



U.S. Department of Energy



Localized Corrosion Due to Dust Deliquescence on the Alloy 22 Waste Package Outer Barrier

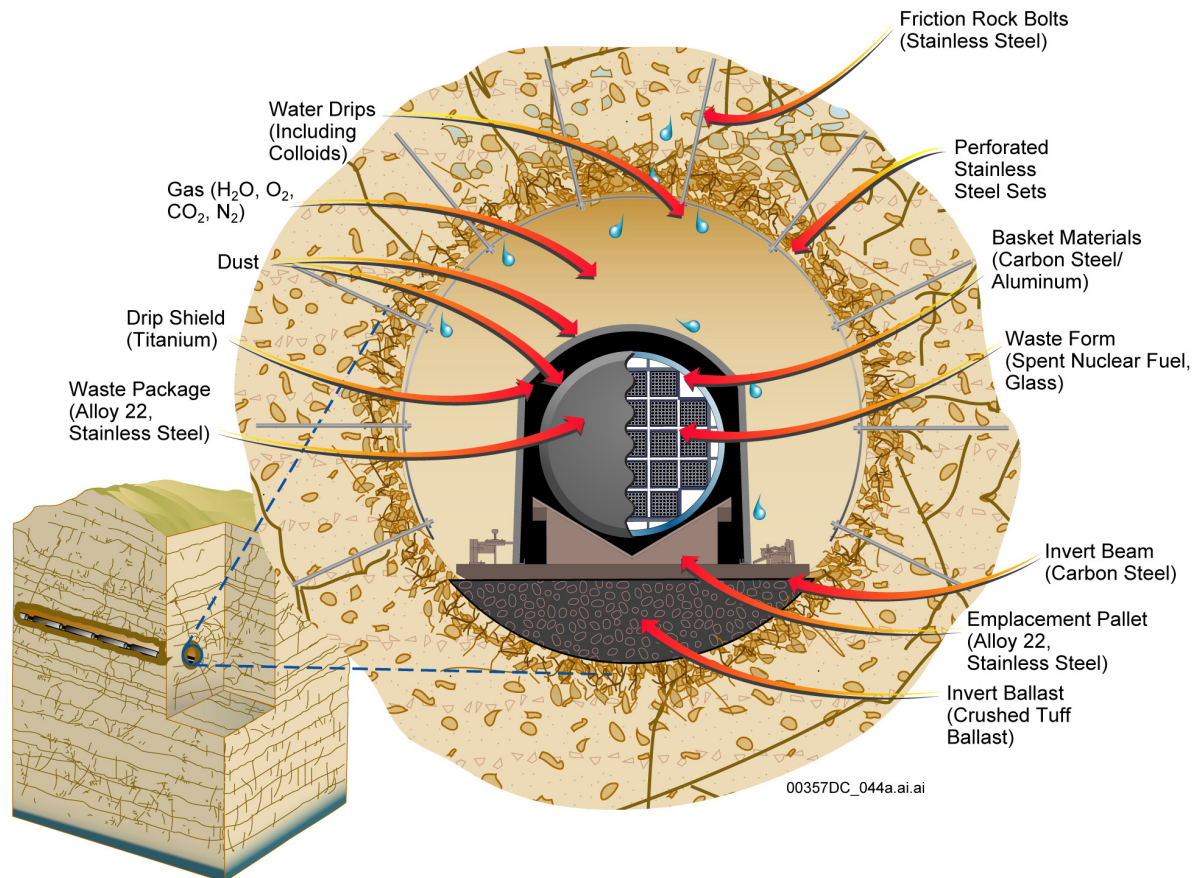
**Presented to:
Nuclear Waste Technical Review Board**

**Presented by:
Charles R. Bryan
Geochemist–Near Field Environment
Sandia National Laboratories**

**November 8-9, 2005
Las Vegas, Nevada**

In-Drift Environment

The environment of the surface of the waste package is characterized by seepage evaporation and deliquescence of salts found in dust



