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Chemistry of Water Contacting Engineered Barriers

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NWTRB Workshop on Localized Corrosion
of Alloy 22 in Yucca Mt. Environments
Las Vegas, Nevada, September 25-26, 2006

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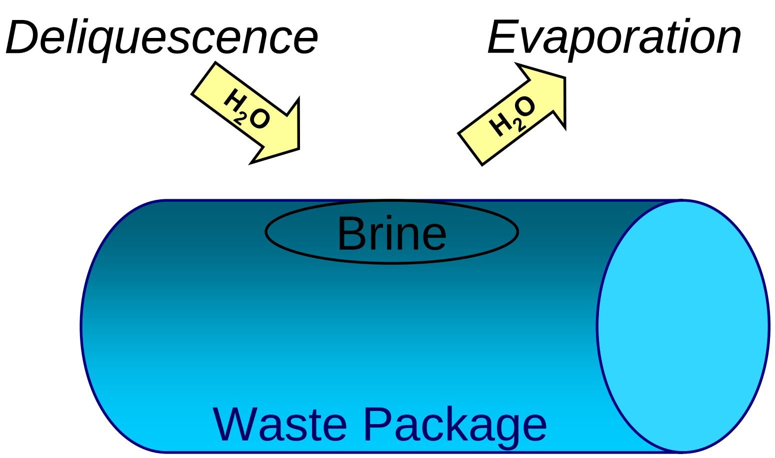
Outline of Presentation

- Introduction
- Objectives of CNWRA Studies on In-Drift Water Chemistry
- Key Points
- Technical Approach
- Results
- Summary

Introduction

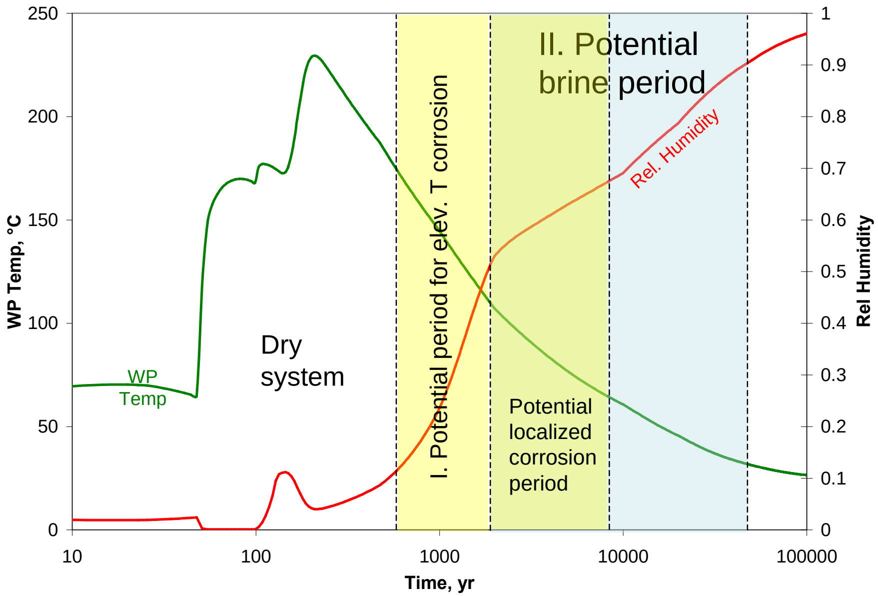
- Mode and rate of corrosion of engineered barriers will depend on water chemistry
- Chemistry of water will be altered by coupled thermal-hydrological-chemical processes
    - Deliquescence of inorganic salts
    - Evaporation of initially dilute seepage water



Introduction (Cont'd.)

