COUPLED HYDRO-GEOCHEMICAL PROCESSES
AND THEIR SIGNIFICANCE FOR YUCCA
MOUNTAIN SITE CHARACTERIZATION

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ABSTRACT

Geochemical processes can result in changes in hydrological properties and processes via modification of pore and fracture volumes. Coupling of these processes must be taken into account when modeling repository evolution. Preliminary calculations have been carried out to determine the distribution of equilibrium vs. kinetically controlled recrystallization domains in the repository block, and what the magnitude of resulting changes in porosity may be. The results suggest that equilibrium may be achieved for most of the hydrological regimes that may develop, except within fractures a few tens of meters from emplacement drifts. Preliminary models suggest total change in porosity may be ca. twenty percent in equilibrium-dominated regimes.

I. INTRODUCTION

Confidence that long term storage of high level nuclear waste in deep geological repositories can be successful must rely on the capability to realistically simulate repository performance. Such simulations require a description of the failure rate of containers, and the rate at which radionuclides are transported from the failed container to areas where human exposure may be possible. To do this requires knowledge of how geochemical and hydrological processes interact to control the thermal properties, water movement, and geochemical characteristics of the evolving site. These parameters are important because they determine 1) container corrosion rates, 2) extent, if any, of waste dissolution, and 3) transport of radionuclides to the accessible environment. This paper discusses efforts aimed at defining the types of the evolving site. These parameters are important because they determine 1) container corrosion rates, 2) extent, if any, of waste dissolution, and 3) transport of radionuclides to the accessible environment. This paper discusses efforts aimed at defining the types of geochemical domains that may influence hydrological properties, and the preliminary results of efforts directed at evaluating the relative importance of various recrystallization processes for hydrological properties.

II. HYDROLOGICAL PROCESSES

Pore water heated by energy transferred from waste packages to surrounding rock will: 1) evaporate as temperature rises, with a corresponding increase in water vapor pressure, resulting in migration of vapor to lower pressure regions in the repository block; 2) change composition as water evaporates, leaving behind solutions that are progressively more concentrated; 3) condense in cooler regions after evaporation and vapor-phase migration; and 4) boil, leaving behind a dried out region when temperatures exceed the nominal boiling temperature. The local heat budget will thus reflect the local balance between convective and conductive processes.

The resulting thermal and hydrological evolution of the site has been modeled extensively using the V-TOUGH code, which computes the coupled transport of water, vapor, air, and heat in fractured, porous media. An equivalent continuum model that considers the bulk permeability (fracture and matrix properties are pore-volume averaged) is assumed to be appropriate. It is assumed that capillary pressure and thermal equilibrium between fractures and matrix is achieved.

A number of simulations were conducted to evaluate the effect of recharge and APD on the evolution of hydrological and thermal regimes that might develop over the lifetime of a repository (10,000 years). For virtually all cases examined, (APD of 20 to 114 kilowatts/acre, recharge flux of from 0.00 to 0.132 mm/year), four hydrological regimes develop within the repository block.

Regime A (Temperature < T boiling) encompasses those areas where the temperature is between ambient and boiling, and therefore is realized for all regions that experience heating. As heating occurs, in situ pore water is heated and evaporation occurs, resulting in higher water vapor pressures and consistently high relative humidity. The increase in water vapor pressure results in movement of vapor down pressure gradients. Pressure gradients as high as 5 bars may develop between intact rock blocks and the fractures that bound them, due to higher gas phase diffusivities in the fractures. Pressure gradients will also develop between low and high temperature regions. Water vapor moving in fractures to lower temperature regions will condense on the cooler fracture surfaces. Provided that full saturation of the rock has not been achieved, the condensed water will be imbibed into the matrix of rock blocks.

Fluid velocities within this regime vary greatly. Within the lower temperature portion of Regime A both gas and liquid movement is restricted to maximum values of millimeters per day in both matrix and fractures. At temperatures approaching the boiling point, gas phase velocities can be as high as tens of meters per day in fractures, and centimeters per day in the matrix.
The duration of these processes at any one location will depend upon the rate of heating, which is related to distance from waste package emplacement locations. Within a few tens of meters of emplacement drift walls, Regime A will persist for a very brief period of time (less than 10 years) due to the rapid rate of heat deposition and attainment of boiling. In contrast, rock that is hundreds of meters from emplacement drifts will heat up slowly, resulting in the persistence of Regime A for hundreds to thousands of years.

