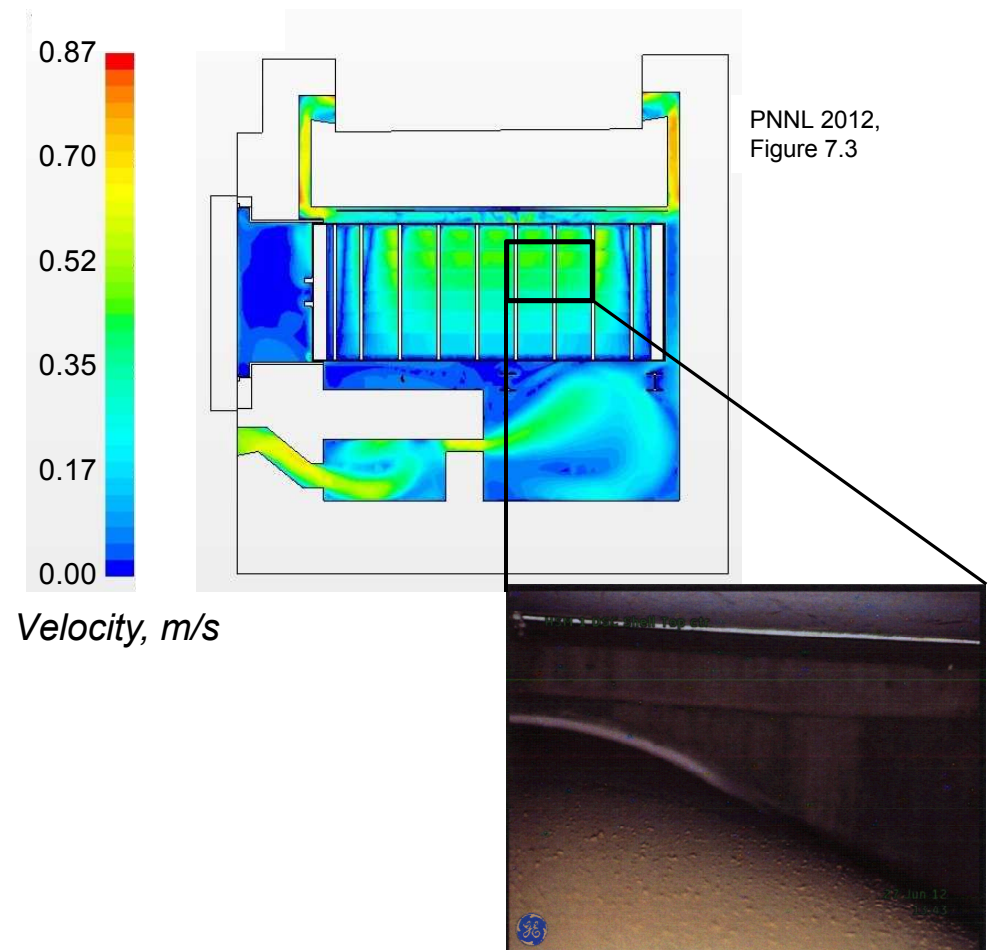
- Presence of an aqueous solution

- 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)

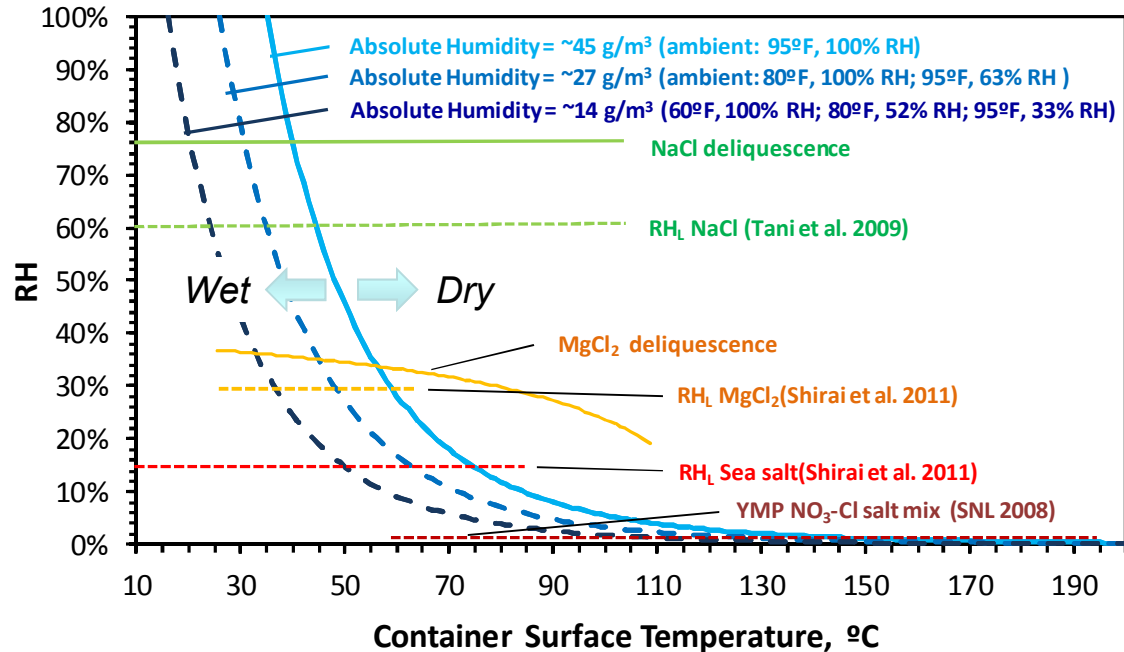
- Salt deliquescence and brine composition are dependent on:

- Temperature at the container surface
 - Relative humidity at the container surface
 - Composition of deposited salts




Parameters Controlling Deliquescence: Temperature, RH, composition

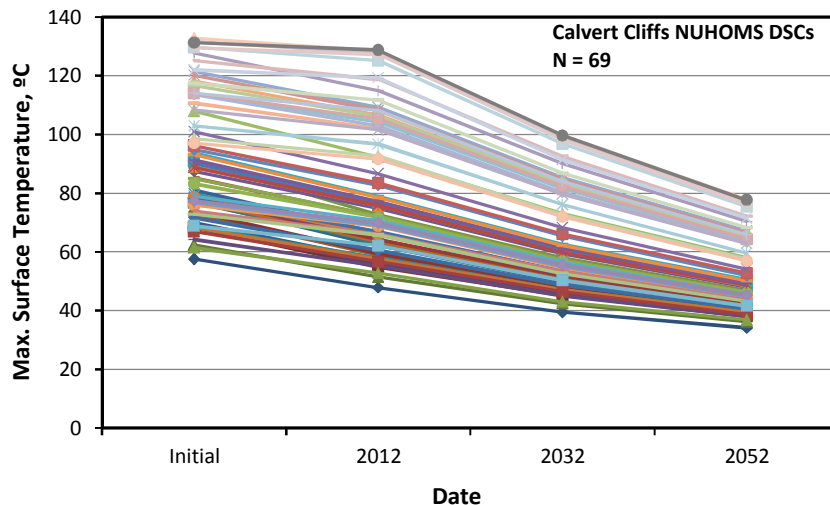
- Salt assemblages have a minimum RH at which they deliquesce (RH_d)
- $RH = P_{\text{water vapor}} / P_{\text{sat}}$
- $P_{\text{water vapor}} = f(\text{Abs. Humid}_{\text{outside air}})$
- $P_{\text{sat}} = f(T_{\text{WP surface}})$
- During cooling, T decreases and $RH_{\text{WP surface}}$ increases 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°C

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., °F	Max. shell T, °C	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	
NUHOMS HSM-HD	24PTH-S-LC	24.0	117	176	C
	32PTH ⁽²⁾	34.8	115	208	
	32PTH ⁽³⁾	32.0	115	201	
HI-STORM	32PTH ⁽⁴⁾	26.1	115	187	D
	MPC-68	38.0	80	233	
	MPC-32	38.0	80	242	

⁽¹⁾Flat stainless steel heat shields

⁽²⁾Finned Al side shields

⁽³⁾Unfined Al side shields

⁽⁴⁾galvanized steel side shields

^ANAC-UMS FSAR, Revision 5 (2005)

^BNUHOMS FSAR, Revision 10 (2008)

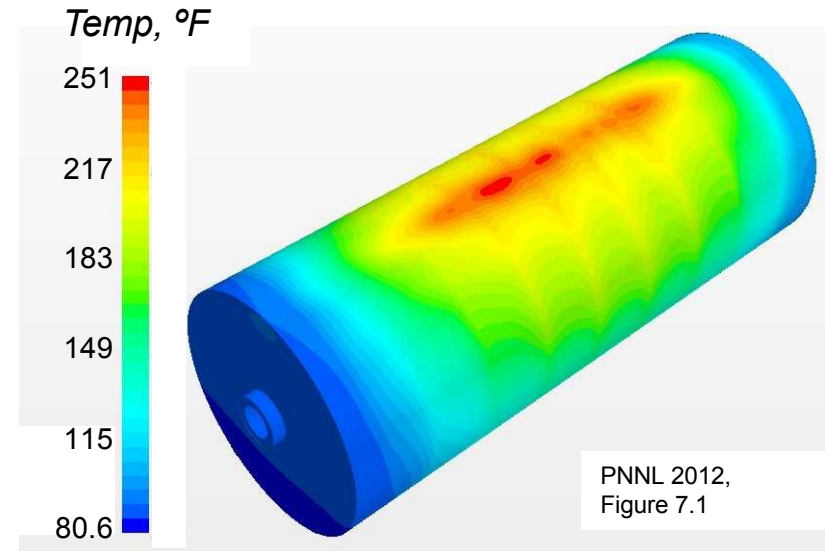
^CNUHOMS-HD FSAR, Revision 0 (2007)

^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 ($>90^{\circ}\text{C}$) on the surface
 - Seasonal temperature fluctuations correspond to similar-magnitude container surface temperature fluctuations

