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# Effect of Capillary Retention by Dusts on the Corrosivity of Deliquescence Brines

X. He, R.T. Pabalan, and L. Yang
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute®

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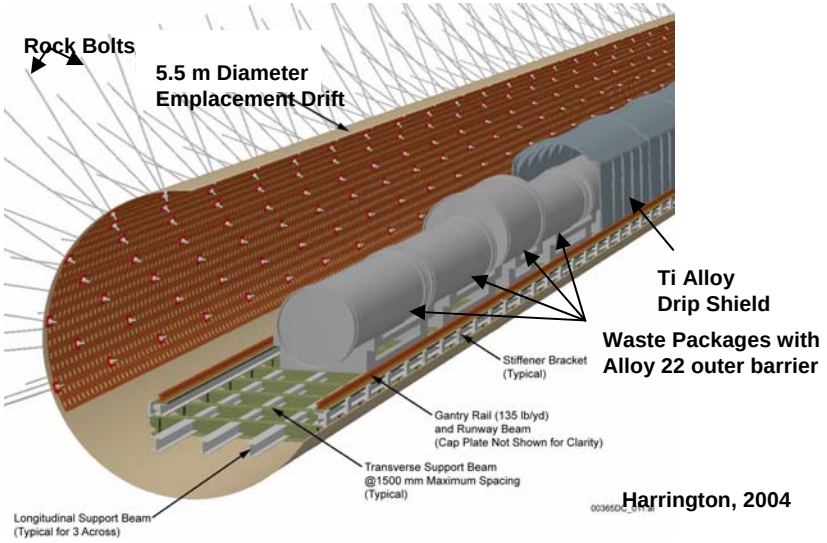
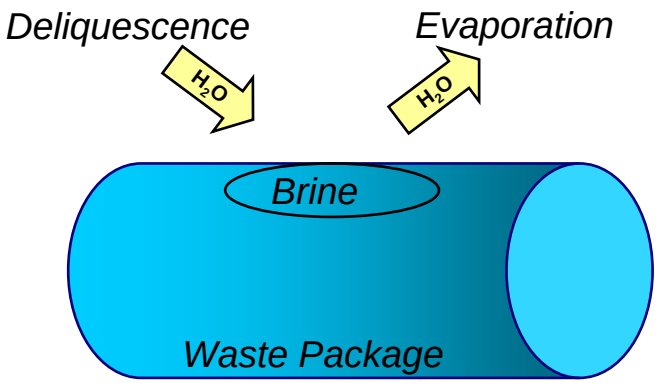
# Background

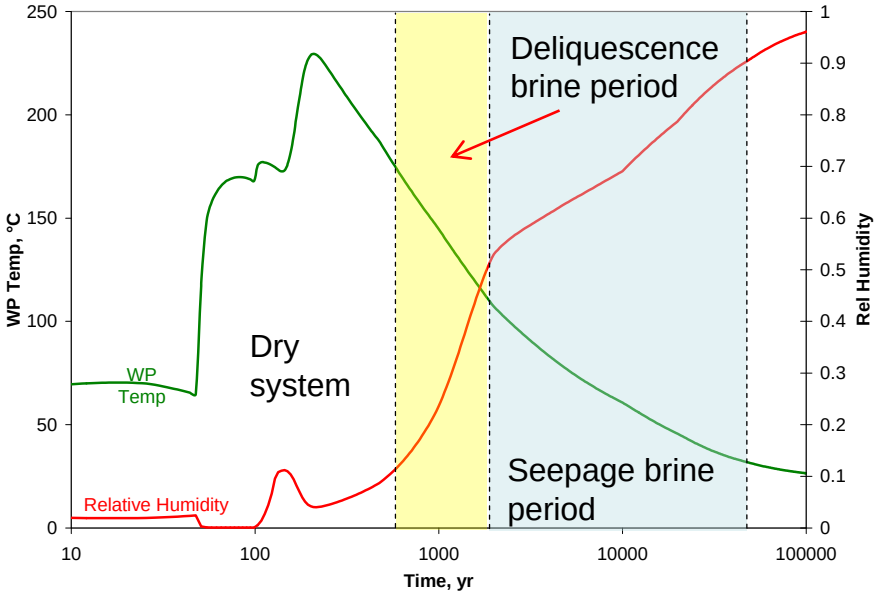
- Engineered barriers at a potential Yucca Mountain, Nevada, high-level waste repository include waste packages and drip shields
- Corrosion due to brines is a potential degradation process
  - Deliquescence of inorganic salts present in dusts
  - Evaporative concentration of seepage water



