



U.S. Department of Energy
Office of Civilian Radioactive Waste Management



Composition of Aqueous Environments

Presented to:

Waste Package Materials Performance Peer Review Panel

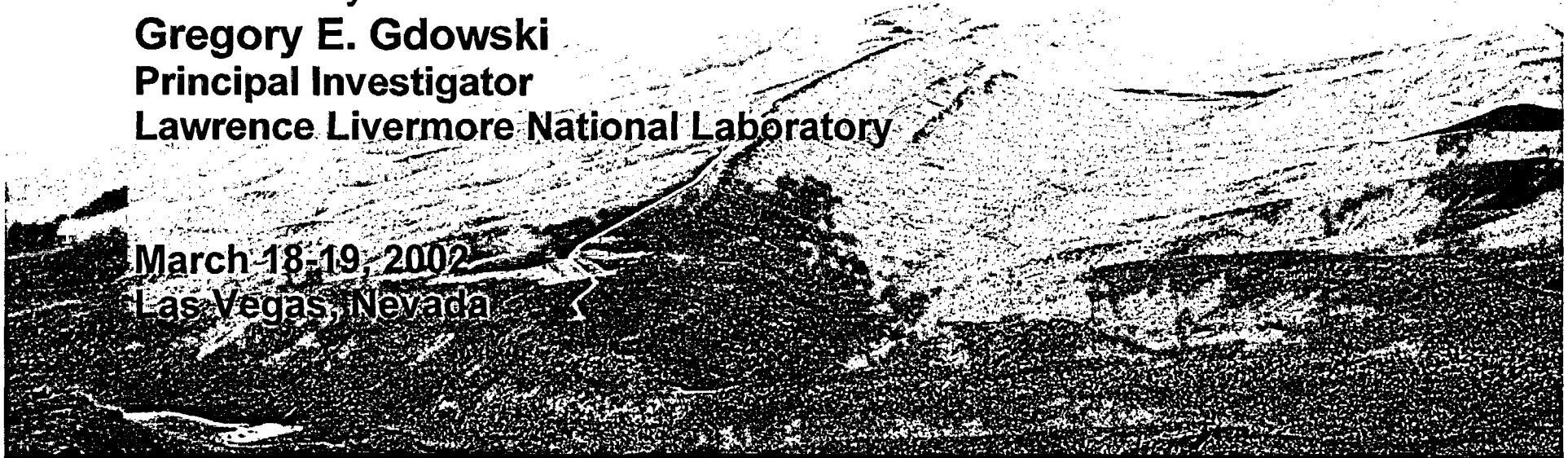
Presented by:

