The In-Drift Chemical Environment During the Above-Boiling Period

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Nuclear Waste Technical Review Board

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• In-drift chemical environment
  ✷ Greg Gdowski, Lawrence Livermore National Laboratory
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Overview of Presentation

- Effect of Thermal-Hydrologic (TH) environment on in-drift chemistry during the above-boiling period
- A first look at salt deliquescence
- Salt minerals in dust in the repository
  - Can they generate CaCl$_2$ or MgCl$_2$ brines?
- Stability of salt minerals at temperature
- Acid gas volatilization from salt assemblages at temperature
- Another look at salt deliquescence
  - How much water is absorbed?
  - What composition brines can develop?
- Conclusions
Effect of TH Environment on In-Drift Chemistry During Above-Boiling Period
In-Drift Chemical Environment During the Above-Boiling Period

- Focus on drift environment where drift wall temperatures are above boiling, which includes:
  - Relatively short heating period that dries out the drift and rock
  - Extended period in which drift wall gradually cools to boiling point—no seepage of water possible

- Issues during this period include:
  - Deliquescence of salt originating from dust accumulated on the waste package
  - Possible generation of acid gases from deliquescent salts and their fate in the drift environment
Above-Boiling Period

Temperature (°C)

Relative Humidity (%)

Time (yr)

I  II  III  IV  V
T-RH Trajectories for Waste Packages
Salt Deliquescence
A First Look at Salt Deliquescence

- Dusts originating in the repository or brought in by ventilation may contain salts that deliquesce at a relative humidity (RH) < 100%

- What is salt deliquescence?
  - Activity of water (x 100) equates to RH
  - Activity of $\text{H}_2\text{O}$ in equilibrium with a saline brine is lower than 1 (pure water), so these brines will absorb $\text{H}_2\text{O}$ when RH (activity of $\text{H}_2\text{O}$ in atmosphere) > activity of $\text{H}_2\text{O}$ in brine
  - For highly deliquescent salts, a brine will exist above the boiling point of pure $\text{H}_2\text{O}$ (boiling point elevation)
Vapor Pressure of Water as a Function of Temperature and Activity of Water
Deliquescence RH for Some Salts

![Graphs showing deliquescence RH for different salts](image-url)
As RH rises in the drift, eutectic for a salt or salt assemblage will be reached.

- First aqueous solution to form will have eutectic composition.
- A bulk composition different from the eutectic composition will cause aqueous solution to migrate along solvus.
Salt Minerals in Dust
Importance of Dusts during the Above-Boiling Period

- Due to lack of seepage during the above-boiling period, salt-bearing dusts are the chief concern because of their potential for deliquescence.
- Small amounts of soluble salts found in repository dust, higher amounts expected if atmospheric dust is more important.
- Chief concern are chloride-bearing salts because of their potential for corrosion of the Alloy 22 waste packages in the repository.
Dust Collection (Phase II) by United States Geological Survey

Dust collected in Phase II by vacuuming surfaces. The amount of dust accumulation ranged from 0.012 to 0.023 gm/cm²
Dust Analysis

- Soluble content of dust analyzed by subjecting samples to a distilled water leach
- Evaporation of leachates yields salt minerals that can be identified
- Primary salt minerals calculated using an equilibrium/mass balance “evaporation” (EQ3/6)
Average of Soluble Cations and Anions

Concentration (milli-equivalents/kg dust)

Ca, Mg, K, Na, Cl, F, NO₃, SO₄, PO₄, CO₃
X-Ray Diffraction Analyses of Salts from Evaporated Dust Leachate

X-ray diffraction analysis of salts precipitated from evaporated dust leachate

<table>
<thead>
<tr>
<th>Salt</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<tbody>
<tr>
<td>NaCl</td>
<td>X</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
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<tr>
<td>KCl</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td></td>
<td></td>
<td>XX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄ 2H₂O</td>
<td>XX</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄ 5H₂O</td>
<td></td>
<td></td>
<td>XX</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄,K)H₂PO₄</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaC₂O₄ 2H₂O</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

XX Major Component  X Minor Component

Analyses conducted at the United States Geological Survey
Salt Mineralogy Calculated with EQ3/6