# Background (Cont'd.)

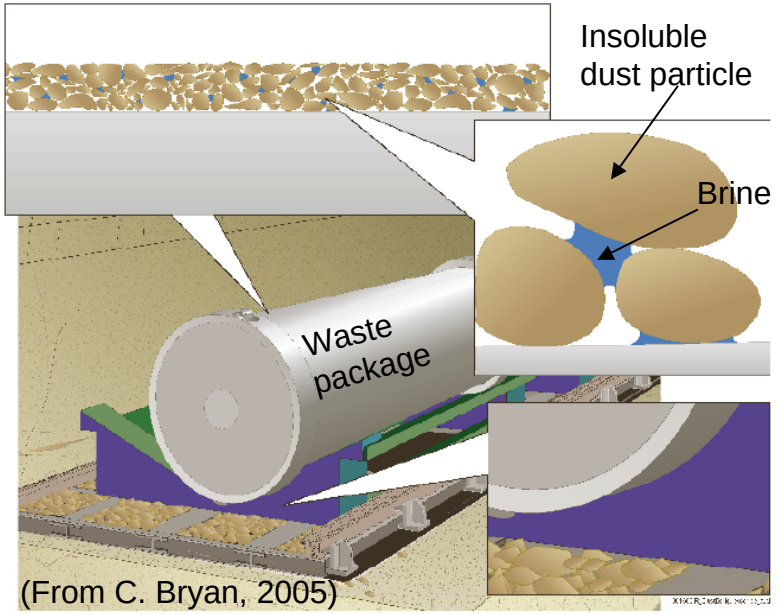
- Deliquescence
  - Rapid absorption of water from humid air by inorganic salts to form a saturated solution
- Potential corrosion of engineered barriers at elevated temperatures
  - $NaCl$-$KNO_3$-$NaNO_3$ salts have deliquescence points exceeding 190 °C [374 °F]
  - These salts are possible deliquescent mineral assemblages at Yucca Mountain (C. Bryan, 2005)




**Calculated Waste Package Temperature and Relative Humidity for a Degraded Drift Scenario**

# Background (Cont'd.)

- Rock dusts could mitigate corrosion by deliquescence brines (C. Bryan, 2005)
  - Physical isolation of salt minerals in the dust may inhibit the formation of eutectic salt mixtures with low deliquescence relative humidity
  - Limited volume of brine
  - Capillary and surface tension effects in the dust will limit brine contact with metal surface



(From C. Bryan, 2005)

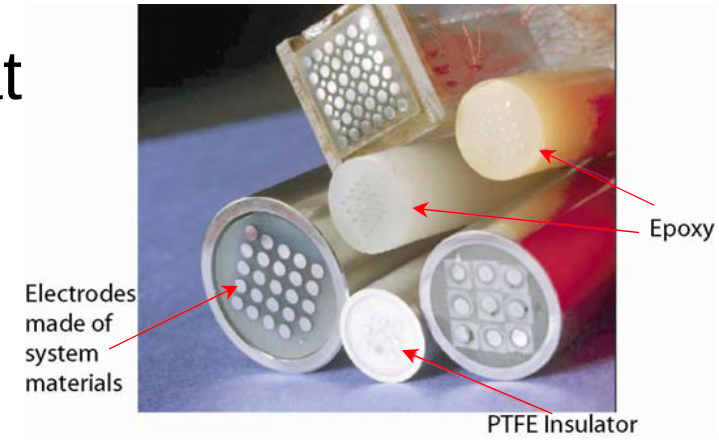
# Objectives of This Study

- Measure corrosion in brines formed by deliquescence of salts mixed with rock dusts
- Evaluate the effect of capillary retention by dusts on corrosivity of deliquescence brines

