Evolution of Waste Package Environments in a Repository at Yucca Mountain

Presented to:
Nuclear Waste Technical Review Board
Workshop on Localized Corrosion

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Evolution of Waste Package Environments in a Repository at Yucca Mountain

Outline

- **Temperature/humidity conditions**

- **Seepage vs. deliquescence comparison**

- **Deliquescence environment**

  - **Source of deliquescent salts**

  - **Salt accumulation and brine volume**

  - **Processes affecting brine**

  - **Importance of small brine volume**

Evolution of Waste Package Environments in a Repository at Yucca Mountain

Outline (cont'd)

- **Seepage Environment**

    - **Near-field water chemistry**

    - **In-drift water evolution and timing**

    - **Representation for Total System Performance Assessment (TSPA)**

- **Summary of Environments**

Evolution of Temperature/Relative Humidity (RH) on the Waste Package (WP) Surface

Deliquescence can occur starting at emplacement
Seepage occurs only after the drift wall temperature cools below 100ºC (T_{WP} ~105ºC)

DTN: SN0508T0502205.015
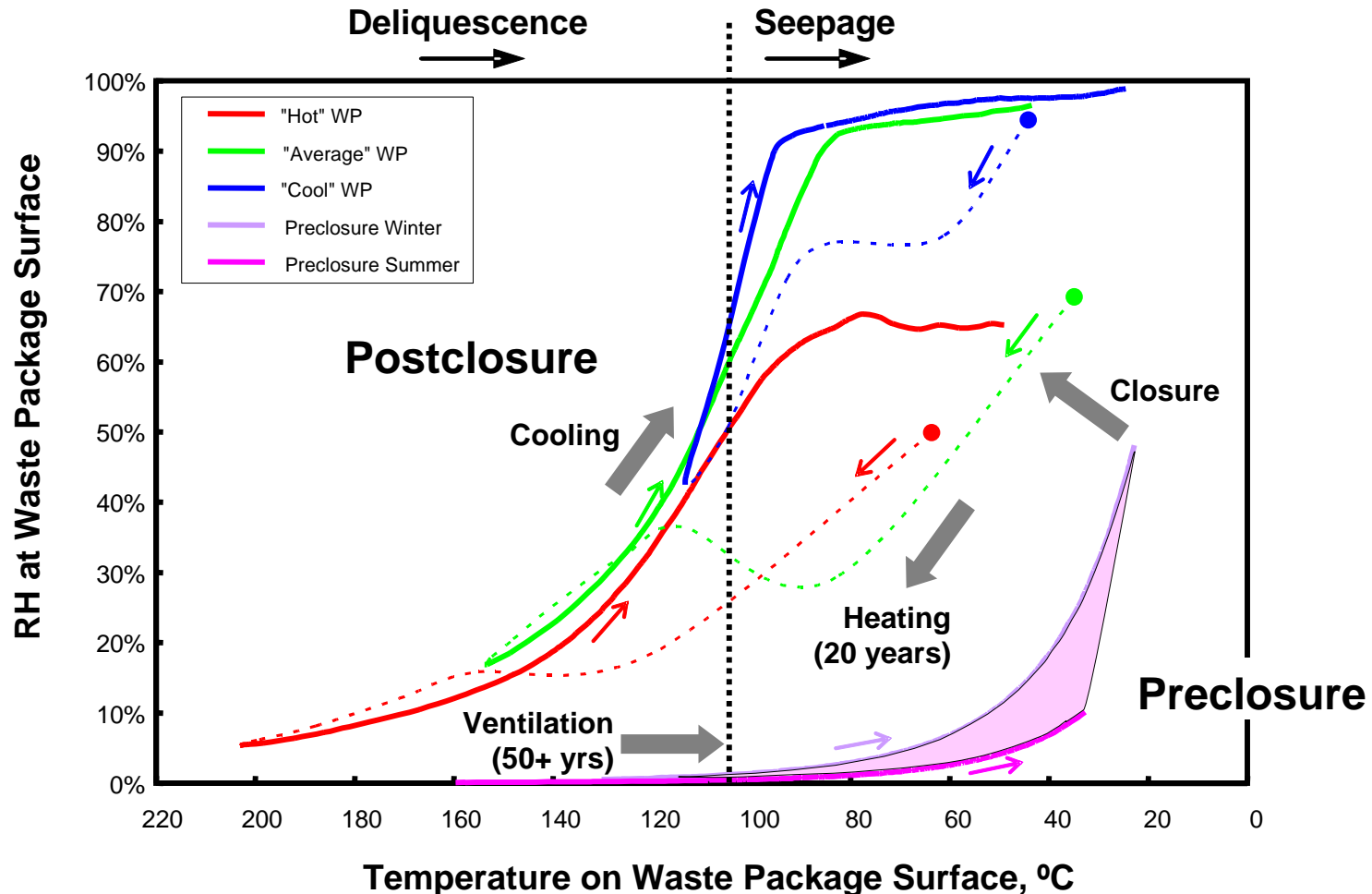
Two Types of Chemical Environments

