

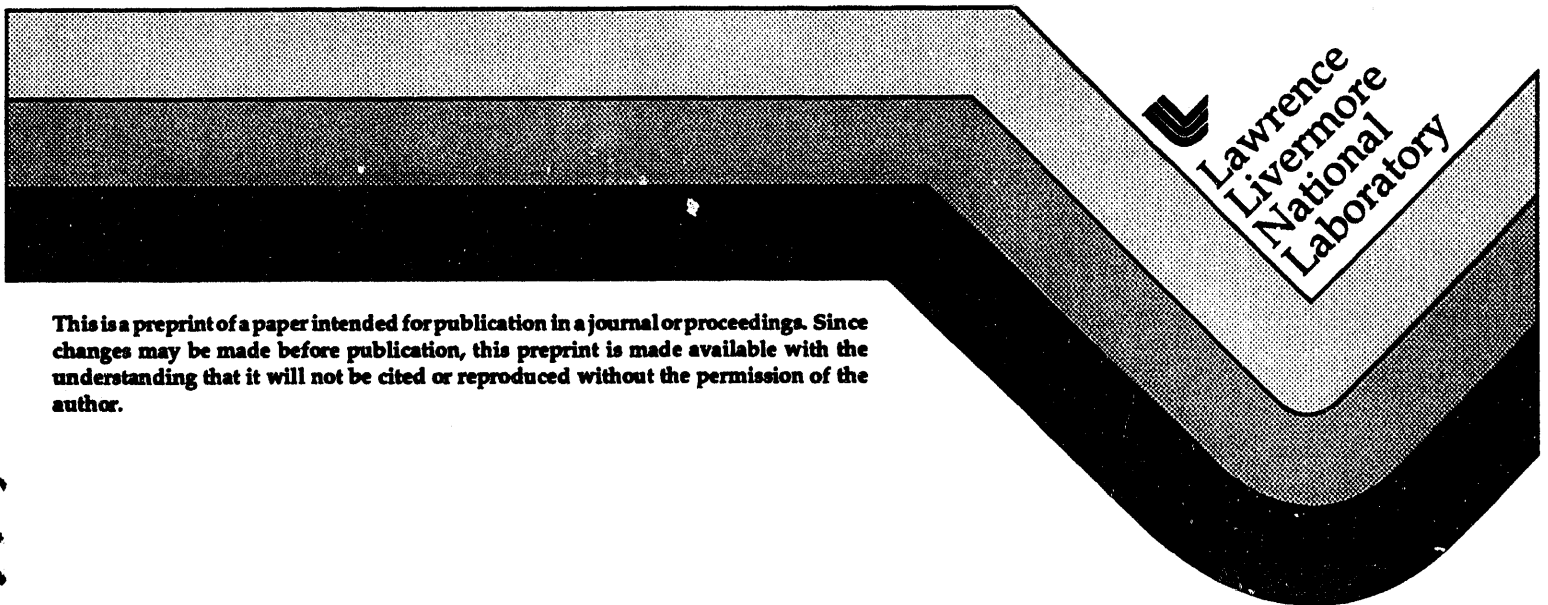
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**TESTING GEOCHEMICAL MODELING CODES USING  
NEW ZEALAND HYDROTHERMAL SYSTEMS**

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TESTING GEOCHEMICAL MODELING CODES USING  
NEW ZEALAND HYDROTHERMAL SYSTEMS

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ABSTRACT

Hydrothermal systems in the Taupo Volcanic Zone, North Island, New Zealand are being used as field-based modeling exercises for the EQ3/6 geochemical modeling code package. Comparisons of the observed state and evolution of selected portions of the hydrothermal systems with predictions of fluid-solid equilibria made using geochemical modeling codes will: 1) ensure that we are providing adequately for all significant processes occurring in natural systems; 2) determine the adequacy of the mathematical descriptions of the processes; 3) check the adequacy and completeness of thermodynamic data as a function of temperature for solids, aqueous species and gases; and 4) determine the sensitivity of model results to the manner in which the problem is conceptualized by the user and then translated into constraints in the code input.