Potential Corrosion Environments

- Environment I
  - No seepage (due to elevated temperature)
  - Brines from deliquescence of inorganic salts
  - Potential corrosion at elevated temperatures
- Environment II
  - Brines formed by evaporation of initially dilute seepage water



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

Objectives of CNWRA Studies on In-Drift Water Chemistry

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- Determine the range in chemistry of waters that could contact the engineered barriers at Yucca Mountain
- Review the DOE technical bases for TSPA abstractions
- Abstract the results into the NRC Total-system Performance Assessment (TPA) code (O. Pensado, this workshop)
- Guide laboratory studies
  - Corrosion of Alloy 22 in salt environments at elevated temperature (L. Yang, this workshop)
  - Integrated tests on corrosion and evolution of near-field chemistry (D. Dunn et al., MRS 2006)
  - Deliquescence of Yucca Mountain dust salts (M. Juckett, Goldschmidt 2006)

Key Points

- Dust deliquescence appears unlikely to promote localized corrosion
  - High proportion of localized corrosion inhibitors in dust samples from Yucca Mountain and vicinity
  - Possible general corrosion and localized corrosion are being studied (uncertain at this time if inhibitors are effective at elevated temperatures)
  - Additional characterization of dust salt chemistry is needed
- Evaporation of seepage waters could form brines that support localized corrosion of Alloy 22
  - Further work is underway to update thermodynamic analyses

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Technical Approach

- Thermodynamic modeling
  - Evaporation of initially dilute seepage waters (e.g., ranges in concentrations of corrosive species and corrosion inhibitors)
  - Deliquescence behavior of salts and salt mixtures (effect of composition; time and temperature of brine formation)
    - Modeling supported by deliquescence measurements (e.g., Yang et al., 2006)
- Sampling and characterization of dusts at Yucca Mountain
  - Chemistry of potential deliquescent salts

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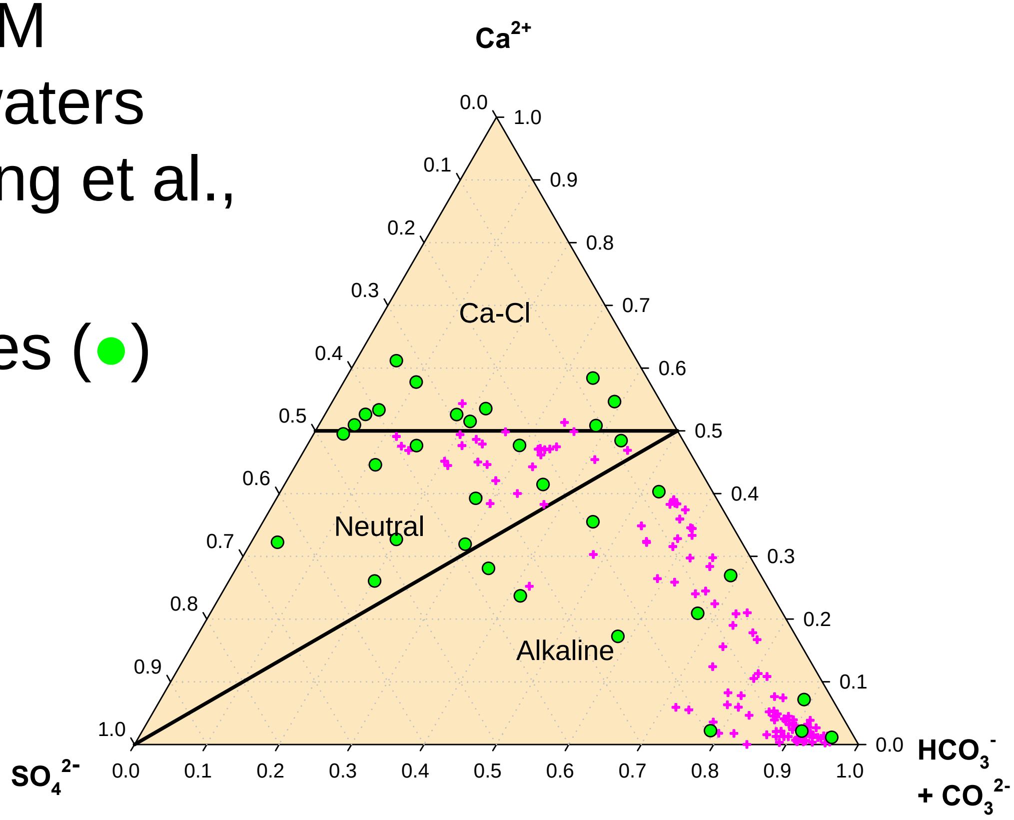
Thermodynamic Modeling