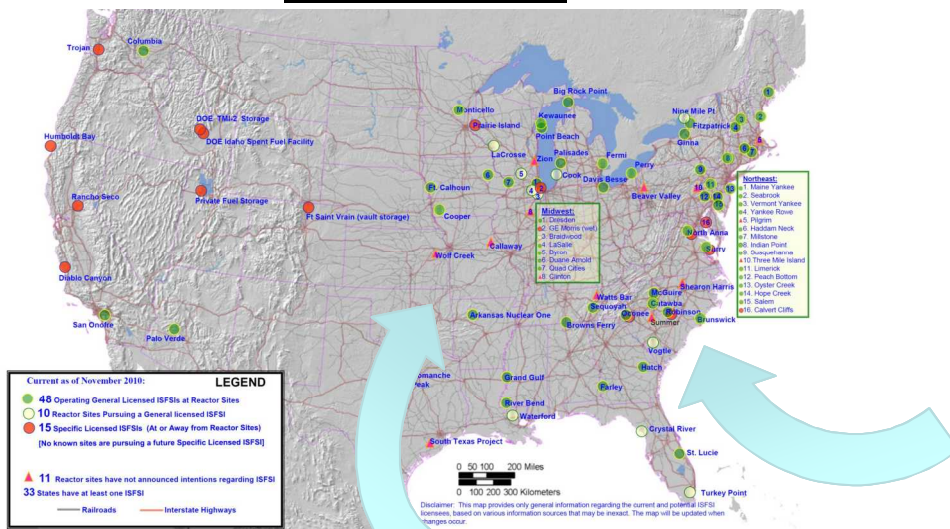
- Timing of initial deliquescence and potential for SCC ($<80\text{--}85^{\circ}\text{C}$) will vary greatly over the container surface
- Corrosion, SCC penetration models based on “time of wetness” would have to be location-specific on the storage container surface



Chemical Environments:

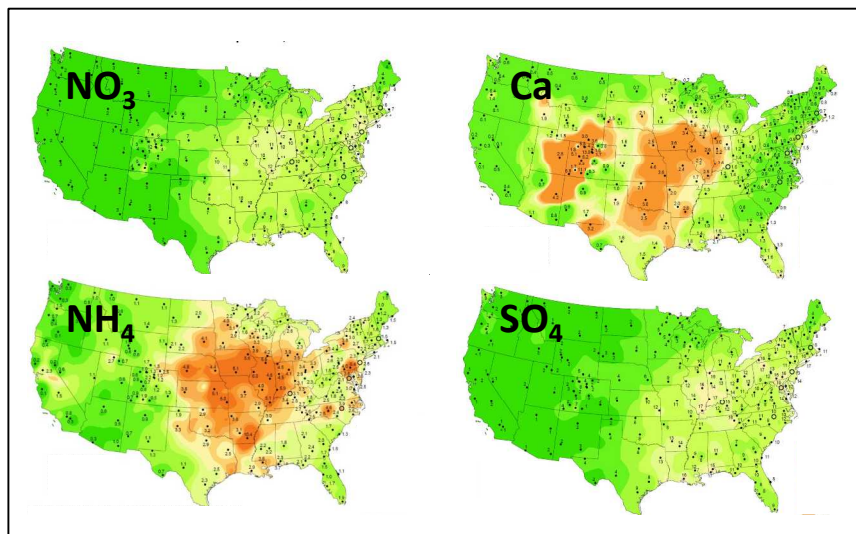
Expected salts vary with location

U.S. ISFSI sites

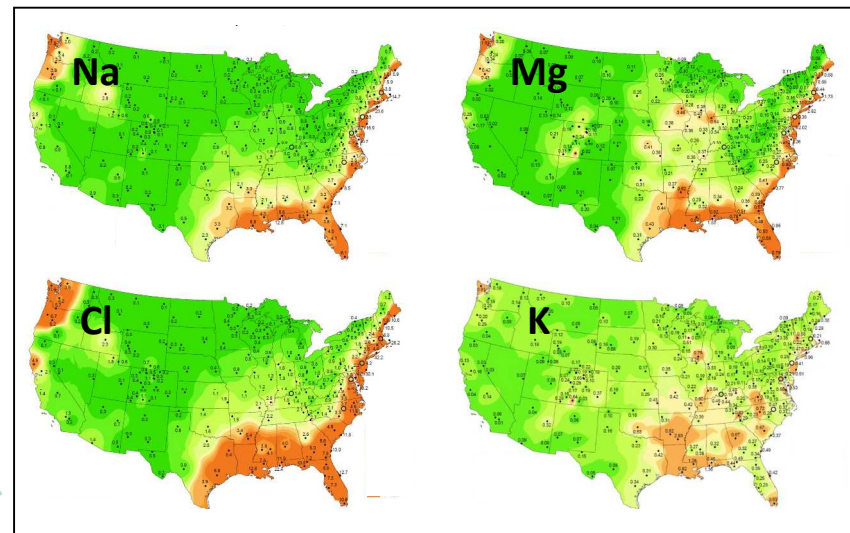


Source: U.S. NRC website

Salt components enriched at inland sites



Salt components enriched in near-marine environments



U.S. National Airfall Deposition Program (NADP) wet deposition maps

Parameters Controlling Deliquescence: Salt Composition

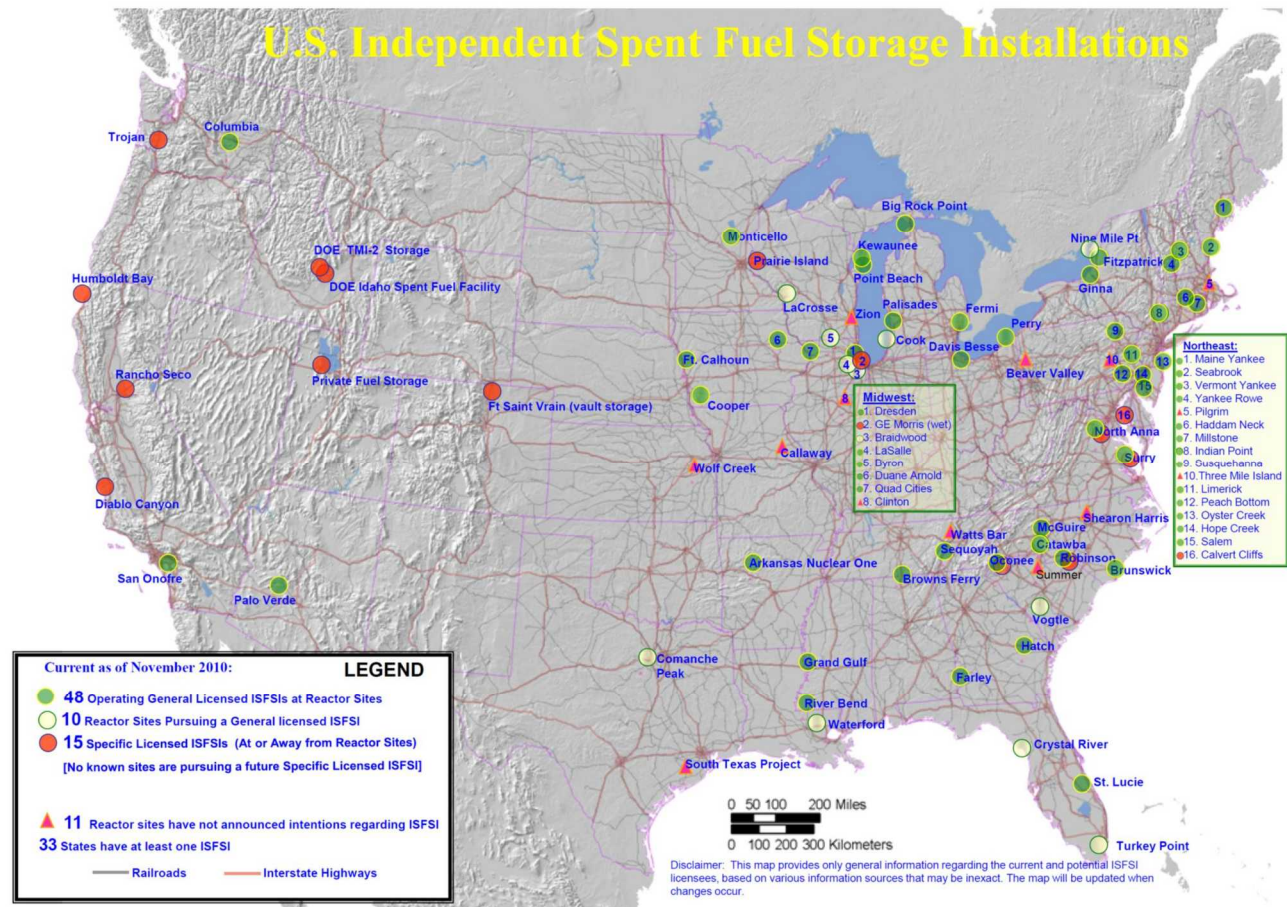
Storage sites can be grouped into two general categories

