U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: GEOCHEMICAL UNCERTAINTIES

PRESENTER: DR. BRIAN E. VIANI

PRESENTER'S TITLE AND ORGANIZATION: CHEMIST
LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA

PRESENTER'S TELEPHONE NUMBER: (415) 423-2001

OCTOBER 8 - 10, 1991

Issues to be Addressed Regardless of Thermal Load

- Can we predict the variation in the composition of groundwater over time and space?
- Can we predict the ability of the rock matrix, fracture coatings, and introduced repository components to sorb radionuclides?
- Can we predict the effect that geochemical reactions have on hydrologic properties?

Geochemical Processes Need to be Known as a Function of Temperature and $p/p^{o}_{H_2O}$ (Relative Humidity)

- Dissolution/precipitation
  - Equilibrium properties
  - Kinetic properties
- Sorption
  - Cation exchange equilibria
  - Surface complexation equilibria
  - Water adsorption equilibria

Results of Experimental and Modeling Studies of Groundwater/Repository-Rock Interaction at Elevated Temperature

- Mineral dissolution/precipitation

Results obtained from experiment (K. Knauss) and modeling (C. Bruton) are consistent:

1. The activity of aqueous silica is the dominant variable controlling the types of minerals expected to form or persist at elevated T
2. Activity of silica is controlled by the least stable silica polymorph
3. High and moderate silica activities (Si controlled by glass and cristobalite solubilities) favor zeolites (clinoptilolite and mordenite) and clays (smectite), phases with significant ion-exchange capacity

Results of Experimental and Modeling Studies of Groundwater/Repository-Rock Interaction at Elevated Temperature

(Continued)

- Mineral dissolution/precipitation (continued)

  4. Low silica activities (Si controlled by quartz solubility) favor analcime and feldspars, phases without significant exchange capacity

  5. Evolution of silica polymorphs is kinetically controlled

  6. The phases expected to form during the reaction of groundwater and Topopah Spring tuff at elevated temperatures are those that already exist as secondary phases present in the rock, namely, zeolites and clays

Results of Experimental and Modeling Studies of Groundwater/Repository-Rock Interaction at Elevated Temperature

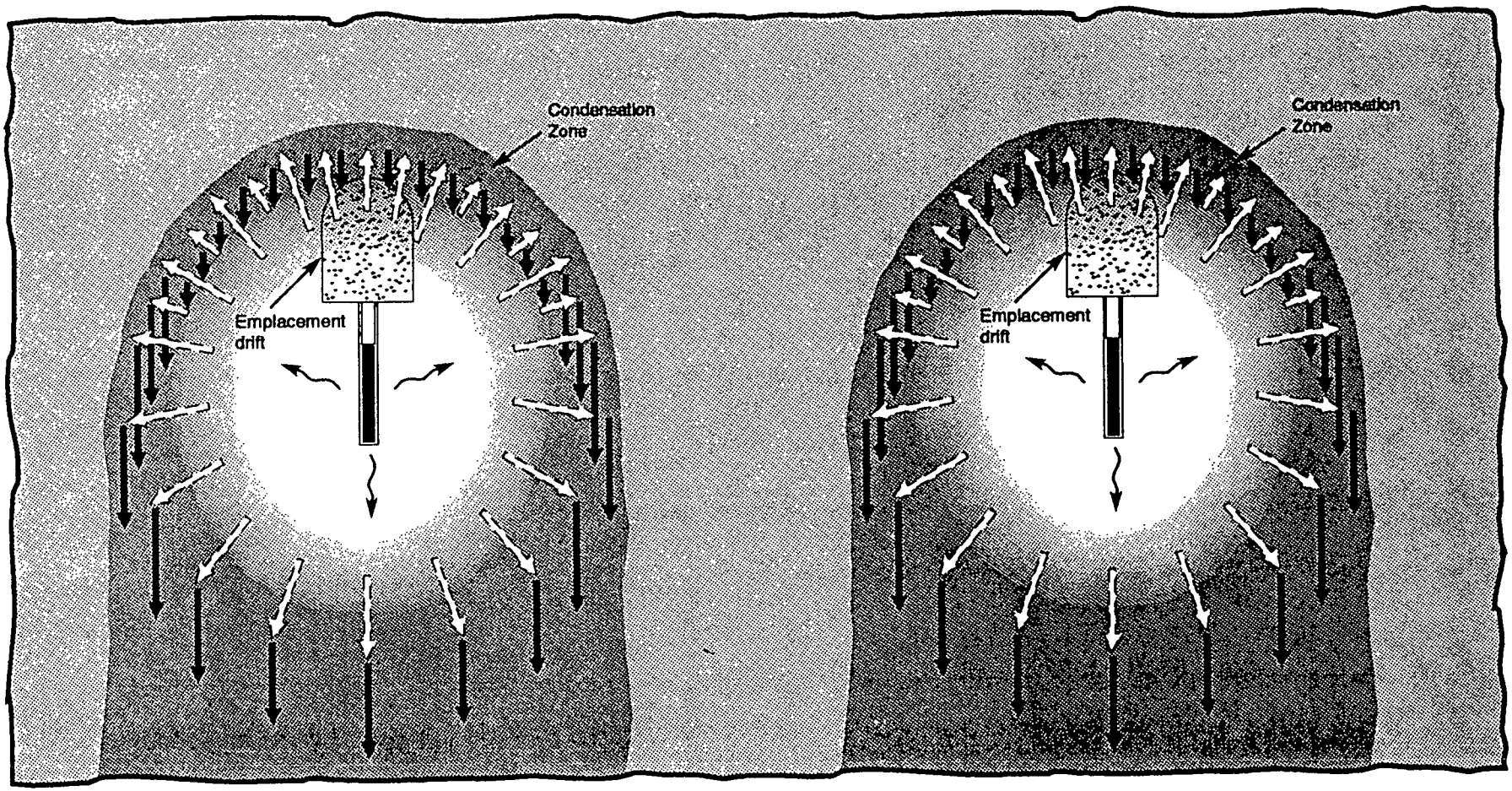
(Continued)

