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VALIDATION OF HYDROGEOCHEMICAL CODES USING THE NEW ZEALAND GEOTHERMAL SYSTEM

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ABSTRACT

Evaluation of the performance of a nuclear waste repository requires that numerous parameters be evaluated over a broad range of conditions using computer codes. The capabilities of these codes must be demonstrated using complex natural systems in which the processes of interest have already occurred or are occurring. We have initiated such a test of geochemical and hydrological simulation codes, using the geothermal areas of the Taupo Volcanic Zone, New Zealand. Areas that have been evolving for a few tens to a few tens of thousands of years are of particular interest. This effort will help determine the extent to which simplified modeling approaches can be used in performance assessment calculations.

To guide the selection of natural systems, we are attempting to map potential repository regions dominated by equilibrium processes and those dominated by kinetically controlled processes. To do so, fluid velocities and temperatures were computed using the V-TOUGH code assuming an equivalent continuum, dual porosity model. These results were then used to compare advective fluid flow rate with silica dissolution/precipitation rates, using Damköhler numbers. Only the first 5000 years of repository operation were considered. The results identify a migrating envelope of kinetically dominated activity several meters wide in the vicinity of waste packages that contrasts with other parts of the repository.

The Lake Rotokawa region, New Zealand, has been used in our first test effort, since it contains environments that are examples of kinetic and equilibrium processes. The results of tests involving equilibrium processes show excellent correspondence between simulated and observed mineral alteration sequences, although discrepancies in some mineral parageneses demonstrate that operator decisions in conducting simulations must be considered an integral part of validation efforts; pure "code validation" is impossible when considering complex natural systems. The extent to which simplification of models may be possible will be evaluated as further simulations are completed.

1. Introduction

Predicting the behavior of nuclear waste repositories over their service lifetimes requires codes that simulate the response of the enclosing geological environment to a broad range of physical and chemical processes. However, it is unrealistic to expect that these codes will rigorously simulate the detailed behavior of these repositories because: 1.) many of the processes of interest are coupled in complex ways that are not yet fully characterized by functional relationships; 2.) many of the parameters that need to be measured are difficult or impossible to obtain (e.g., the rate of precipitation of mineral phases in the natural setting, or the surface roughness of pore spaces); 3.) probabilistic functions that describe the distribution of properties or parameters can seldom be determined due to the variability of the natural setting, and the fact that the number of points at which the parameters can be evaluated is insufficient to satisfy statistical requirements for representative sampling. Furthermore, the number of separate computer runs required to provide a statistically valid probabilistic model of the performance of a repository is prohibitively large.

It thus becomes necessary to determine the extent to which models of natural processes can be simplified. To do this requires determining which parameters have a significant influence on the performance of the repository, and defining the precision that is required for characterizing or measuring these significant parameters.

Simulations of processes in natural settings are particularly important for accomplishing this task. Natural systems are the only "experiments" available for evaluating the relative importance of specific parameters in complex, heterogeneous environments, and in which the time duration is comparable to repository lifetimes. The principle shortcoming of such systems is that they are difficult to characterize, since they seldom have sufficient information preserved to allow adequate measurement of the parameters of interest.

To address some of these issues, we have begun a long term study of geochemical and hydrothermal processes at the active Taupo Volcanic Zone on the North Island of New Zealand[1]. The intent of this study is to determine the extent to which geochemical and hydrothermal models can be simplified and still provide accurate predictions of geochemical and hydrological properties. This effort is also designed to accomplish rigorous code validation by comparing the results of simulations with observed processes.

2. Definition of the Problem

Processes and characteristics that are important for nuclear waste repositories include, but are not limited to, reaction kinetics, ion exchange and sorption, aqueous speciation, rock and fracture permeability, imbibition characteristics, connectivity, and fracture roughness. Values for these variables span many orders of magnitude. Evaluation of the ability of a code to simulate processes in a nuclear waste repository thus requires that the natural systems used for study somehow provide a test of the capabilities required to simulate repository behavior.

There are specific characteristics of the proposed repository design at Yucca Mountain that are useful in selecting natural sites for study. Rocks and packing material in the vicinity of waste packages will undergo a period of rapid heating followed by a long cool-down period (Fig. 1). In the fractured rocks that may make up the repository, fluid velocities will be very different between intact blocks and the fractures, and these velocities will vary greatly as heating and cooling proceed. This situation generates two distinct domains that will be important for understanding the evolution of chemical and hydrological environments.