# Experimental Method

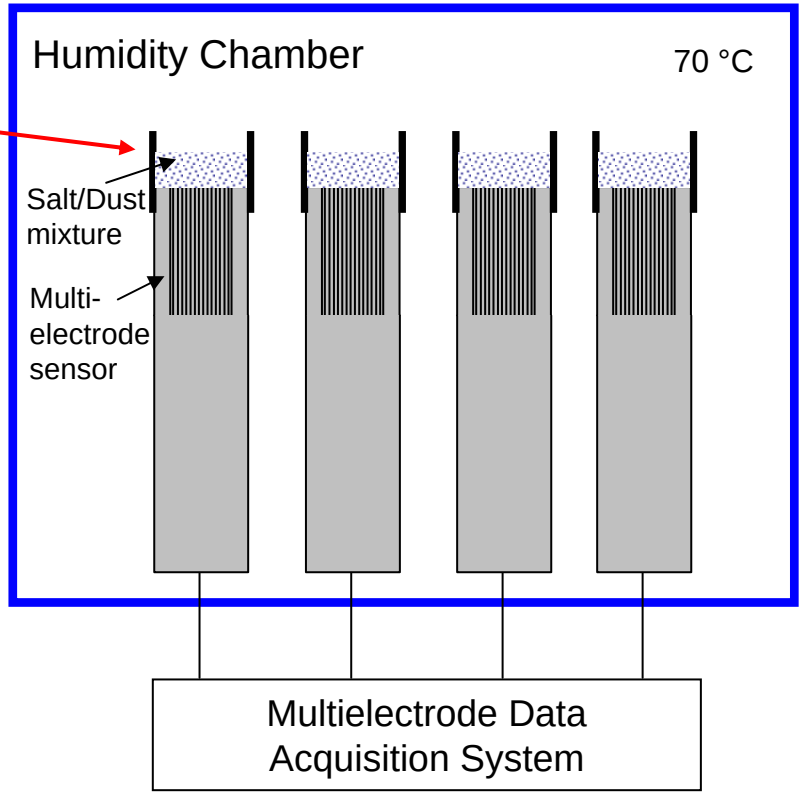
- Corrosion was monitored using a coupled multielectrode array sensor (MAS) probe developed at SwRI® (Yang et al., 2002)
  - Carbon steel electrodes for higher sensitivity to corrosivity of brine
- Deliquescent salt: NaCl
- Rock dust: Topopah Spring Tuff
  - Potential repository host rock
  - Crushed and sieved to <74 μm [<0.003 in] diameter
- Quartz powder used for comparison
  - Ground and sieved to <250 μm [<0.01 in] diameter
  - Acid washed