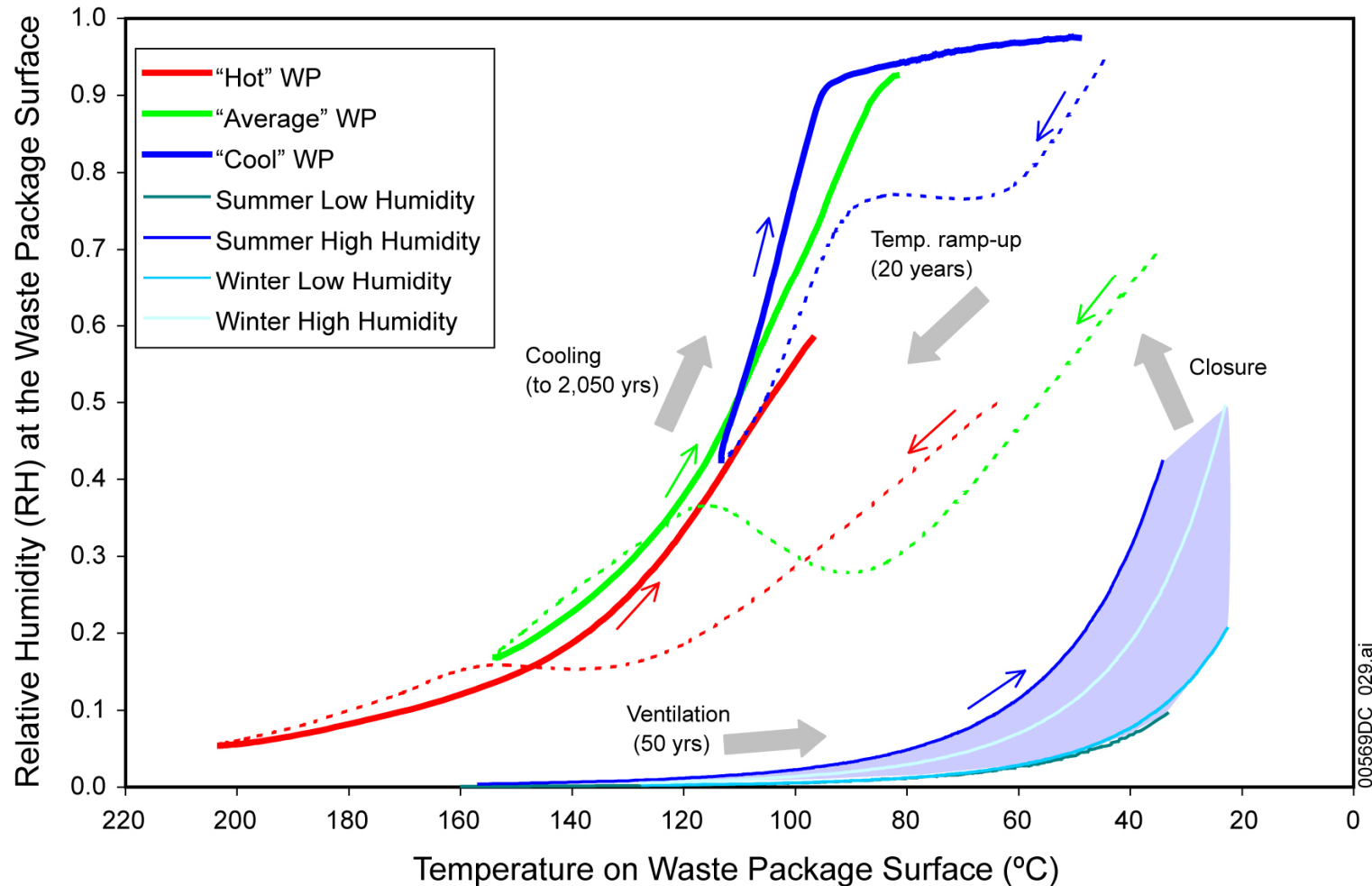
Overview

Evaluate the potential for penetration of the Alloy 22 waste package outer barrier by localized corrosion (LC) due to deliquescence of salts in dust on the waste package surface.

- **Can multiple-salt deliquescent brines form at elevated temperatures?**
- **If deliquescent brines form at an elevated temperature, will they persist?**
- **If deliquescent brines persist, will they be corrosive?**
- **If potentially corrosive brines were to form, would they initiate localized corrosion?**
- **If localized corrosion were to be initiated, would penetration of the waste package outer barrier occur?**



Temperature/RH on the Waste Package Surface



00569DC_029.ai

DTN: SN0508T0502205.015



1. Can multiple-salt deliquescent brines form at elevated temperatures?

- **To evaluate the potential formation of deliquescent brines at high temperatures:**
 - Identify relevant dust sources and compositions
 - Determine salt assemblages controlling deliquescence
 - Determine conditions of deliquescence



Yucca Mountain Tunnel Dusts

- **Dominantly rock powder**
(Peterman et al., 2003, *IHLRWM Conf. Proceedings*)
- **<1% highly soluble salts**
- **Important deliquescent mineral assemblages:**
(based on chemical analyses of dust leachates and EQ3/6 modeling)
 - **NaCl-KNO₃**
 - **NaCl-KNO₃-NaNO₃**
 - **NaCl-KNO₃-NaNO₃-Ca(NO₃)₂**



Atmospheric Dusts

- **Site-specific data (Reheis and Kihl, *JGR*, 1995)**
 - 6 locations at Yucca Mountain
 - Highly soluble salt load—10.5% (avg)
 - Carbonate content—9.5% (avg)
- **Solubles—NADP regional precipitation data (represents the salt compositions of atmospheric aerosols)**

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 mg/L
NV00-2002	0.48	0.044	0.013	0.059	0.26	1.14	0.09	0.46
NV00-2001	0.66	0.068	0.042	0.113	0.69	2.15	0.16	1.01
NV00-2000	1.21	0.137	0.055	0.263	1.01	3.24	0.36	1.35

NADP/NTN 2000 [DIRS 172977], Part 2.