Dust leachate solutions are “evaporated” computationally with EQ3/6 to yield a primary assemblage of deliquescent salts

<table>
<thead>
<tr>
<th>Main Predicted Salts</th>
<th>Occurrence %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-NaNO₃-KNO₃-KBr</td>
<td>28</td>
</tr>
<tr>
<td>NaCl-KNO₃-KBr</td>
<td>68</td>
</tr>
<tr>
<td>Ca(NO₃)₃-NaCl-NaNO₃-KNO₃-KBr</td>
<td>4</td>
</tr>
</tbody>
</table>

No CaCl₂ or MgCl₂ salts predicted
Different Soluble Salt Contents in Atmospheric and ESF Dust

**Atmospheric Dust**  
(Reheis, 2003)

- Average = 13.3
- Stdev = 8.1
- n = 66

**ESF Dust**  
(Peterman et al., 2003)

- Average = 0.373
- Stdev = 0.175
- n = 51
Can Salt in Dust Generate CaCl$_2$ Brines?

- A CaCl$_2$ brine is possible only if the following conditions on the soluble salt fraction are both satisfied:
  - $\text{Ca} > \text{SO}_4 + \text{CO}_3$ (CaSO$_4$ and CaCO$_3$ are relatively insoluble)
  - $\text{Cl} > \text{Na} + \text{K}$ (NaCl and KCl will precipitate before CaCl$_2$)

- ~96% of the tunnel dusts fail to satisfy the first condition
- The remainder (~4%) satisfy the first condition, but not the second
Can Salt in Dust Generate MgCl₂ Brines?

- The formation of an MgCl₂ brine requires the following three conditions **all** be satisfied:
  - Mg > CO₃ (MgCO₃ is relatively insoluble)
  - Cl > Na + K (NaCl and KCl will precipitate before MgCl₂)
  - A “low silica” environment, since Mg is likely to be tied up by the silica in the soluble fraction

- These conditions do not occur in the repository
The Presence of CaCl$_2$ or MgCl$_2$ Minerals in Outside Dust Is Very Unlikely

- The minerals are known to exist on the earth’s surface at only a few places (e.g., CaCl$_2$:6H$_2$O in Antarctica)
- The few known surface occurrences appear to be ephemeral
  - Very low RH conditions (<25%) required to preserve these salts in situ
  - Low RH conditions even harder to maintain during transport of salts
Is Equilibrium Relevant for Salts in Dust?

- Salts in dust on the metal barrier surfaces may be a mechanical mixture and therefore not in thermodynamic equilibrium
- However, a disequilibrium salt assemblage would almost immediately equilibrate upon initial deliquescence, leading back to a dry state via a reaction such as:

\[ \text{CaCl}_2(aq) + \text{Na}_2\text{SO}_4(c) = \text{CaSO}_4(c) + 2 \text{NaCl}(c) \]

  - Experimental studies indicate reaction times on the order of 2 days or less
  - The reaction products have higher Deliquescence RH points (causing them to dry out) because of their greater thermodynamic stability and lower solubility
Soluble Ionic Ratios (mol/mol) Are Very Similar Among Tunnel Dusts and Nevada Rainfall

<table>
<thead>
<tr>
<th></th>
<th>Tunnel Dusts¹</th>
<th>Nevada Rainfall²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P07</td>
<td>P14</td>
</tr>
<tr>
<td>Na/Cl</td>
<td>2.699</td>
<td>4.069</td>
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<tr>
<td>K/Cl</td>
<td>1.221</td>
<td>1.528</td>
</tr>
<tr>
<td>NH₄/Cl</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Mg/Cl</td>
<td>0.072</td>
<td>0.305</td>
</tr>
<tr>
<td>Ca/Cl</td>
<td>8.472</td>
<td>6.389</td>
</tr>
<tr>
<td>NO₃/Cl</td>
<td>4.002</td>
<td>1.671</td>
</tr>
<tr>
<td>SO₄/Cl</td>
<td>3.123</td>
<td>3.293</td>
</tr>
<tr>
<td>CO₃/Cl</td>
<td>4.839</td>
<td>4.737</td>
</tr>
</tbody>
</table>

