U.S. Department of Energy
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Thermal Experiments on Atmospheric and Subsurface Dust at Yucca Mountain, Nevada

Presented to:
Nuclear Waste Technical Review Board

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USGS science for a changing world

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  - Zell Peterman (PI), Thomas Oliver, Leonid Neymark, Brian Marshall, Loretta Kwak, Kiyoto Futa, Joseph Whelan
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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 NO_3/Cl Ratios of Dust from Various Environments

Dust	Salt (%)	NO_3/Cl
ESF-2	0.5	2.2
ECRB	0.1	1.1
Surface (exposed)	0.1	3.1
Surface (protected)	0.2-7.0	0.5-7.7
Atmospheric (cyclone)	2.3-5.5	10
Regional (Reheis, USGS)	13	--

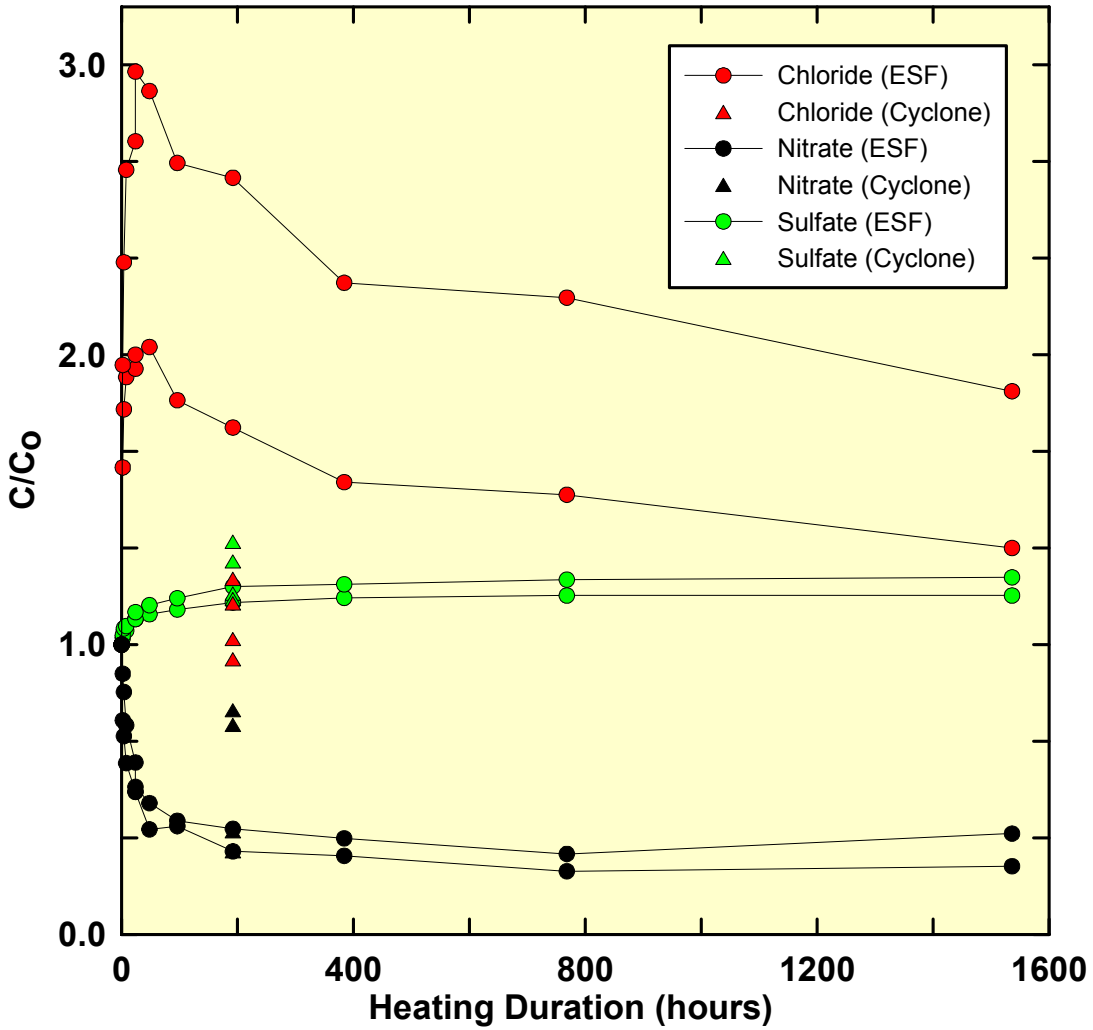
USGS Experimental Studies

- **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 (C_o)**
- **Pure salts and mixtures were also heated and analyzed**