Preliminary predictions of mineral assemblages in equilibrium with fluids sampled from wells in the Wairakei geothermal field suggest that affinity-temperature diagrams must be used in conjunction with EQ6 to minimize the effect of uncertainties in thermodynamic and kinetic data on code predictions. The kinetics of silica precipitation in EQ6 will be tested using field data from silica-lined drain channels carrying hot water away from the Wairakei borefield.

INTRODUCTION

Active hydrothermal systems can be used as field-based tests of geochemical modeling codes such as EQ3/6<sup>1,2</sup>. In the Taupo Volcanic Zone, North Island, New Zealand, heated fluids have been reacting with silicic rocks, volcanic glasses and man-made materials in hydrothermal systems for long periods of time. Many of the physical and chemical phenomena occurring in the systems today are analogs to processes that may occur in potential nuclear waste repositories where emplaced nuclear waste may heat surrounding fluids, cause fluid flow and result in fluid-solid interactions over extended time periods.

The extent to which computer codes adequately represent natural processes relevant to siting of a nuclear waste repository can be tested by comparing computer simulations of fluid-solid interactions with compositional data from hydrothermal systems. The well-studied New Zealand hydrothermal systems are especially appropriate for these types of studies because of

their lithologic characteristics and duration of activity. We are carrying out a set of field-based modeling exercises using data from New Zealand that will test the capabilities of the EQ3/6 geochemical modeling computer codes. This effort will help to determine the accuracy and uncertainty associated with geochemical models used in performance assessment calculations.

The process of code testing (i.e. "validation") involves three elements: comparing predictions and observations, ascertaining whether the process being modeled is accurately represented, and judging how well the prediction matches the observation. Use of a natural system in which the processes of concern are active and can be monitored, such as the selected sites in the Taupo Volcanic Zone, provides the best opportunity to obtain well-constrained data on processes of interest, and to determine the accuracy of models that describe particular processes. What remains problematic is the determination of whether the match between prediction and observation is "good enough".

The intent of the exercises we are pursuing is to identify problem areas of geochemical process modeling, and to establish confidence intervals around predictions. This effort thus focuses on mismatches between observation and prediction, with the ultimate goal of reducing the mismatches as we refine our database, modeling approaches, and analytical capabilities. As a result, what is meant by "good enough", and by implication, the uncertainties associated with predictions, must change as the exercises proceed.

GOALS OF MODELING EXERCISES

Comparisons of the observed state and evolution of a hydrothermal system with predictions of fluid-solid equilibria made using geochemical modeling codes will: 1) ensure that we are providing adequately for all significant processes occurring in natural systems; 2) determine the adequacy of the mathematical descriptions of the processes; 3) check the adequacy and completeness of thermodynamic data as a function of temperature for solids, aqueous species and gases; and 4) determine the sensitivity of model results to the manner in which the problem is conceptualized by the user and then translated into constraints in the code input. Exercises must be used to find ways to minimize the effect on model results of unavoidable uncertainties in field observations and thermodynamic and kinetic data required to run the computer models.

There will not be one definitive exercise; nor will there be any damning exercise. All exercises will provide us with new information useful in refining modeling strategies. Hence, when a prediction does not match field observations, it becomes a guide to help us find what parts of the puzzle we are missing, and may ultimately be more rewarding and useful than a superficially adequate match.

During the course of this project, developments and/or refinements required in EQ3/6 and its thermodynamic data base will be identified. This information can then be used to constructively guide and prioritize future code development. The project will also point to additional data needs from site characterization that would permit more realistic performance assessment calculations.

An added benefit of this project is the opportunity to examine in a field-scale setting the consequences of physical and chemical phenomena that have been identified as critical to repository performance. In the process of testing the geochemical models in situations that are relevant to the repository, we identify areas where the process of interest is thought to be occurring. Data are then collected to better define the processes and their impact on the environment. Not only does such data define the "ground truth" for the models, but it also is extremely useful information in its own right that can be used to forecast system response to various repository scenarios.

