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INTRODUCTION

EQ3/6 is a set of related computer codes and data files for use in geochemical modeling of aqueous systems. The creation of EQ3/6 began in 1975, for the purpose of modeling the reaction of sea water and basalt in mid-ocean ridge hydrothermal systems (1). EQ3/6 has since been adopted for further development and application to problems in geologic disposal of high-level nuclear waste by both the Nevada Nuclear Waste Storage Investigations (NNWSI, tuff repository program) and the Office of Nuclear Waste Isolation (ONWI, salt repository program). The code package is currently operational at Lawrence Livermore National Laboratory, other U.S. national laboratories, several universities, and in private industry.

The EQ3/6 package centers around two large computer codes, EQ3NR and EQ6, which are supported by a common thermodynamic data base. EQ3NR (2) is a speciation-solubility code, whose function is to compute a model of the state of an aqueous solution. This code is very flexible in terms of the input that it will accept. Input may consist of analytical measurements, assumptions (such as that the fluid is in equilibrium with specified minerals), or some mixture of measurements and assumptions. The output contains the distribution of aqueous species, their thermodynamic activities, and saturation indices for various solids. If the input contains the assumption that the fluid is saturated with some mineral, the output also gives the total concentration of some element which makes up that mineral (e.g., the solubility of uranium in contact with schoepite). The output also normally includes a calculation of the electrical balance of the fluid, which is a useful indicator of the quality and completeness of aqueous solution analyses.

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EQ6 (3) is a reaction-path code, which calculates models of changes in aqueous systems as they proceed toward a state of overall chemical equilibrium. These models are divisible into three types: 1) "instant" equilibration of a system not at equilibrium, such as a water that is supersaturated with respect to several solids, 2) reaction-path calculations using arbitrary kinetics to describe mass transfer for reactions that do not follow instantaneous equilibrium (these calculations essentially represent titrations), and 3) reaction-path calculations using actual kinetic rate laws. EQ6 runs are initialized by entering a description of the starting aqueous fluid (from EQ3NR) and defining the constraints for the reaction path (i.e., identifying the irreversibly reacting materials and specifying the controls on their rate of reaction; temperature/pressure changes may also be included).

At the present time, EQ6 models correspond to two physical scenarios: 1) a closed system, which best approximates a rocking autoclave, and 2) a flow-through open system, which follows the progress of a single packet of water as it traverses a reacting medium (this is a pseudo-one-dimensional model). There are tentative plans to add a third model, which would deal with a flow-through open system approximating a leaching cell (also pseudo-one-dimensional). A full one-dimensional model, in which the code would keep track of reaction in a series of boxes, appears feasible, but is not currently planned for EQ3/6 development.

RECENT IMPROVEMENTS

With the adoption of EQ3/6 by the NNWSI and ONWI, development has accelerated in the period FY83-84, and several major steps have been made to improve the adequacy of the code package for use by the waste programs. One major step forward is that a series of detailed user's guides (2-5) has been produced. This documentation has been produced specifically to satisfy NRC software requirements (6).

EQ3/6 prior to FY83 had no capability for modeling brines, because the approximations for calculating the thermodynamic activity of water and the activity coefficients of the solute species were restricted to low ionic strengths ($\leq$1.0 molal). Under ONWI sponsorship, we have added an option (4,7) to use Pitzer's equations (8-11) for such calculations. These equations, based on a semi-empirical approach using virial coefficients, represent a proven methodology for modeling the thermodynamics of brines. Fig. 1 shows an example of this option, in which Pitzer's equations have been used to calculate the solubility of gypsum as a function of NaCl concentration in the system $CaSO_4$-NaCl-H_2O at 25°C.

At present, EQ3/6 contains two alternate Pitzer coefficient data bases. The first, drawn largely from sources other than solublity data (largely Ref. 10), contains sufficient species to account for acid-base equilibria, but does not include any ion-pairs as component species. The second is taken from a source (11) which has been partially optimized to