¹Three Phase I samples, each representing a different key salt assemblage

²National Atmospheric Deposition Program, 2002 Annual Mean Data
(CA95=Death Valley, NV00=Red Rock, NV05=Great Basin)
Stability of Salt Minerals at Temperature
Stability of CaCl$_2$, MgCl$_2$, and NaCl Salts

- Although not expected based on preceding arguments, the stability of CaCl$_2$ and MgCl$_2$ has been evaluated experimentally.
- Stability of NaCl, which is expected to be present in small amounts, has now been investigated experimentally.
- Salt stability evaluated using thermogravimetric analysis (TGA) under controlled temperature and RH conditions at Lawrence Livermore National Laboratory.
Deliquescence Brines Studied with Thermogravimetric Analysis at LLNL

- Sensitive to weight changes as small as “tens of micrograms”
- Operation at temperatures up to 150°C
Deliquescence and Stability of CaCl$_2$ and MgCl$_2$ Salts in TGA Experiments

- **100°C**: CaCl$_2$ aqueous films are stable for duration of test
- **125°C**: CaCl$_2$ solution evolves slowly, forming insoluble precipitates
- **150°C**: CaCl$_2$ solution evolves rapidly, forming insoluble precipitates and acid gas
- **MgCl$_2$**: transforms within hours at all temperatures, becoming non-deliquescent
Deliquescence and Stability of NaCl and NaCl-KNO₃

- Deliquescent NaCl is stable at 105°C (boiling point of a NaCl-saturated solution is 108.7°C)
- NaCl-KNO₃ may be transforming slowly
Deliquescent Brines – Deposit Formation

- Electron dispersive spectroscopy (EDS) analysis indicates precipitates contain Ca, Cl, and O.
- EDS and wet-chemical analyses indicate a loss of Cl relative to Ca (HCl volatilization).
- Raman spectroscopy indicates that precipitates are not Ca(OH)$_2$ or CaCO$_3$.
- Precipitates are possibly CaOHCl.
Summary of TGA Results

- TGA experiments conducted at controlled temperature and RH show CaCl₂ transforms to non-deliquescent phases at temperatures and RH conditions of test.
- Deliquescent MgCl₂ unstable at all temperatures > 100°C.
- Transformation of these salts is a result of HCl volatilization.
- Strong temperature dependence to volatilization of HCl.
- NaCl is stable at 105°C.
Volatilization of Acid Gases in the Drift Environment
Generation of Acid Gas in the Above-Boiling Period

- Instability of CaCl₂ and MgCl₂ (to the extent they are present) is due largely to degassing of HCl
- HNO₃ gas less volatile than HCl gas
- What will happen to any acid gas generated in the drift environment?
- How much acid gas will be generated?
Fate of Acid Gas in the Drift Environment

- Under open system conditions, any HCl gas that is generated will disperse in the drift—this will occur at high temperatures when drift environment is dry.
- Reactive gases will migrate along fractures in rock until encountering liquid water, where partitioning into the aqueous phase will occur.
- Migration and dissolution behavior of gases in rock confirmed in the Drift-Scale Test.
- Condensation will not occur on waste packages since they are the hottest spots.
Simulations to Demonstrate Fate of Acid Gas in the Drift Environment

Inject HCl gas above waste package under 2 scenarios
1) Drift wall just below boiling, waste package above boiling,
2) Drift wall and WP below boiling, water vapor transported into drift from higher T

Use mass of dust measured in tunnels to determine amount of dust covering a waste package

Use measured chloride content of dusts and assume all of the chloride volatilizes as HCl
Waste Package Above Boiling, Drift Wall Below Boiling (No Condensation in Drift)

- HCl gas disperses rapidly in the drift environment
- Over slightly longer time periods, HCl gas dissolves into the aqueous phase in the rock, thus lowering its concentration in the drift atmosphere

Simulations conducted at Lawrence Berkeley National Laboratory
Drift Wall and Waste Package Below Boiling, Water Vapor Transported from Hotter Region

- When water condenses on the drift wall, its pH is lowered by the dissolution of HCl gas
- Continued water condensation raises pH with time through dilution
- No condensation of any water on waste package