Coupled Multielectrode Array Sensors

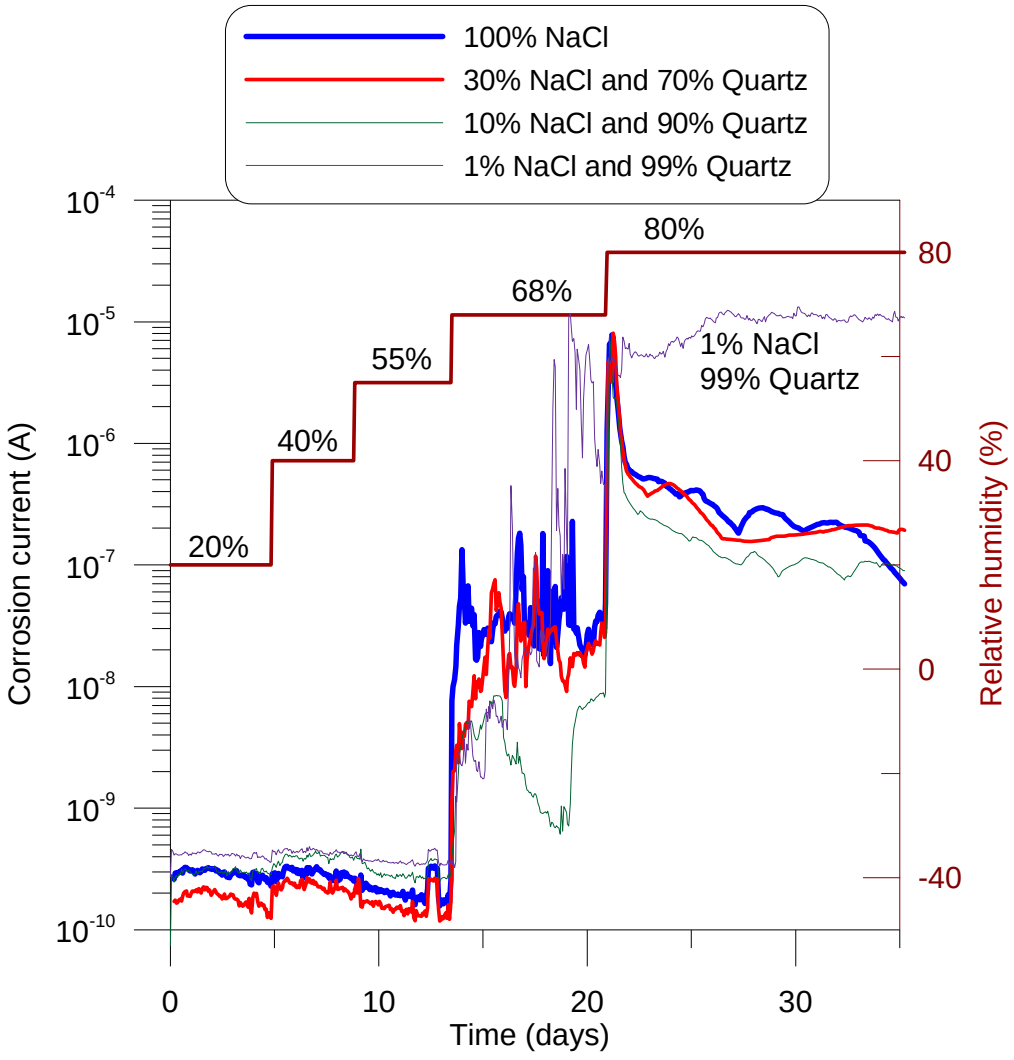


# Experimental Setup

- Salt/dust mixture placed inside Tygon® sleeve above the MAS probe
  - 10 g [0.35 oz] total mass
  - Relative amount of NaCl varied from 0.4  to 100 wt%
- Controlled temperature-humidity chamber (ESPEC)
  - Temperature = 70 °C [158 °F]
  - Relative humidity raised stepwise from <20% to above the deliquescence point of NaCl (75% at 70 °C [158 °F])



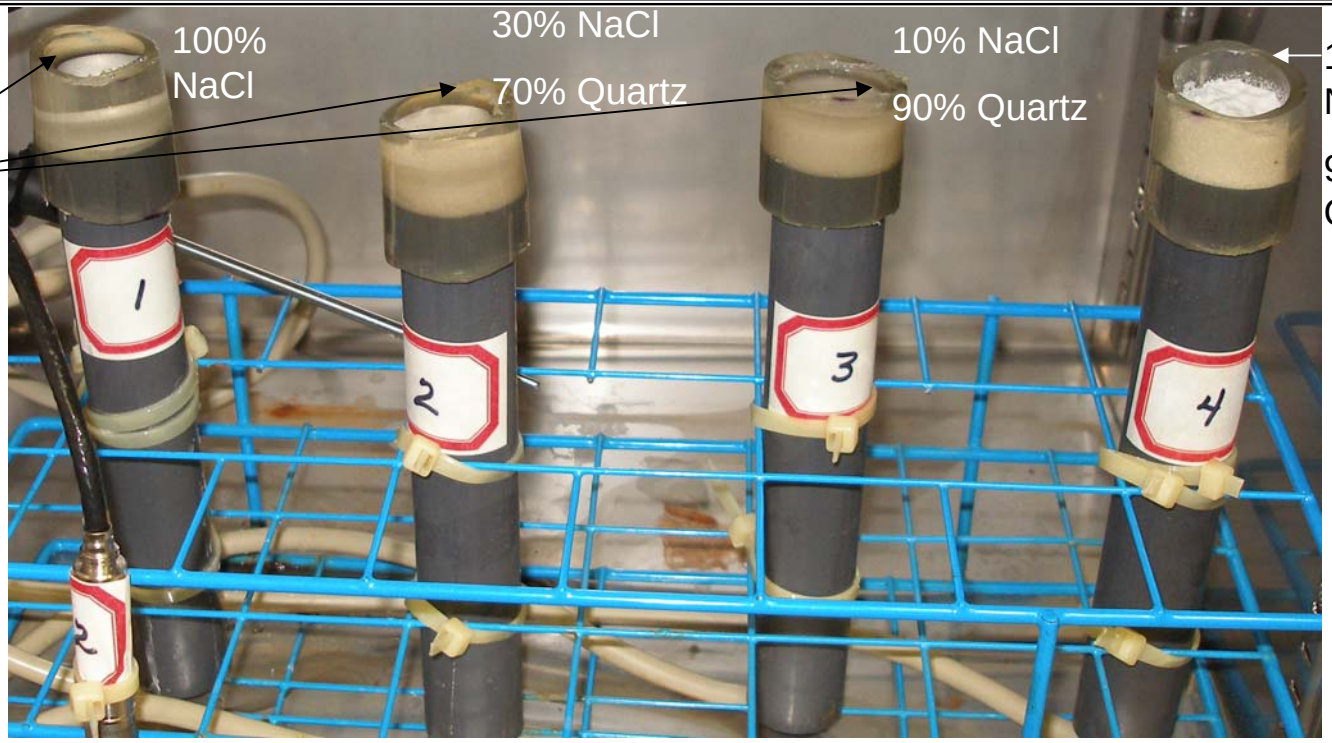
# Results–Test 1: NaCl/Quartz Mixture




- Brine started to form at 68% RH, below the NaCl deliquescence relative humidity (75% RH)
- Brine from 1%-NaCl/99%-quartz mixture is the most corrosive
  - Possibly due to very thin electrolyte film where oxygen transport is not a limiting factor
  - Calculated volume of deliquescence brines (per 10 g of solid)
    - 100% NaCl: 31 mL
    - 30% NaCl: 9.3 mL
    - 10% NaCl: 3.1 mL
    - 1% NaCl: 0.31 mL