- Cation exchange

1. Cation exchange modeling results (LLNL) agree with experiments (LANL) for sorption of Cs and Sr from groundwater onto tuff
2. Compositions of clinoptilolite formed during hydrothermal alteration of tuff are consistent with predictions based on exchange modeling
3. Cation exchange modeling predictions suggest that cation exchange equilibria, and therefore, sorption, will be sensitive to temperature
4. Experimental data for cation exchange (and surface complexation) are lacking at elevated temperatures. Modeling results are based on estimated thermodynamic data

Glass Dissolution Features And Clinoptilolite Formed From Solution During Zeolitization Of Vitric Tuff Under Hydrothermal Conditions at 250°C

A "Hydrothermal Umbrella" is Established Along Each of the Emplacement Drifts Due to Condensate Being Shed Off of the Boiling Zone



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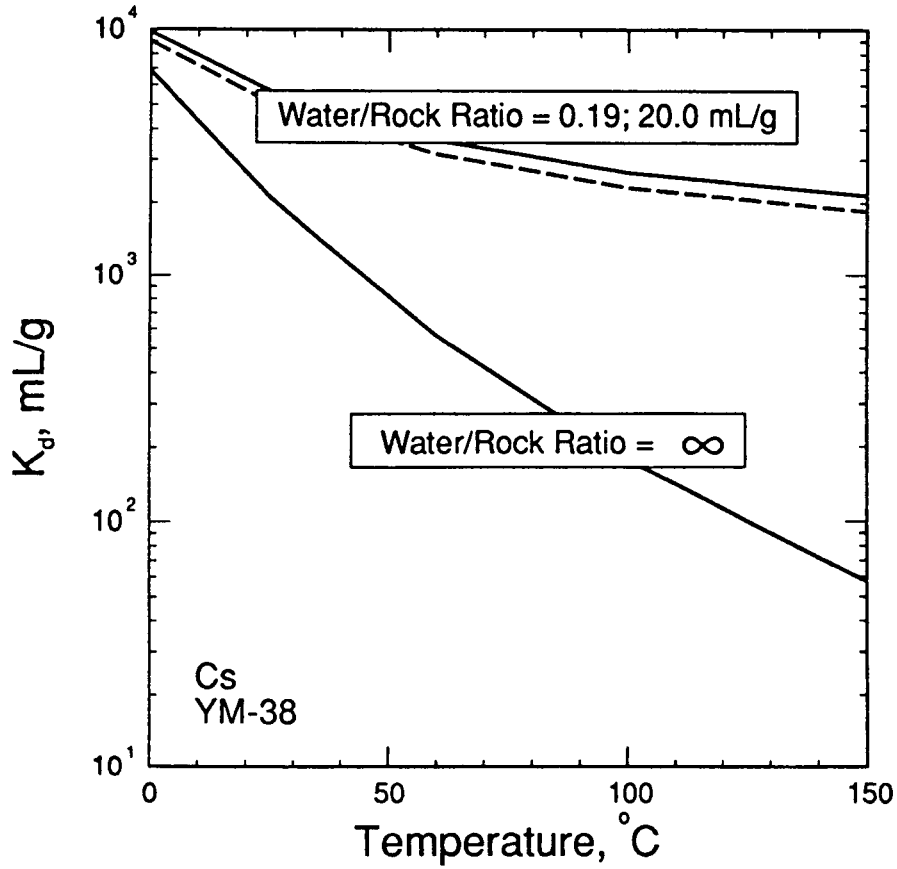
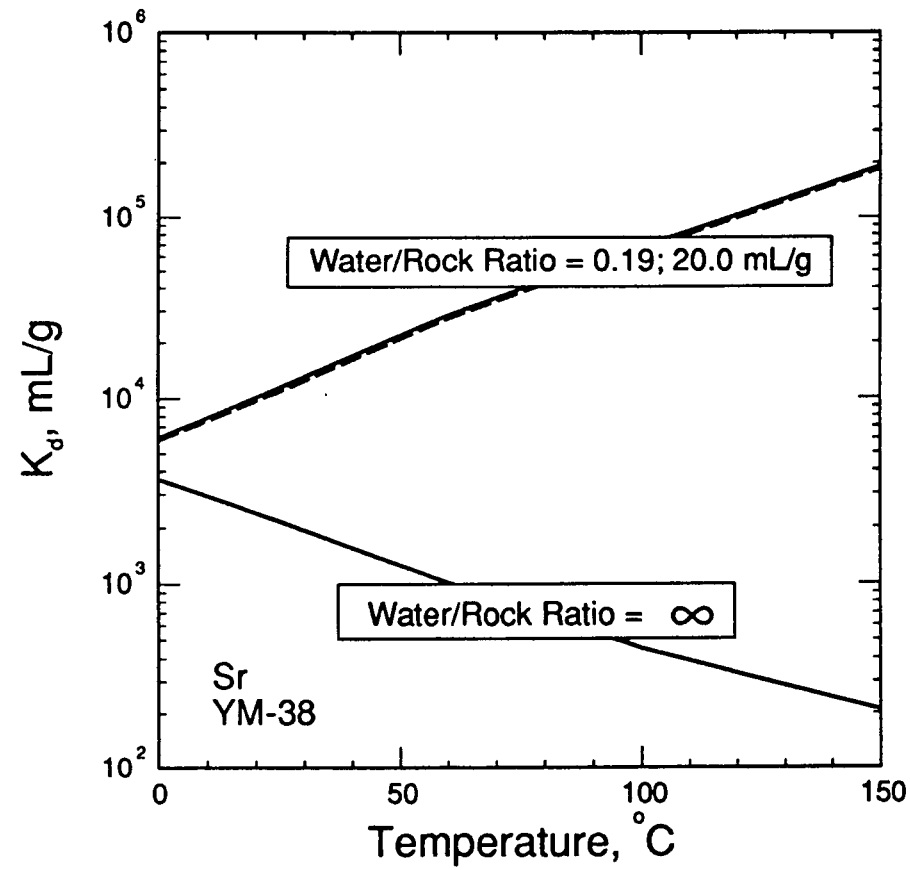
Examples of Coupled Geochemical/Hydrologic Scenarios