Of particular interest to us is the extent to which chemical equilibrium will be achieved within domains of the repository. We have compared the different flow regimes by computing, as a function of time and position with respect to a waste package, the distance a fluid would be required to move to achieve chemical equilibrium.

The computations were carried out in a two dimensional array that extends away from waste packages 24 meters in a vertical direction, and 18 meters in a horizontal direction. The simulations first established the flow regime and thermal history, using the VTOUGH code[2]. The resulting fluid velocities and temperatures were then used to compute the distances over which fluid must flow before equilibrium would be closely approached, by inverting the Damkohler Group 1 number for length. The Damkohler Group 1 number is a dimensionless number that is the ratio between reaction rate and

fluid velocity, for the temperature, fluid velocity, exposed reactive surface area, distance over which the fluid flows, reaction rate function, and the equilibrium fluid composition for the system being considered[3], and is expressed as:

$$D_I = v_{ij} S_j K_j (a_{H+})^n \, L/c_{eq} V,$$

where v_{ij} is the stoichiometry of the ith component in the jth reaction, S_j is the surface area, K_j is the reaction rate, $(a_{H+})^n$ is the hydrogen ion activity for the respective nth order reaction, c_{eq} is the equilibrium concentration of the ith component, and V is the fluid velocity.

Large Damkohler numbers (> 1000) characterize systems that will approach thermodynamic equilibrium, while small Damkohler 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, that the solution remains near neutral in pH, and solved for the equilibrium length. This allowed us to map those regions in the vicinity of waste containers in which fluid velocities were high enough to require large equilibrium lengths. Regions that had this feature would be unlikely to achieve chemical equilibrium, and provided us with a guide for selecting particular types of systems in New Zealand for detailed study and use in code validation activities.

3. Equilibrium Regimes and Implications for Study Sites

Within a few years after waste emplacement, fluid velocities in *fractures* a few meters away from the waste containers are high enough (>1 meter/year) to result in very large length values (10-10,000 meters; shaded region in Fig. 2). This regime migrates outward over a period of about 100-400 years, and into regions where equilibrium may have been achieved. As it migrates the halo eventually dissipates in regions that are at the same elevation as the waste containers. Above and below the containers, however, these areas persist until they eventually dissipate at about 400 years. In contrast, there are no regions in which the velocity of fluids in the rock *matrix* requires lengths greater than a millimeter. This suggests that equilibrium will be achieved in the rock matrix.

With these features in mind, the initial site we selected for reconnaissance study was Lake Rotokawa in the Rotokawa geothermal field[4]. Lake Rotokawa fills a 6000 year old hydrothermal eruption vent. The lake water has a slightly elevated temperature, with a pH of 2.3. The high pH is due to condensation and oxidation of upwardly streaming H_2S-rich fluids that are interacting with atmospheric gases. The H_2S fluids are derived from boiling alkaline chloride fluids that are at deep levels in the hydrothermal system. Sulfur, which is one of the oxidation reaction products, is actively being deposited at the site.

The upward flowing fluids have caused the development of alteration zones that represent different degrees of rock-water interaction. These zones represent different liquid to rock ratios, and can be used as a means of testing the ability of codes to accurately model fluid-rock interaction.

This system is phenomenologically similar to those that may develop in regions surrounding waste packages, at the potential repository site at Yucca Mountain, where increased saturation may develop in response to pore-fluid vaporization, migration and condensation. The attractive aspect of the Rotokawa site for testing geochemical

simulation capabilities is the ability to monitor the kinetics of reactions in natural systems, and the quantity of reaction products that develop.

4. Modeling Approach

Our initial effort focused on modeling the evolution of the fluids and solid reaction products, as a function of fluid-rock ratio and temperature. Our goal was to determine the conditions under which sulfur would be deposited in the relative proportions observed at various temperatures using the observed gas and liquid compositions at the site, and to compare the observed mineral assemblages at the site with the minerals predicted to occur by the reaction path geochemical modeling code EQ3/6[5,6].

Since it was unknown the extent to which sulfur deposition reflected free evolution of atmospheric gases and volcanic fluids, or interaction of fluids with rock, we considered several different scenarios. The cases we considered allowed free evolution of the fluids (volcanic gases/waters and atmospheric gases) with and without controls on certain gas species. We then repeated the simulations, but included the local rock (Taupo ignimbrite) as a reactant.

Under no conditions did sulfur form in the simulations, if any of the gas fugacities were fixed at some constant value. If the gas fugacities are allowed to freely evolve (i.e., are unbuffered by any mineral assemblages) sulfur deposition occurs. Of course, it was only in the runs that had the Taupo ignimbrite present that secondary alteration mineral sequences formed.