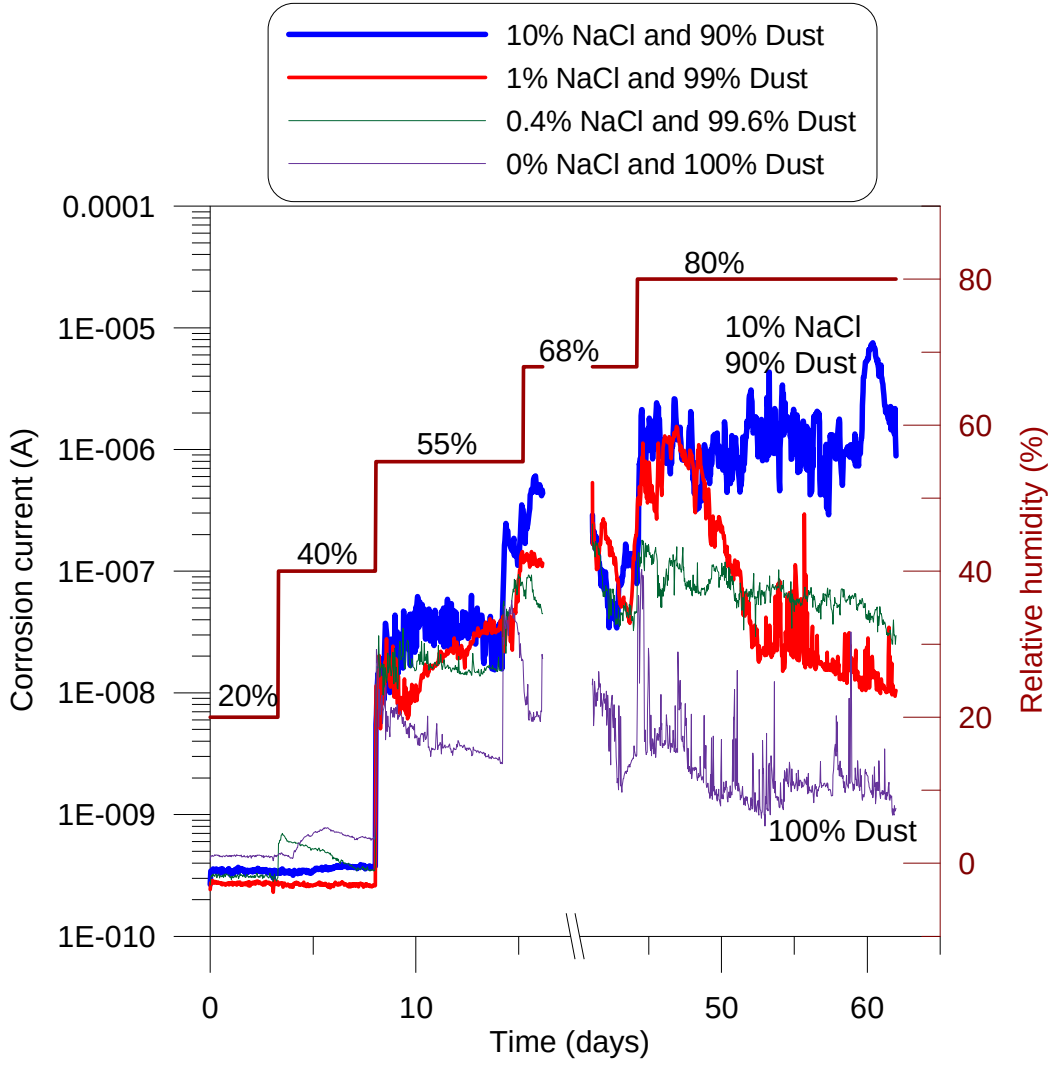
# Test 1 (NaCl/Quartz): Post-Test Observations

- Deliquescence brines formed at 68% RH and 80% RH
- $H_2O$ overflow observed at 80% RH for probes 1, 2, and 3, but not on probe #4