Deliquescence

- **Soluble salts deposited on the WP during preclosure**

- **Drip shields control post-closure dust accumulation**

- **Multi-salt assemblages control deliquescence at higher T**

- **Brine compositions become dilute as T$\downarrow$, RH$\uparrow$**

- **Amount of brine contacting metal surfaces is limited**

- **Chemistry is moderated by contact with rock-forming minerals in dust**

- **Brines change with time-- degassing, deliquescence**

Seepage

- **Seepage may occur after cooldown (T$_{WP}$ < 105ºC)**

- **WP outer barrier is protected by drip shields**

- **Residence time (equilibrium with T, RH at WP surface) controls corrosion environment**

- **Chemical conditions (pH, Cl$^-$, NO$_3^-$, NO$_3^-$/Cl$^-$) are potentially corrosive early during cooldown**

- **Chemical fractionation may occur during transport**

Relevant Dust Sources and Composition

Current model is based on two sources of dust:

- ## Yucca Mountain tunnel dusts

  - Mostly rock forming minerals, <1% soluble salts

  - Important deliquescent mineral assemblages:

    - $NaCl$-KNO_3
    - $NaCl$-KNO_3-$NaNO_3$
    - $NaCl$-KNO_3-$NaNO_3$-$Ca(NO_3)_2$

- ## Atmospheric dust

  - Site-specific data, 6 locations near YM (Reheis and Kihl, *JGR*, 1995)

    - Highly soluble salts 10.5% (avg.); carbonate 9.5% (avg.)

  - Solubles—NADP regional precipitation (rain-out) data:

Sample #	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	NH_4^+ mg/L	NO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^-/Cl^-
NV00-2002	0.48	0.044	0.013	0.059	0.26	1.14	0.09	0.46	7.3
NV00-2001	0.66	0.068	0.042	0.113	0.69	2.15	0.16	1.01	7.7
NV00-2000	1.21	0.137	0.055	0.263	1.01	3.24	0.36	1.35	5.2

NADP/NTN 2000, Part 2.
NADP/NTN 2001, Part 2.
NADP/NTN 2002, Part 2.

Site-Specific Dust Samples for Planned Update

- **South pad cyclonic collector (300 cfm)**

    – **Began operating 6/29/2005**

    – **Moisture sensor and controller stop the blower during rainstorms**

    – **Two collectors in series:**

        ◆ **Cyclone separator for large particles (>5 μm)**

        ◆ **Torit filtration separator for smaller particles (to <0.5 μm)**
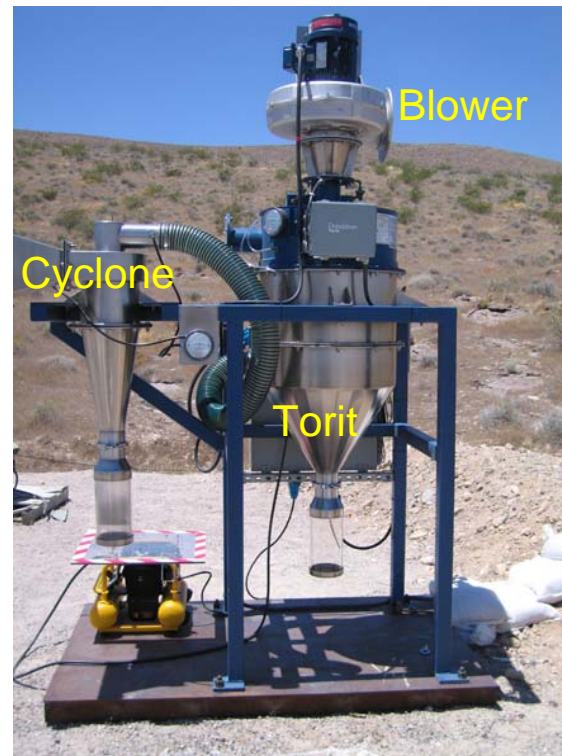
Analyses (averages of duplicated analyses)