■ Near-marine

- A large component of sea salt in dust/aerosols

■ Inland

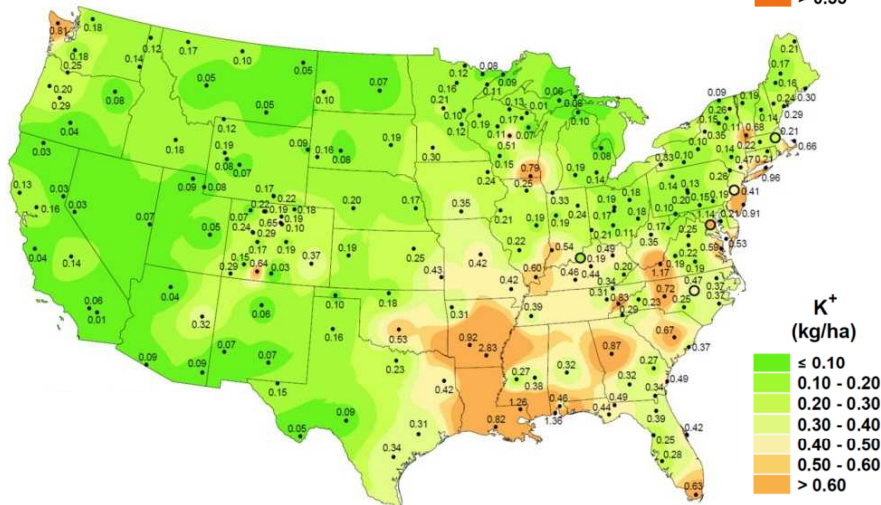
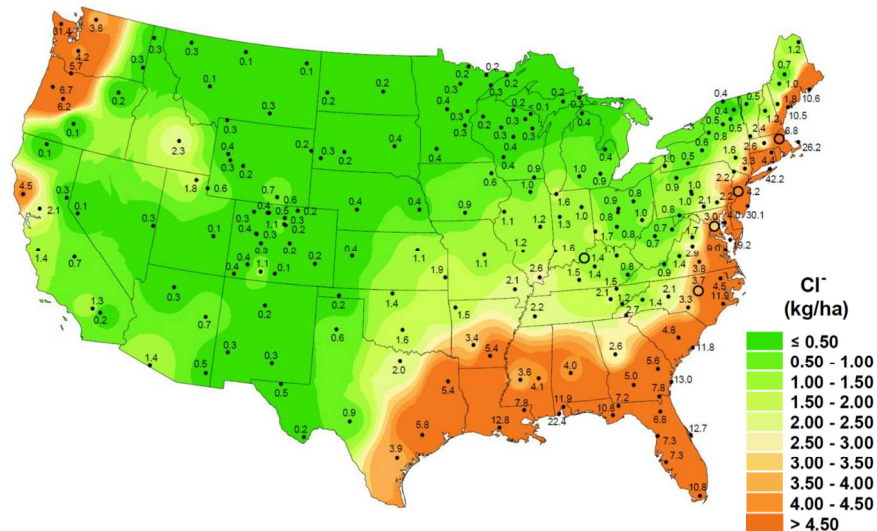
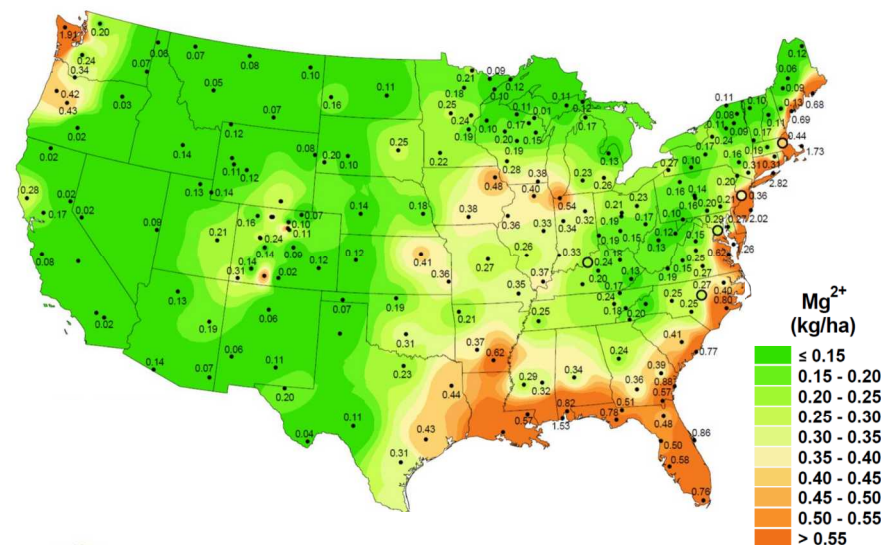
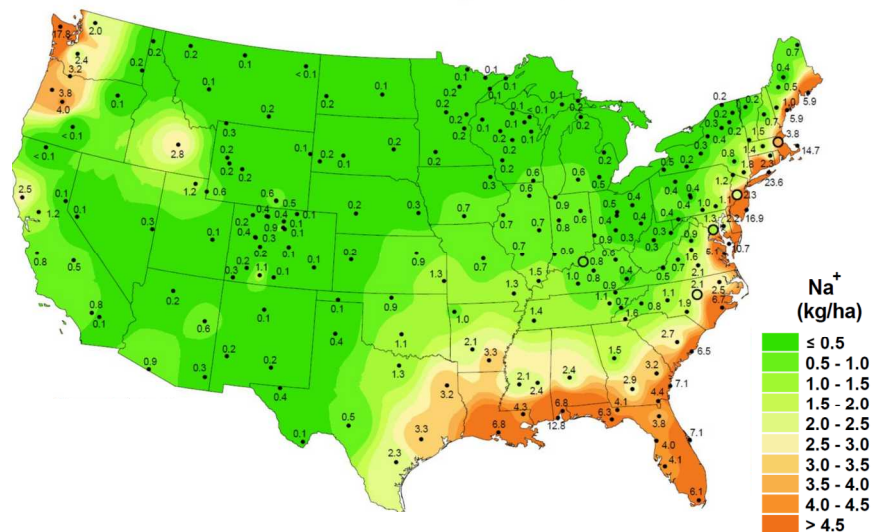
- Salts largely derived from anthropogenic activities, terrestrial sources, and atmospheric reactions with marine salts



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

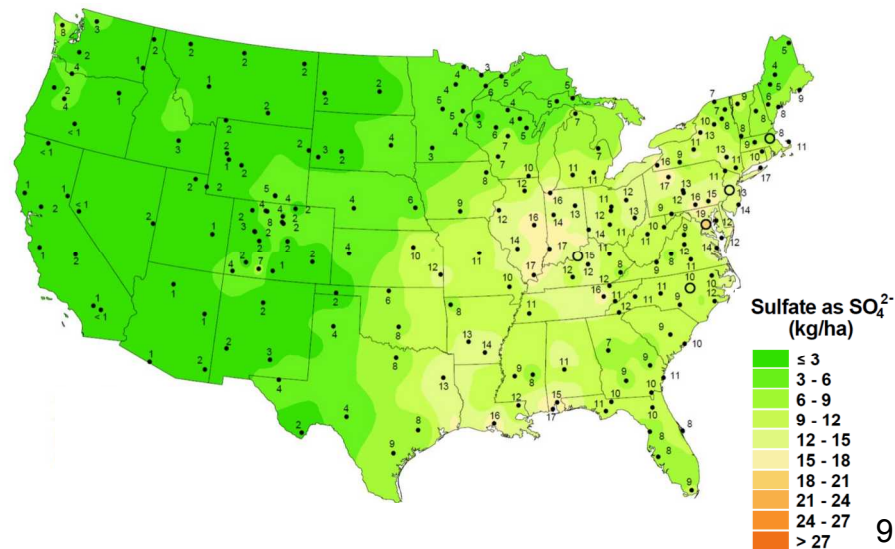
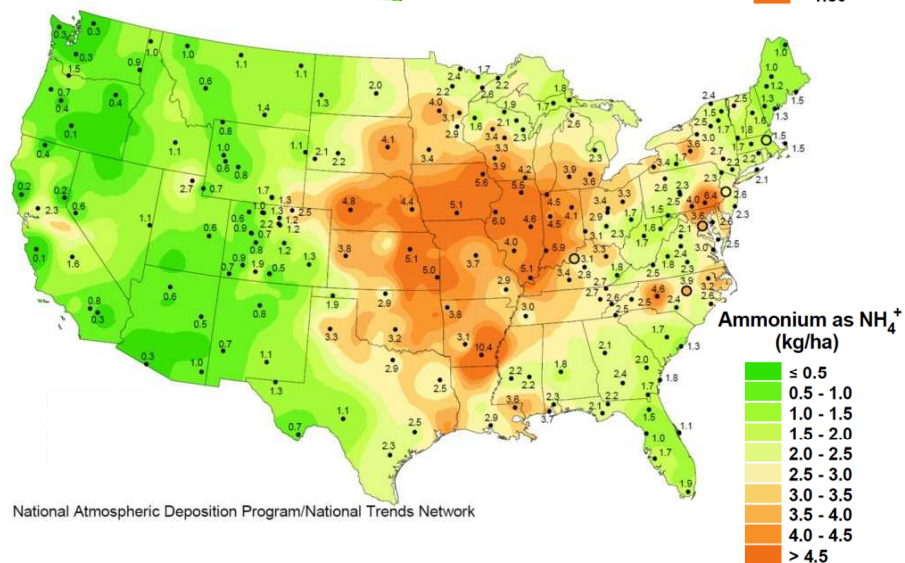
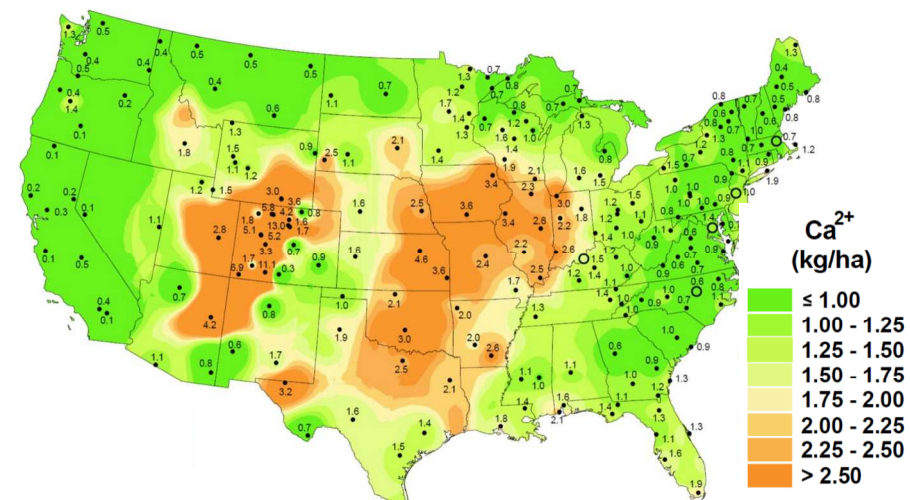
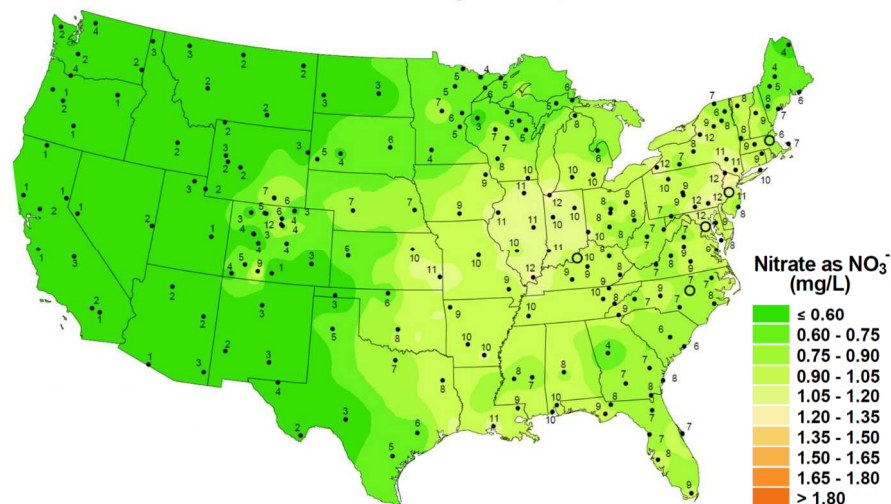
Salt compositions: Species enriched in near-marine areas