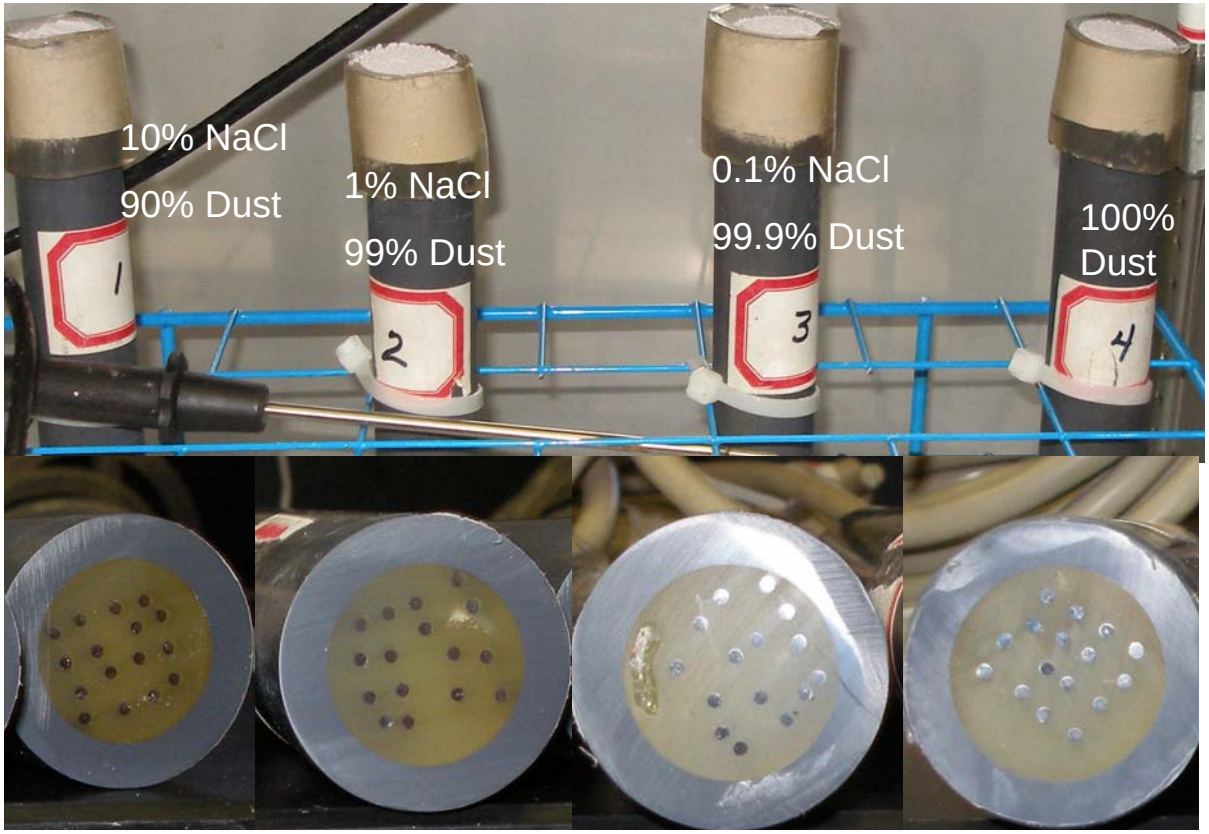

Corrosion was observed on each probe indicating solution contacted the metal surface

# Results–Test 2: NaCl/Dust Mixture




- Brine formed at 55% RH, below that observed for NaCl/quartz mixture (68% RH) and much lower than NaCl deliquescence point
  - Possible moisture absorption on dust
- Dust reduced the corrosion current, but did not prevent brine from contacting the metal surface