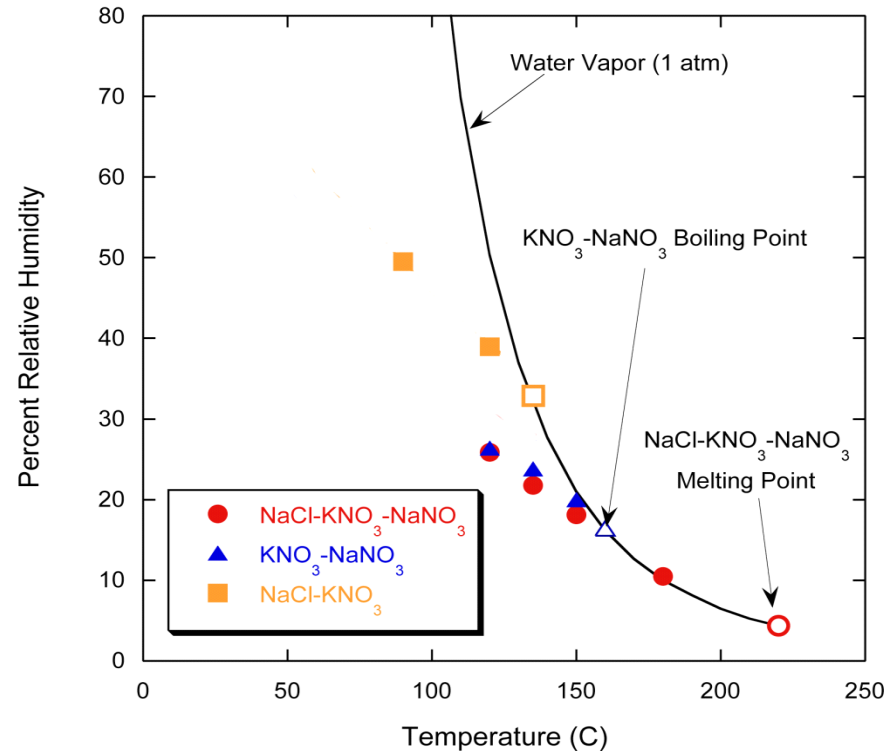| Collection Date Ending:	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	NH_4^+ mg/L	NO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^-/Cl^-	HCO_3^- mg/L	TDS %
03-Aug-05	2260	525	852	950	59.8	6690	548	1580	7.0	2820	1.68
08-Sep-05	1190	301	664	644	97.6	3100	389	725	4.6	291	0.79
10-Jan-06	598	1290	1640	12500	112	29000	2600	15600	6.4	449.5	6.97
18-May-06	4370	1040	1580	4510	232	16500	1840	6150	5.1	4310	4.12
07-Jun-06	3240	758	1530	2940	446	11400	1510	4080	4.3	4930	3.14

PRELIMINARY DATA - DTN TBD

Conditions of Deliquescence

Experimental Data:

- **Ammonium salts thermally decompose and won't contribute to deliquescent mineral assemblages**

- **NaCl - KNO$_3$ $\Rightarrow$ 134°C**

- **NaCl - KNO$_3$- NaNO$_3$ $\Rightarrow$ Transition to hydrous melt at 220°C, Dryout at ~300°C**

- **NaCl - KNO$_3$- NaNO$_3$- Ca(NO$_3$)$_2$ $\Rightarrow$ Boiling point > 400°C**

- **Maximum WP surface temperature: 203°C**
  (ANL-EBS-MD-000038 Rev. 03)

Graph: Percent Relative Humidity vs. Temperature (C). Labels: Water Vapor (1 atm); KNO$_3$-NaNO$_3$ Boiling Point; NaCl-KNO$_3$-NaNO$_3$ Melting Point. Legend: NaCl-KNO$_3$-NaNO$_3$; KNO$_3$-NaNO$_3$; NaCl-KNO$_3$.

DTNs: LL050903412251.150
LL050901931032.009
LL050800623121.053

Processes Affecting Brine on the WP Surface

- **Acid degassing — $H^+_{(aq)} + Cl^-_{(aq)} \Rightarrow HCl_{(aq)} \Rightarrow HCl_{(g)}$**
  - **Ca-Chloride brines degas and dry out (TGA experiments)**
  - **Multiple-salt assemblages can deliquesce at higher temp.**
    - Acid-degassing may occur initially, but less as pH increases
    - Brines may not degas sufficiently to dry out
    - NO_3^-/Cl^- minimum ratio is controlled by temperature

- **Reactions with silicate minerals in dust**
  - **Silicate dissolution buffers pH**
  - **Ca, Mg removed from brine as silicate phases**
  - **Deliquescence RH generally increases (brines may dry out)**
  - **Possible consumption of chloride by silicates**
    - Scapolite-, cancrinite-, sodalite-, prehnite-group minerals
    - Clays (exchange for hydroxides)