Thermal Experiments Using Salts
(at 180°C for 48 hours)

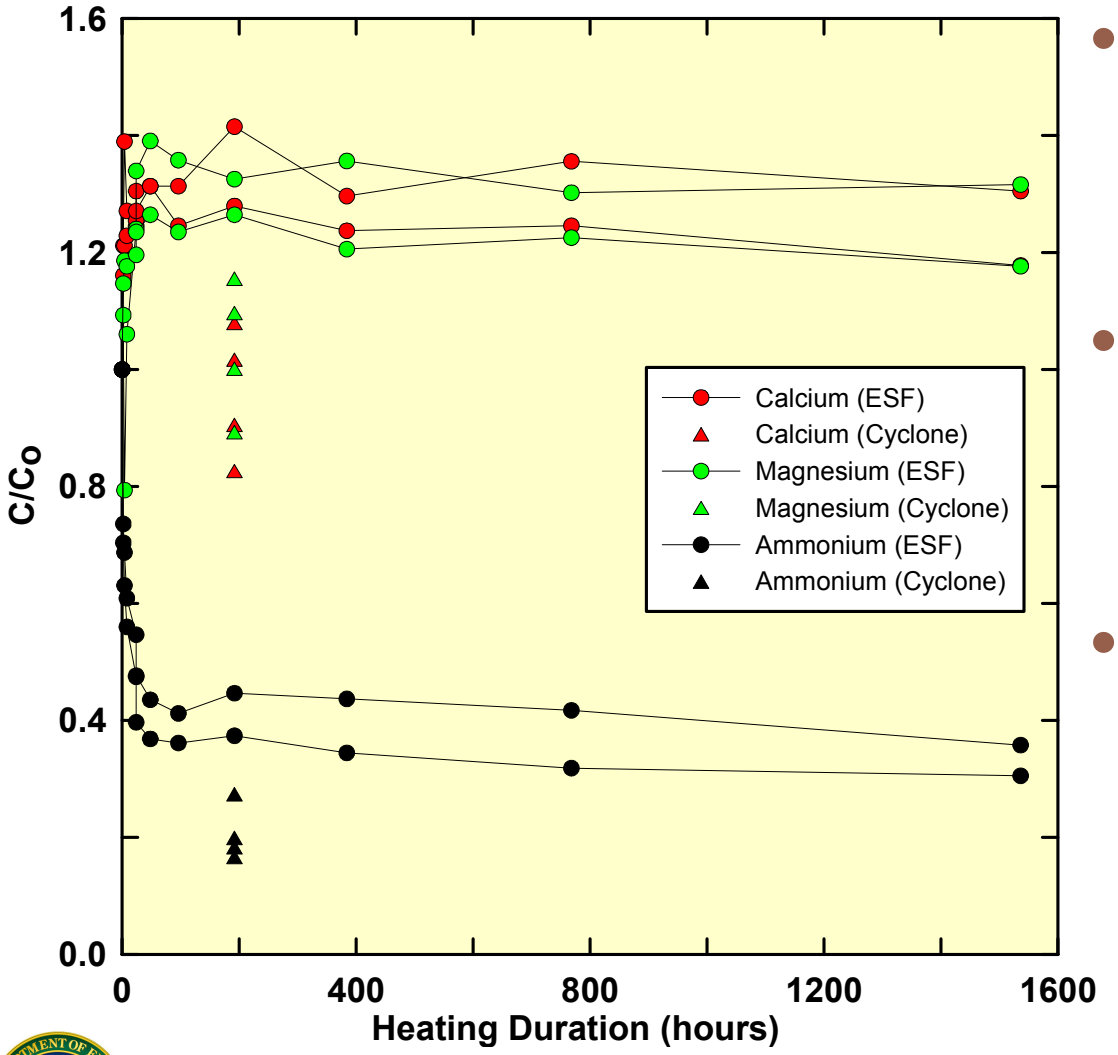
- Salts used are NaCl, KCl, $NaNO_3$, KNO_3, $Ca(NO_3)_2 \cdot 4H_2O$
- Individual salts
  - $Ca(NO_3)_2 \cdot 4H_2O$—formed a solid bead
  - Salts lost moisture but no nitrate loss
- Mix of nitrate salts only
  - Salt mix liquefied
  - Salts lost moisture but no nitrate loss
- Nitrate salts plus chloride 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