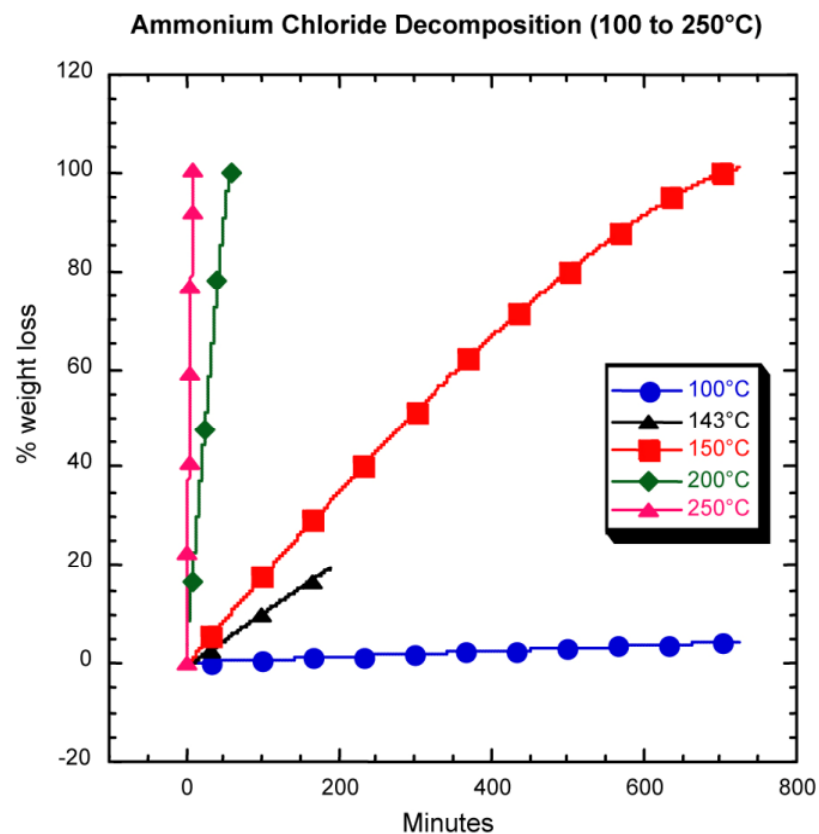
NADP/NTN 2001 [DIRS 172976], Part 2.

NADP/NTN 2002 [DIRS 173141], Part 2.



Fate of Ammonium Minerals

- Ammonium salts thermally decompose:
 - $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HNO}_3(\text{g})$ (fast)
 - $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ (fast)
 - $(\text{NH}_4)_2\text{SO}_4(\text{s})$ —stepwise decomposition (slow)
- If the salt minerals represent an equilibrium assemblage, NH_4NO_3 and NH_4Cl decomposition increases NO_3/Cl in the residual
- Deliquescent mineral assemblages following ammonium mineral decomposition are similar to tunnel dust assemblages.



DTNs: LL050301723121.050
LL050205223121.048



Maximum Deliquescence Temperatures

January, 2005 letter to the NWTRB; M. Chu notes: “Although we agree that calcium chloride type brines are very unlikely to exist or be stable at Yucca Mountain, *other chloride brines with varying amounts of corrosion inhibitors, such as nitrate and sulfate, may be present at elevated temperatures.*”

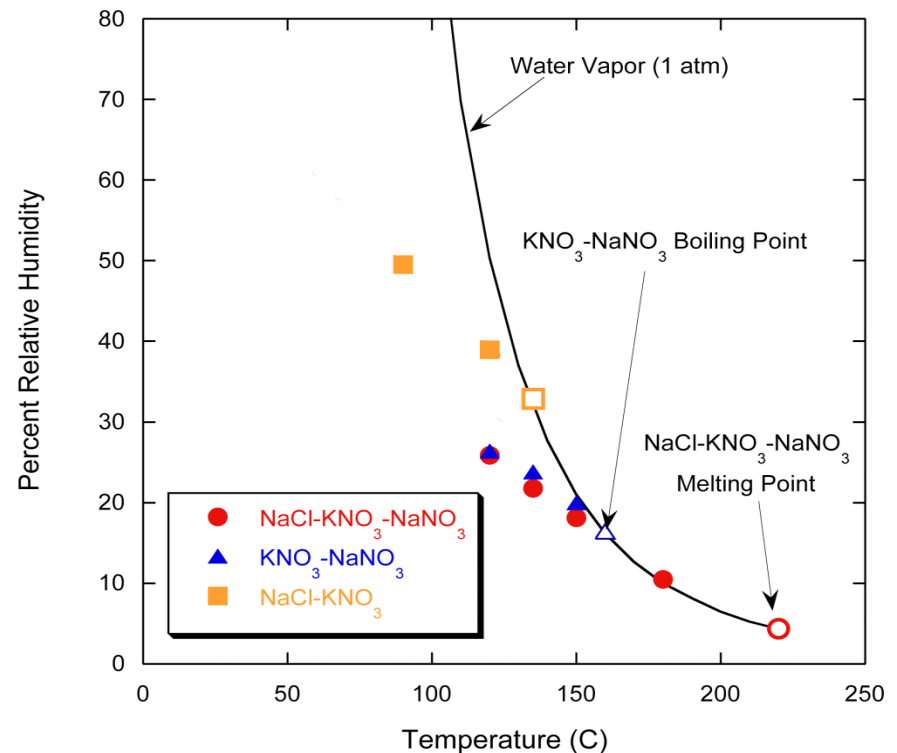
Experimental data:

NaCl-KNO₃ — 134°C

**NaCl-KNO₃-NaNO₃ —
transition to hydrous melt at
220°C, dryout at 300°C**

**Maximum temperature at the
waste package surface: 203°C**

(ANL-EBS-MD-000049 Rev. 03, Table 6.3-38)