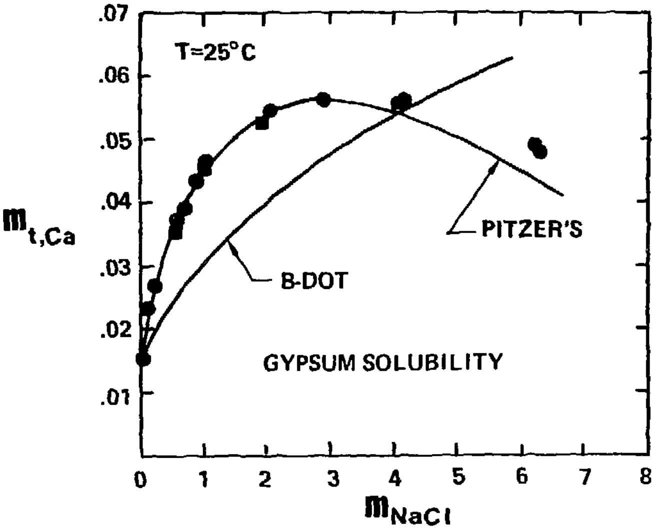

Fig. 1. The solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in NaCl solution at 25°C, calculated using the Pitzer option in the EQ6 code (solid line marked "PITZER'S"). Small squares represent the experimental data of Block and Waters (14); circles those of Marshall and Slusher (15). The Pitzer coefficients were taken from Harvie et al. (11). The second line shows the solubility calculated using the B-dot equation, which was formerly the only activity coefficient model in EQ3/6.

fit solubility measurements and which includes some ion pairs as component species. There are temperature coefficients on the first data file, but none yet on the second.

Other improvements have been made to the basic thermodynamic data file which supports EQ3/6. The EQ3/6 data base includes all data which can be generated from the SUPCRT data base (12,13, and subsequent updates), which includes many simple ions and most of the common rock-forming minerals. All other thermodynamic data are handled through MCRT (5). This code has its own thermodynamic data base, which exists in a supporting role to the the main EQ3/6 data base. Both data bases are internally documented. MCRT functions as a thermodynamic consistency checker, a temperature extrapolator, and a generator of data blocks for insertion into the EQ3/6 data base. Its data file is a master repository of information, which includes not only good thermodynamic data, but also references to alternate numbers which may be good, and documentation of discredited species and bad data as well. In the last two years, the MCRT code itself has been improved, and its data base has been considerably expanded, both to add new elements (such as actinides) and also to allow replacement of

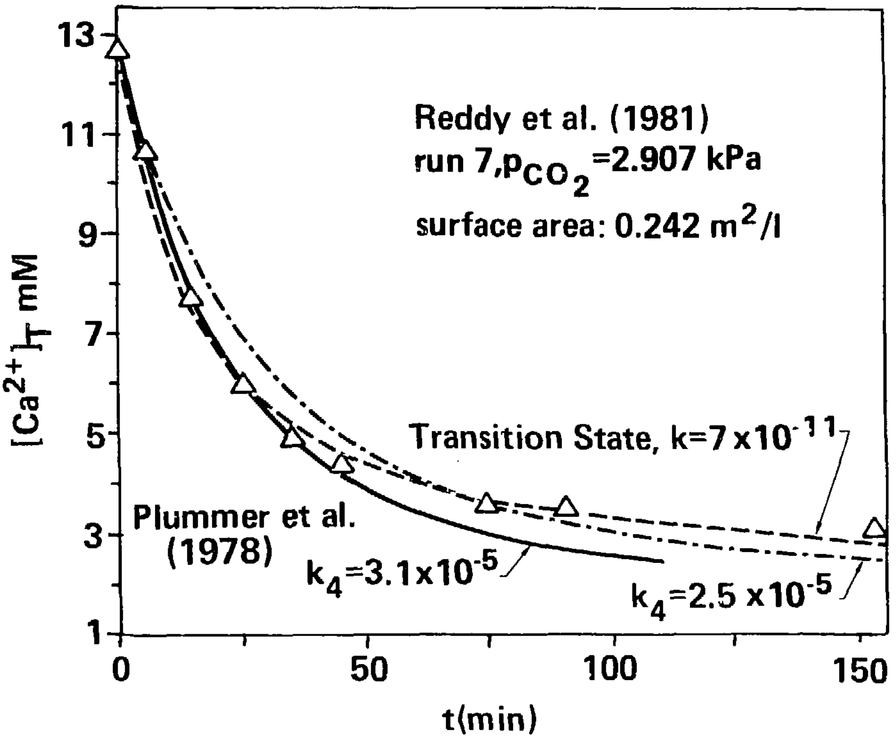

Fig. 2. The precipitation kinetics of calcite, modeled using the new capability in EQ6 (16). Symbols represent the experimental data reported by Reddy et al. (19). Two of the lines were generated using the four term rate law of Plummer et al. (20), using different values for the k_4 constant.

The third line was generated using a simple transition state theory equation with only one rate constant.

old and undocumented data for ion pair and complex dissociation reactions that existed in the EQ3/6 data file.

Several improvements have been made to the EQ6 code. Prior to FY83, the code could run models of mineral dissolution kinetics, but could not calculate models of precipitation kinetics. This problem has recently been overcome by additional code development (16). Fig. 2 shows the results of some attempts of modeling calcite $[CaCO_{3(s)}]$ precipitation using this capability. For a general review of kinetics in geochemistry, see Lasaga and Kirkpatrick (17).