The secondary minerals that form, and the quantity of sulfur deposited depends directly on the amount of fluid-rock interaction (Fig. 3). The correspondence between observed and simulated secondary mineral assemblages is excellent. The absence of anhydrite in the simulations, however, is an important contrast between models and observed phase relationships, since it represents the presence of an oxidized sulfur species. This suggests that the models do not accurately represent fluid-rock-atmospheric gases interaction.

5. Implications of These Preliminary Results for Future Work

With respect to code validation activities, this exercise emphasizes the well known problem that there is seldom sufficient information available from natural sites to allow a test of codes modeling capabilities alone. Validation activities also become a test of the knowledge of the individuals designing the validation runs. In this particular instance, guesses had to be made as to how gases behaved during evolution of the system (i.e., were gas fugacities buffered or were they allowed to evolve as the system evolved?). Such situations may be advantageous, however, since the computer simulations generate vast bodies of predictive information that can be tested by further field work. When conducting simulations for validation efforts, plans should therefore include field studies that will be conducted after the simulations, in order to test code predictions.

With respect to the simplification issue, it is apparent that the greater the number of variables that can be treated as constants during the simulations, the simpler are the computations. The effort we are undertaking in New Zealand is focused on this problem, with the intent of establishing the range of values for particular chemical parameters of importance to the system, as a means of defining limits for chemical conditions. It is not yet known, however, if it will be possible to accomplish significant simplification of the systems we are studying; the preliminary results we have to date

have not provided any clear indication of particular chemical variables that may be amenable to such a treatment.

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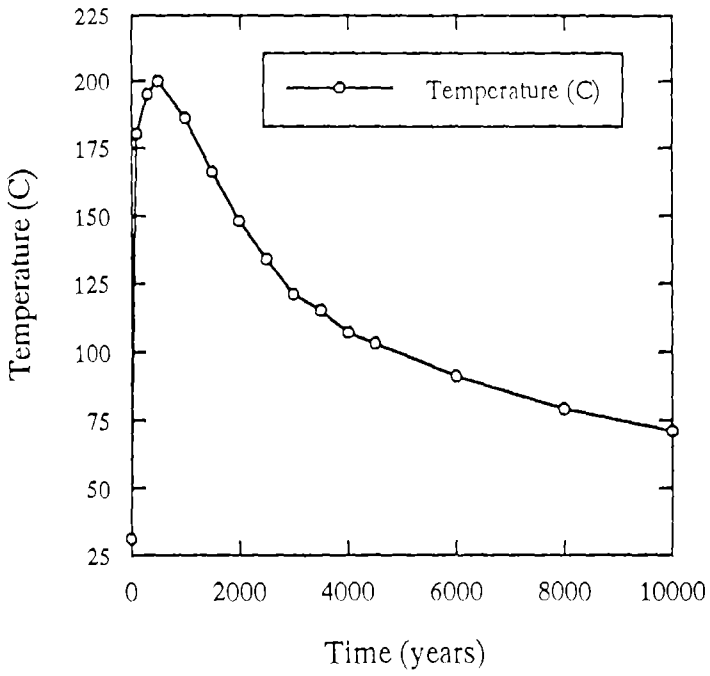

Figure 1. Temperature of the center of a high level radioactive waste repository at the potential repository site at Yucca Mountain, Nevada, as a function of time. Temperatures computed for 30 year old fuel, and an assumed areal power density of 114 kw/acre, with no recharge flux (computed by J. Nitao and T. Buscheck, using the VTOUGH code[2]).