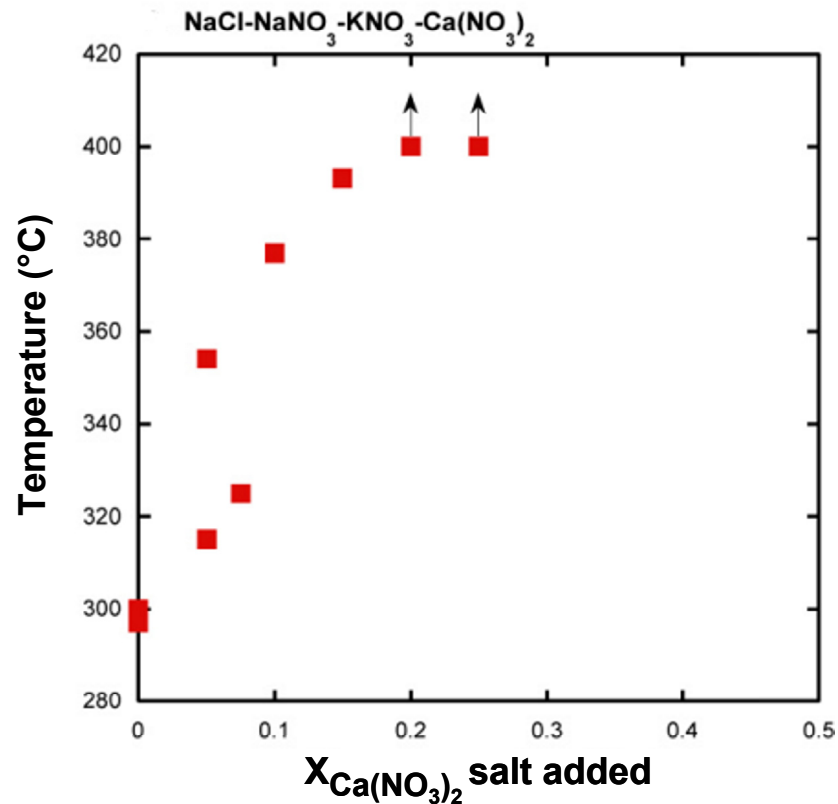
DTNs: LL050903412251.150, LL050901931032.009, LL050800623121.053



Maximum Deliquescence Temperatures

Experimental data:

NaCl-KNO₃-NaNO₃-Ca(NO₃)₂—boiling point >400°C



DTNs: LL050901931032.009



2. If deliquescent brines form at an elevated temperature, will they persist?

Acid degassing – $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \Leftrightarrow \text{HCl}(\text{aq}) \Leftrightarrow \text{HCl}(\text{g})$

- **Ca-chloride brines at high temperatures (May, 2004 NWTRB)**
 - A (OH, Cl) phase precipitates, buffering pH
 - Acid gas partial pressures remain high enough to result in dryout (a less deliquescent compound precipitates)
- **Deliquescent brine assemblages in dust**
 - **Monovalent salt brines**
 - ♦ pH rises to ≥ 10 , then buffered by Na-carbonate precipitation
 - ♦ Acid gas partial pressures high initially, but drop as pH rises—brines will not degas sufficiently to dry out
 - ♦ NO_3/Cl ratio increases with degassing
 - **Monovalent salt brines with $\text{Ca}(\text{NO}_3)_2$**
 - ♦ Buffered to near-neutral pH by calcite precipitation
 - ♦ Acid gas partial pressures remain high—continued degassing may occur
 - **No experimental evidence for acid degassing or dryout of these assemblages**



Other Processes on the Waste Package Surface

Reactions with silicate minerals (EQ3/6 modeling)

- **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)**



3. If deliquescent brines persist, will they be corrosive with respect to localized corrosion?

- **Initial deliquescent brines**
 - **NaCl-KNO₃ ± NaNO₃ ± Ca(NO₃)₂ - systems**
 - **Nitrate-rich**
 - **Nitrate-chloride ratio increases with temperature**
- **Modification of brines on the waste package surface**
 - **Acid degassing**
 - ◆ **raises pH**
 - ◆ **increases the nitrate-chloride ratio in the remaining brine**
 - **Reactions with silicate minerals—may buffer pH, remove divalent cations**

