Composition of Aqueous Environments

Presented to:
Waste Package Materials Performance Peer Review Panel

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Strategy

- Characterize the aqueous environments in contact with the Waste Package (WP) into aqueous solution "types" that can be classified according to their "corrosive nature"
  - Establish bounds on parameters given the constraints of the system
Aqueous Solution Parameters Important for Corrosion

- Dripping water including transient behavior
- Deliquescence of deposited salts
- Ionic composition as a function of relative humidity
- Minor constituents
- Electrochemical potential, Eh; Thermodynamic and kinetic considerations
- pH
- Crevices: Metal-to-metal, under-deposit, & dust
- Microbes
- Thermal gradients on surfaces due to mineral scale deposits
Aqueous Environment Evolution Characterization Strategy

- Temperature and Relative Humidity
  - Seepage water
  - Entrained matter in ventilation
  - Rock dust
  - Microbes
  - Radiation

- Mild or Carbon Steel
- Grout
- Drift Debris
- Drip Shield
- Backfill (optional)

Waste Package Surface Aqueous Environment
(moist dust; mineral scale; metal to metal crevices)
Illustrative Example of Aqueous Environment Evolution

- Seepage water contacting silicate base materials before contacting a waste package
- Silicate base materials:
  - Rock dust
  - Backfill (optional)
Aqueous Environment Evolution
Characterization Strategy

Temperature and Relative Humidity

Seepage water

Entrained matter in ventilation

Rock dust

Microbes

Radiation

Mild or Carbon Steel

Grout

Drift Debris

Backfill (optional)

Waste Package Surface Aqueous Environment
(moist dust; mineral scale; metal to metal crevices)
Illustrative Example: Seepage Water - Rock Dust - Interaction

- Seepage water reacts with rock dust before contacting the Waste Package

- Considerations
  - Three types of brine
    - Na-Cl-F-NO3-SO4-CO3
    - Na-Ca-Mg-Cl-NO3
    - Na-Mg-Cl-SO4-NO3
  - Rock dust is silicate base
  - Temperature and relative humidity effect on aqueous solutions composition
Illustrative Example: Seepage Water - Rock Dust - Interaction
(continued)

- **Na-Ca-Mg-Cl-NO3 + “silicates”**
  - Clay mineral formation
    - Mg-smectite (Na0.3(Al,Mg)2Si4O10(F,OH)2)
  - “Silicate” deposition on the metal surface

- **Na-Mg-Cl-NO3-SO4 + “silicates”**
  - Clay mineral formation
  - “Silicate” deposition on the metal surface
Seepage Water - Rock Dust or Silica Backfill - Interaction

- Na-Cl-NO₃-SO₄-CO₃ + "silicates"
  - High pH of brine moderated by silica dissolution
  - "Silicate" deposition on the metal surface; more prevalent under higher pH conditions
  - Clay mineral formation
    - Mg-smectite (Na₀.₃(Al,Mg)₂Si₄O₁₀(F,OH)₂)
    - Kanyataite (NaSi₁₁O₂₀·₅(OH)₄·₃H₂O)
Silica Solubility Dependence on pH

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- Crevices
  - Metal-to-metal, under-deposit, & dust
- Microbes
Solution Composition Dependence on Relative Humidity

- Type of corrosion process that occurs is dependent on solution composition
  - Localized corrosion (e.g. crevice corrosion) susceptibility in concentrated solutions is a function of occurs ratio of aggressive ion concentration to inhibitor ion concentration
- Thermodynamic database based on the Pitzer formulation is being developed for relevant species at high temperatures
  - Database for sodium species is nearing completion
  - Database for calcium and magnesium is being developed
Phase Diagram for Mixture of NaCl + NaNO₃

- Deliquescence point of any salt mixture is lower than the deliquescence point of any pure salt in the mixture.
- Pitzer database developed to model high ionic strength aqueous solutions.

Calculated with EQ3/6 Thermodynamic Code; Tom Wolery, LLNL.
Relative Humidity - Temperature Dependence of Aqueous Solution Properties

- General corrosion susceptibility at deliquescence of salt mixture
- Localized corrosion susceptibility for sodium base salt may occur at relative humidities much higher than mixture deliquescence

Calculated with EQ3/6 Thermodynamic Code; Tom Wolery, LLNL
Thin Film Corrosion Testing on Metal Surfaces

- Testing under conditions that result in very high ion strength solutions at temperatures up to 170°C
  - Thermogravimetric analyzer and environmental chamber apparatus modified for elevated temperature testing
  - Analyze corrosion products and mineral scale
- Water drip tests at elevated temperature and constant relative humidity (environmental chamber and heated coupons)
  - Allow evaporation to dryness between drips
- Thermogravimetric analysis (TGA); continuous measurement of weight change vs time
  - Metal coupon with salt deposits (e.g. CaCl2) under constant temperature and relative humidity
Aqueous Environment Evolution Characterization Strategy

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Mild or Carbon Steel

Grout

Drift Debris

Drip Shield

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Evaporative Drip Testing

- Apparatus modified for higher temperature operation (170°C)
- Testing will include interaction of test aqueous solutions with "grout" and "carbon steel" prior to interacting with waste package candidate material
Summary

- Strategy is to characterize the aqueous environments in contact with the Waste Package (WP) into aqueous solution “types” that can be classified according to their “corrosive nature”
- Identified and consider those parameters that are important for corrosion and potential sources that affect those parameters
- Aqueous solution modeling effort is continuing
- Extending the thin film aqueous solution testing to higher temperatures