- Thermodynamic codes: Environmental Simulation Program (ESP) and StreamAnalyzer
  - Steady-state process simulators for evaluating aqueous chemical processes in industrial and environmental applications (OLI Systems, Inc., Morris Plains, NJ)
  - Large thermodynamic database
  - Temperature and pressure limits: 300 °C, 1500 bar
  - Concentration limit
    - ~ 30 molal (standard electrolyte model)
    - Pure (fused) salt (mixed-solvent electrolyte model)

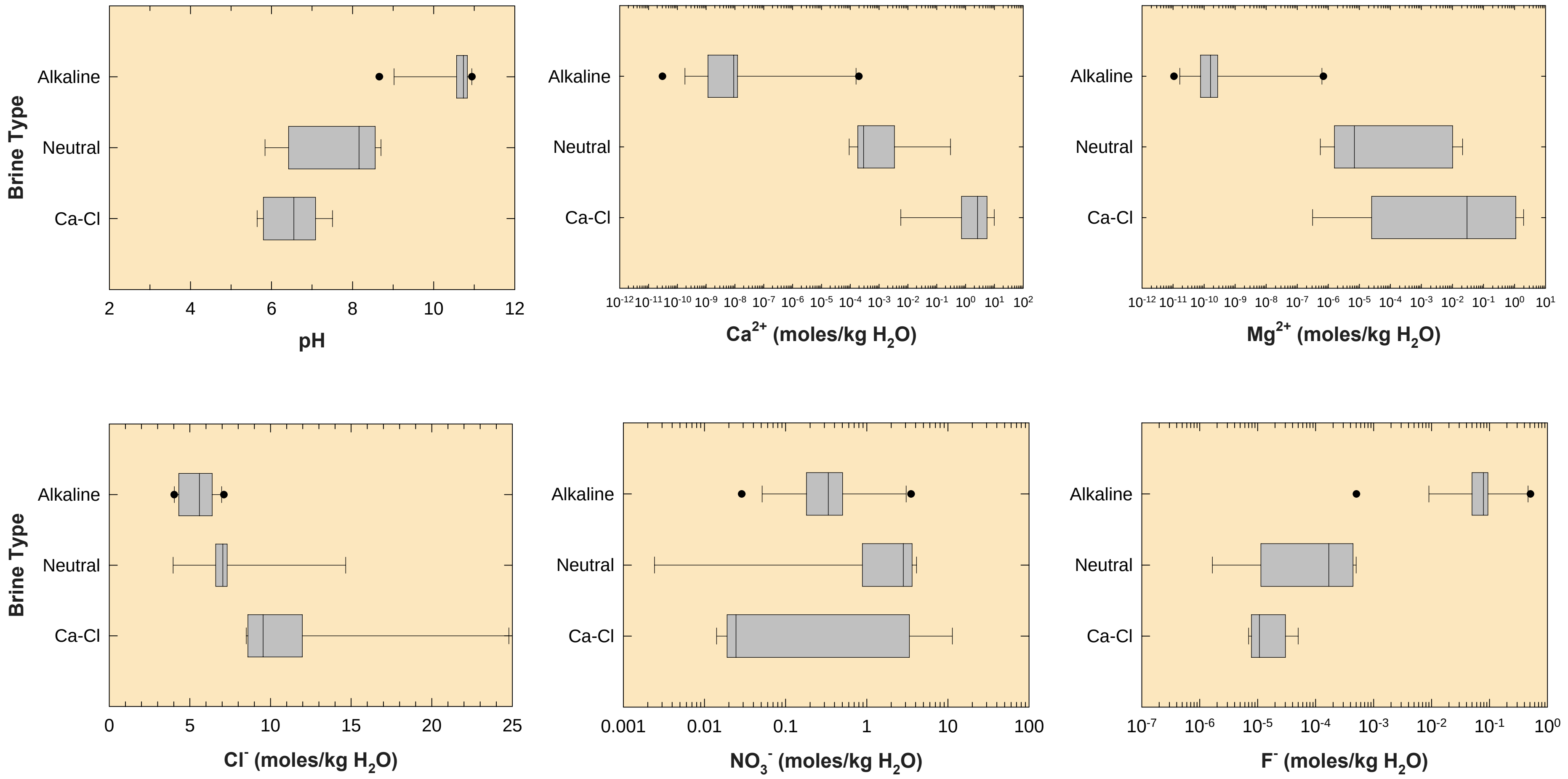
Thermodynamic Modeling of Seepage Water Evaporation