Gregory E. Gdowski

Principal Investigator

Lawrence Livermore National Laboratory

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Main-70

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**

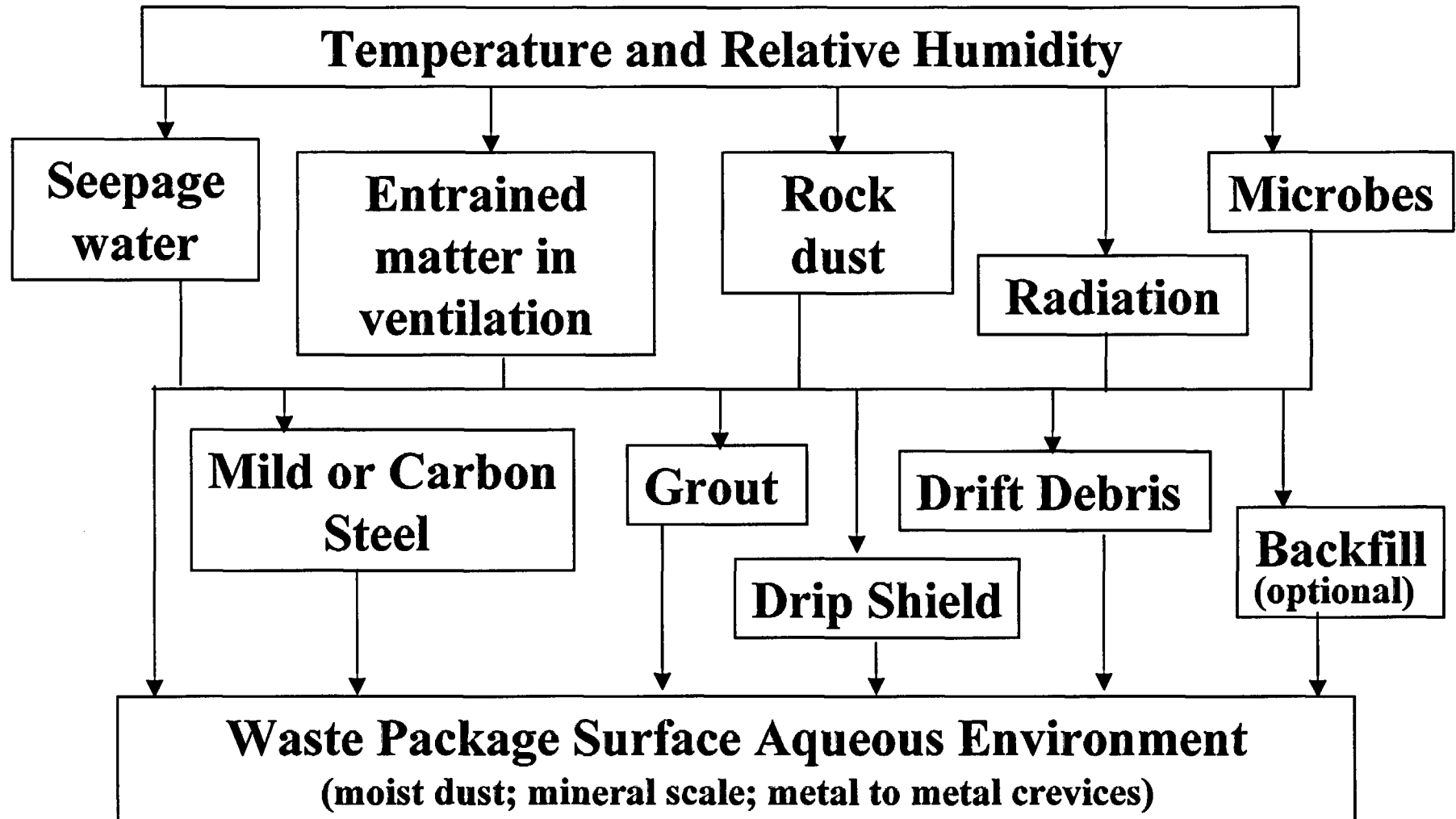


Aqueous Solution Parameters Important for Corrosion

- **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

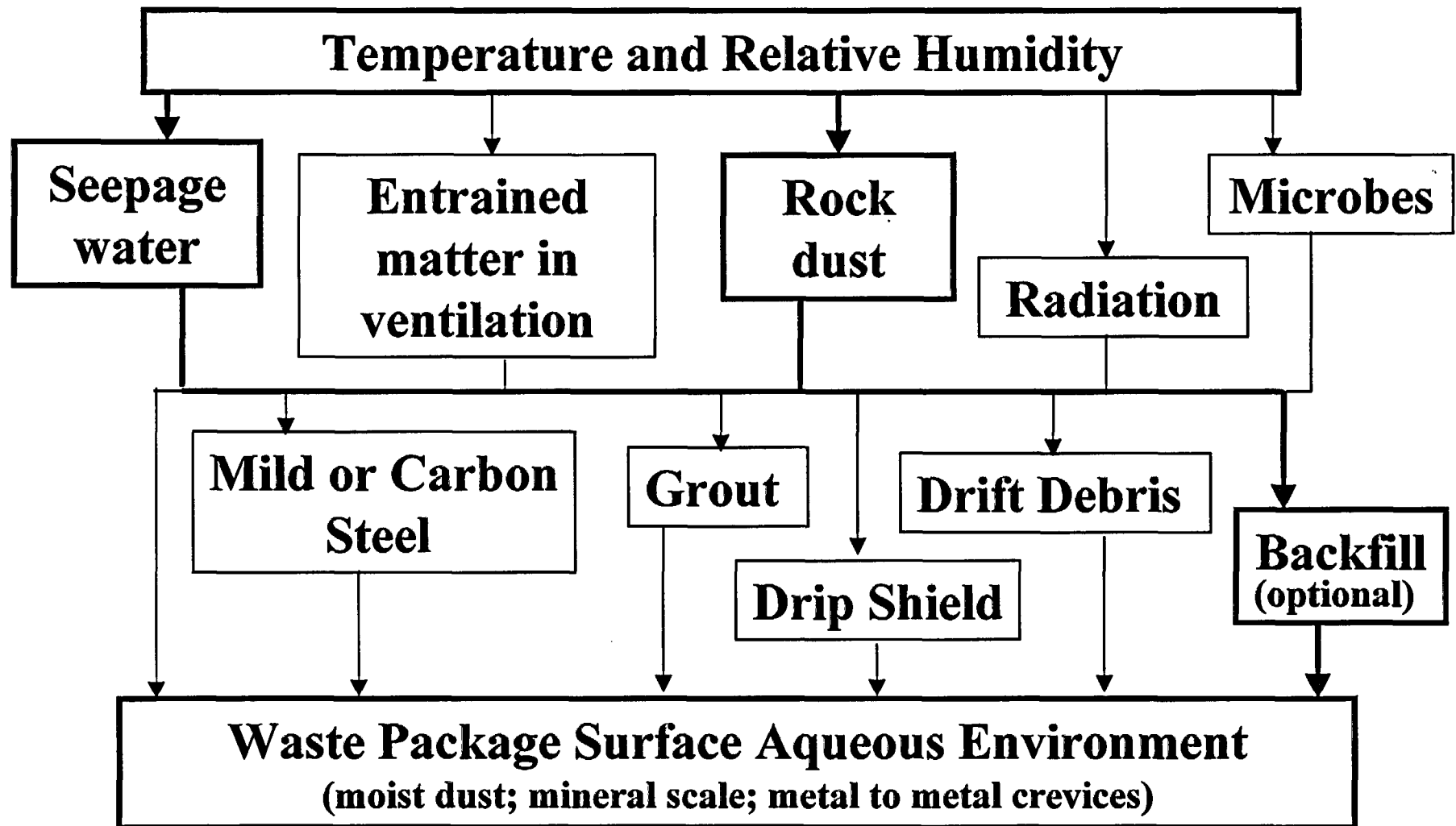


Illustrative Example of Aqueous Environment Evolution

- **Seepage water contacting silicate base materials before contacting a waste package**
- **Silicate base materials:**
 - **Rock dust**
 - **Backfill (optional)**



Aqueous Environment Evolution Characterization Strategy



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 ($\text{Na}_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2$)
 - “Silicate” deposition on the metal surface
- **Na-Mg-Cl-NO₃-SO₄ + “silicates”**
 - Clay mineral formation
 - “Silicate” deposition on the metal surface