- **Dilution with decreasing temperature, increasing humidity**

Salt Amount and Brine Volume

- **Estimated amount and composition of dust on WPs**

  - **Atmospheric dust concentration (site-specific): 22 µg/m^3 (typical)**

  - **Drift and ventilation design parameters**

  - **Upper-bound particle size (10 and 30 µm)**

  - **Deposition on first waste package in drift**

  - **Ventilation period: 50 years**

  - **Dry particle deposition model (Sehmel 1980)**

- **Estimate brine volume**

  - **Dust soluble salt content (site-specific): 10.5%**

  - **Ammonium minerals volatilize (~1/2 of total salts)**

  - **Thermodynamic modeling with Pitzer database**

# Salt Amount and Brine Volume

DTN: SN0508T0502205.016
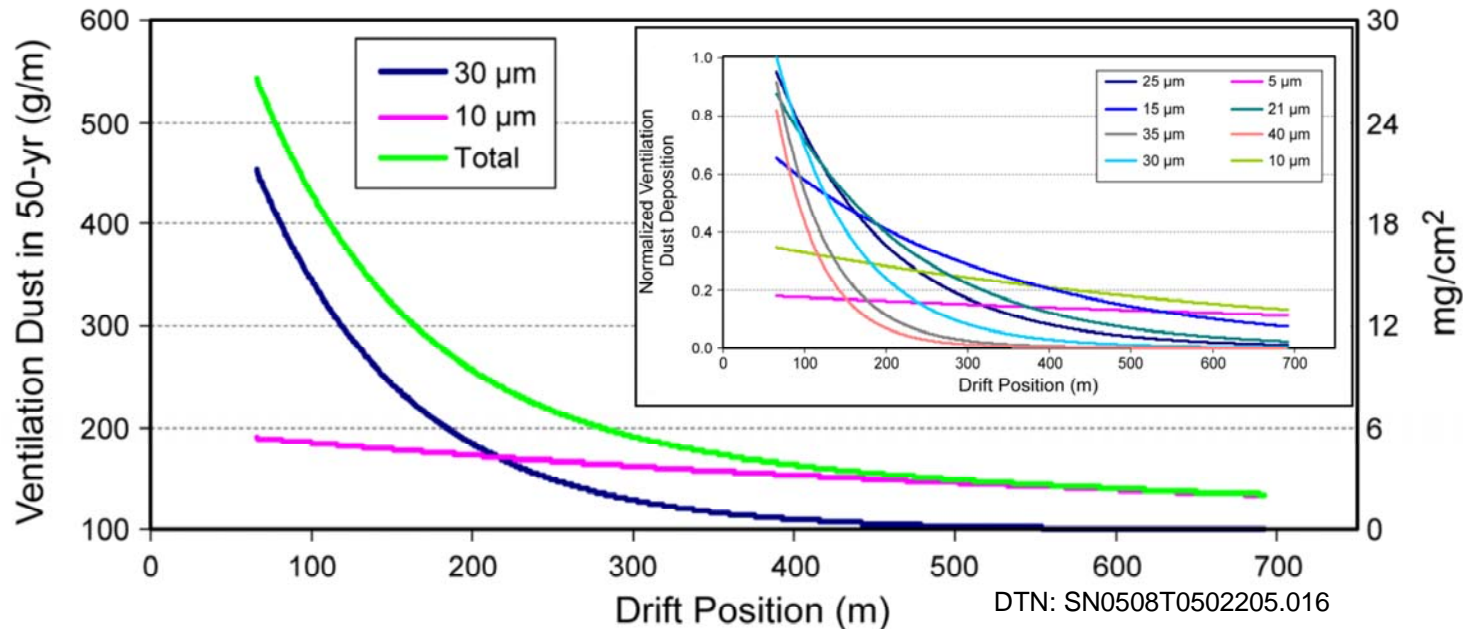
- **Upper bound for dust deposited: 26 mg/cm^2**
  - **260 µm thick layer for bulk density 1 g/cm^3**
  - **Rock dust may add mass, not soluble salts**
- **Upper bound brine volume: 1.8 µL/cm^2 (18 µm thick layer)**
  - **At 120°C; less volume at higher temperatures**
  - **Assumes all salts are internally mixed (no geometric isolation)**
  - **Average liquid saturation for dust layer ~ 11% for porosity of 60%**
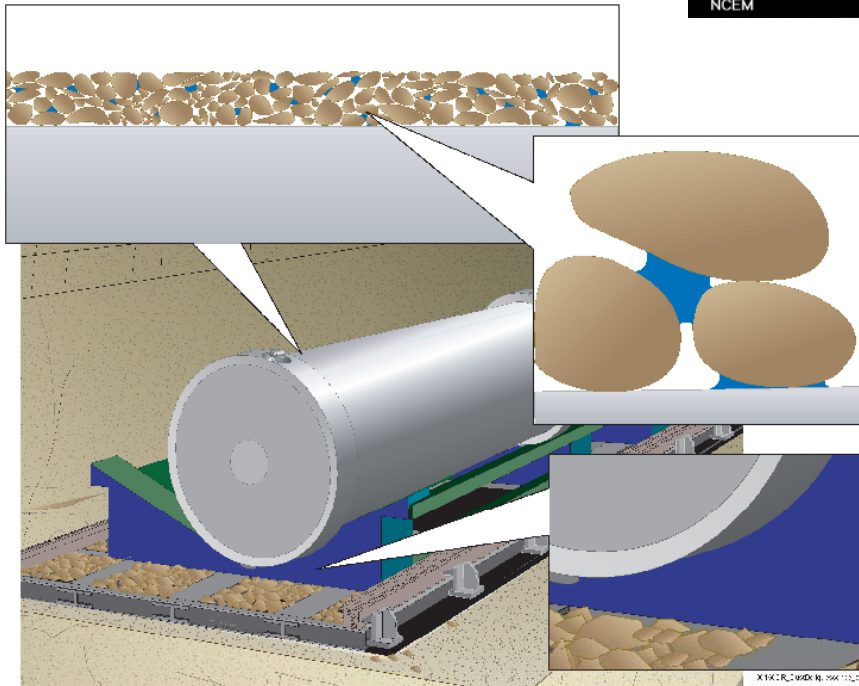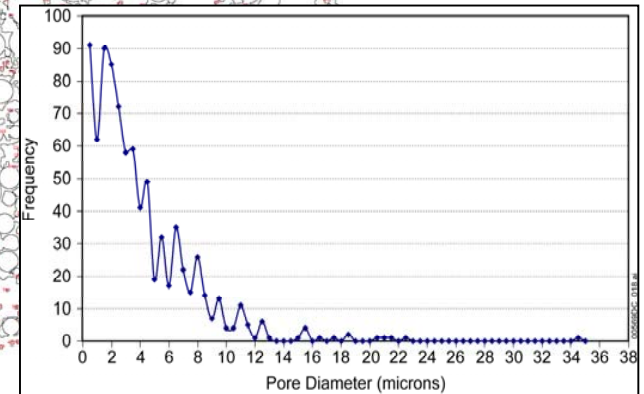- **Lower bound approx. 1 order of magnitude less at 200°C**