- Chemistry data (+) on YM unsaturated zone porewaters published by USGS (Yang et al., 1996, 1998, 2003)
- Data on selected samples (●) used as input
  - Seepage water assumed similar to ambient YM porewaters
  - Neglected interactions with natural and in-drift engineered materials



- Supplemented by chemical divide approach
  - Three brine types: calcium-chloride, neutral, and alkaline

Thermodynamic Modeling of Evaporation — Results for 110 °C and 0.85 atm



Thermodynamic Modeling of Seepage Water Evaporation — Results (Cont'd.)

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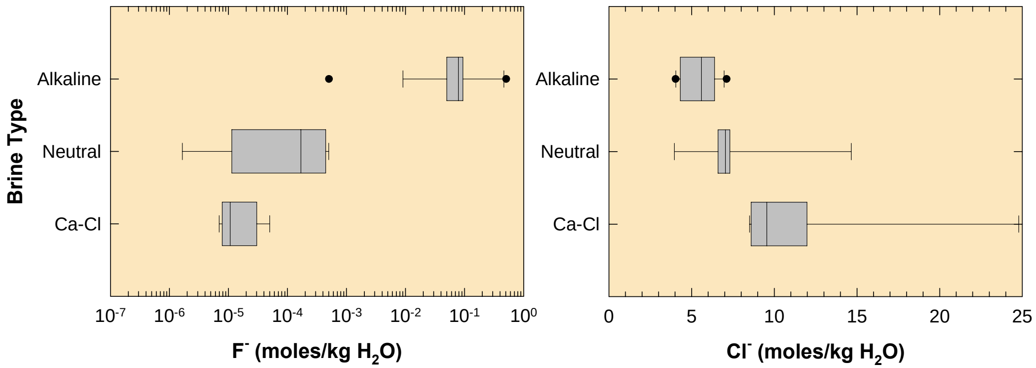

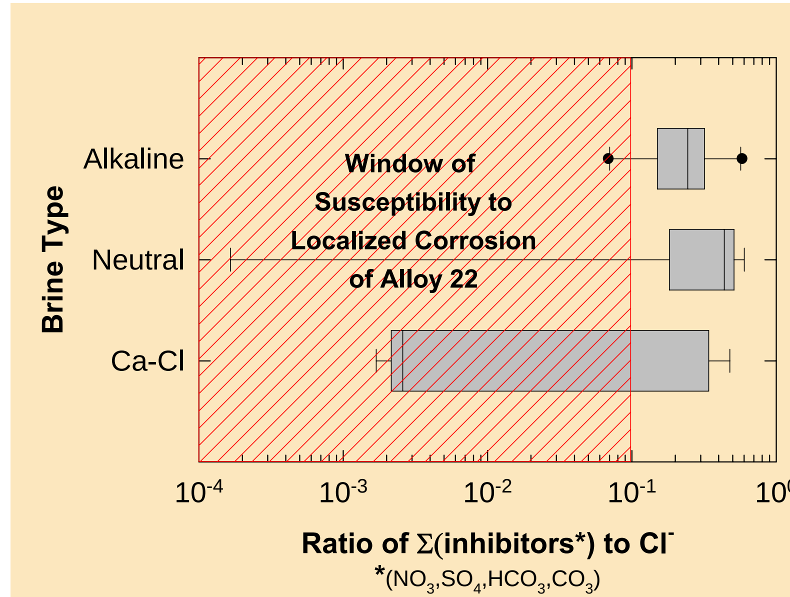

Note: Low ratio of Σ(inhibitors) to Cl^- is partly due to formation of $CaNO_3^+$ and $NaNO_3$ aqueous complexes, which have uncertain thermodynamic data