Experimental data (<160°C) indicate nitrate-rich brines do not initiate LC



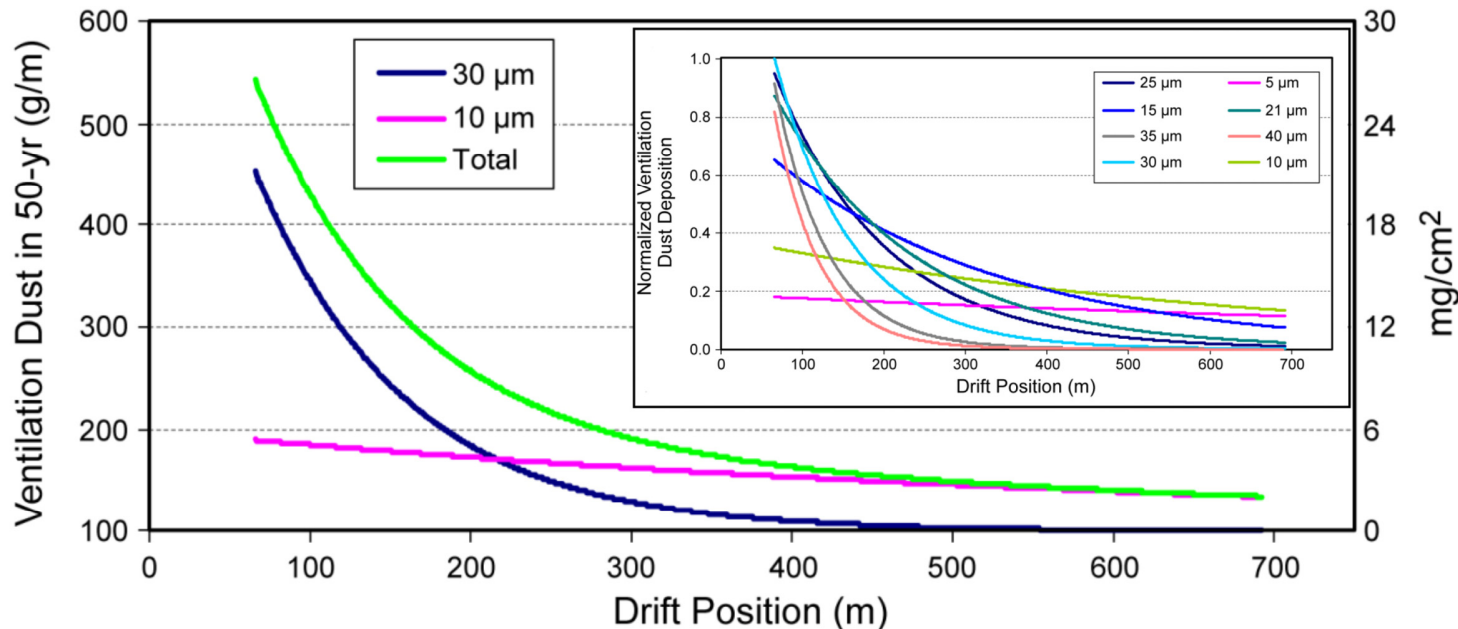
4. If potentially corrosive deliquescent brines were to form, would they initiate localized corrosion?

Scale limitations related to small brine volumes may inhibit LC initiation. To estimate brine volumes:

- **Estimate the amount and composition of dust deposited**
 - Atmospheric dust load (site-specific data) : $22 \mu\text{g}/\text{m}^3$
 - Drift and ventilation design parameters
 - Ventilation period: 50 years
 - Dry particle deposition model of Sehmel (1980)
- **Estimate brine volumes (EQ3/6)**
 - Dust soluble salt content (site-specific data): 10.5%
 - Ammonium minerals (~1/2 of total salts) subtracted out
 - Thermodynamic modeling with Pitzer database



Dust Deposition and Brine Volumes



DTN: SN0508T0502205.016

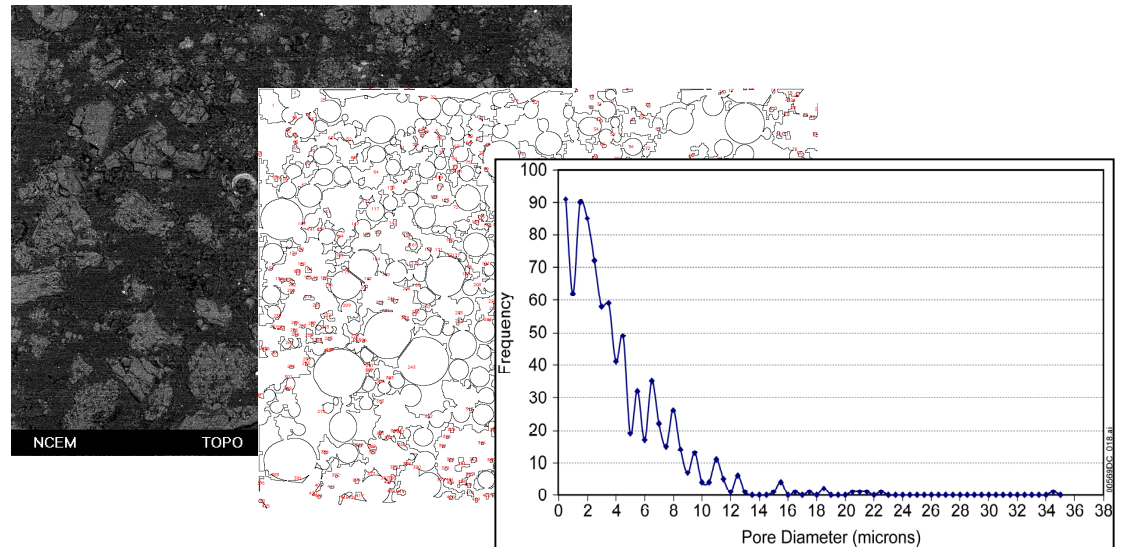
- **Upper bound for dust deposited**
 - First waste package in drift
 - Particle size distribution that yields highest deposition
 - Assumes all salts are in mutual contact (no geometric isolation)
 - **26 mg/cm²**
- **Upper bound brine volume: 1.8 µL/cm² (18 µm thick layer)**
(at 120°C—less at higher temperatures)