Importance of Very Small Brine Volume

- **Dust capillary response: ~ 1μm**

- **Capillary retention in dust limits brine contact with metal surface**
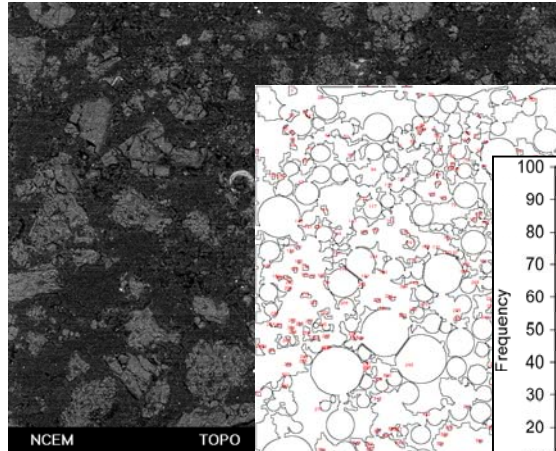
Confocal image of tunnel dust

- **Dust layer is unsaturated $\Rightarrow$ rapid gas diffusion into/out of dust**

- **Scale limitations on development of compositional gradients (e.g., O_2)**
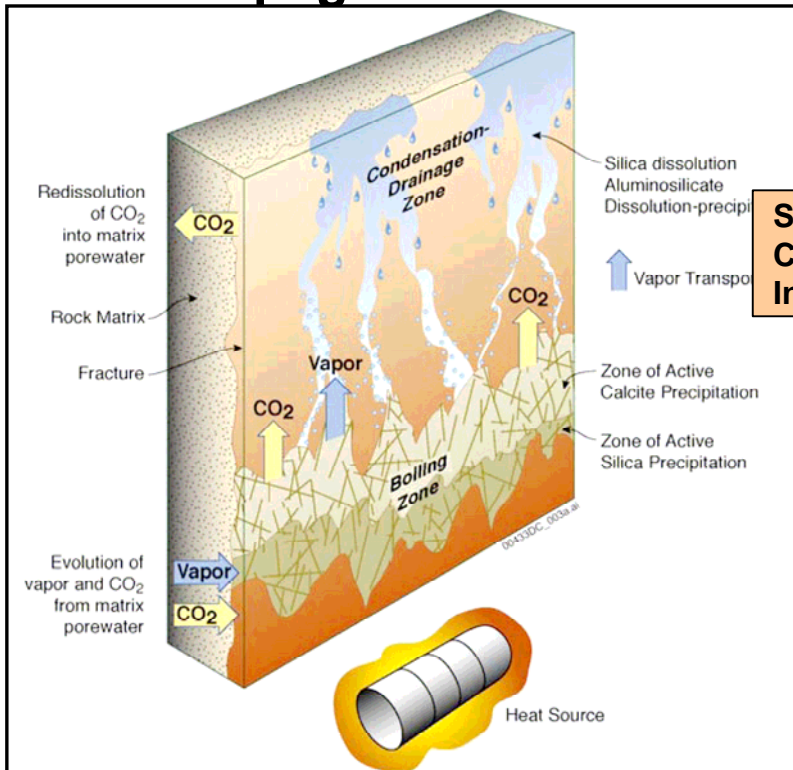
Capillary hold-up in dust layer
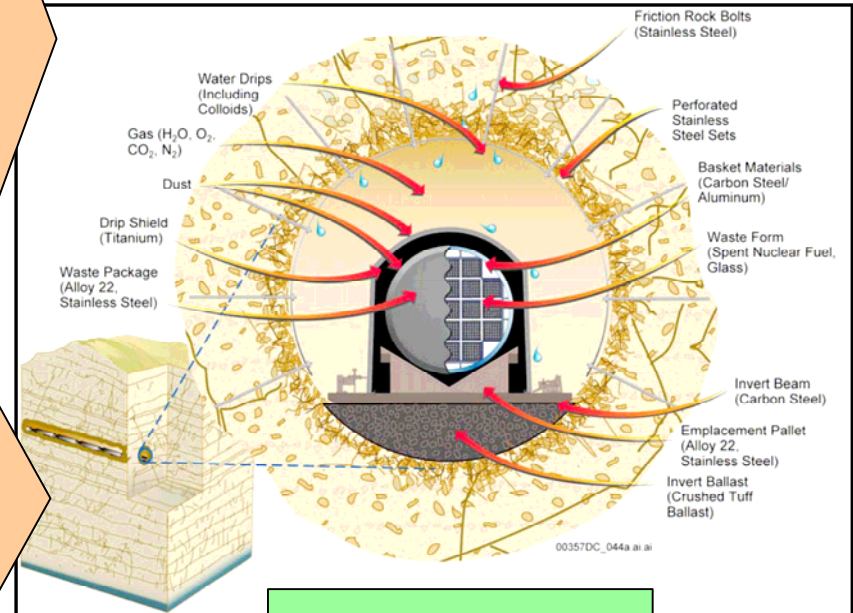
Seepage Chemical Environment