- Reactions accompanying the flow of condensate via a fracture network to the saturated zone
  - Dissolution of fracture minerals at point of condensation
  - Precipitation of minerals in fracture as fluid moves and cools
  - Alteration of zeolite and clay mineral exchange ion compositions along fracture
- Reactions accompanying the "refluxing" of water along the boiling isotherm
  - Dissolution of matrix and fracture minerals by condensate
  - Precipitation of secondary phases upon boiling of previously condensed fluid
  - Development of a region in which permeability and porosity have been altered

Predicted Effect of Temperature on Sorption of Cs and Sr on Calico Hills Tuff at Different Water/Rock Ratios





Water: J13; Cs and Sr concentration = 1E-11 molal
Rock: Calico Hills; Sample YM-38; 49% clinoptilolite
Model: EQ3 with 1-site Vanselow exchange model
Data: Data at 25 ° C from published isotherms; data at other temperatures are estimated
Water/rock ratio = 0.19 mL/g equivalent to fully saturated rock with 30% porosity; *matrix case*
Water/rock ratio = 20.0 mL/g equivalent to LANL batch sorption experiments
Water/rock ratio = ∞ ; *fracture case*

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Concluding Comments

- There are both benefits and detriments related to the interaction of repository rock, introduced materials, and groundwater at the temperatures defined by "hot" and "cold" scenarios. Uncertainties are associated with <u>both</u> benefits and detriments

- Geochemical processes and geochemical/ hydrological scenarios are expected to be qualitatively similar over the thermal regime encompassed by the hot and cold scenarios

Concluding Comments

(Continued)

- Uncertainties associated with fundamental geochemical processes are similar for hot and cold scenarios
- Coupling geochemical processes to specific hydrological scenarios introduces greater complexities and hence, greater uncertainties

Resolution of Issues

- Existing scientific plans pertaining to the near-field environment are of wide enough scope so that the uncertainties associated with geochemical processes can be addressed

- Integration of geochemistry and hydrology must take place via analysis of specific scenarios

- Elements of a near-field geochemistry program required to resolve issues:
  - Modeling applications
  - Experimental-rock/water interaction
  - Thermodynamic and kinetic data acquisition and development
  - Model development
  - Natural analogue studies