#### SUITABILITY OF NEW ZEALAND HYDROTHERMAL AREAS

Hydrothermal systems in the Taupo Volcanic Zone (TVZ) of New Zealand (Figure 1) possess many characteristics which make them ideal candidates for analog study. They are well-characterized, and occur within rock types (silicic volcanics) and at temperatures (~10 - 300°C) appropriate to Yucca Mountain scenarios. TVZ hydrothermal systems have been active over about 500,000 years, which spans the time scales important in repository models. Alteration mineralogies include zeolites such as mordenite, clinoptilolite, laumontite and wairakite, clays, feldspars, epidote, and silica polymorphs, all of which have, or may, play a role in the evolution of the repository host rock

Many physical and chemical processes have been hypothesized to occur in a potential nuclear waste repository, including mineral dissolution/precipitation, changing fluid chemistry, boiling, condensation, fluid flow, glass alteration, degradation of man-made materials, and so on. All of these processes can be found in various parts of the TVZ thermal systems, and will afford us the opportunity to test many potential functions of the computer codes. Our intent is not to use TVZ hydrothermal systems as total system performance analogues, but to use them to test selected process modules in EQ3/6.

Much of the required information about TVZ hydrothermal systems is already available, which saves us the expense and time of gathering it. In addition, the active exploitation of the hydrothermal systems for geothermal power gives us the added advantage of being able to collect additional data, such as fluid and rock samples, as needed. We are collaborating with scientists from New Zealand's Institute of Geological and Nuclear Sciences (IGNS) who have extensive field, experimental and modeling

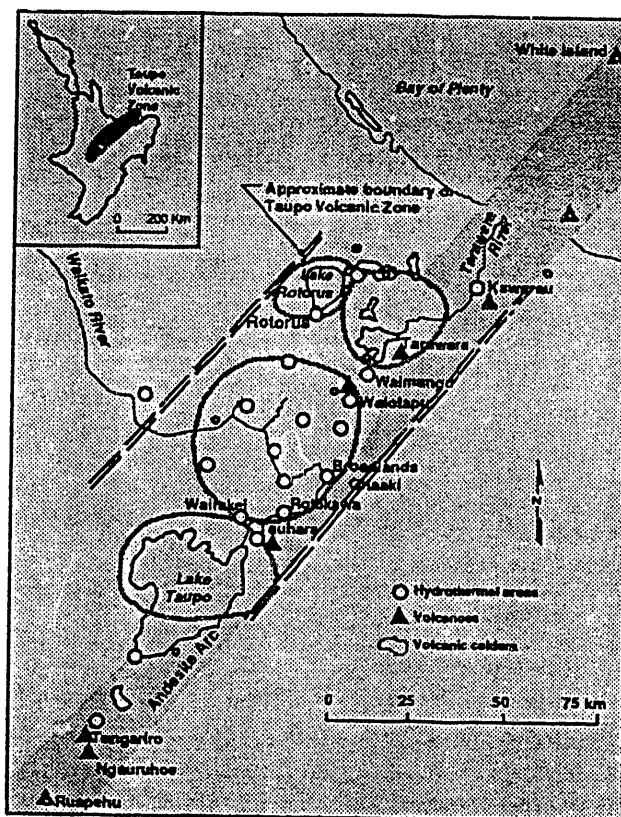


Figure 1. Location map of Taupo Volcanic Zone, North Island, New Zealand with selected hydrothermal areas and volcanic features. Dark shaded strip represents the andesitic arc. Adapted from <sup>4</sup>.

experiences with hydrothermal processes in the TVZ.

Added benefits of working on actively exploited TVZ hydrothermal systems are: 1) the ability to couple predictions of rock alteration and changes in fluid chemistry with studies of the interactions with man-made materials; and 2) the chance to study the impact that utilization has had on the hydrothermal systems.

In the course of utilizing geothermal power, a variety of man-made materials such as cements and metals have been introduced through drilling and production. The interaction of these materials with fluids at elevated temperature over tens of years will be characterized, evaluated and modeled in coordination with other tasks of the LLNL Yucca Mountain Project such as Man-Made Materials.

Utilization of the fields for geothermal power since 1953 has also resulted in striking changes in hydrothermal areas which we can use to test our ability to model man-induced perturbations in natural systems. For example, production from the Wairakei borefield has resulted in field drawdown and the formation of a steam zone where water once used to exist. Cooler waters are beginning to flow back into rocks which were originally at higher temperature. In some cases, abundant silica precipitates seal individual fractures. All of these processes have been suggested to occur at various points in the thermal evolution of the potential repository. The TVZ provides a unique opportunity to test our

ability to model these processes on time scales unattainable in the laboratory.