Equilibrium Thermodynamic (Pitzer) Model for Evaporative Evolution

Physical & Chemical Environment Model

THC-Seepage Model


Seepage Composition; In-Drift P_{CO_2}

To TSPA:

Composition of Evaporated Seepage Water on the Waste Package Surface, $f(T, P_{CO_2}, RH)$

pH, I, [Cl], (NO_3^-/Cl^-)

THC Seepage Model

Model Approach

- **Initial/boundary conditions selected from available porewater analyses**
  - **Approx. 100 porewaters analyzed**
  - **NO_3^-/Cl^- ratios typically > 0.5**
  - **Group in 2-3 clusters based on chemical divides and statistics**
- **Thermal-hydrologic-chemical model**
  - **Repository center and edge conditions**
  - **Identify potential seepage waters, compositions**
  - **Validation using drift scale test results**
- **Abstracted output:**
  - **Compositions for potential seepage waters**
  - **CO_2 fugacity vs. time**
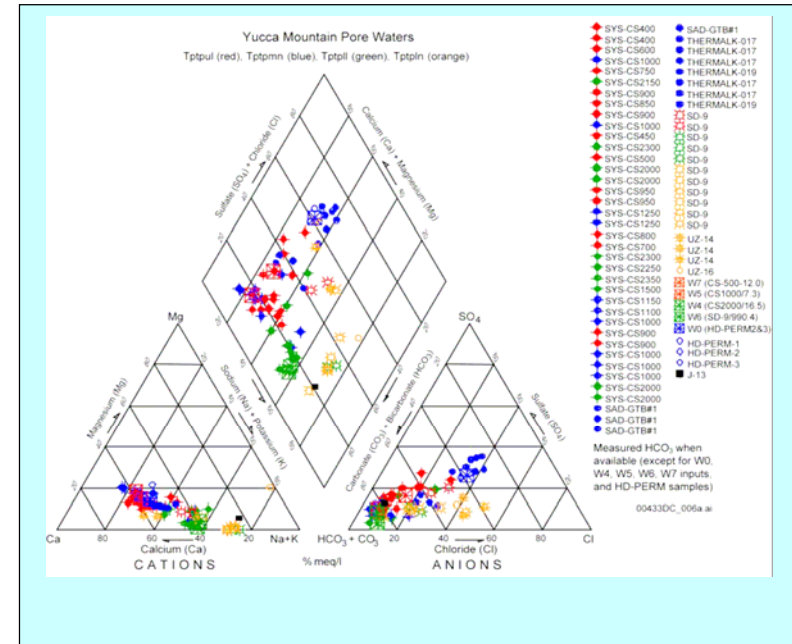
PRELIMINARY INFORMATION FROM DTNs: GS030408312272.002, GS020408312272.003, GS020808312272.004, GS031008312272.008, and MO0005PORWATER.000.
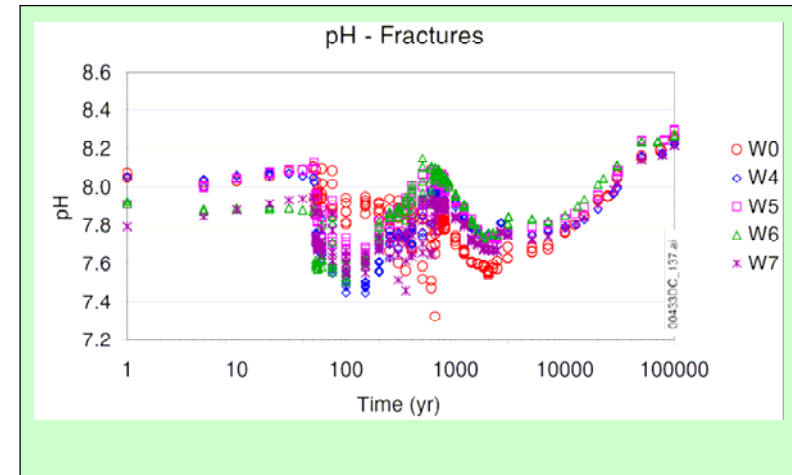
PRELIMINARY INFORMATION FROM DTNs: LB0302DSCPTHCS.002, LB0307DSTTHCR2.002

Physical and Chemical Environment (P&CE) Model

- **Corrosion environment**
  - **Evaporative equilibrium**
  - **Salt separation effect**
- **Binning approach**
  - **Bins based on chemical divides and other similar characteristics**
  - **Statistical median water for each bin**
  - **Create "bin history tables" by mapping bins to THC runs**
- **Preliminary results - 11 bins**
  - **Lookup tables wrt T, P_{CO2}, RH**
  - **Outputs NO_3^-, Cl^-, pH, ionic strength**
  - **Uncertainty propagated**