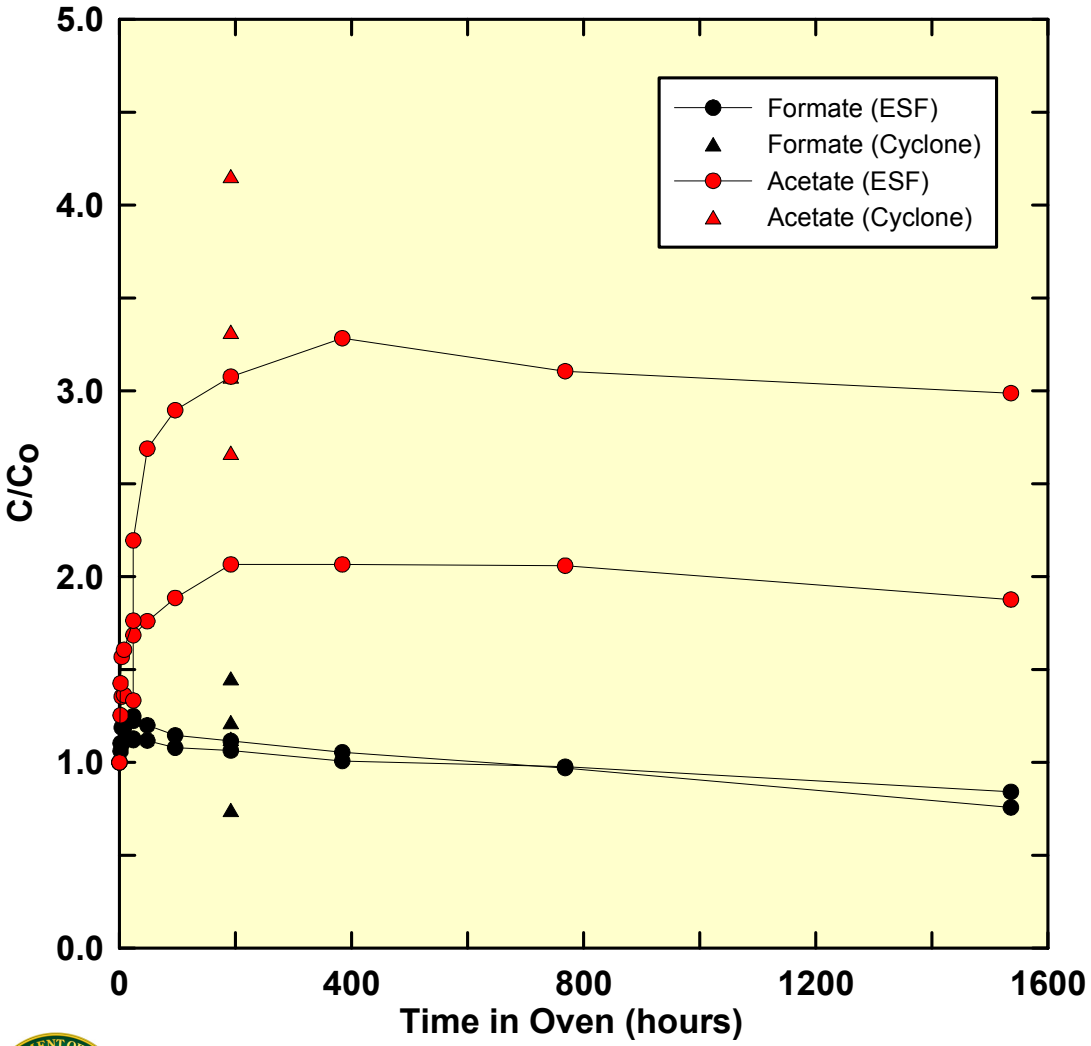
- **Chloride**
  - Increase in soluble chloride possibly caused by degradation of neoprene particulates
  - Subsequent loss possibly by acid degassing
- **Nitrate**
  - After 200 hours, 70 percent of soluble nitrate is lost from ESF dust
- **Sulfate**
  - Increase in soluble sulfate possibly caused by 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:

$$NO_3^- \rightarrow NO_2^- \rightarrow N_{2(g)} \rightarrow NH_4^+$$

- Nitrate can be reduced by reactions of the type:

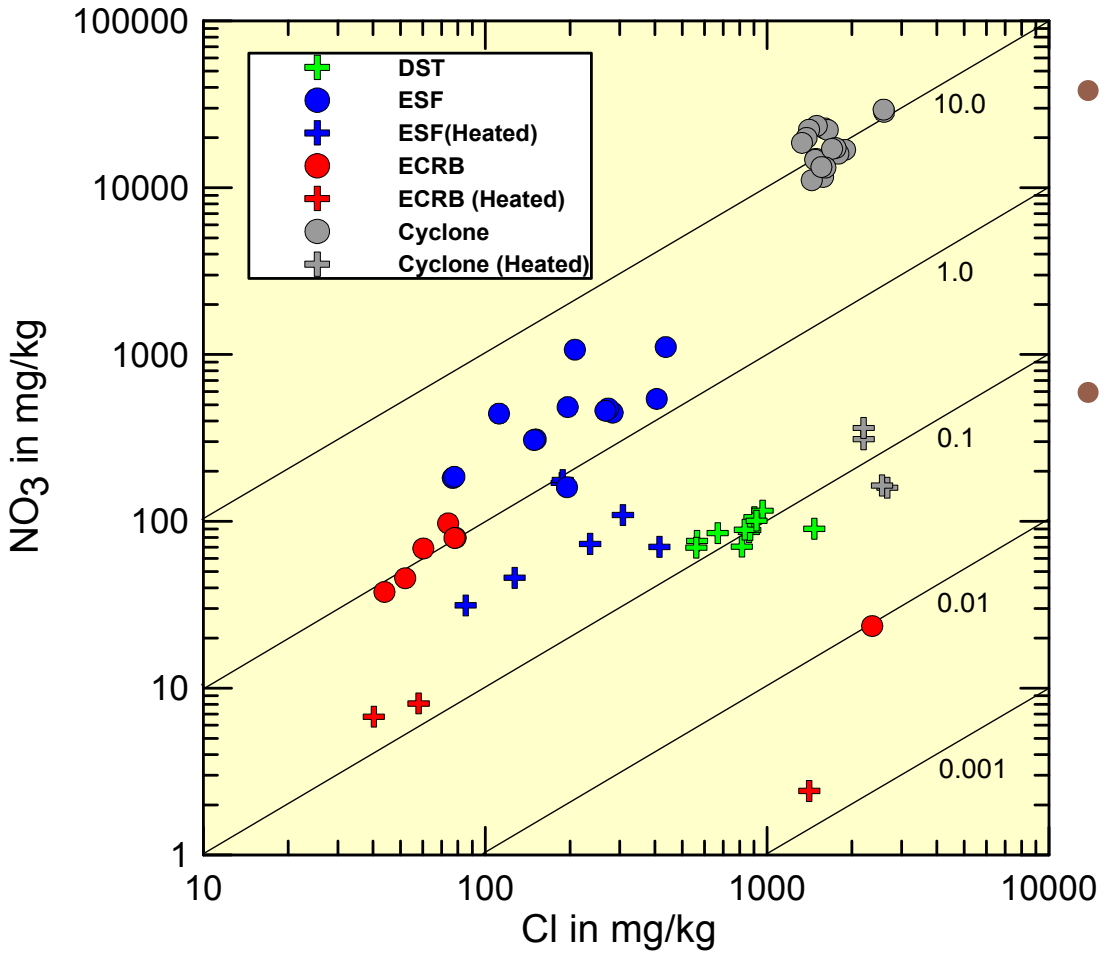
$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2\uparrow + 6H_20$$