- Some brines have high Cl^- and F^- concentration
- Most have high ratio of corrosion inhibitors (NO_3^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}) to corrosive Cl^-
- Chemistry information abstracted into NRC TPA code (O. Pensado, this workshop)

Thermodynamic Modeling of Deliquescence Behavior of Salts

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- Deliquescence relative humidity (DRH) is a function of salt composition and temperature
- Limited data at elevated temperatures (>80 °C)
- Deliquescence relative humidity, DRH, is given by

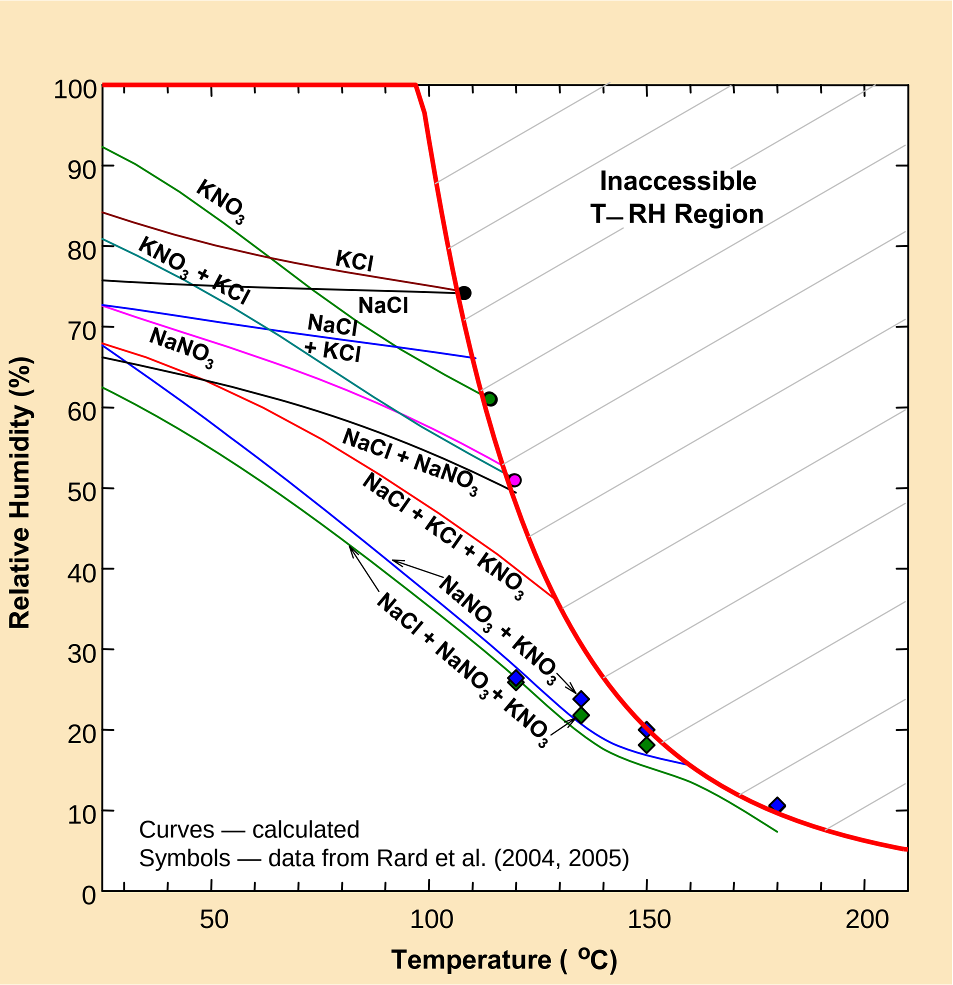
$$DRH = pH_2O_{sat}/pH_2O^o$$

where pH_2O_{sat} is the vapor pressure of a saturated salt solution and pH_2O^o is the vapor pressure of pure water