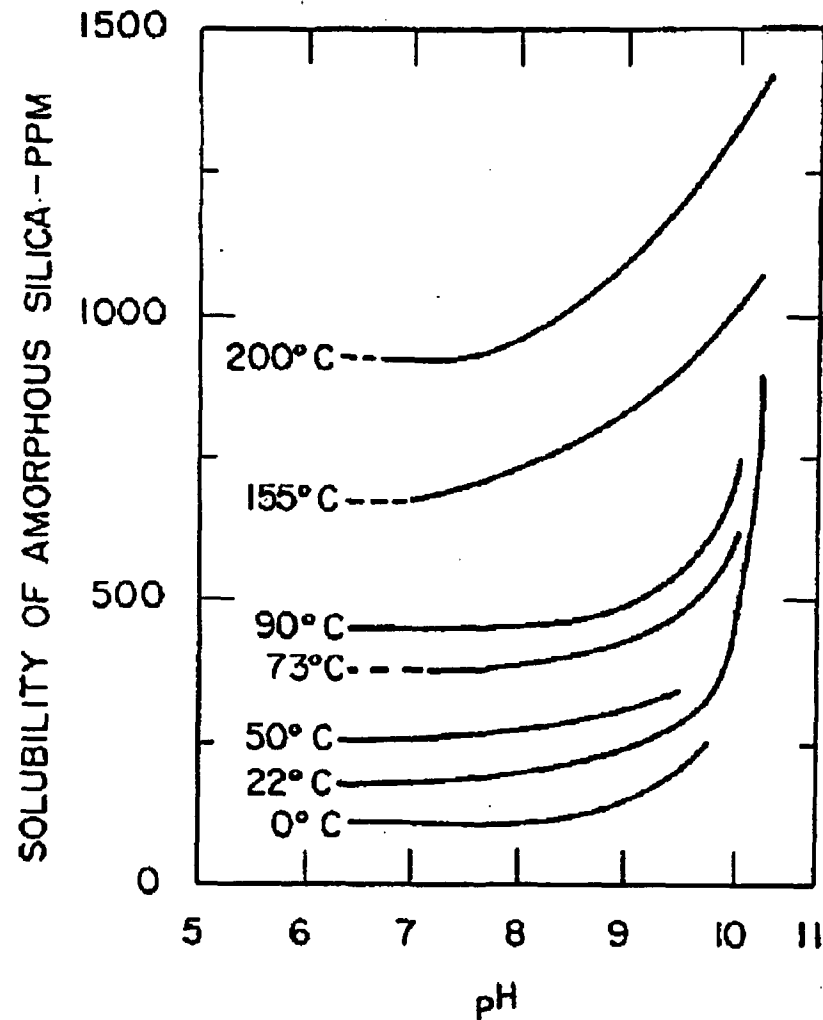
YUCCA MOUNTAIN PROJECT

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 ($\text{Na}_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2$)
 - ♦ Kanyataite ($\text{NaSi}_{11}\text{O}_{20.5}(\text{OH})_4 \cdot 3\text{H}_2\text{O}$)



Silica Solubility Dependence on pH



RK Iler, The Chemistry of Silica, John Wiley & Sons, Inc., New York, 1979.



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
 - Thermodynamic and kinetic considerations
- pH
- Crevices
 - Metal-to-metal, under-deposit, & dust
- Microbes