Simulations conducted at Lawrence Berkeley National Laboratory
Conclusions Concerning Acid Gases

- In the unlikely event that CaCl$_2$ or MgCl$_2$ are present, HCl gas can be generated during the above-boiling period
  - If this occurs, it is expected to be during the period when the entire drift temperature > ~125$^\circ$C—no condensation can occur
- Amounts of acid gas possible are small
- Any acid gases generated will be dispersed widely in the drift environment
- Upon dispersal, acid gases will dissolve into liquid water in the rock beyond the drift
- If condensation of liquid water occurs (accompanied by scavenging of HCl gas), it will take place in coolest parts of the drift (not the waste packages)
Another Look at Salt Deliquescence

- How much water is absorbed?
- What composition brines can develop?
Salt Deliquescence in Multicomponent Systems

- Salts present in dust expected to contain both nitrate and chloride
- Reversed multicomponent deliquescence experiments used to validate geochemical model
- Mass of $\text{H}_2\text{O}$ adsorbed by deliquescent salt is very small
- At high temperature and low RH, eutectic composition has high $\text{NO}_3:\text{Cl}$ ratio due to thermodynamics of deliquescence
Validation of Geochemical Model at 120°C

- Reversed deliquescence experiments at 120°C
- Reversal occurs within about 48 hours in most cases, indicating rapid reaction rates

Experiments conducted at Lawrence Livermore National Laboratory
Deliquescence in Na-K-Cl-NO$_3$ System

- While concentrated brines can develop due to deliquescence, brine volumes are small

For a salt mass of 0.35 g
Thermodynamic Control of $\text{NO}_3/\text{Cl}$ Ratios in NaCl-NaNO$_3$ system

![Graph showing thermodynamic control of NO$_3$/Cl ratios in NaCl-NaNO$_3$ system.](image)
Nitrate-Chloride Ratios in Dust Leachate

- When salts dissolve completely at higher RH, solution $\text{NO}_3/\text{Cl}$ ratios are equal to ratio in original salt assemblage.
- In Na-K-Cl-$\text{NO}_3$ system, these ratios are minimum values--at lower RH, the thermodynamics of the system drive solution to higher $\text{NO}_3/\text{Cl}$ ratios.

Data collected and analyzed by the United States Geological Survey
Chemistry of Brines in Na-K-NO$_3$-Cl System

Temperature-RH history of a waste package limits range of possible brine compositions
Range of Possible NO$_3$/Cl Ratios During the Above-Boiling Period

During the above-boiling period, NO$_3$/Cl ratios remain $> 0.5$
Conclusions

- Due to lack of seepage during the above-boiling period, the deliquescence of salts in dust is the chief issue.

- CaCl$_2$ and MgCl$_2$ salts are extremely unlikely to be present in the repository, but if present, will rapidly transform to non-deliquescent phases due to their instability at temperature.

- Any acid gases generated due to salt deliquescence will be dispersed in drift environment and dissolved into water in the rock.

- If condensation of liquid water occurs accompanied by scavenging of acid gases, it will take place in coolest parts of the drift, not on the waste packages.
Conclusions

• Only NO$_3^-$ dominant brines will form during the above-boiling period due to the thermodynamics of deliquescence in Na-K-Cl-NO$_3$ system

• Mass of H$_2$O taken up by salts is very small
Catholic University
Distillation Experiments

- Distillation experiment involving extensive boiling of Ca-Mg-Cl-N0₃ water shows condensation of low pH water, leading to metal corrosion
- Is the experiment relevant to the drift environment?
Catholic University Distillation Experiment

Features of the distillation experiment that do not apply to the drift environment at Yucca Mountain

- Highly localized condensation due to closed system—refluxing of condensed acids back into boiling liquid
- Corroding metal coupons at lower temperature than boiling brine
- Experiment involves the equivalent of about 14,000 liters of dilute seepage water
- Very large temperature gradients

The Catholic University distillation experiment is irrelevant to the drift environment at Yucca Mountain
Backup Slides
Reactive Transport Modeling of Distillation Experiment

ToughReact (Pitzer) modeling of Catholic University experiment conducted at Berkeley National Laboratory