- Reduction of nitrate by organic matter is well documented:

$$5CH_2O + 4NO_3^- \rightarrow 2N_2\uparrow + 4HCO_3^- + CO_2\uparrow + 3H_2O$$

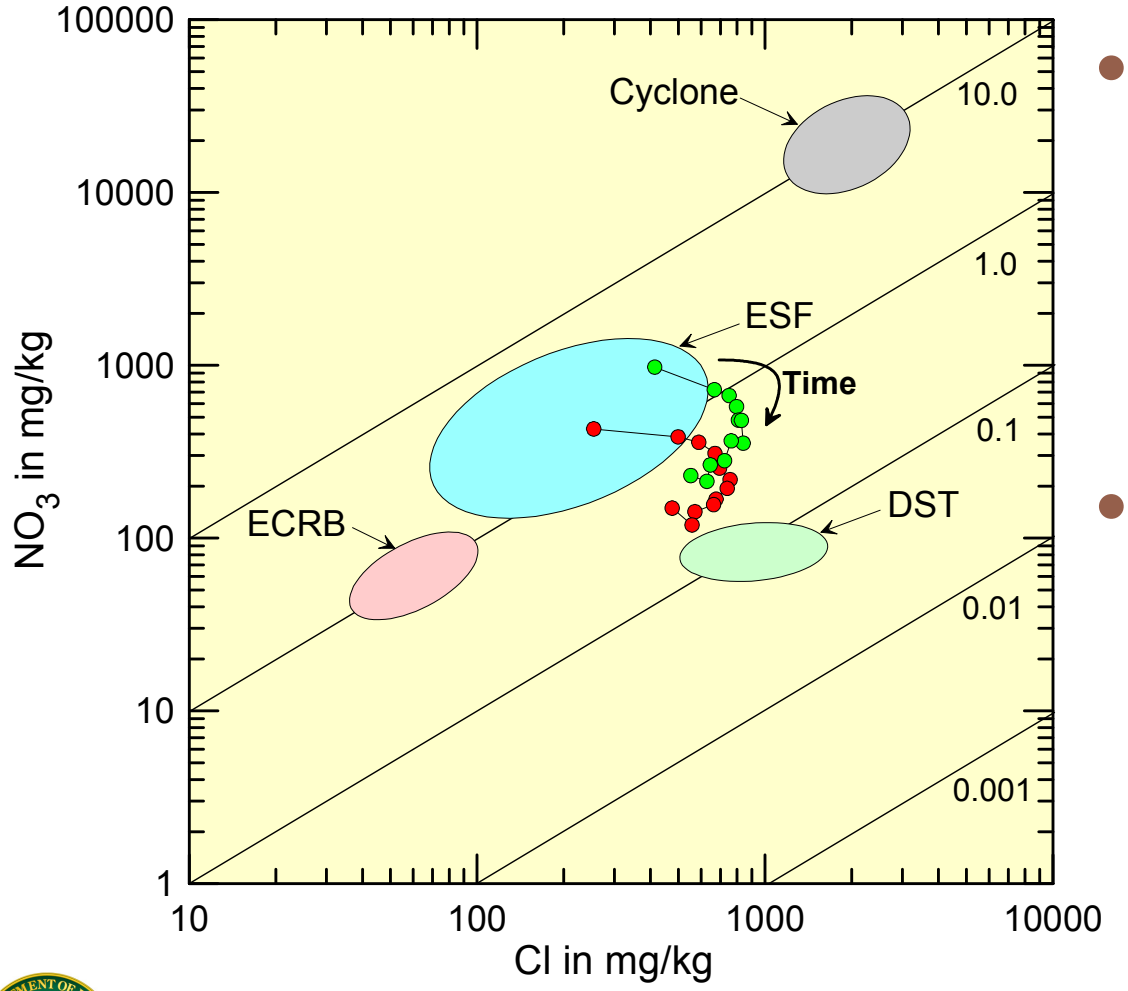
*Appelo, C.A.J., and Postma, D., 1994, Geochemistry, Groundwater and Pollution: A.A. Balkema, Rotterdam, p. 250, 270

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 to3 and then gradually decreases with prolonged heating in ESF dust samples**