GAS-WATER-ROCK GEOCHEMISTRY

AT THE PROPOSED YUCCA MOUNTAIN REPOSITORY
UNDER VARIOUS THERMAL LOADS: RELATIONS TO FLUID FLOW

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Presented to the United States Nuclear Waste Technical Review Board
Full Board Meeting on Thermal Loading: The Integration of Science and Engineering
Denver, Colorado, July 13, 1993

This presentation, documenting work conducted for the U.S. Nuclear Regulatory Commission (NRC) under contract NRC-02-88-005, is an independent product and does not necessarily reflect the views or regulatory position of the NRC. Notable acknowledgments are due Richard B. Codell (NRC) for flow and transport modeling, George F. Birchard (NRC) for program direction, and Christopher J. Goulet for computing assistance.
KEY GEOCHEMICAL PROCESSES AND PARAMETERS
FOR THE REPOSITORY AT YUCCA MOUNTAIN

Gas-water-rock interactions affect repository performance through:

Containment: Waste package degradation processes;
Source Term: Waste form alteration and dissolution,
Radioelement solubilities;
Transport: Hydrologic and transport properties,
Radioelement speciation,
Distribution of radioelements (retardation).

Temperature affects equilibria and rates of chemical reactions.
Pressure affects liquid phase stability.
Materials control variations in phase compositions.
Oxidation state affects material stability, reaction rates and speciation.
Gas flow and gas-phase transport affect H₂O, CO₂, and O₂ pressures.
Liquid flow affects aqueous transport.
Evaporation (condensation) affects solution concentrations and
precipitation (dissolution).
Vapor pressure lowering affects moisture distribution.
LIKELY GEOCHEMICAL EFFECTS OF HEATING AT YUCCA MT.

Volatileization and redistribution of CO₂ and H₂O:
With increasing temperature CO₂ and H₂O are strongly partitioned into the gas phase.

pH increase:
Due mainly to depletion in carbonic acid, increases in pH modify mineral stabilities, reaction rates and aqueous speciation.

Precipitation, then dissolution of calcite:
Temperature-retrograde and pH-dependent solubility and fast reaction rate of calcite lead to initial precipitation, then redissolution at long times.

Dissolution of feldspars, cristobalite, tridymite, and glass:
Increasing temperature and pH increase rates of reaction and solubilities.

Increase in sodium bicarbonate concentration:
Dissolution of feldspar and glass leads to increasing sodium bicarbonate concentrations.

Growth and ion exchange of zeolites and clay minerals (and quartz growth?):
Low solubility leads to precipitation of hydrated secondary alumino-silicates. Changes in aqueous ion activity ratios and differing temperature effects on thermodynamics lead to ion exchange between solid and aqueous solutions. Metastably supersaturated solutions may precipitate quartz lowering the silica activity.

Brine and salt formation and dissolution:
Drying at elevated temperatures leads to brine formation and precipitation of salts such as NaHCO₃ and NaCl. Vapor pressure lowering over the salts stabilizes water at temperatures above the nominal boiling point. Rehydration dissolves precipitated salts.
GEOCHEMICAL MODELING:
KEY CONCEPTS FOR THE YUCCA MOUNTAIN REPOSITORY

Staged modeling: Natural system -- Nonisothermal system -- Evaporative system

System components: 
- (Na,K)A1Si3O8 -- feldspar
- SiO2 -- cristobalite/quartz
- H2O/CO2 -- liquid/vapor
- NaCl -- electrolyte
- CaCO3 -- calcite
- (Na2,K2,Ca)A12Si10O24•8H2O -- clinoptilolite
- (Na.33,K.33,Ca.165)A12.33Si3.67010(OH)2 -- smectite

Natural model: Recharging water from the soil zone is saturated with calcite. CO2 gas pressure is buffered. Feldspar/glass dissolution promotes clinoptilolite growth.

Nonisothermal model: Temperature-time relations are derived from heat flow modeling. Initial conditions are derived from ambient system modeling. Variations in CO2 gas fugacity are derived by gas flow and transport modeling coupled with a local-equilibrium chemical model. Reaction progress-time relations are derived from kinetic modeling.