W0 Time	W0 Crown	W4 Time	W4 Crown	W5 Time	W5 Crown
10	4	10	10	10	7
51	5	51	11	51	11
53	5	53	11	53	11
55	6	55	11	55	11
60	6	60	11	60	11
75	5	75	11	75	11
100	5	100	11	100	11
150	4	150	11	150	11
200	4	200	11	200	11
250	3	250	11	250	11
300	3	300	11	300	11
350	3	350	11	350	11
400	3	400	11	400	11
500	4	500	5	500	9
600	4	600	5	600	11
650	5	650	11	650	11
700	11	700	11	700	11
751	11	751	11	751	11
790	11	801	11	785	11
801	11	804	11	801	11
1001	11	1001	11	1001	11
1201	11	1201	11	1201	11
1401	11	1401	11	1401	11
1601	11	1601	11	1601	11
1801	11	1801	5	1801	5
2001	4	2001	4	2001	4
2202	11	2202	11	2202	11
2402	11	2402	11	2392	11
3002	11	2597	11	2402	11
5003	11	3002	11	3002	11
7005	6	5003	11	5003	11
10007	6	7005	9	7005	9
12310	7	10007	7	10007	10
15010	7	12598	7	12304	7
20013	8	15010	8	15010	7
50035	8	20013	8	20013	8
		50035	8	50035	8

Bin History Tables From P&CE Model
(DTN: MO0312SPAPCESA.002)

Department of Energy • Office of Civilian Radioactive Waste Management
bryan_NWTRB_9/25-26/06.ppt
www.ocrwm.doe.gov

Summary: Seepage Environment

- **Waste package temperature < 105ºC**

- **RH varies from approx. 40% to 99+%**

- **Salt separation effect implemented for RH < 77%**

- **NO_3^-/Cl^- controlled by ambient water composition**

- **Ca-Cl brines predicted during peak thermal period**

- **Wide range of pH (4.5 to 10.5 plus uncertainty)**
  - **Higher pH after cooldown (T_{dw} < 100ºC)**
  - **Increasing pH as repository cools**

- **Greatest potential for corrosive seepage chemistry occurs early during cooldown**

- **Open system with respect to gases (background acid gas concentrations low)**

Summary: Deliquescence Environment

- **Brines can form only in small amounts at elevated T**

- **Physical environment**
  - **Unsaturated**
    - **Open system with respect to gases**
  - **Capillary and adsorptive retention in the dust layer further decreases available brine volume**

- **Chemical environment**
  - **NaCl – KNO$_3$ (– NaNO$_3$) (– Ca(NO$_3$)$_2$) salt systems**
    - **Deliquescence at higher temp. requires multiple-salt assemblages**
  - **Nitrate-rich; NO$_3^-$/Cl$^-$ increases with higher temperature**
  - **Acid degassing**
    - **May occur initially; less as pH increases; unlikely to dry out**
    - **Background acid-gas pressures are very low**
    - **NO$_3^-$/Cl$^-$ minimum ratio is controlled by temperature**
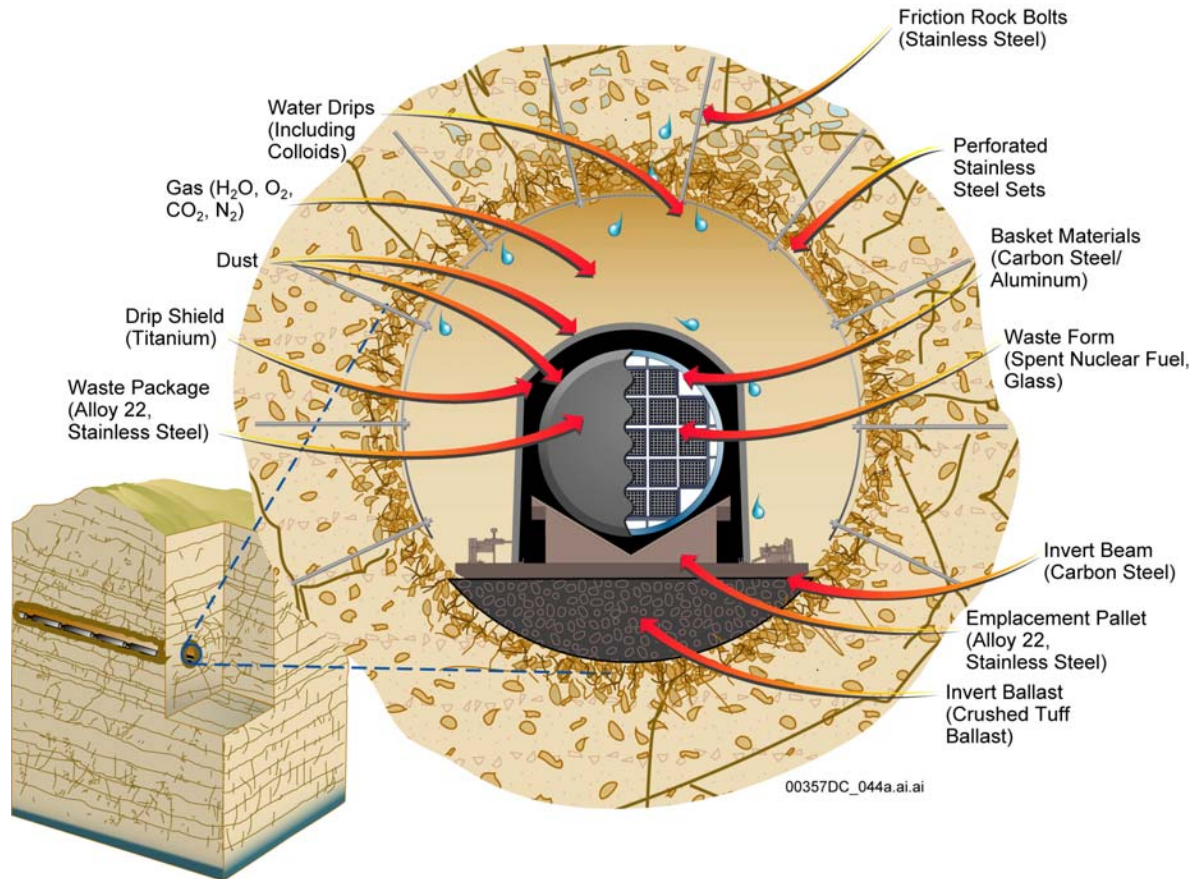 - **Reaction with silicates buffers pH, removes divalent cations**