## TESTING CODE MODULES

Geochemical modeling codes embody mathematical representations of specific physical and chemical processes with provision for coupling of the processes. In EQ3/6, these processes include kinetics of solid dissolution/precipitation, homogeneous equilibrium within the fluid phase, and solid-solution and cation-exchange phenomena in solids of variable composition (e.g. zeolites, clays, carbonates). Although the process models are founded on fundamental principles, we sometimes lack critical model parameters needed for specific systems. For example, the kinetics of dissolution are critically dependent on the surface area of solids, but surface areas measured in the laboratory do not correlate well with effective surface areas calculated from natural systems. Lacking models for processes such as nucleation kinetics, user-specified rules are used to determine the order of solid precipitation. Validation exercises should be designed not only to test models in which we have reasonable confidence, but should also determine how best to cope with unavoidable uncertainties in model parameters and field data.

## FIELD-BASED MODELING EXERCISES

In our initial collaborations with IGNS, we reviewed potential study areas for data availability, quality and extent of characterization and presence of geochemical processes that would test existing models in EQ3/6. We selected Wairakei, Waitapu, Waimangu and Kawerau geothermal areas as initial study areas. IGNS has completed a summary of the open literature data on fluid chemistry, rock types, mineralogy, mineral chemistry, well data and other information about the Wairakei geothermal area. Initial work was directed toward identifying sets of coexisting water analyses and mineral assemblages along fractures and flow zones that could be used to test for fluid-rock equilibrium (see below).

The information was used to specify the first tests of the EQ3/6 codes: A) water-rock equilibrium in Wairakei boreholes; and B) rates of silica precipitation.

All calculations described in this paper were carried out using version 7.1 R125 of EQ3<sup>1</sup> and version 7.1 R154 of EQ6<sup>2</sup> together with version R16 of the SUPCRT subset of the GEMBOCHS thermodynamic data base. Pressures of all EQ3/6 calculations were set equal to the vapor pressure of water along the liquid/vapor saturation curve.

### A. Water-rock equilibrium in Wairakei boreholes

1. *Modeling test.* One of the most fundamental modeling exercises is the situation in which a fluid of known composition is believed to be in equilibrium with a documented mineral assemblage. In this exercise, the chemical model is run to determine the extent to which the measured fluid chemistry can be used to identify the minerals and their compositions in equilibrium with the fluid. Conversely, the mineralogy is used to place constraints on the fluid chemistry in equilibrium with the mineral assemblage.

This exercise tests the schemes by which codes select which

precipitates are most likely to form, reveals the extent of supersaturation maintained in natural systems (or, alternately, inaccuracies in the thermodynamic data), checks for the existence of local equilibrium, and tests models of solid solution and cation exchange. Selected systems should encompass a wide range of fluid chemistries, different classes of minerals (e.g. zeolites, clays, anhydrous framework silicates, etc.) and temperature.

2. *Wairakei geothermal system.* Mineral-fluid relations in the well-characterized Wairakei geothermal system will be used to illustrate the testing process described above. At Wairakei, alteration assemblages have formed along fractures which focus fluid flow through the host rhyolitic ignimbrites. Production is from wells that intersect these feed zones.

Studies have shown that alteration of primary minerals at Wairakei<sup>4,5,6</sup> has produced a variety of silicates, zeolites, carbonates and clays as secondary minerals. Excluding the acid condensate zones, the secondary minerals include epidote, calcite, pyrite, smectite, chlorite and silica polymorphs, plus the zeolites wairakite, mordenite, clinoptilolite and laumontite. The alteration mineralogy as a function of temperature at Wairakei tends to be uniform across the field in different boreholes. Water chemistry has changed little throughout the field's over 30 year production history, except for perturbations such as dilution caused by production.