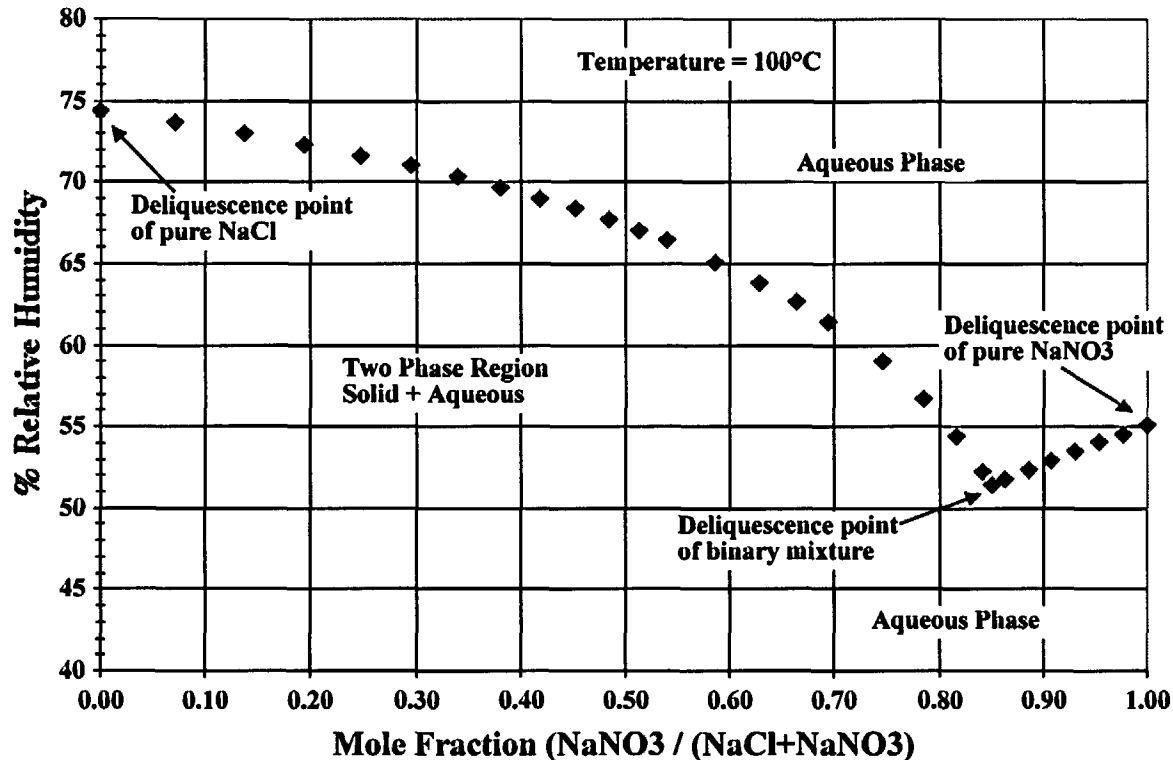


Solution Composition Dependence on Relative Humidity

- **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

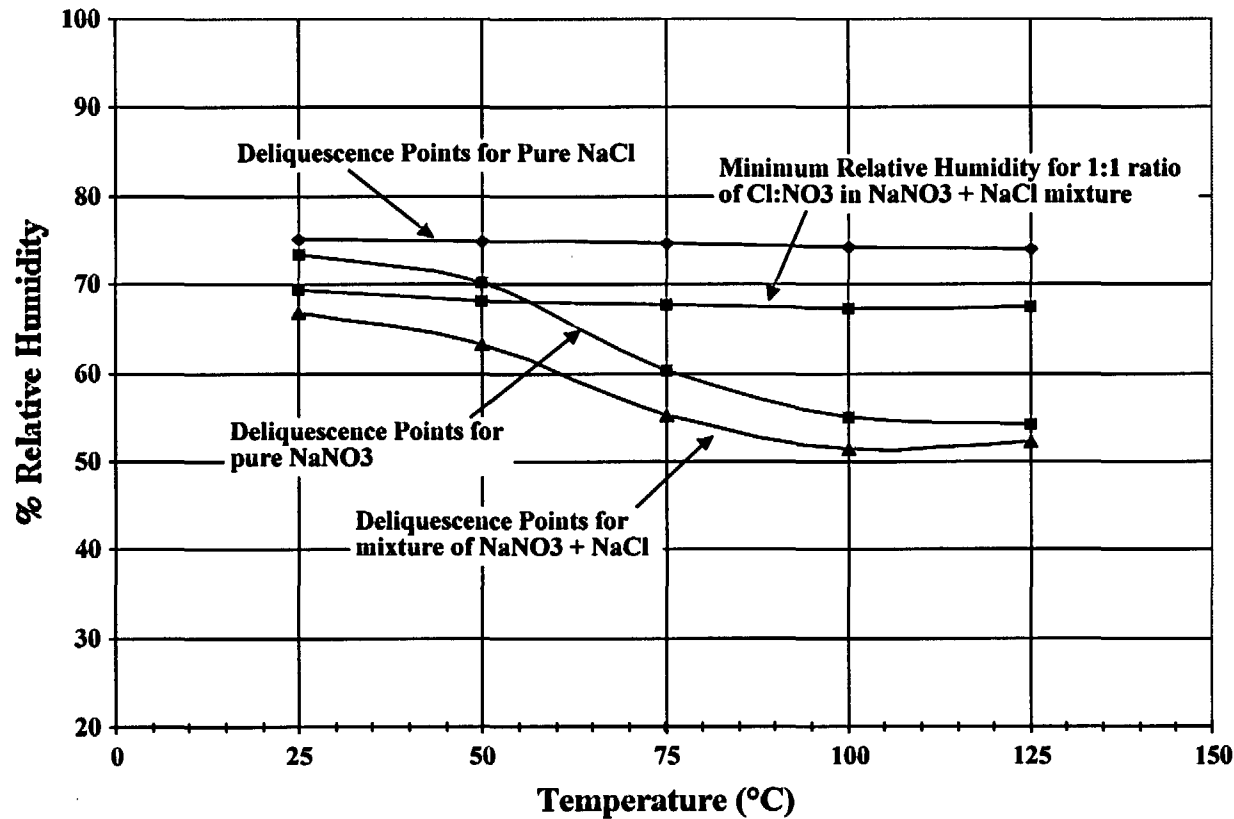


- Deliquescence point of any salt mixture is lower than the deliquescence point of any pure salt in the mixture
- Pitzer database developed to model high ionic strength aqueous solutions