- pH_2O_{sat} and pH_2O^o calculated using Environmental Simulation Program or StreamAnalyzer (mixed-solvent electrolyte model)

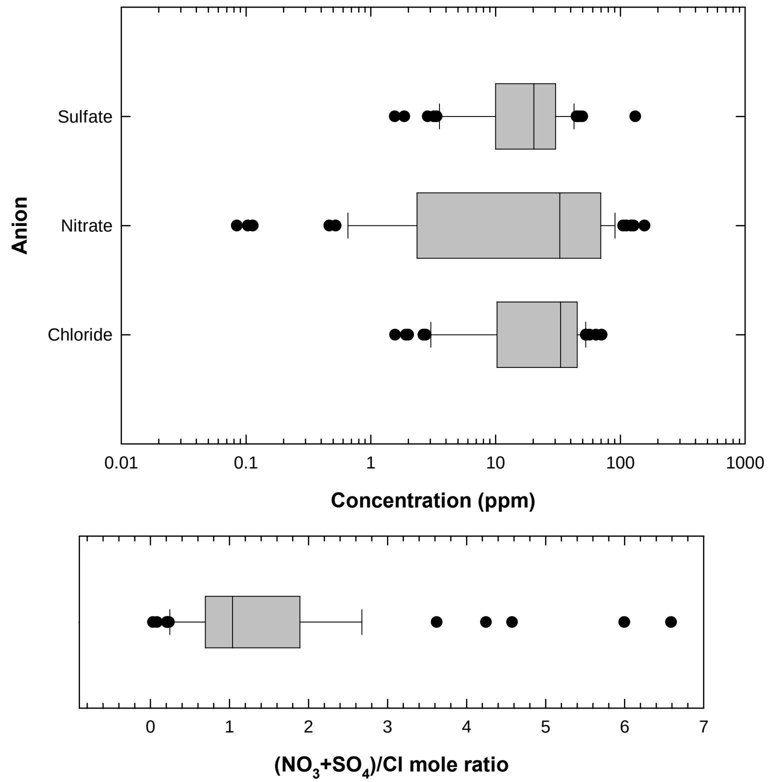
Thermodynamic Modeling of Deliquescence Behavior of Salts (Cont'd.)

- Results for salts in the Na-K-Cl-NO_3 system
  - Likely dominant composition in YM in-drift environment
  - Significant decreasing trend of DRH with temperature
  - Very low DRH possible (thus, brine formation at early times and high temperatures)



Characterization of Dust from Yucca Mountain and Vicinity

- Literature data on chemistry of dusts collected in the vicinity of Yucca Mountain (Reheis, 2003)
  - Dominant anions are chloride, nitrate, and sulfate
  - Significant concentrations of oxyanions (NO_3^-, SO_4^{2-}) that potentially can mitigate localized corrosion of Alloy 22
  - Highly variable $(NO_3+SO_4)/Cl$ mole ratio, but mostly greater than 0.1.



Characterization of Dust from Yucca Mountain and Vicinity (Cont'd.)

- Samples collected by the CNWRA from the Exploratory Studies Facility (underground tunnel) and at the Yucca Mountain surface
- Samples provided by U.S. Geological Survey (Z. Peterman)
- Samples were characterized
  - Ion chromatography
  - ICP-MS
  - Scanning electron microscopy
  - Energy dispersive X-ray spectrometry
  - X-ray diffraction analysis

Dust sample collectors setup (a) outside and (b) inside the Exploratory Studies Facility at Yucca Mountain

Characterization of Dust from Yucca Mountain and Vicinity (Cont'd.)

