Thermal Experiments on Atmospheric and Subsurface Dust at Yucca Mountain, Nevada

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Nuclear Waste Technical Review Board

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• Team members on dust project
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  – The statements expressed in this paper do not necessarily reflect the views or policies of the U.S. Department of Energy
Dust Deliquescence and Corrosion

- **FEP (Features, Events, and Processes)**
  2.1.09.28.0A “Deliquescence on Waste Package Outer Barrier”
  - Subsurface and atmospheric dust contain small amounts of soluble salts (chlorides, nitrates, and sulfates)
  - In a humid environment, salts in dust may deliquesce (absorb moisture) and form brines which may cause localized corrosion of the outer barrier of the waste package
Enrichments in Bulk Underground Dust Relative to Host Rock

- Underground dust is 90 to 95 percent comminuted host rock (mostly rhyolite)

- Excess major elements
  - FeO (introduced as metallic iron), CO$_2$ and F (from fracture minerals), organic C and Cl (neoprene abraded from conveyor belt and introduced materials), and Cl (from pore water)

- Excess trace elements
  - Bi, Cd, Co, Cr, Mo, Ni, Sb, V, Zn (metallic elements introduced during construction)
Soluble Salt Contents and NO₃/Cl Ratios of Dust from Various Environments

<table>
<thead>
<tr>
<th>Dust</th>
<th>Salt (%)</th>
<th>NO₃/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESF-2</td>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>ECRB</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Surface (exposed)</td>
<td>0.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Surface (protected)</td>
<td>0.2-7.0</td>
<td>0.5-7.7</td>
</tr>
<tr>
<td>Atmospheric (cyclone)</td>
<td>2.3-5.5</td>
<td>10</td>
</tr>
<tr>
<td>Regional (Reheis, USGS)</td>
<td>13</td>
<td>--</td>
</tr>
</tbody>
</table>
USGS Experimental Studies

- Heating experiments are being conducted on natural dust (ESF and cyclone)
  - 250 mg carefully split aliquots of ESF dust were heated at 180°C for up to 64 days
  - Because of limited sample size, a 50-mg aliquot each of 4 cyclone dust samples were heated for 8 days
  - Aliquots were removed from heating, leached with deionized water (20:1 or 40:1), and analyzed for anions, cations, and some organics
  - Concentrations of ions in leachates (C) are compared with concentrations in the unheated aliquots (C₀)

- Pure salts and mixtures were also heated and analyzed
Thermal Experiments Using Salts
(at 180°C for 48 hours)

- Salts used are NaCl, KCl, NaNO₃, KNO₃, Ca(NO₃)₂·4H₂O
- Individual salts
  - Ca(NO₃)₂·4H₂O—formed a solid bead
  - Salts lost moisture but **no nitrate loss**
- Mix of nitrate salts only
  - Salt mix liquefied
  - Salts lost moisture but **no nitrate loss**
- Nitrate salts plus chloride salts
  - Salt mix liquefied
  - Salts lost moisture but **no nitrate loss**
Changes in Soluble Fraction of ESF and Cyclone Dust when Heated at 180°C

- **Chloride**
  - Increase in soluble chloride possibly caused by degradation of neoprene particulates
  - Subsequent loss possibly by acid degassing

- **Nitrate**
  - After 200 hours, 70 percent of soluble nitrate is lost from ESF dust

- **Sulfate**
  - Increase in soluble sulfate possibly caused by oxidation of sulfur in neoprene
Changes in Soluble Fraction of ESF and Cyclone Dust when Heated at 180°C (cont’d)

- After 24 hours, about 60 percent of soluble ammonium is lost from ESF dust
- Soluble calcium and magnesium in ESF dust increase by about 30 percent
- Cyclone dust loses soluble ammonium but little change in calcium and magnesium
Changes in Soluble Fraction of ESF and Cyclone Dust when Heated at 180°C (cont’d)

- Soluble formate increases slightly and then gradually decreases
- Soluble acetate increases by a factor of 2 to 3 and then gradually decreases
- Changes in formate and acetate in cyclone dust are generally consistent with those for ESF dust
Reduction of Nitrate by Organic Material*

- Nitrogen occurs in nature with valences of +5 in NO$_3^-$ to -3 in NH$_4^+$ and a reduction series can be written as:

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2(\text{g}) \rightarrow \text{NH}_4^+
\]

- Nitrate can be reduced by reactions of the type:

\[
2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 \uparrow + 6\text{H}_2\text{O}
\]

- Reduction of nitrate by organic matter is well documented:

\[
5\text{CH}_2\text{O} + 4\text{NO}_3^- \rightarrow 2\text{N}_2 \uparrow + 4\text{HCO}_3^- + \text{CO}_2 \uparrow + 3\text{H}_2\text{O}
\]

Nitrate-to-Chloride Relations in Heated Dust

- Underground and atmospheric dust typically have NO$_3$/Cl ratios between 1 and 10.
- NO$_3$/Cl ratios are reduced 1 to 2 orders of magnitude due to loss of NO$_3$ upon heating to 180°C for 64 days.
Trajectory of Soluble Chloride and Nitrate Concentrations in ESF Dust Samples when Heated at 180°C for 64 Days

- Soluble nitrate and chloride in two ESF samples shown by red and green circles
- Initial increase in chloride is followed by substantial decrease in nitrate
Summary

• Heating experiments for 64 days reveal systematic changes in amounts of soluble cations and anions in ESF and cyclone (atmospheric) dust samples
  – Nitrate-to-chloride ratios are reduced 1 to 2 orders of magnitude
  – Soluble sulfate increases with heating in ESF and cyclone dust samples
  – Soluble chloride increases by a factor of 2 to 3 and then gradually decreases with prolonged heating in ESF dust samples