Impact of Small Brine Volumes

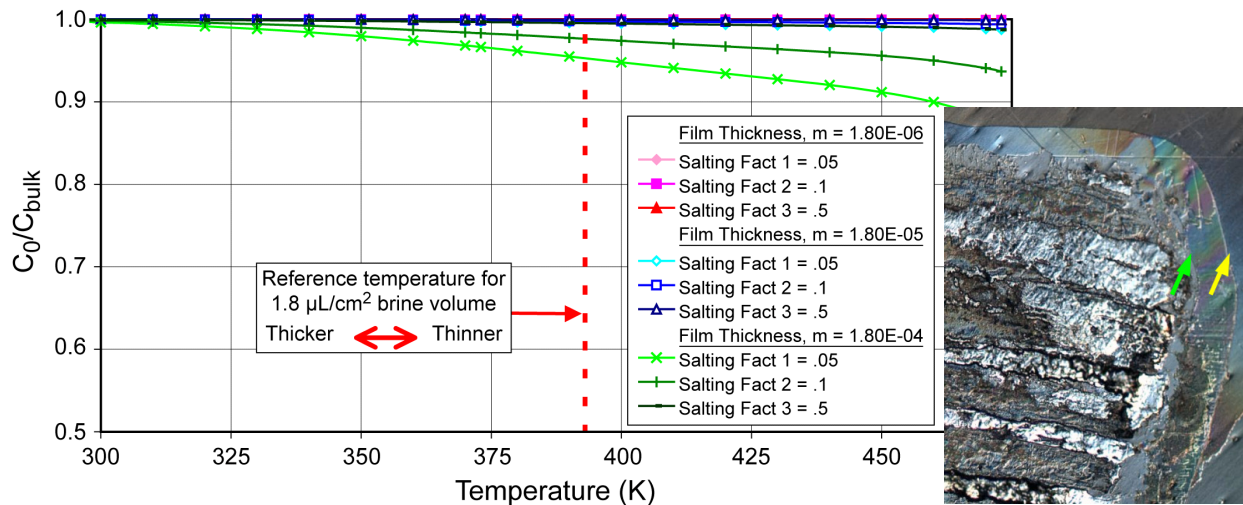
- **Capillary retention in dust:**

- limits contact with metal surface
- Dust capillary response: $\sim 1\mu\text{m}$



DTN: LB0503DUSTIMAG.001
LB0503DUSTPCAP.001

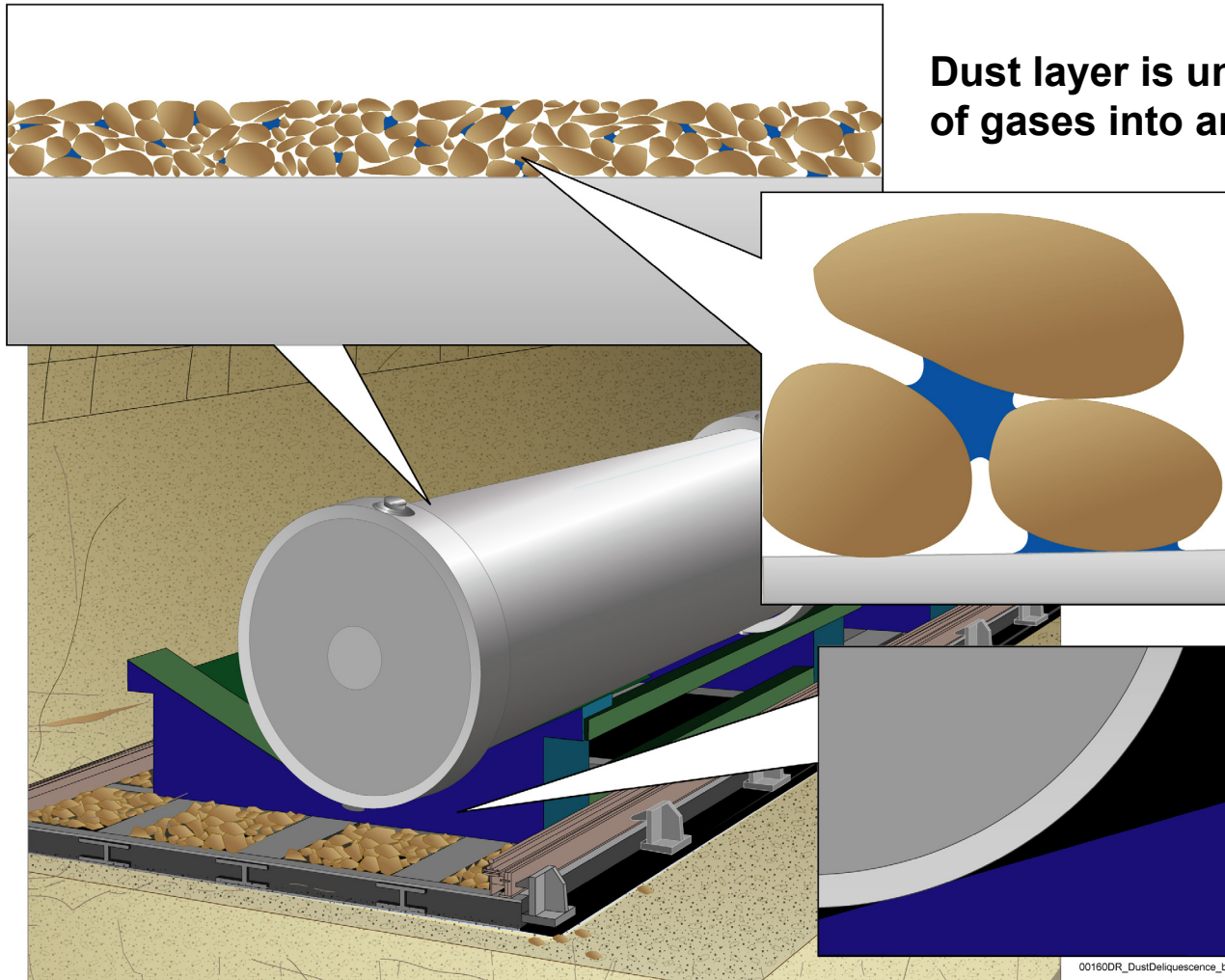
- **Scale limitations on development of compositional gradients (e.g., O_2)**