Evaporative model: Rayleigh fractionation versus CO2 buffered systems models. Equilibrium precipitation versus supersaturation models. Vapor pressure lowering stabilizes liquid water at elevated temperatures.
CHEMICAL PRINCIPLES AND COMPUTATIONAL METHODOLOGY

CARBON SYSTEM MODELS

Conductive heat flow
Averaged one-dimensional gas flow
CO₂ transport by advection
Local equilibrium among gas, aqueous, and calcite phases based on mass conservation, electroneutrality, and mass action relations
Aqueous activity coefficients based on an extended Debye-Hückel formulation

Computations were performed with codes written by Codell, Goulet, and Murphy and thermodynamic data from DATA0.COM (Johnson et al.).

PARTIAL EQUILIBRIUM REACTION PATH MODELS

Equilibrium among gas, aqueous, and secondary minerals based on mass conservation, electroneutrality, and mass action relations
Aqueous activity coefficients based on an extended Debye-Hückel formulation
Dissolution and growth of feldspar and cristobalite based on rate expressions
Time obtained by integrating rate equations for increments of mass transfer
CO₂ gas fugacity controlled as a function of time and temperature

Computations were performed with the EQ3/6 software (Wolery et al.) and modified DATA0.COM data.
Figure 5 - Carbon content of gas, liquid and solid phases between the water table and the ground surface.
VARIATION IN TEMPERATURE AND CO$_2$ FUGACITY
75 METERS ABOVE THE REPOSITORY HORIZON

![Graph showing temperature and CO$_2$ fugacity variations over time.](image-url)
VARIATION IN pH, FELDSPAR DISSOLUTION, AND SMECTITE PRECIPITATION 75 METERS ABOVE THE REPOSITORY HORIZON

DOTTED LINES = LOW pCO₂
SOLID LINES = HIGH pCO₂

MOLES/KG WATER

TIME, YEARS

pH

FELDSPAR

SMECTITE
VARIATION IN MAJOR SOLUTION COMPONENTS
75 METERS ABOVE THE REPOSITORY HORIZON

- UPPER CURVE = HCO$_3^-$
- LOWER CURVE = Na

- HIGHER RATE, HIGHER pCO$_2$
- LOWER RATE, HIGHER pCO$_2$
- HIGHER RATE, LOWER pCO$_2$

MOLAL CONCENTRATION

TIME, YEARS
ECTS OF BOILING ON WATER CHE, TRY WITH MINERAL PRECIPITATION AT 100°C AND CO₂ PRESSURE AT 10⁻².14 BAR.

**A**
- MOLAL CONCENTRATION
- FRACTION BOILED
- Lines: Na, TOTAL CARBON, HCO₃⁻

**B**
- pH
- IONIC STRENGTH
- FRACTION BOILED

**C**
- MOLALITY
- FRACTION BOILED
- Lines: Na, TOTAL C, HCO₃⁻, K, Si, Cl, Ca

**D**
- pH
- IONIC STRENGTH
- FRACTION BOILED
**YUCCA MOUNTAIN REPOSITORY GEOCHEMISTRY: RELATIONS TO THERMAL LOADING AND FLUID FLOW**

**FLUID FLOW:**
Redistribution of H$_2$O and CO$_2$ by gas phase flow would affect aqueous solution properties on a large (e.g., mountain-sized) scale.
Zeolitization of bedded vitric tuffs could affect hydraulic properties.
Precipitation of calcite (or other minerals) could affect hydraulic properties.
Most chemical reactions would occur in the matrix, where the water is, and most flow of significance to repository performance would be in the fractures. However, alteration of fracture lining minerals could affect flow and transport.

**INCREASED THERMAL LOADING:**
Time and space scales of thermal effects would increase with increasing thermal loading.
At elevated temperature and decreased H$_2$O vapor pressure, hydrated minerals could dehydrate and smectites could alter to illite, which could affect sorption or hydraulic properties.
Heating could affect near-field materials, e.g., dehydration or cracking of grout and corrosion of rock bolts.