NADP wet deposition maps



Salt compositions: Species enriched at inland sites

NADP wet deposition maps

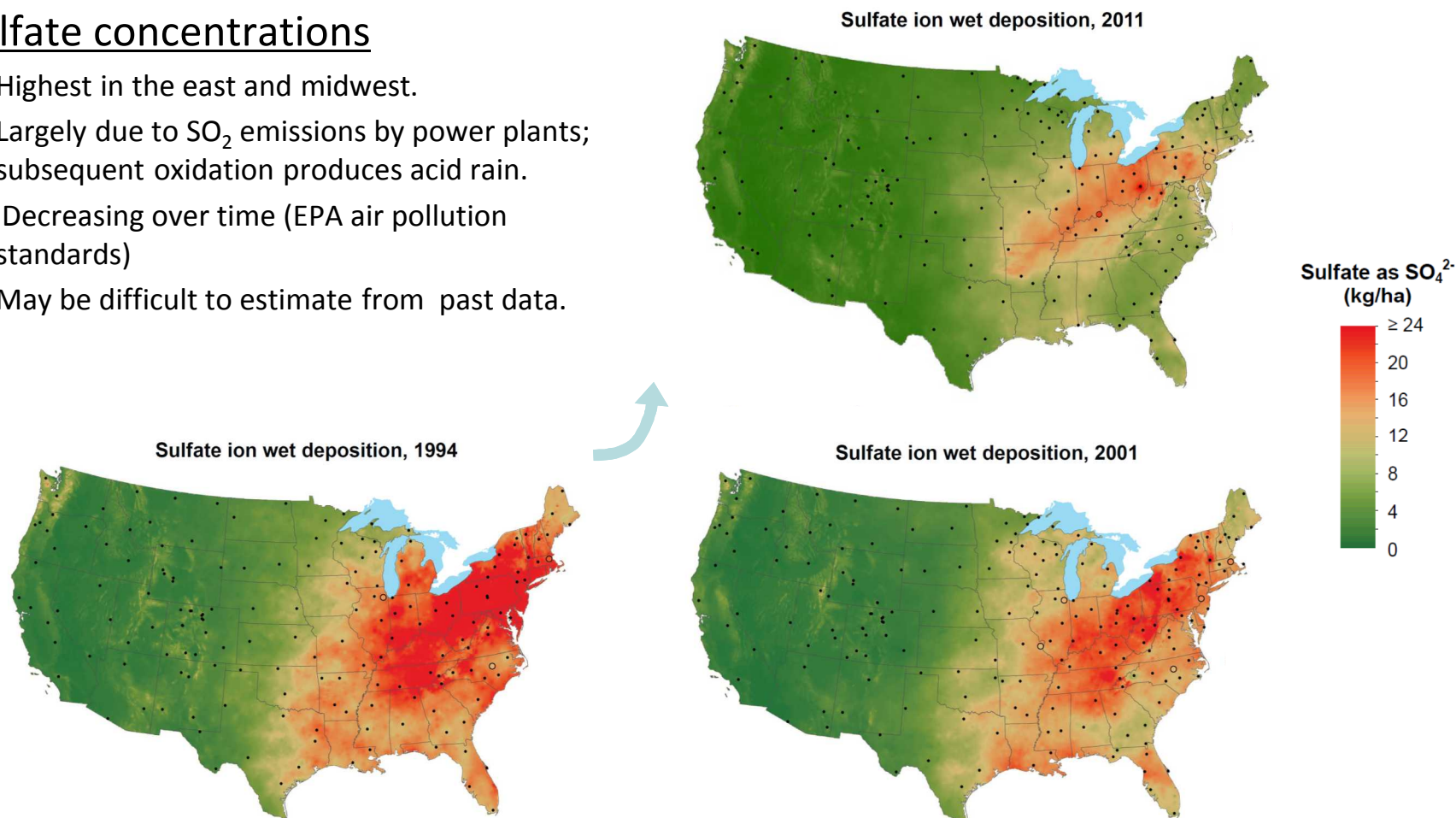


National Atmospheric Deposition Program/National Trends Network

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.



SCC Experiments with Sea Salt and Sea Salt Components

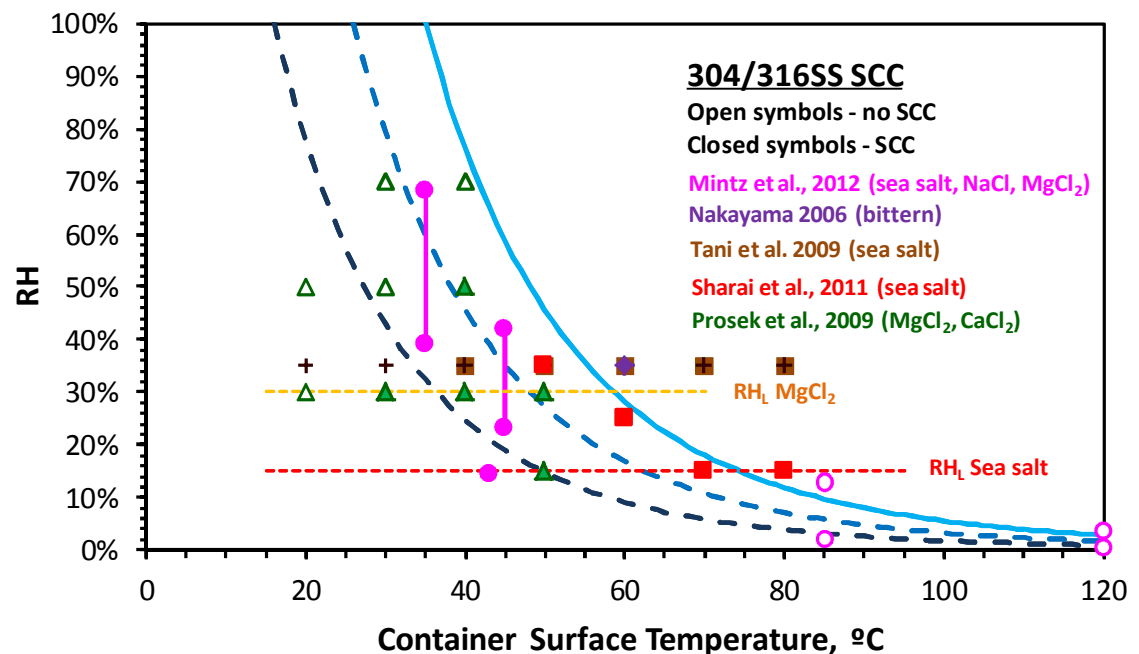
Sea salt/spray—generally simulated with synthetic ocean water (ASTM D1141-98)

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

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., $\mu\text{eq/L}$
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)

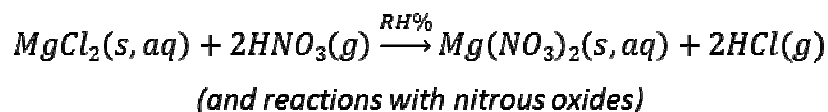
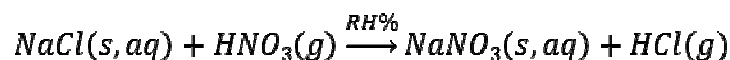
- Recent NRC/CNWRA scoping study assessed corrosion by NH_4NO_3 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and $[\text{NH}_4\text{NO}_3 + (\text{NH}_4)_2\text{SO}_4]$ mixtures (He et al., 2013)
 - U-bend samples of as-received, sensitized, and welded 304SS
 - Tests at 35°C, 72% RH; 45°C, 44% RH
 - Samples exposed to NH_4HSO_4 (very acidic solution; pH = -0.79) had extensive general corrosion; welded samples also showed grain boundary attack.
 - $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3$
 - $\text{SO}_4:\text{NO}_3 = 0.5$: minor pitting observed
 - $\text{SO}_4:\text{NO}_3 = 1.0, 3.0$: 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 (e.g., Gibson et al., 2006):



- Reactions are 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:



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

T (°C)	NH ₄ Cl			NH ₄ NO 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.