3. *Field data.* After critiquing collected data, Wairakei well WK-28 was chosen for detailed study. WK-28 has a temperature of 248°C at the main producing horizon. Mineral assemblages identified at downhole temperatures of 240-260°C in the main feed zones at Wairakei include: wairakite, adularia, epidote, wairakite ± quartz, quartz + adularia, wairakite+epidote+calcite, albite+quartz+epidote+chlorite+calcite, prehnite and wairakite+prehnite<sup>6</sup>.

The as-sampled composition of the produced water from WK-28, affected by steam and gas loss during production, is shown in the left hand column of Table 1. Most water samples from producing fields were obtained from weirboxes at atmospheric pressure. Fluid analyses are available from 1960 onward for WK-28. The chemical composition of the vapors discharged from WK-28 are shown in Table 2, in units of  $\mu\text{mol gas/mol water}$ .

Prior to making equilibrium calculations, the fluid composition must be corrected for the steam and other gases lost because of decreases in pressure during production. Enthalpy balance calculations<sup>7</sup> were used to estimate the amount of H<sub>2</sub>O (steam) loss, and the resultant concentration of dissolved species in the produced waters. At this time, only the most reactive and abundant gases CO<sub>2</sub> and H<sub>2</sub>S were considered out of the ones listed in Table 2. EQ6 was used to add the gases back into the fluid. H<sub>2</sub>S gas added back into the fluid was assumed to contribute to sulfide species, but not sulfate, on the assumption that the kinetics of sulfur oxidation in the aqueous phase is slow relative to rates of production.

The calculated downhole fluid composition at the subsurface temperature of 248°C, corrected using EQ6, is shown in the right hand column of Table 1. Al and Fe were assumed to be controlled by equilibrium with respect to K-feldspar and pyrite at depth,

TABLE 1. Major constituents of discharge from Wairakei well WK-28 sampled on 03/78 (in mg/kg)<sup>6</sup>.

Component	As-sampled*	Corrected**
Na	1195	846
K	186	132
Ca	19	13
Mg	0.01	0.007
Fe	-	0.58e-4
Al	-	0.15
Rh	2.32	1.64
Li	11.1	7.86
Cs	2.14	1.52
B	28.2	20
Cl	2035	1441
HCO <sub>3</sub>	-	102
SO <sub>4</sub>	31	22
HS	-	48
SiO <sub>2</sub>	590	418
pH	7.8	5.9***

\* temperature=ambient; from <sup>5</sup>

\*\* corrected for steam and gas loss and assuming equilibrium with pyrite and K-feldspar at 248°C

\*\*\* calculated after correction; temperature = 248°C

TABLE 2. Chemical composition of vapors discharged from Wairakei well WK-28 on 3/78 (in  $\mu\text{mol/mol}$  water)<sup>6</sup>.

Component	
CO <sub>2</sub>	30
H <sub>2</sub> S	26.1
NH <sub>3</sub>	1.0
Hc	0.0003
H <sub>2</sub>	0.090
Ar	0.014
O <sub>2</sub>	< 0.002
N <sub>2</sub>	0.54
CH <sub>4</sub>	0.095

respectively, because of the ubiquitous presence of both of these minerals at depth in the Wairakei field. Redox state was set by the SO<sub>4</sub>/H<sub>2</sub>S buffer, assuming an initial content of 0.3 mg/kg of aqueous H<sub>2</sub>S based on concentration data from nearby wells. The H<sub>2</sub>S value was then supplemented by the addition of H<sub>2</sub>S back into solution to obtain the subsurface H<sub>2</sub>S concentration. These assumptions represent the first phase of testing conceptual models and modeling strategies.

4. *Simulation results.* The corrected downhole fluid composition in Table 1 was used in EQ6 to calculate a measure of the degree of saturation with respect to all potential minerals in the chemical system. The measure of saturation is the affinity for dis-

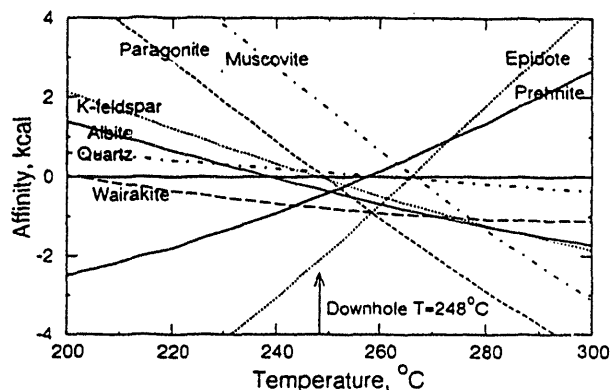


Figure 2. Affinity of selected silicates as a function of temperature in water from Wairakei well WK-28.

solution or precipitation, defined in EQ3/6 as  $\text{RTlog}(Q/K)$  where R is the gas constant, T is temperature in degrees Kelvin, Q is the ion activity product of the mineral hydrolysis reaction under consideration, and K is the equilibrium constant at the temperature of interest.