Regime B (T = T boiling) forms between Regime A and the waste packages, where temperatures will eventually reach the boiling point for virtually all scenarios with APD's greater than 20 kW/acre. When this condition is met, processes become dominated by boiling of pore water, migration of the resulting steam through pores to fracture surfaces, transport of the steam along fractures, and condensation of steam at the edge of the boiling zone. Imbibition of the condensed steam into the matrix of fracture-bound blocks will eventually result in complete saturation of fractures. This region thus becomes one in which temperature is essentially constant at the nominal boiling point (96°C), at 100% saturation.

Once 100% saturation is achieved, steam that condenses will deposit water on fracture walls that will not imbibe into the saturated rock blocks, but will, instead flow along fracture surfaces under the influence of gravity. Above the repository, this may lead to a region of water refluxing in which water will cycle from the boiling zone to the condensation front (as vapor), and back again (as liquid). Below the repository, refluxing will not occur, but the saturation zone will be widened as condensed hot water flows downward along fractures, and heats the rock as the latent heat of vaporization is released.

Regime B grows in volume as long as the thermal envelope around the repository is expanding. The regime thickness varies with time, being virtually zero at the edge of emplacement drift walls when the boiling point is first reached, and reaching thicknesses in excess of 100 meters several hundred years after the repository is closed. This regime will persist for long time periods (10's to hundreds of years).

Regime C (T > T boiling) is bounded by the boiling point isotherm and the repository, and represents the region within which temperatures are above the boiling point and relative humidity is low (< 9). Vapor pressure lowering due to increased salinity of trapped water in restricted pores, and boiling point elevation associated with high vapor pressures in block interiors where vapor migration to fractures may be restricted, may result in local persistence of thin films of water to very high temperatures, perhaps as high as 150-210°C. In general, however, it is expected that this regime will be one dominated by drying of the rock, with a persistent but very small volume of water residing in geometrically constrained sites.

Regime D (T < T local max) develops after the local thermal maximum has been achieved. It encompasses rock that has been physically modified during the heat-up period, either as a result of mineral dissolution and/or precipitation, or due to mechanical effects. These effects will be evident as changes in bulk and fracture porosity and permeability. In those regions where saturation values exceed pre-emplacement ambient values, slow dehydration will occur. Those regions which experience decreased saturation at the local thermal maximum, relative to pre-emplacement ambient saturations, will begin to slowly rehydrate. Modeling suggests that the rates of resaturation are so slow that it will take hundreds of thousands of years before pre-emplacement ambient saturations are approached.

III. GEOCHEMICAL AND MINERALOGICAL PROCESSES

The geochemical processes that affect hydrological processes in particular regimes are primarily continuous and discontinuous reactions that result in changes in mineral assemblages and mineral compositions which effect changes in the volumes of primary and secondary phases. The following discussion focuses on these processes.

A. Continuous Reactions

Dehydration reactions involving single hydrous mineral phases can be expected to occur in all regimes in the repository block. The rates of these reactions is sufficiently fast such that equilibrium dehydration states for single phases will likely be achieved for all portions of the repository affected by temperature changes or changes in relative humidity. The impact of these processes on pore and fracture volumes may be locally significant where concentrations of hydrous minerals is large, and temperatures or relative humidities exceed critical values.

Although continuous precipitation of material during evaporation and boiling is likely to occur, preliminary simulations with EQ3/6 suggest that the total volume of precipitated material will be much less than 0.1% of the initial water volume (C. Bruton, personal communication, 1993).

Exchange reactions and sorption are also important continuous reactions that influence water chemistry and retardation properties of the repository materials. However, these reactions have very small volume changes associated with them and would tend to be a second order effect on hydrogeological properties.