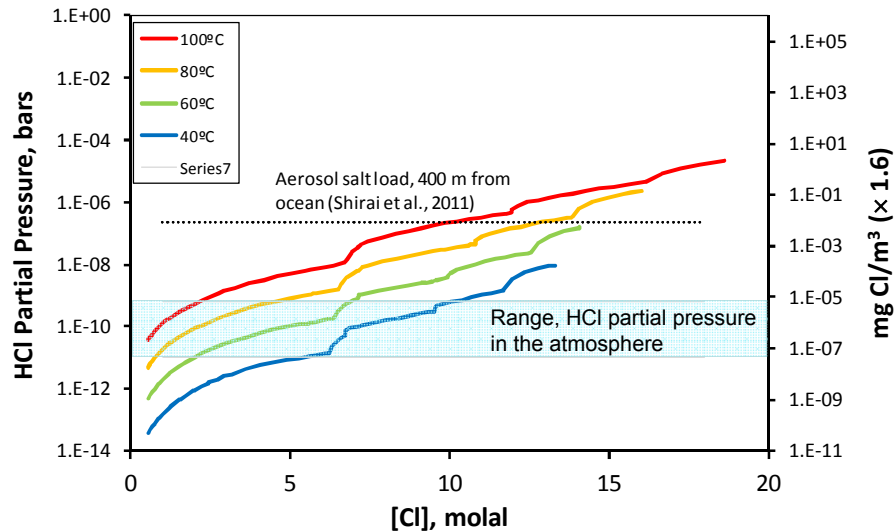
After deposition: once temperatures drop and deliquescence occurs:

- Salt deposition continues
- Ammonium salts
 - Ammonia/anion loss is no longer stoichiometric
 - 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
 - SO₂, nitric acid gas-to-particle conversion reactions resume
 - Acid degassing and adsorption of CO₂, 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)

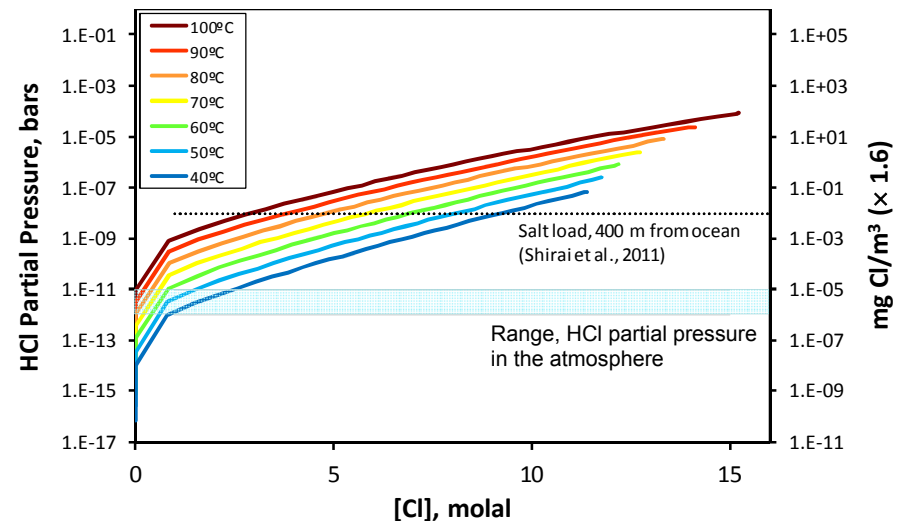
Acid Degassing After Deliquescence

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.

Summary: Existing environments may not be well constrained

- 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.

Sampling of In-service Interim Storage Canisters

Joint program with the Electrical Power Research Institute (EPRI)

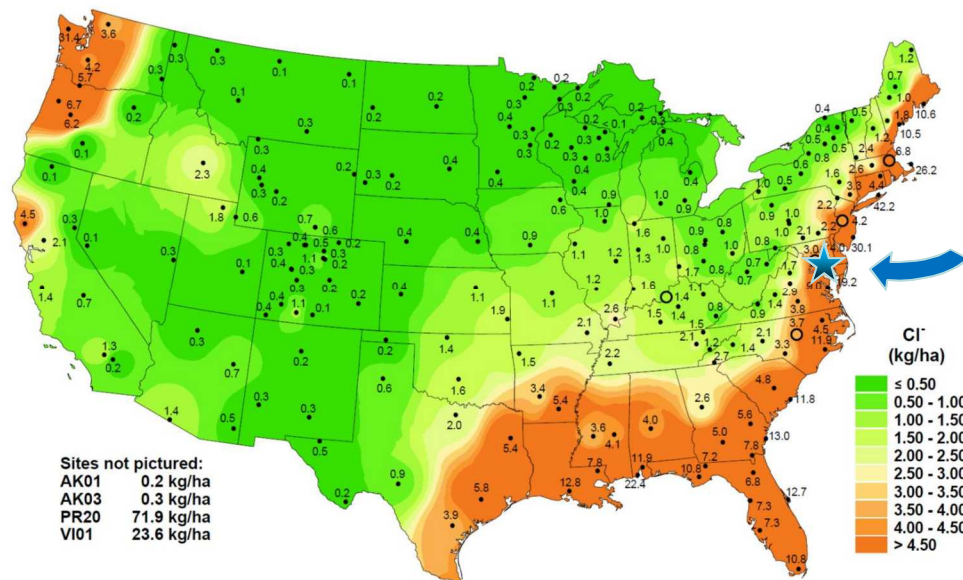
- EPRI collects dust samples, Sandia characterizes the samples via wet chemistry, XRF, XRD, SEM EDS, other methods.
- Analysis of samples from Calvert Cliffs ISFSI is ongoing. Two other sites, Hope Creek and Diablo Canyon, will be sampled soon

Calvert Cliffs ISFSI

- One overpack opened June, 2012
- Four samples collected with an abrasive pad/filter assembly
- 2 dust samples (#1 – 11:00; #4 – 7:00) sent to Sandia



NUHOMS horizontal storage system



Calvert
Cliffs site

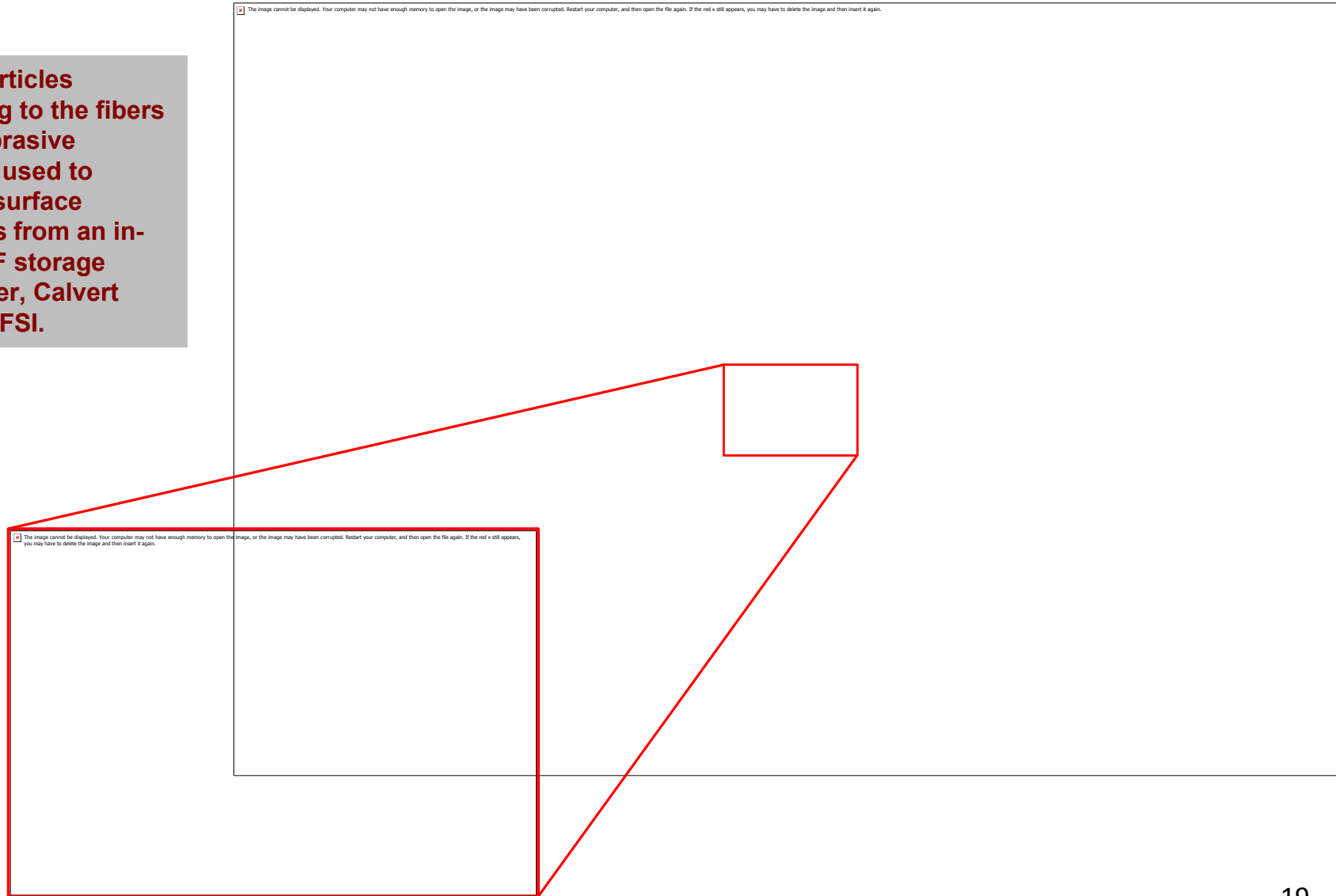


Dust on storage container surface

Chemical Environment

Sampling of dust on in-service storage canisters

**Dust particles
adhering to the fibers
of an abrasive
sponge used to
collect surface
samples from an in-
use SNF storage
container, Calvert
Cliffs ISFSI.**