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

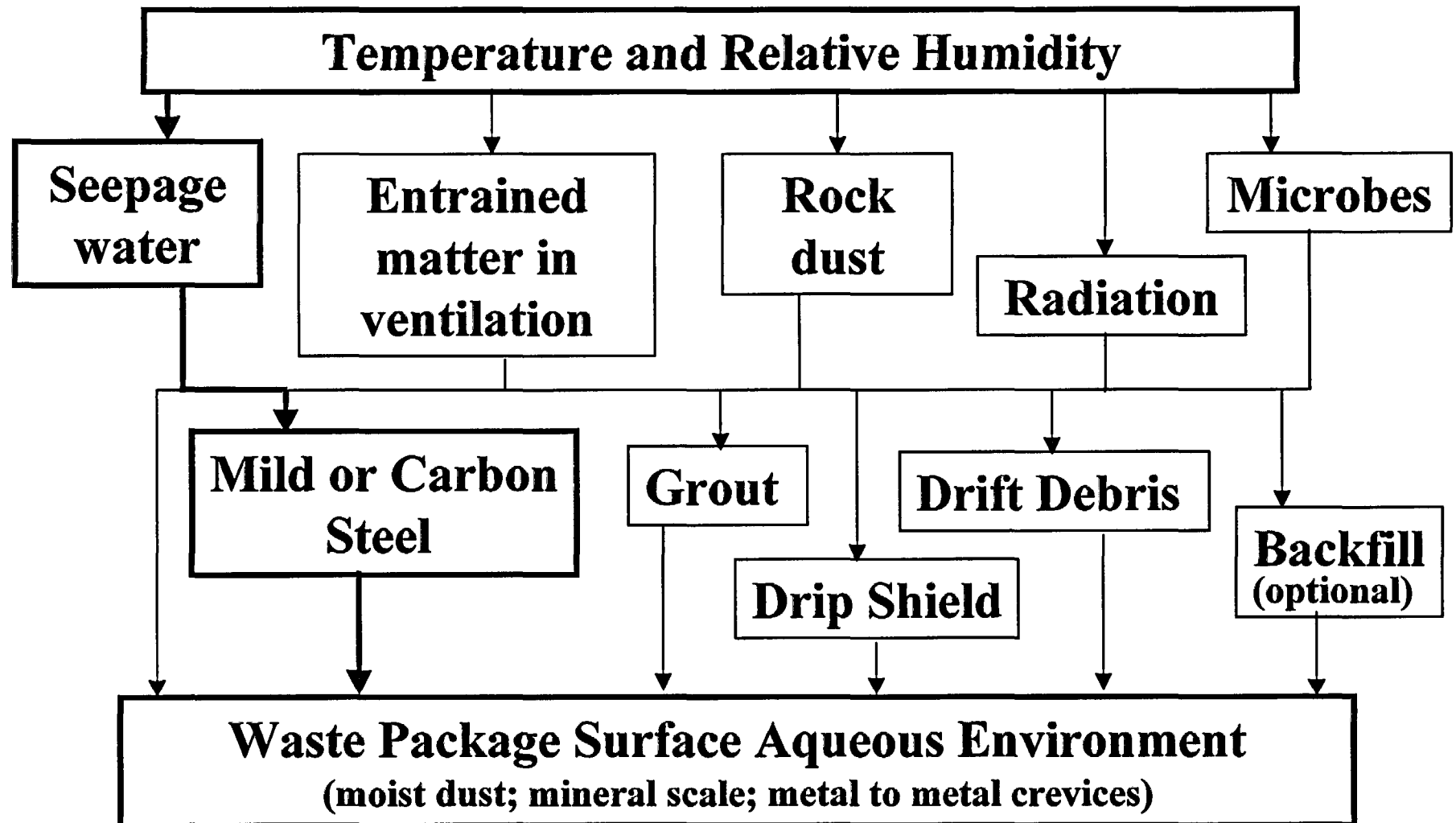


Thin Film Corrosion Testing on Metal Surfaces

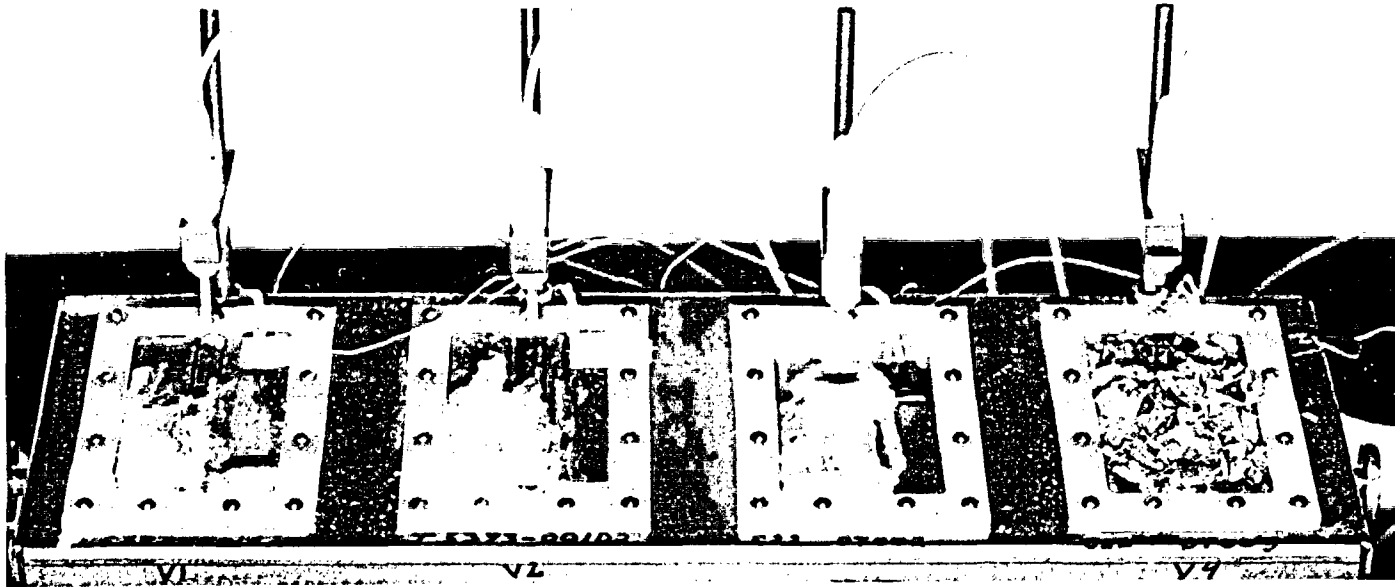
- **Testing under conditions that result in very high ion strength solutions at temperatures up to 170°C**
 - Thermogravimetric analyzer and environmental chamber apparatus modified for elevated temperature testing
 - Analyze corrosion products and mineral scale
- **Water drip tests at elevated temperature 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. CaCl_2) under constant temperature and relative humidity



Aqueous Environment Evolution Characterization Strategy



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**