When the affinity of a mineral equals zero, the code would predict that the phase is in equilibrium with the fluid. This does not mean, however, that the mineral necessarily occurs in the actual mineral assemblage. Common ion effects, such as the competition among saturated minerals for available chemical components required for their precipitation, limit the number of minerals that actually will precipitate even though a significantly greater number of minerals may be saturated or supersaturated. The kinetics of precipitation may also impact the appearance of a mineral phase.

The affinity runs were made at temperatures ranging from 200 to 300°C. Results for selected minerals are shown in Figure 2. Minerals shown were selected on the basis of their proximity to saturation and their relevance to the Wairakei geothermal field. As Reed and Spycher<sup>8</sup> point out, this type of diagram is useful for indicating whether the fluid is in equilibrium with a mineral assemblage, what that assemblage may be, and the temperature of the assemblage.

A number of minerals appear to be close to equilibrium (within 500 cal) with WK-28 waters at the downhole temperature (Figure 2), including quartz, albite, K-feldspar, prehnite and paragonite. K-feldspar should, and is, in equilibrium at 248°C because the fluid was assumed to be in equilibrium with it in order to estimate the concentration of Al in the water. Muscovite is predicted to be supersaturated, whereas wairakite is undersaturated throughout the entire temperature range. Epidote is also undersaturated; however, this could be related to complex issues relating to the assumption that Fe concentration in the system is controlled by pyrite, and to the estimate of subsurface redox conditions using the SO<sub>4</sub>/H<sub>2</sub>S buffer.

To complement the affinity calculations, EQ6 was used to predict what specific mineral assemblage is stable in equilibrium with the fluid at depth. This calculation fully accounts for competition among supersaturated minerals for available chemical com-

ponents, but does not take into account kinetics of precipitation. The calculations were carried out at 20°C increments.

From 200 to 248°C, muscovite, pyrite and quartz were calculated to be the stable assemblage, whereas at higher temperatures, anhydrite along with epidote and prehnite comprise the new phase assemblage. Diopside also precipitates at 300°C. These results are consistent with the relations in Figure 2, although diopside is not shown in the figure. The apparent stability of anhydrite is problematic; we are not sure at this stage if its stability merely reflects an inappropriate choice of redox constraints in our input parameters.

At this stage, we must now evaluate whether the predicted 248°C pyrite-muscovite (considered a proxy for muscovite/illite)-quartz assemblage accurately reflects the assemblage in equilibrium with the fluids. Additional detailed petrographic studies are in progress by IGNS to address this question.

In the meantime, the above results show why figures such as Figure 2 will be important when we try to predict mineral stability from computer simulations. A mineral such as muscovite may be very supersaturated, such that its precipitation precludes precipitation of other saturated minerals, which would not be apparent from a cursory examination of a simple EQ6 precipitation run. If the thermodynamic data for that mineral were suspect, or the mineral is not favored to form because of kinetic constraints, we might never have identified the other minerals as potential precipitates.

Figure 2 also suggests that a variety of mineral assemblages can be close to equilibrium with a given fluid chemistry. Small energetic differences separate these assemblages, such that small changes in fluid chemistry can have a significant impact on mineral assemblages. Perhaps this phenomena is reflected in the varying combinations of a limited number of minerals noted in Wairakei wells and other hydrothermal areas.