DTN: MO0508SPA0XYGE.004



Unsaturated Environment in Dust on the WP Surface



Dust layer is unsaturated—rapid diffusion of gases into and out of the dust.

Formation of aggressive crevice solutions is not possible (no stagnant zone, no separation of metal dissolution and oxide precipitation regions)

However, relevance to engineered crevices is uncertain.

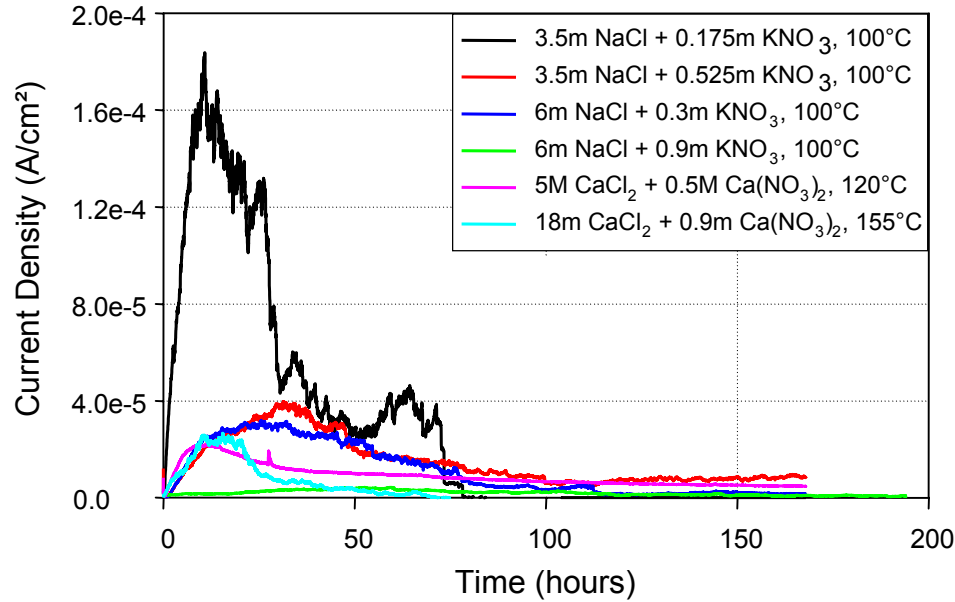


5. If localized corrosion were to initiate, would penetration of the waste package outer barrier occur?

- **Processes occurring after initiation of LC would limit extent of corrosion**
 - **Corrosion stifling—power rate law for corrosion penetration**
 - **Physical retention of brine in corrosion products**
 - **Chemical sequestration of brine components in corrosion products**

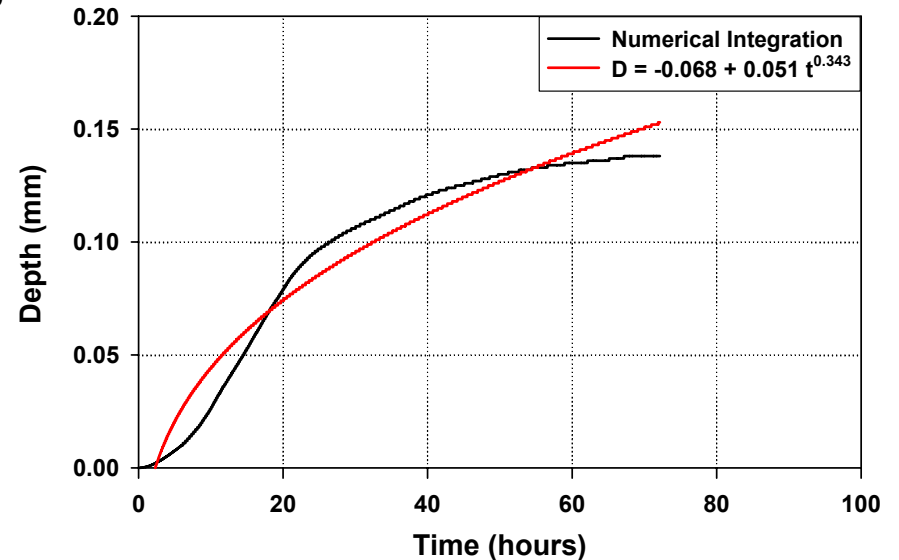


Corrosion Stifling



Constant Potential Testing of As-Welded Alloy 22 Prism Crevice Assembly Specimens