B. Discontinuous Reactions

Discontinuous reactions may occur when water composition, temperature, and/or pressure changes are of sufficient magnitude to exceed the stability limits of individual phases or mineral assemblages. The specific reactions that will occur will depend on local mineral assemblages and lithological properties. Within Regimes A and B, most of the discontinuous reactions of interest will proceed via dissolution and precipitation mechanisms. The extent to which equilibrium will be approached will depend upon temperature, surface area to fluid volume ratio, fluid flow rate, and fluid composition, particularly the pH and solution ionic strength. For single phase dissolution and precipitation reactions the same parameters will determine the extent to which equilibrium will be approached, in addition to the saturation index in the fluid of the relevant...
single phases. Within Regime C, where liquid water may no longer be present in significant quantities, the mechanism whereby discontinuous reactions may occur is via diffusion, or via solid state "breakdown" of mineral phases usually through reactions in which hydrous mineral phases react to form other solid phases and a vapor phase. For these reactions, the extent to which equilibrium will be approached will depend upon the kinetics of the diffusional processes involved, and the rate of solid state "breakdown" of the reactant phases. The impact of all of these reactions on hydrological properties may be large due to the large molar volumes of the minerals that are potential reactant and product phases.

IV. COUPLED HYDRO-GEOCHEMICAL PROCESSES

To determine the geochemical impact on hydrological properties in any particular environment, it must first be determined whether chemical and mineralogical equilibrium is closely approached or achieved. If locations within the repository block can be identified where equilibrium is likely to be achieved, for any given set of conditions at any given time, the anticipated changes in the hydrological properties, particularly porosity and permeability, can be established by determining the equilibrium mineral assemblages and mineral abundances that result from rock-water interaction in pores and on fracture surfaces during fluid flow. Otherwise, the role of reaction kinetics in controlling the pore and fracture volume changes associated with mineral dissolution and precipitation must also be considered. We have undertaken several reconnaissance studies to determine where in the repository block it is likely equilibrium will be achieved, and what might be the expected changes in total porosity for low temperature rock-water interactions during heating of the repository block.

In regions where fluid flow velocities are known, the extent to which equilibrium will be approached can be determined by considering the Damköhler number of the system, which relates reaction rate \( k_j \), reaction stoichiometry \( v_{ij} \), surface area \( S_j \), hydrogen ion activity \( a_{H^+} \), reaction order \( n \), distance traveled by the fluid \( L \), fluid equilibrium concentration \( C_{eq} \), and fluid velocity \( V \), for the \( i \)th component of the \( j \)th reaction, through the relationship

\[
D_I = \frac{v_{ij}S_jk_j(a_{H^+})^n}{L/C_{eq}V}.
\]

Large Damköhler numbers (> 1000) characterize systems that will be very close to thermodynamic equilibrium, while small Damköhler numbers (< 1) characterize systems that will be dominated by kinetics.

We assumed a \( D_I \) value of 1000, the reaction kinetics appropriate for cristobalite dissolution and precipitation\(^5\), near neutral solution pH, and solved for the equilibrium length. Fluid velocities were taken from simulations of flow regimes in the vicinity of waste containers\(^5\). The results of the calculation (Fig. 1) demonstrate that within Regime B, velocities in fractures are such that fluid would have to travel distances greater than 10,000 meters before equilibrium would be achieved. Within matrix material, however, velocities are so low that equilibrium would be attained over distances of less than a few millimeters.

These results suggest that equilibrium in matrix blocks probably will be achieved for most conditions that develop in the near vicinity of waste packages, but equilibrium is unlikely to be attained in coexisting fractures.

At greater distances from waste containers fluid velocities are, in general, sufficiently low so that equilibrium distances calculated from \( D_I \) are only a few millimeters. Whether equilibrium will be approached will then depend on the rate of change of temperature conditions, relative to reaction rates. This can be evaluated by comparing reaction rate time constants \( (\tau_c) \) for dissolution and precipitation reactions, with the amount of time a given location will exist at temperature. Using silica dissolution and precipitation kinetics\(^5\), and temperatures computed from hydrothermal models\(^1\), one can compute the ratio of the amount of time a particular location will be at a given temperature vs. the time required for reaction to approach completion \((5\tau_c) \) at that temperature:

\[
R_i = \frac{1}{[(5/((10^{-0.707/2.598}0/T)))/(6.3072*10^8)]}
\]