The downhole temperature of the fluids can be estimated using Figure 2, as noted by <sup>8</sup>, by noting the temperature at which the affinity curves converge on 0. The measured downhole temperature seems to agree fairly well with that estimated using the mineral affinities provided muscovite is not considered. Muscovite is supersaturated because equilibrium with respect to K-feldspar was specified to control Al. Muscovite would have buffered Al activity at a lower activity given the solution composition; hence its supersaturation. Results such as these are being used to define guidelines for making appropriate and reasonable assumptions that will adequately provide for gaps and uncertainties in field data, such as the lack of an Al analysis.

#### B. Rates and amounts of silica precipitation with time

Field operators at Wairakei flow waste water through concrete drains to cool it before disposal. The waters, at a temperature of about 80°C, contain large masses of aqueous silica that precipitate along the drain walls to form massive silica sinter. This sinter must be frequently scraped from the drain's interior. Modeling of silica precipitation will test the ability of the code to predict the masses of silica that precipitate with time from a fluid originally in contact with high silica rocks at elevated temperature. With regard to a potential repository, this work will test the

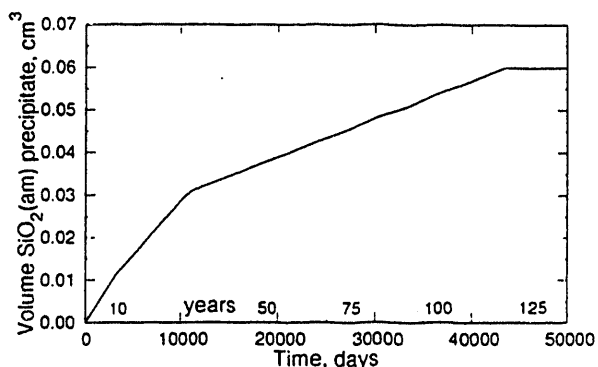


Figure 3. Volume of amorphous silica precipitated per kg of Champagne Pool water at 76°C assuming a surface area of 1000 cm<sup>2</sup>/kg of water and a pH-independent rate law of precipitation<sup>10</sup>.

adequacy of the EQ3/6 submodels for mineral precipitation kinetics, and will test theories of precipitation kinetics.

Data will be collected regarding the masses and rates of fluid flow through the drains, the masses of silica sinter produced through time, and fluid chemistry and temperature. The precipitation kinetics option of EQ3/6 will then be invoked using rate equations and constants from Rimstidt and Barnes<sup>10</sup> and others to try to predict the masses of silica precipitate through time for comparison to the field data.

Figure 3 demonstrates the general modeling approach to be taken. Because the present-day fluid chemistry from the drains was not yet available, the composition of a fluid from Champagne Pool in the Waiotapu geothermal field was used in its stead. Champagne Pool water is considered to be representative of the deep geothermal reservoir water at Waiotapu. An arbitrary surface area of 1000 cm<sup>2</sup>/kg of fluid was used prior to obtaining the wetted contact area of the drains. The amounts of silica scraped from the drains over the years can be directly compared to the calculated results as exemplified in Figure 3.

Garibaldi and Freeston<sup>11</sup> immersed stainless steel cylinders and a plate into the Wairakei drains and monitored the rates of silica deposition over 20 days. Rates ranged from about 0.29 to 3.88 mg/cm<sup>2</sup>/day. Water chemistry, pH and temperature were constant over this time. EQ6 will be used to try to model their results as a further code test. These exercises will test the adequacy of our models for silica precipitation, and help to set guidelines for the choice of meaningful surface areas.

In related studies by the Man-Made Materials task at LLNL, we hope to obtain samples of the concrete drain to examine the degradation caused by contact with flowing, heated fluids over extended time periods.



## CONCLUDING REMARKS

The hydrothermal areas of the Taupo Volcanic Zone provide unparalleled opportunities for testing geochemical models of fluid-rock interaction in long-lived natural systems. We are conducting these tests in the TVZ because physical and chemical phenomena operating in the field bear resemblance to potential Yucca Mountain processes. Such phenomena can be used as guides to potential system response to emplacement of nuclear waste in a geologic repository.

Preliminary calculations with available data are defining approaches to constraining code input to reduce the impact of uncertainties in field data. Diagrams such as the affinity-temperature diagram allow us to better predict the consequences of fluid-rock interaction by minimizing the effect of uncertainties in thermodynamic data and kinetics of mineral precipitation.

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