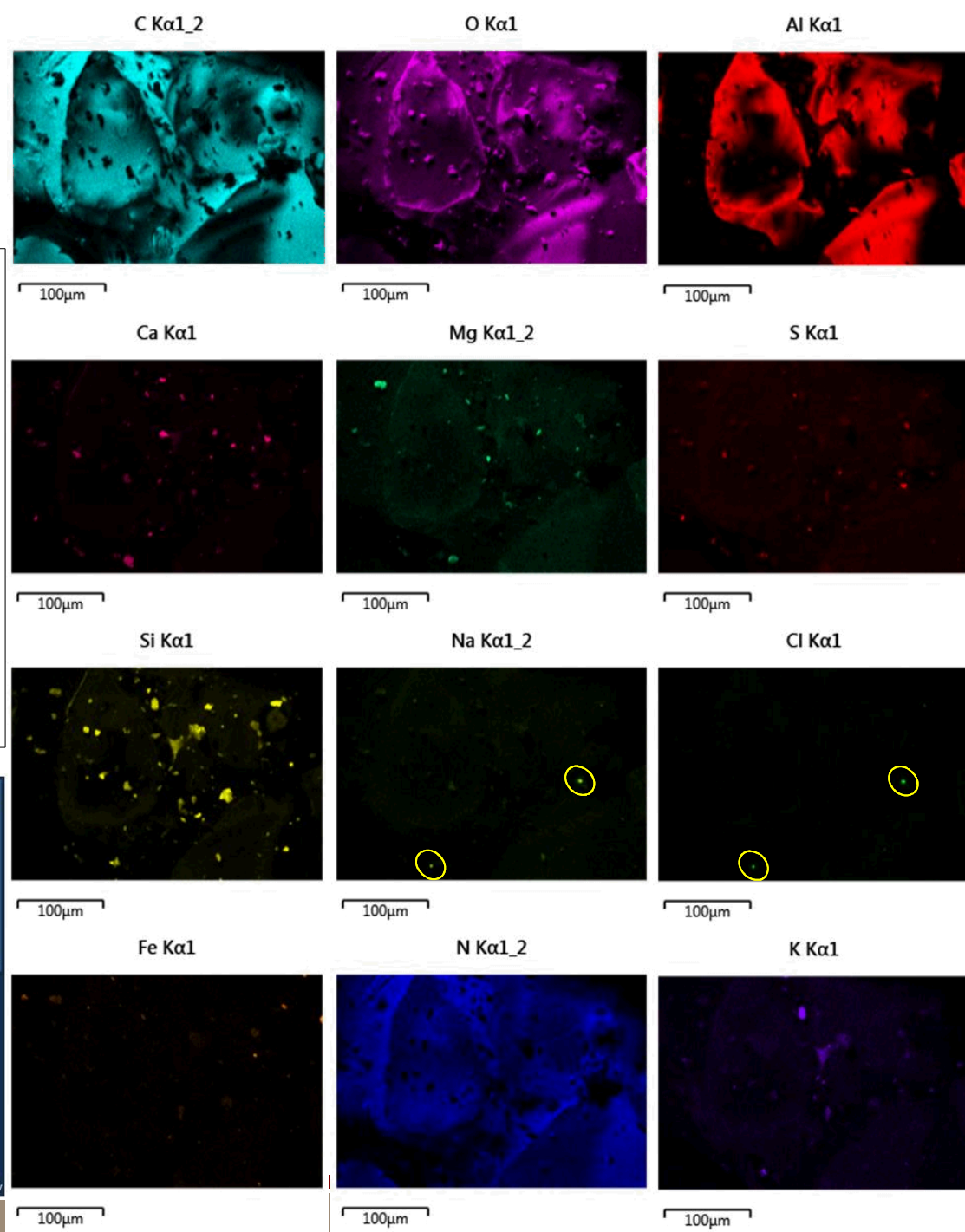
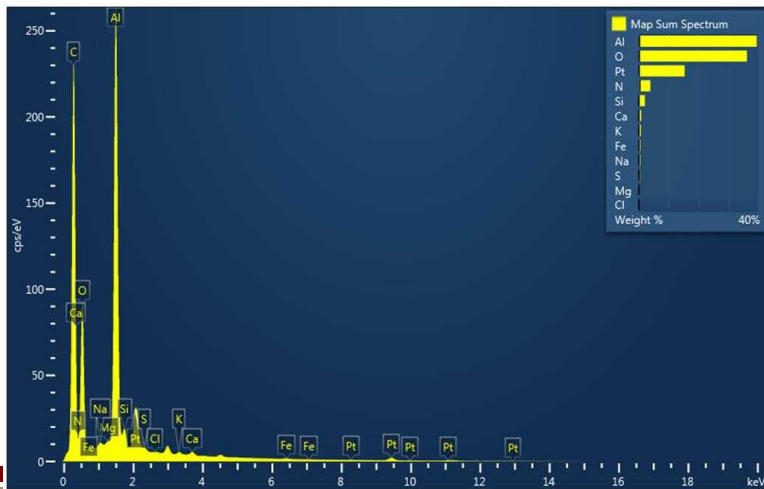
SEM/EDS Analysis

EPRI #1 Pad

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NaCl

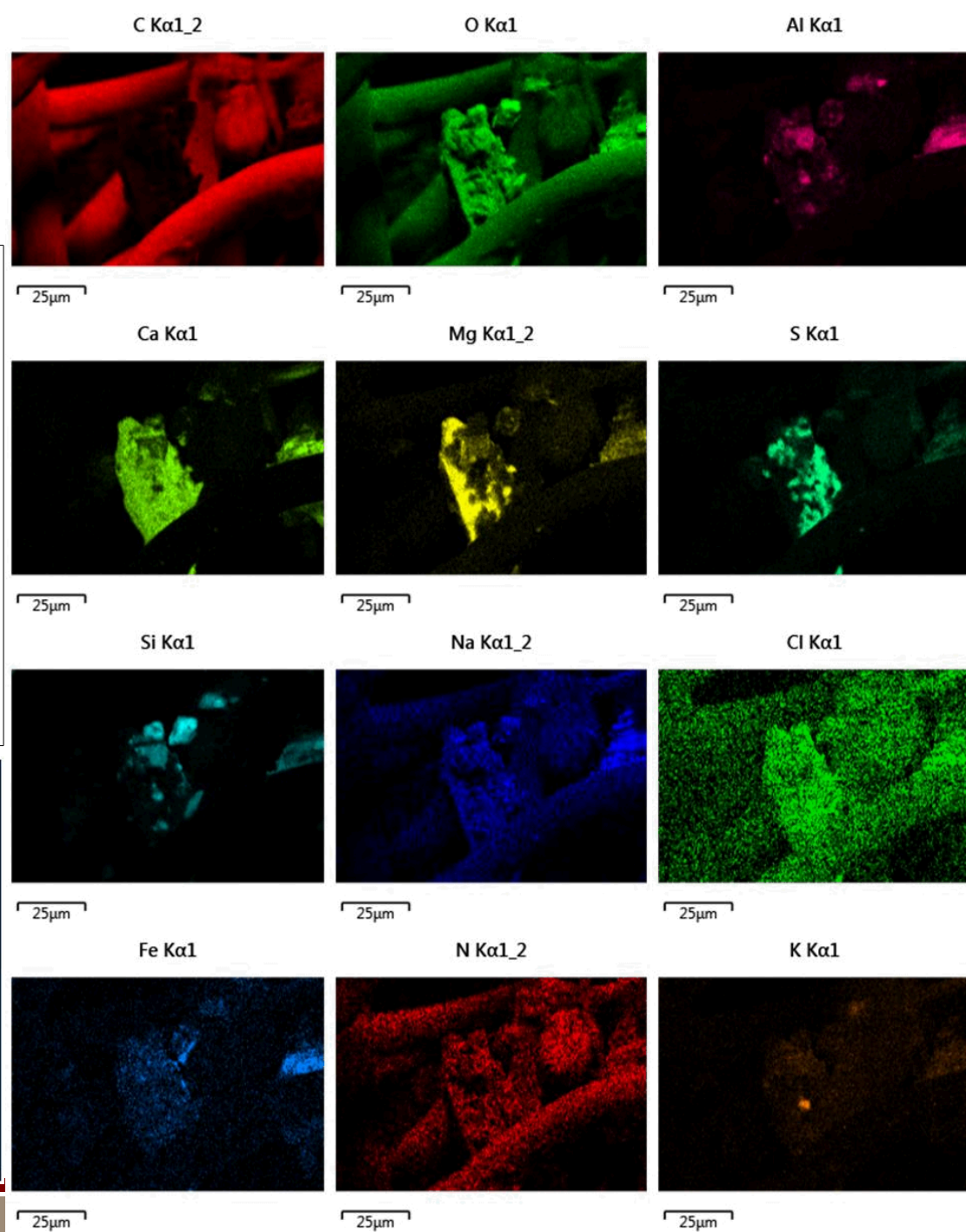
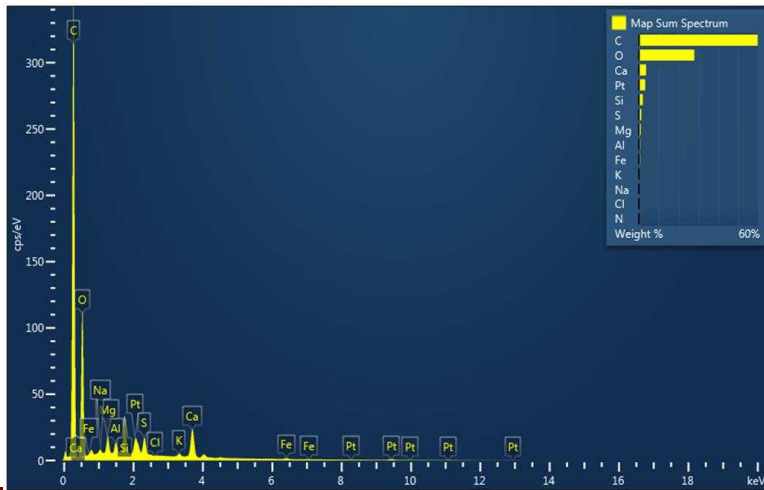
NaCl