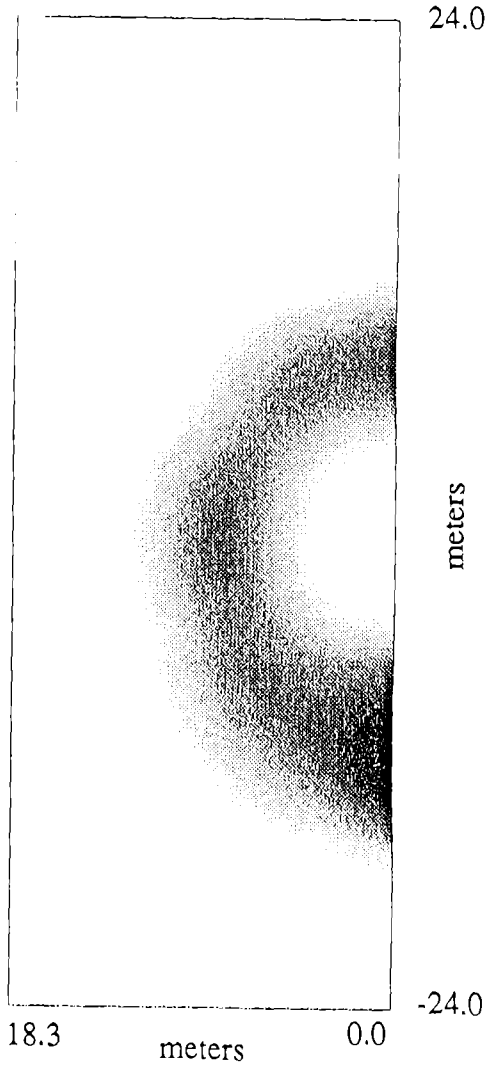

Figure 2. Fluid flow distances in fractures 25 years after waste emplacement. Darkest shading is for distances >10,000 meters, lightest shading is for distances of 10m.

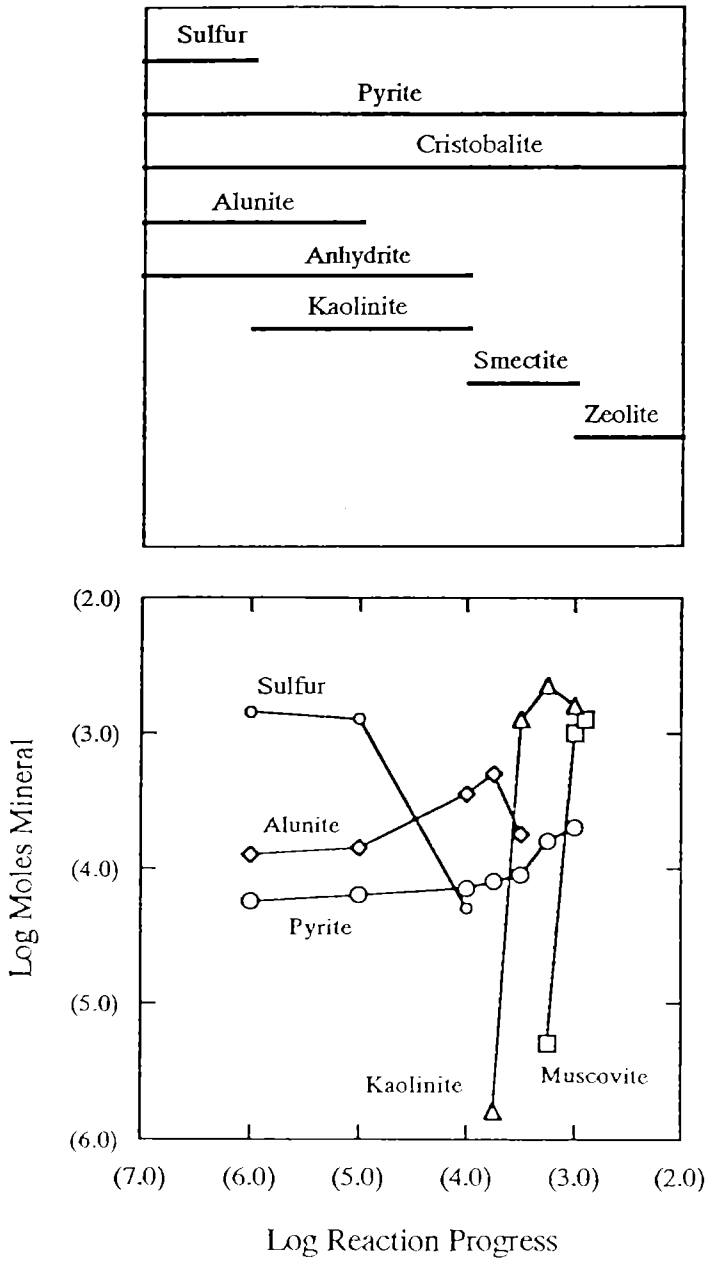

Figure 3. Comparison of the observed mineral assemblages at the Rotokawa geothermal system (top) with the assemblages predicted to occur in the EQ3/6 simulations (bottom). The horizontal axis in the top figure is schematic, and represents the transition from water-dominated conditions (left side of figure) to rock-dominated conditions (right side of figure). Bars identify approximate conditions over which different minerals coexist. Numbers in parentheses in the bottom figure are negative.