Evolution of Waste Package Environments in a Repository at Yucca Mountain

Environment - Backup Slides
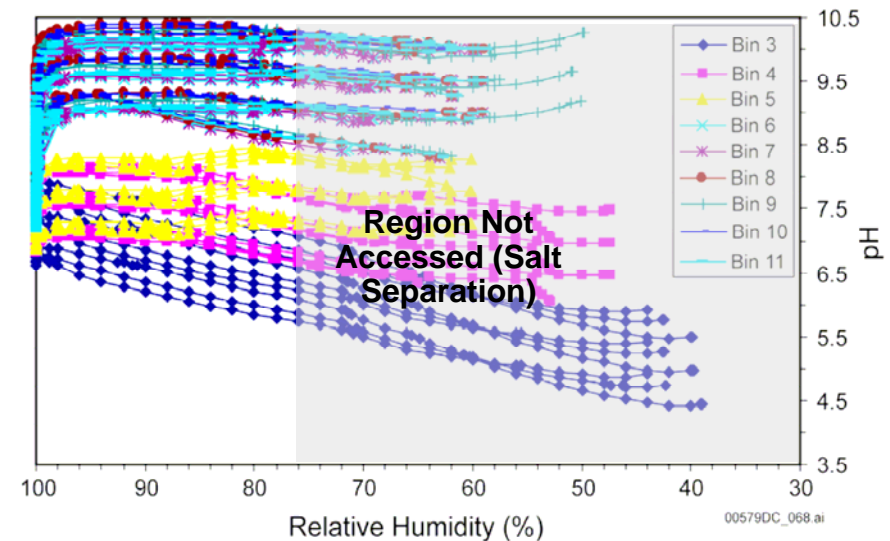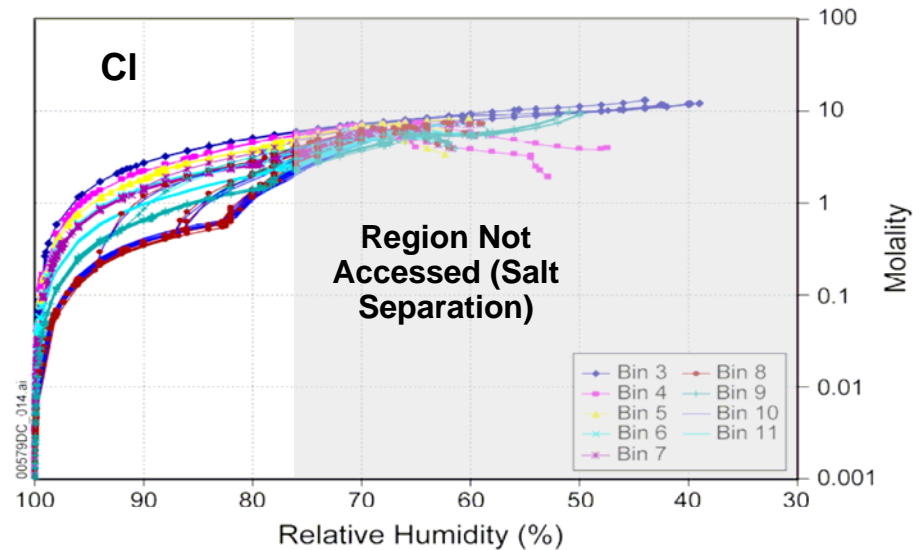
In-Drift Environment

An aqueous environment can form on the surface of the waste package by deliquescence of salts found in dust, or by seepage

TSPA Implementation

Evaporated Water Compositions for Input to the Localized Corrosion Model

- Interpolate Lookup Tables for pH, Ionic Strength, Cl⁻, and NO_3^- (Fcns of T, RH, P_{CO2})
- Salt Separation Effect
  - Halite precipitates if seepage contacts WP for RH < 77%
  - Chloride separates from nitrate; localized corrosion initiates
- Apply Uncertainties
  - Model uncertainty
  - Statistical binning uncertainty

DTN: MO0312SPAPCESA.002.