SEM/EDS Analysis

EPRI #1 Filter

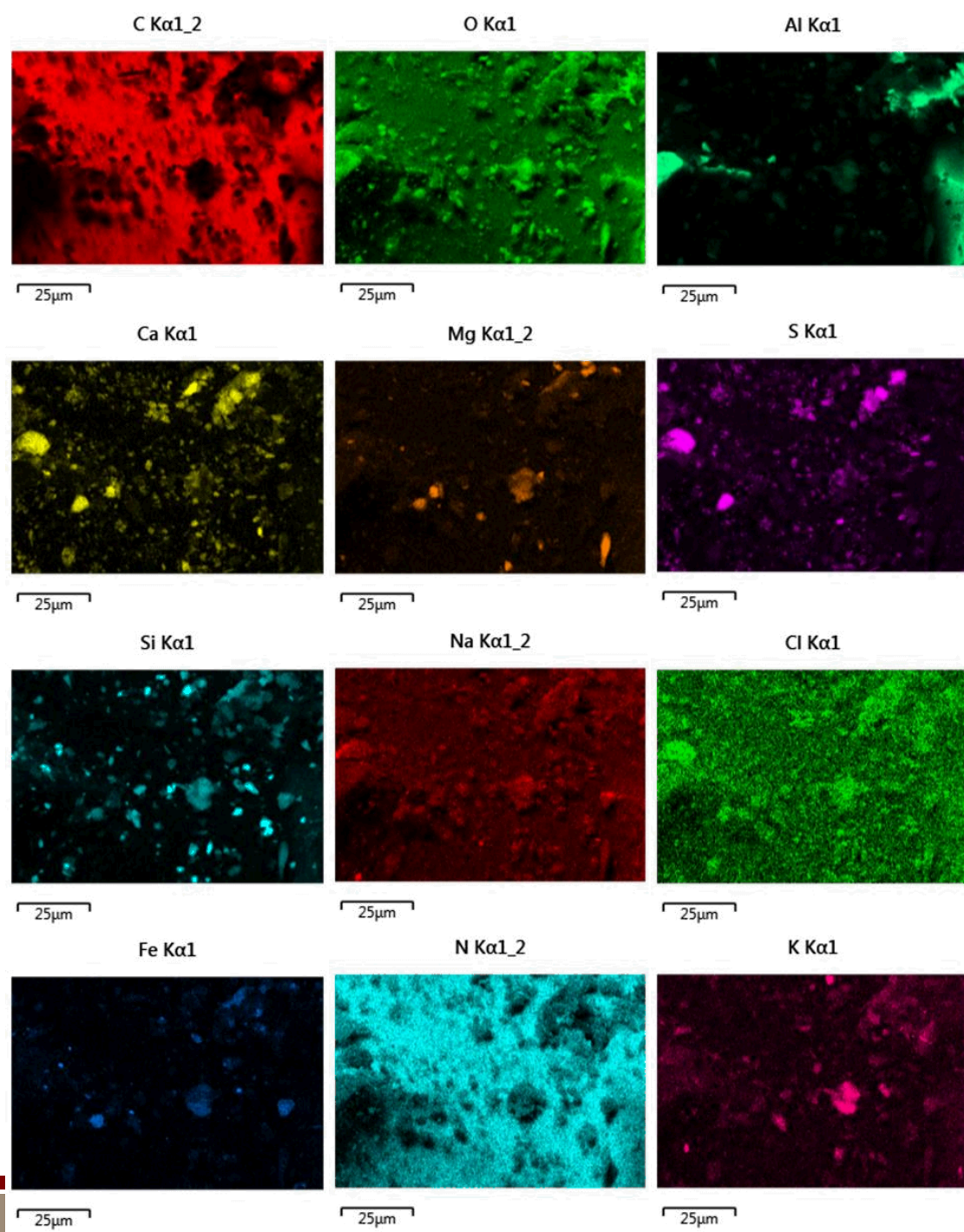
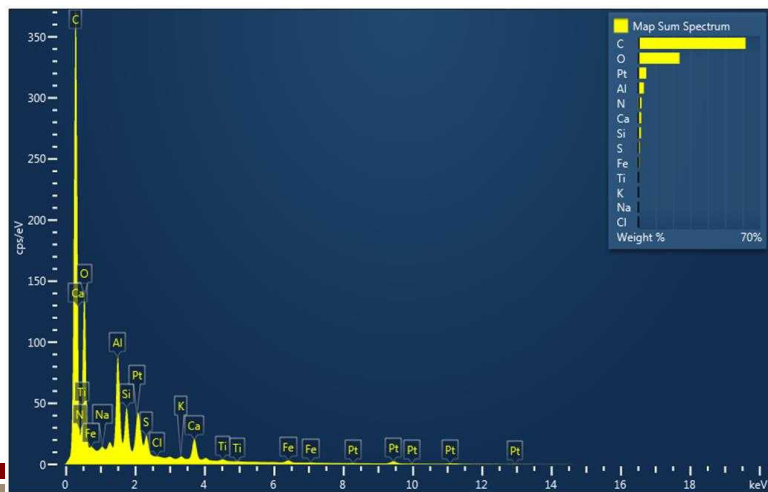
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SEM/EDS Analysis

EPRI #4 Pad

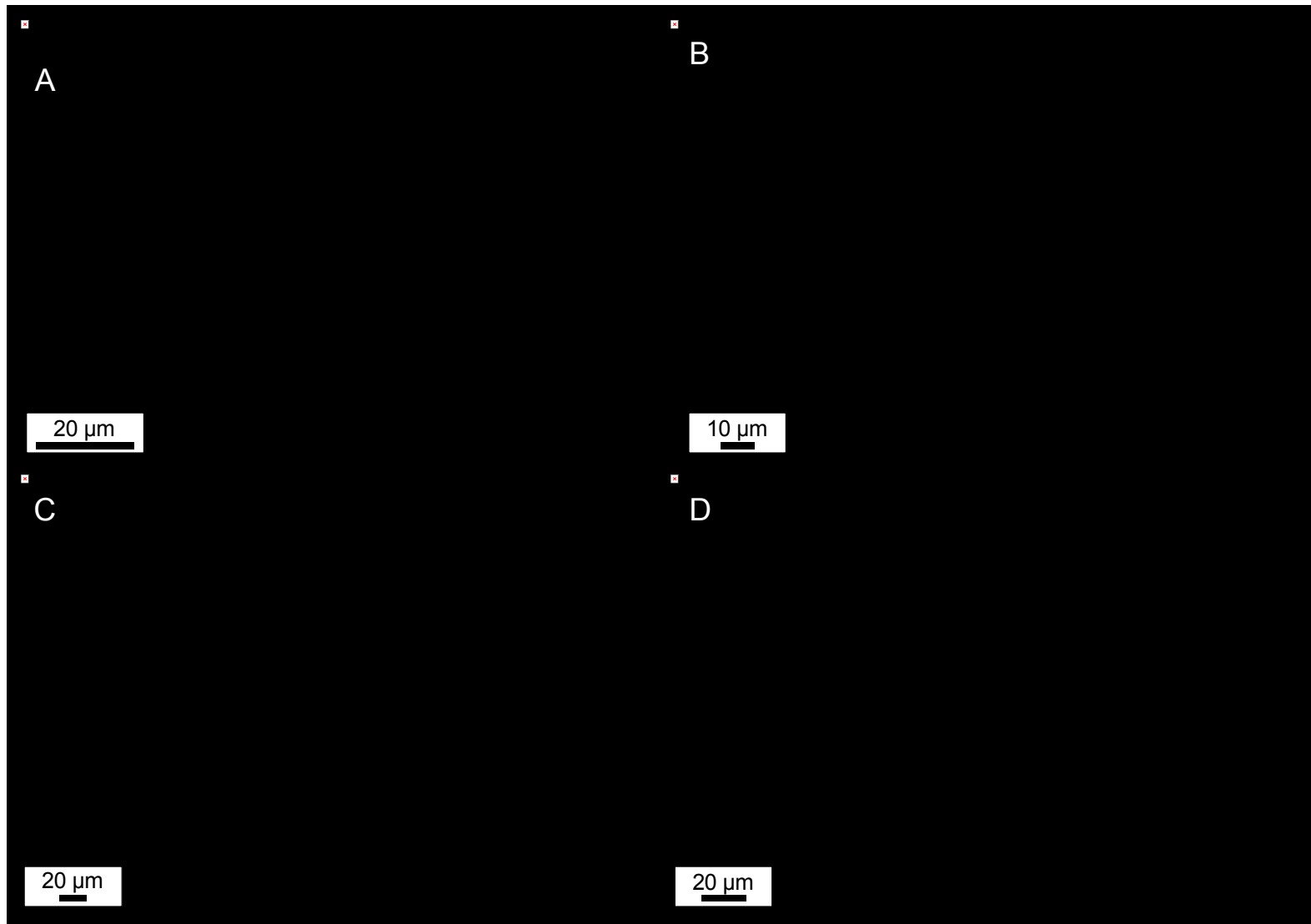
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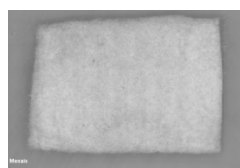
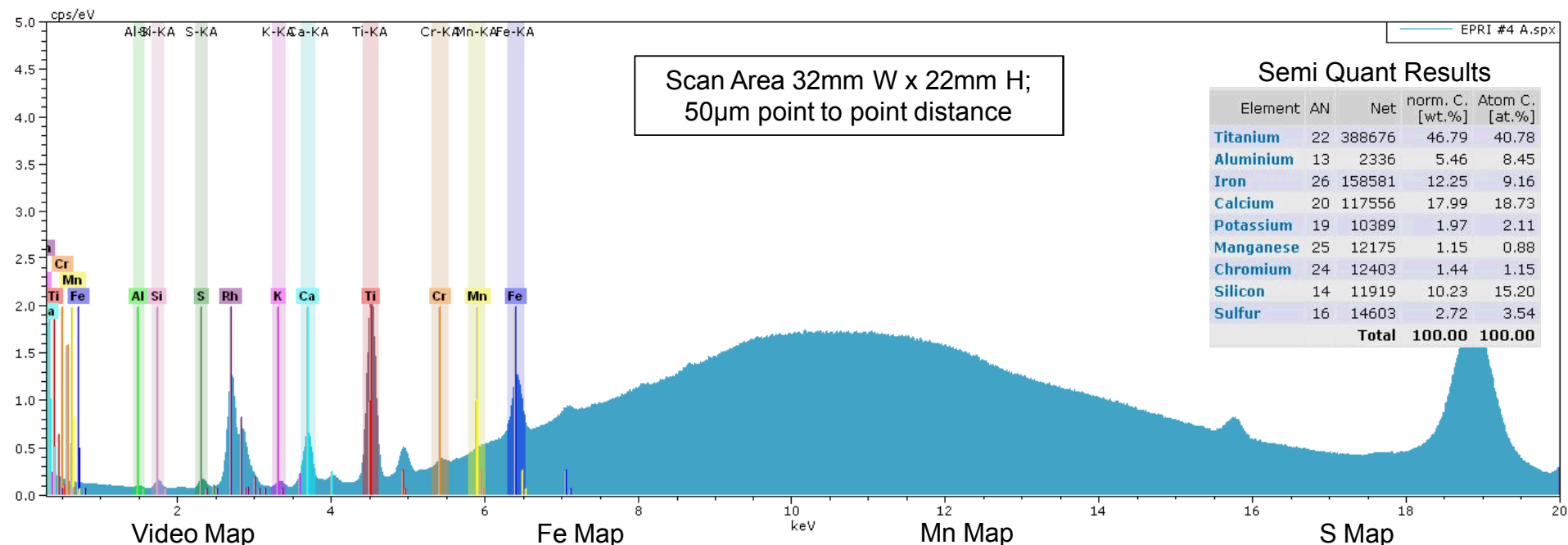
SEM/EDS Analysis

EPRI #1 Filter

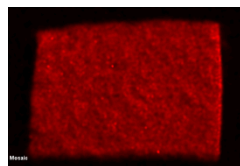
Coarse dust particles in the EPRI #1 sample (collected at the 11:00 position) are largely pollen.