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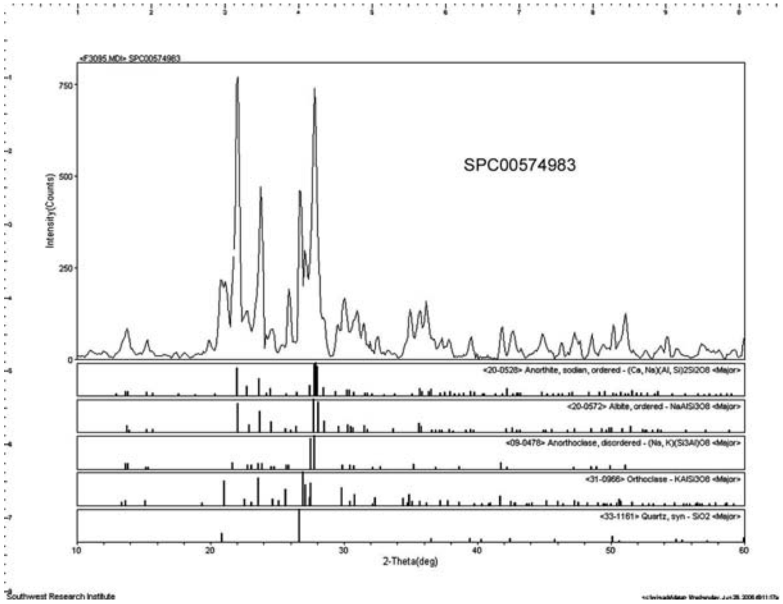
- Results of soluble fraction analyses
  - Very low fraction of soluble salts (<1% of total sample)
  - $(NO_3+SO_4)/Cl$ greater than 0.1
  - Localized corrosion of Alloy 22 could be mitigated in the presence of sufficient nitrate and sulfate

Analysis	Surface Sample (mg/kg)	Tunnel Sample (mg/kg)
Calcium	56.5	918
Sodium	17.8	686
Potassium	31.2	205
Magnesium	8.84	101
Silicon	42.9	21.9
Sulfate	19.6	1920
Nitrate	1.69	218
Chloride	8.59	2350
$(NO_3+SO_4)/Cl$ Ratio	0.95	0.23
Soluble Fraction (wt%)	<0.1%	0.69%

Characterization of Dust from Yucca Mountain and Vicinity (Cont'd.)

- Dusts are mostly insoluble minerals
  - Feldspars (e.g., anorthite, albite, microcline, anorthoclase)
  - Silica (quartz, cristobalite)
- Likelihood for brine to contact the waste package would be reduced due to the small volume of brine mixed with rock dusts



X-ray diffraction pattern of dust sample taken from inside the Exploratory Studies Facility

- CNWRA experiments are ongoing to evaluate corrosion by small amount of salts mixed with rock dusts

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Summary

- Chemistry of water that could contact engineered barriers at the potential YM repository was evaluated
  - Evaporation of initially dilute seepage waters
  - Deliquescence of inorganic salts
- Evaporation of seepage waters could form brines that support localized corrosion of the Alloy 22 waste package material
  - Ranges in brine chemistry were proposed to support NRC total system performance assessments.
  - Thermodynamic analyses will be updated based on results of CNWRA coupled thermal-hydrological-chemical simulations
  - Effect of drift degradation on water chemistry will be evaluated

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Summary (Cont'd.)

- Some salt mixtures can deliquesce at elevated temperatures and form brines
  - CNWRA experiments to evaluate potential corrosion at high temperatures by Na-K-Cl-NO_3 salts are ongoing
- There is limited chemistry data on dust samples from the Yucca Mountain surface and tunnels
  - Soluble salts have significant concentrations of corrosion inhibitors nitrate and sulfate
  - Proposed NRC performance assessment model assumes no localized corrosion due to salt deliquescence
  - Further sampling and characterization of Yucca Mountain dust samples are planned
  - Experiments are underway to evaluate potential corrosion by small volumes of brines mixed with rock dusts

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Acknowledgment

- The work presented here was performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety, under Contract No. NRC–02-02-012.

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

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