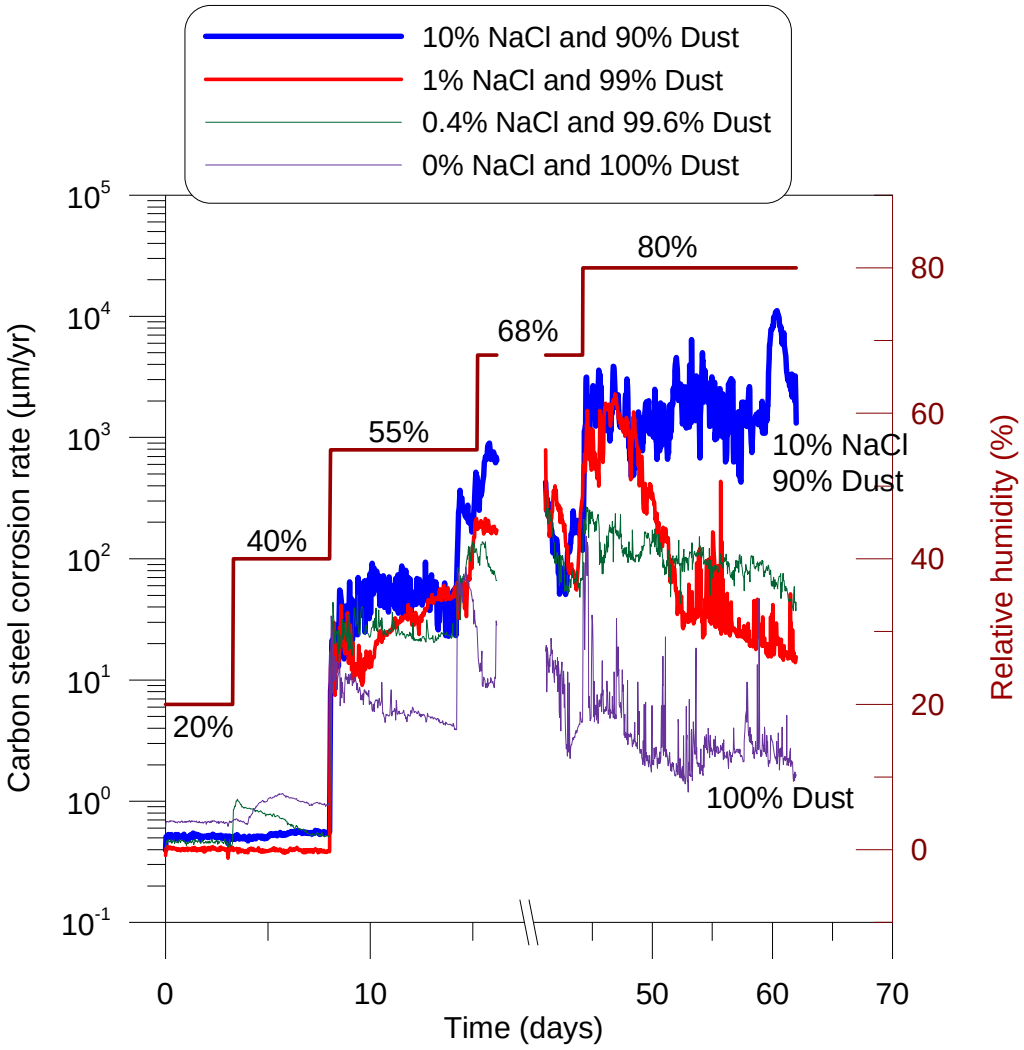
# Test 2 (NaCl/Dust): Post-Test Observations




All the probes were corroded indicating liquid formed at each test condition

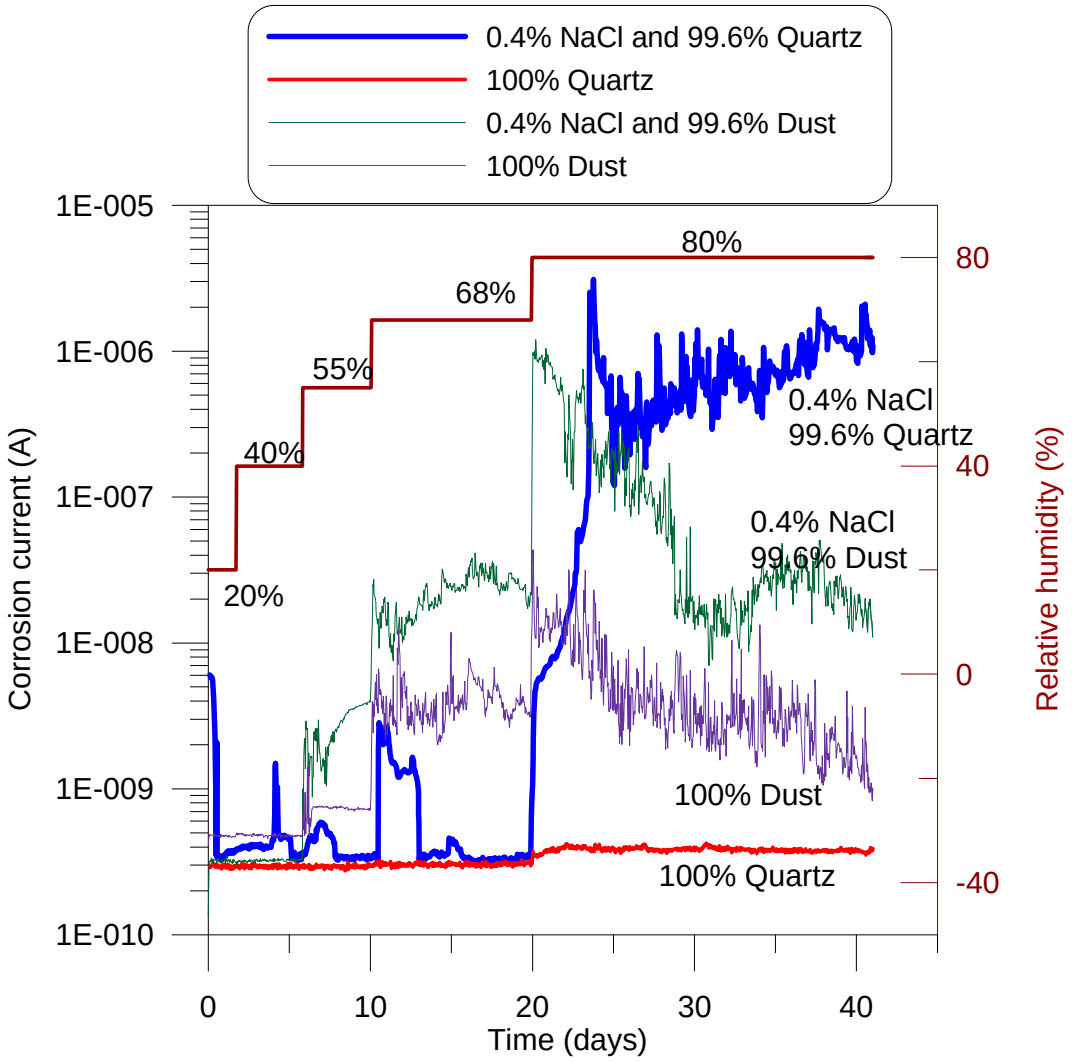
- Calculated volume of deliquescence brines (per 10 g of solid)
  - 10% NaCl: 3.1 mL
  - 1% NaCl: 0.31 mL
  - 0.4% NaCl: 0.12 mL
- No visible liquid formed even at 80% RH, but the solid mixtures were damp