Figure 1 - Distance water would travel to satisfy \( D_I = 1000 \), contoured in meters/year. The kinetics for cristobalite dissolution\(^5\), surface area for a 20 micron fracture, temperatures and fluid velocities computed from V-TOUGH for a horizontally emplaced waste package, and neutral pH are assumed. The location of the waste package is shown by the solid circle. Vertical and horizontal scales are equivalent: the solid bar at the top of the figure represents 5 meters.
where $T$ is degrees Kelvin, and $t$ is total time at temperature. The temperature-dependent power function used is that for precipitation kinetics of silica polymorphs. Similar results are obtained for the dissolution kinetics of silica polymorphs. In this treatment, it was assumed that reaction rates are insignificant at temperatures less than 60°C, and above 100°C (the latter because of the nominal absence of water). In addition, for the sake of conservatism, $t$ was treated as cumulative time between 60 and 100°C, and $T$ was assumed to be 60°C. Values of $R_i$ greater than 1.0 indicate conditions in which sufficient time exists for reactions to proceed to near completion. Mapped in Figure 2 are the results of this calculation, for a 20 micron fracture, and areal power density of 114 kW/acre, along the repository center line, out to 12,000 years. This figure demonstrates that conditions appropriate for equilibrium are progressively attained as the repository block heats up, encompassing all rock within ca. 300 meters above below the repository horizon, within about 1000 years after closure.

Assuming equilibrium is approached at low flow rates (< 1.0 mm/year), the changes in pore volumes due to rock-water interactions can be computed using the EQ3/6 reaction path modeling code. The mineralogy of the repository horizon $T_p$, and the chemistry of J-13 water are assumed in this calculation (see 6 for details). It is further assumed that sufficient water is present to allow reactions to go to completion (in the calculations, the initial water to rock volume ratio is ca. 20:1). This assumption is tantamount to the scenario in which water is continually replenished as reaction proceeds, allowing complete

Figure 2 - Contour diagram showing the dimensionless ratio of cumulative time at conditions between 60 and 100°C, to time required to achieve 99.3% of the equilibrium state for silica polymorph precipitation, along a center line through the repository from the ground surface to 800 meters below the ground surface. The calculation is done from the time of repository closure to 12,000 years into the future. Contour interval is 400, starting contour value is 100. All values greater than 1 indicate locations where the time available exceeds by the indicated amount the time required to achieve equilibrium. The repository depth is assumed to be 340 meters. The central "valley" in the figure locates conditions above 100°C; equilibrium is calculated to be achieved for rocks in this region within 1000 years after closure.
equilibrium to be attained. This calculation thus overestimates the actual change in porosity expected, since the integrated water:rock volume ratio in the repository block is unlikely to achieve such large values, except perhaps in regions of vigorous refluxing.

Plotted in Figure 3 is the total percent change in porosity, assuming an initial porosity of 10%. The dramatic change in porosity at about 70°C is due to the absence of clinoptilolite, which is a major product phase at lower temperatures, in the higher temperature product assemblage. Although the actual changes in mineral assemblages may differ from those seen in these simulations, particularly at low water activities, the results point out that significant differences in porosity change can occur at relatively low temperatures during the thermal evolution of the repository.

CONCLUSIONS

The preliminary simulations described in this paper suggest that equilibrium conditions may be obtained for rock matrix in most regions of the repository block within a few thousand years after closure. The primary exception to this conclusion is the region defined by Regime B in the vicinity of the waste packages, where fluid velocities in fractures are likely to be too high to allow equilibrium to be attained. However, whether this preliminary conclusion is valid will depend upon the number of refluxing cycles to be expected for an average packet of condensate within the refluxing zone.

If equilibrium is achieved, the changes in porosity (and consequently, permeability) will depend upon the mineral assemblage that forms. Preliminary results suggest that porosity can be significantly enhanced or diminished, depending upon local temperature and lithologic properties.

The results demonstrate that adequate modeling of these coupled processes requires the ability to consider both thermodynamic equilibrium and kinetically controlled systems in a wide range of flow regimes. Currently, the ability to model fully coupled hydrology and geochemistry has not been sufficiently developed to accomplish this.

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REFERENCES