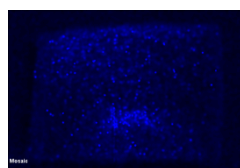
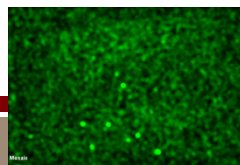
XRF Analysis: EPRI #4 filter



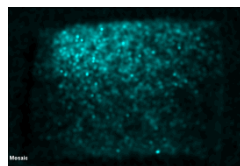
Ti Map



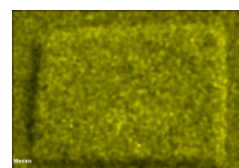
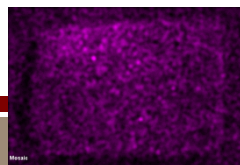
Al Map



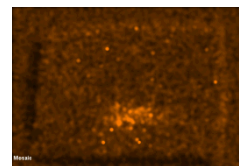
Ca Map



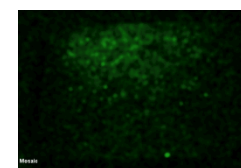
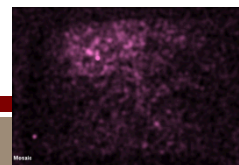
K Map



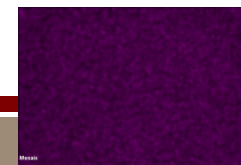
Cr Map



Si Map



Rh Map- X-ray tube source

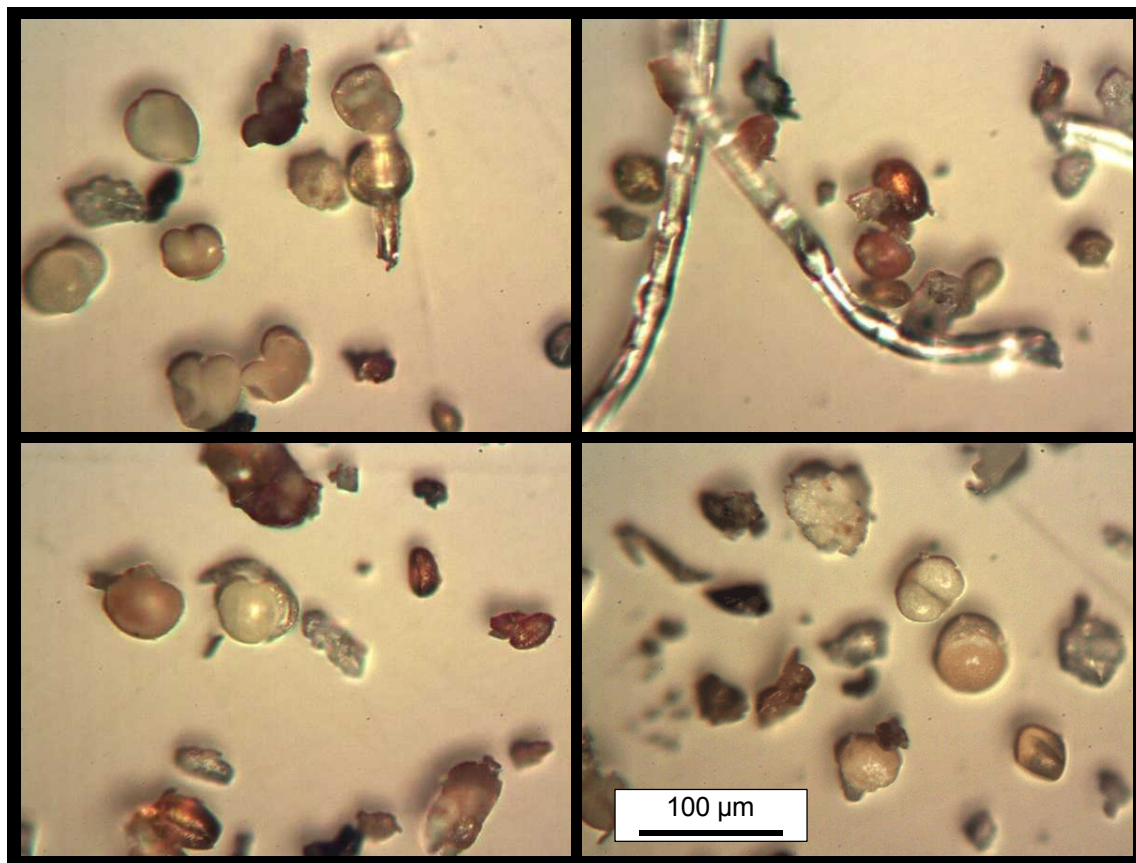
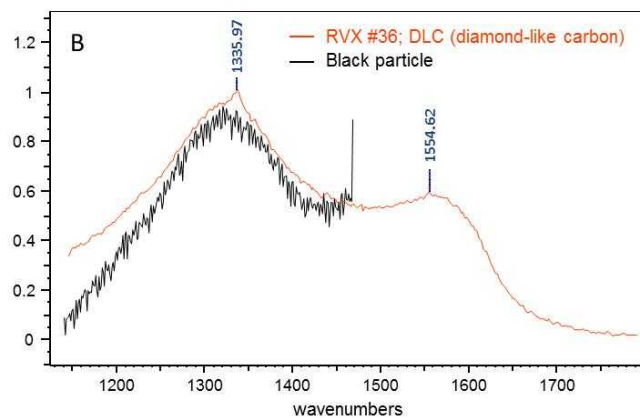
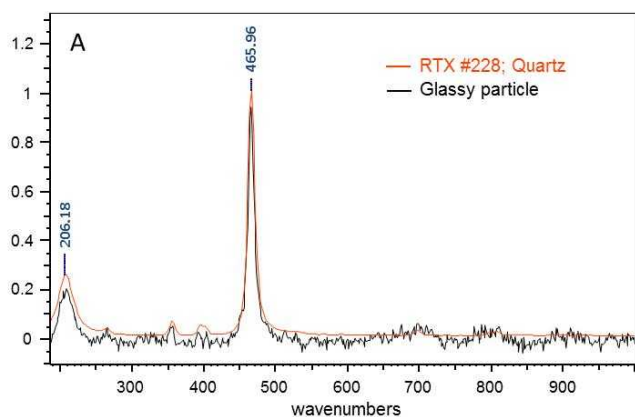


EPRI #1 Filter: Micro-Raman analysis

Photos taken during Micro-Raman analysis show that the coarse fraction of the dust consists mostly of pollen

Other phases identified:

- Quartz
- Soot



Chemical Analysis: Soluble Salts

Water soluble salts:

- 30 minute leach with deionized water
- Cations: $\text{Ca}^{2+} \gg \text{Na}^+, \text{Mg}^{2+}, \text{K}^+$
- Anions: $\text{SO}_4^{2-} \gg \text{NO}_3^- > \text{Cl}^-$

Salts do not appear to have a large marine component:

- Low Na^+ , Cl^- , high Ca^{2+} , SO_4^{2-}
- Conversion after deposition via particle-gas conversion reactions? Does not explain low Na
- Preferential deposition of deliquesced Ca-Cl salts, followed by conversion to sulfates and chloride-loss?

Ion	EPRI #1 filter	EPRI #1 pad	EPRI #4 filter	EPRI #4 pad
Na^+	19.2	14.8	n.d.	11.3
K^+	18.1	13.7	1.05	7.75
Ca^{+2}	77.1	20.6	24.1	153
Mg^{+2}	16.9	6.0	1.95	17.6
F^-	0.30	0.61	n.d.	n.d.
Cl^-	5.64	n.d.	n.d.	3.10
NO_3^-	21.3	9.09	4.34	14.2
SO_4^{-2}	89.7	51.5	48.0	291
PO_4^{-3}	6.68	2.05	0.45	n.d.
Total mass, μg	255	118	80	498

Chemical Analysis: Insoluble Fraction

Insoluble fraction:

- Dominated by SiO_2 , CaO , MgO
- The large amount of SiO_2 implies *quartz* is a major phase (confirmed by SEM)
- Other phases observed (SEM):
 - *K-aluminosilicate, Na-aluminosilicate (feldspars)*
 - *Mg, Mg-Fe aluminosilicates (clays?)*
 - *Fe-oxide*
 - *Fe-metal (spherules – fly ash or welding residue?)*
- Many grains composite or coated, making mineralogical identification difficult

Element	EPRI #1 filter	EPRI #1 pad	EPRI #4 filter	EPRI #4 pad
Na_2O	18.3	8.93	5.42	9.00
K_2O	26.9	14.7	5.55	14.6
CaO	307	119	66.6	123
MgO	134	49.7	35.8	58.9
Fe_2O_3	114	45.5	41.1	56.3
Al_2O_3	195	78.8	41.4	89.3
SiO_2	293	600	100	1452
Total	1088	916	296	1803

Summary of Dust Sampling Results

Dust samples were collected from the surface of an in-service interim storage container at Calvert Cliffs, MD, USA.

- The sample collected from the upper surface (11:00 location) consisted largely of pollen and other particles that settled gravitationally onto the package. The sample from the 7:00 position was finer-grained, and lacked the plant materials.
- The soluble salts in both samples are Ca and SO₄ rich. Gypsum is the dominant salt phase present.
- Chlorides comprise a small fraction of the total salt load, and are dominantly NaCl (a single grain of KCl was observed by SEM)

Despite the proximity to the coast and prevailing winds from the east, the dusts sampled from in-service containers at Calvert Cliffs do not appear to have a large sea salt component. Chesapeake Bay is brackish, and may be sheltered sufficiently to limit wave-generated sea-salt aerosols.

BACKUP SLIDES

SEM/EDS Analysis

EPRI #4 Pad