# Test 2 (NaCl/Dust): Corrosion Rate




- For all mixtures (even for NaCl-free system), carbon steel corrosion rate increased above 1 µm/yr once relative humidity exceeded 55%
  - Brine formed by deliquescence is sufficient to support ionic transport
  - Sufficient leachable salt present in pure rock dust to initiate corrosion of carbon steel

# Results–Test 3: NaCl/Quartz and NaCl/Dust Mixtures




- In 100% quartz test (no NaCl), no deliquescence brine was formed
- In 100% rock dust test (no NaCl), corrosion was observed indicating deliquescence brine was formed
- Deliquescence brine formed at lower relative humidity (55% RH) in NaCl/dust mixture compared to NaCl/quartz mixture (RH 68%)
- Carbon steel corrosion rate increased above 1 µm/yr once relative humidity exceeded 55%

# Conclusions

- Capillary retention by rock dust reduces the amount of deliquescence brine contacting the metal surface
- For carbon steel, however, capillary retention does not prevent corrosion by brines formed by salt deliquescence
- Future tests are planned using Alloy 22 material for the MAS probes at temperatures >70 °C [158 °F]

# Acknowledgment

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This presentation is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

# References


- Bryan, C.R. "Localized Corrosion Due to Dust Deliquescence on the Alloy 22 Waste Package Outer Barrier." Nuclear Waste Technical Review Board Meeting. November 8–9, 2005. Las Vegas, Nevada: Nuclear Waste Technical Review Board. http://www.nwtrb.gov/meetings/nov%202005/bryan.pdf
- Juckett, M.R. "Deliquescence Relative Humidities of Salts and Natural Dusts Present in the Proposed Underground Repository at Yucca Mountain, Nevada." M.S. Thesis. San Antonio, Texas: The University of Texas at San Antonio. 2006.
- Peterman, Z.E. et al. "Geochemistry of Dust in the Exploratory Studies Facility, Yucca Mountain, Nevada." Proceedings of the 10th International High-Level Radioactive Waste Management Conference (IHLRWM). La Grange Park, IL: American Nuclear Society. pp. 637–645. 2003.
- Reheis, M.C. "Dust Deposition in Nevada, California, and Utah, 1984–2002." Open-file Report 03–138. U.S. Geological Survey. 2003.
- Reheis, M.C. and R. Kihl. "Dust Deposition in Southern Nevada and California, 1984–1989: Relations to Climate, Source Area, and Source Lithology." Journal of Geophysical Research, Vol. 100. pp. 8893–8918. 1995.
- Yang, L. et al. "Comparison of Localized Corrosion of Fe-Ni-Cr-Mo Alloys in Chloride Solutions Using a Coupled Multielectrode Array Sensor." CORROSION/2002. Paper No. 02545. Houston, Texas: NACE International. 2002.