Power law for LC penetration:
 $\text{Depth} = A + B t^n$



DTN: MO0505SPASTIFL.001

Department of Energy • Office of Civilian Radioactive Waste Management

YMBryan_NWTRB_1108-0905.ppt

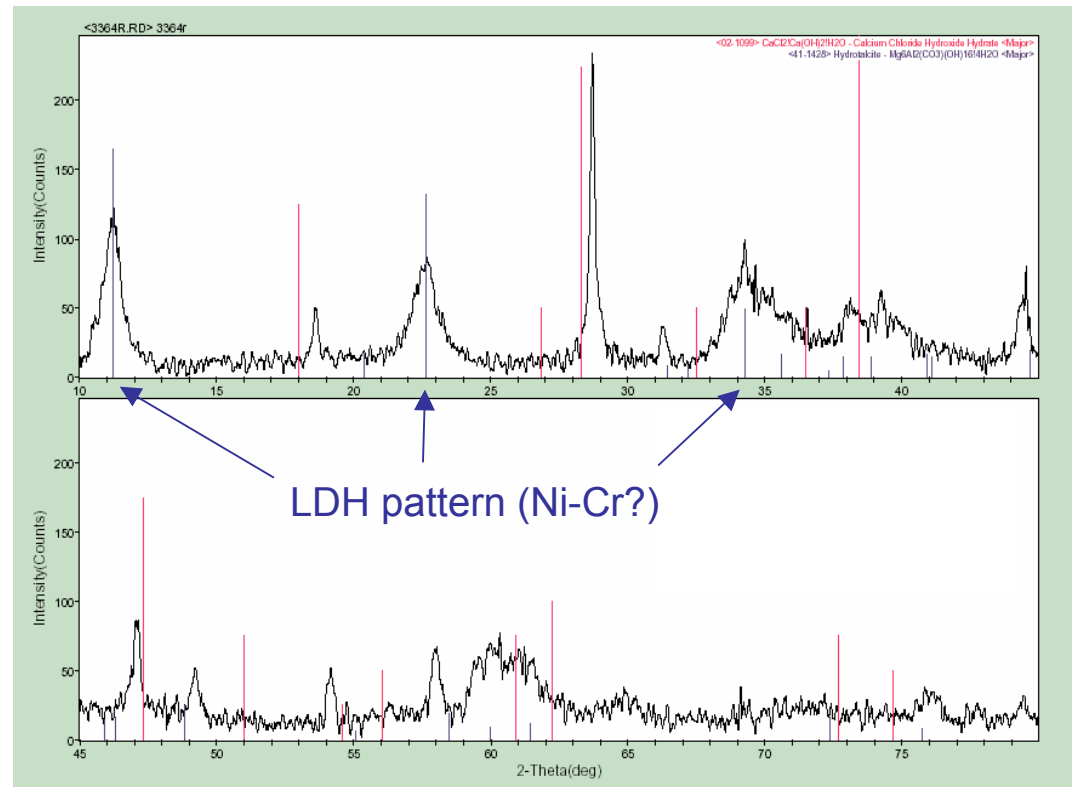
Physical Retention of Brine in Corrosion Products

- Brine volumes are small (max 1.8 $\mu\text{L}/\text{cm}^2$)
- Maximum corrosion product volumetric liquid content that permits penetration to occur (hemispherical, conical penetrations): <0.1%
- Such low levels of saturation are unlikely:
 - Fluid inclusions alone are generally 0.1 to 0.5% in crystalline materials. (Perry et al. 1984, *Perry's Chemical Engineers' Handbook*)
 - Measured porosity in steel and iron analogs (aged 800 years to modern): 10-15%, about half as <50 nm pores (Dillman et al., 2004, *Corrosion Science*)



Chemical Sequestration in Corrosion Products

- Salt loads are small. Max values:
 - 0.11 mg Cl/cm²
 - 1.29 mg NO₃/cm²
- Alloy 22 outer barrier:
 - 5.9 g/cm² (conical penetration)
- Concentration in corrosion products required to consume Cl prior to penetration: <20 ppm
- Potential Cl-containing phases: Layered double hydroxide (LDH) phase observed experimentally



DTN: LL050302823121.051



Summary: Physical and Chemical Environment Associated with Dust Deliquescence

- **Physical Environment**
 - Unsaturated dust (open system with respect to gases)
 - Thin films and small droplets, in part suspended in dust
 - Limited solution volume
- **Chemical Environment**
 - NaCl-NaNO₃-KNO₃-Ca (NO₃)₂ brines (ammonium mineral phases decompose prior to deliquescence)
 - Brines can form in small amounts at high temperatures (>160°C)
 - Initial brines are nitrate-rich
 - Degassing will result in increase in pH, increased NO₃/Cl
 - Limited salt/brine components



Conclusions

1. Can multiple-salt deliquescent brines form at elevated temperatures? **Yes**
2. If deliquescent brines form at an elevated temperature, will they persist? **Yes**
3. If deliquescent brines persist, will they be corrosive? **No (<160°C)**
4. If potentially corrosive brines were to form, would they initiate localized corrosion? **No**
5. If localized corrosion were to be initiated, would penetration of the waste package outer barrier occur? **No**

On the basis of this screening argument, the process of localized corrosion due to dust deliquescence has been screened from the Total System Performance Assessment for the License Application