The speed of non-kinetic EQ6 calculations has recently been enhanced by the creation of two new calculational modes, economy mode and super economy mode. Economy mode gives essentially the same informaton density as before. In super economy mode, however, the code skips over phase boundaries (points where minerals appear and disappear along the reaction path), and consequently gives somewhat less information. The ability to analyze the output of EQ6 has been greatly improved by the addition of a graphics postprocessor (18).

A calculational mode to simulate systems open to large gas reservoirs has also been developed (21). This option, called fixed fugacity mode, is directly pertinent to some kinds of experimental configurations, and is thought to be more applicable than a simple closed system to the situation in the proposed NNWSI repository zone, which lies in the unsaturated zone. Here O_2 and CO_2 in the void spaces may be expected to quickly replenish any such gas lost in localized reaction, such as around a waste canister.

PLANNED DEVELOPMENT

A detailed plan for further EQ3/6 development has been drawn up (22). Planned major improvements include:

- Site-mixing models of solid solutions. These are needed to more accurately model the thermodynamics of such phases as clays, zeolites, and feldspars.
- Provision in EQ6 for redox disequilibrium and redox kinetics. The plan calls for extending this capability to handle radiolysis.
- Sorption models. Sorption here is defined as distinct from precipitation and solid solution. There is presently no sorption modeling capability in EQ6. Such a capability is required to treat mass balances in reacting systems, especially for trace components. There is also a need to look into the coupling between mineral surface chemistry and the kinetics of dissolution/precipitation processes.

Other planned tasks include:

- Enhancements to the precipitation kinetics capability.
- Addition of any special capabilities required to model interactions involving glasses. These needs are currently being evaluated.
- Inclusion of a gas phase in EQ6. The code presently has no capability to handle the presence of a possible gas phase.

Possible additional tasks, to be carried out according to programmatic need, include:

- Pressure corrections to the thermodynamic data. The data are now parameterized with pressure as a function of temperature, a constant 1.013 bar up to 100°C, and the liquid/vapor equilibrium pressure for water at higher temperatures.

- Isotopic fractionation. Work in this area has already been carried out in an EQ6 development external to LLNL (23).
- "Leaching cell" flow-through open system.
- True one-dimensional flow-though model.

RATIONALE FOR CODE DEVELOPMENT

Some discussion is called for concerning the rationale behind such ambitious code development, and how it may be expected to tie in to technical progress in waste disposal. EQ3/6 functions primarily as an integrator of submodels. For example, a situation to be modeled might involve simultaneously several very different kinds of processes and phenomena, such as aqueous complexing, mineral dissolution and precipitation, sorption, and thermodynamic non-ideality. Some processes might be described by thermodynamic equilibrium, and others by kinetics. If these phenomena occurred independently of one another, then geochemical modeling would be relatively straightforward and something as sophisticated as EQ3/6 would be unncessary. In fact, these phenomena tend to be coupled, and furthermore, the mathematical relations pertinent to each vary considerably in form. One might say that the equations describing geochemical behavior are not "user-friendly". Hence codes such as EQ3NR and EQ6 must be called upon.

In general, much basic work needs to be done to develop appropriate submodels for such things as kinetics and sorption. We lock upon EQ3/6 as a device to allow one to test specific submodels in the presence of other submodels, as well as a device for integrating existing information. A good analogy is to consider EQ3/6 as a small computer, a general phenomenon (such as dissolution kinetics) as a circuit board, and a specific submodel (such as a particular rate law) as a chip which can be plugged into that board for testing. In EQ3/6 development, we are eschewing the adoption of specific submodels as the "right" ones in favor of programming in various options, from which the user may choose, or to which the user can add.

APPLICATIONS

In terms of applications, EQ3/6 is like a Swiss army knife. The uses range from making simple solubility calculations to carrying out sophisticated kinetic simulations. We will briefly discuss here some applications that are completed, continuing, or planned at Lawrence Livermore National Laboratory. However, we will first point cut that EQ3/6 has been used elsewhere to model the natural tuff-groundwater interactions at the NNWSI repository site (24), the formation of ore deposits (25-27), and interactions between oceanic crust and hydrothermal sea water (1,23,28,29).

RUTHENIUM MIGRATION AT THE CAMBRIC SITE

Although ruthenium is not a prominent element of concern in high-level nuclear waste management, this example is nevertheless a good illustration of the application of geochemical modeling using EQ3/6 to shed some light on a migration problem involving an element with complex chemistry. Coles and Ramspott (30) report the following case history of discrepancy between field and laboratory studies of the migration of this element. Cambric was an underground nuclear explosive test below the water table at the Nevada Test Site. To study the leaching and possible migration of radionuclides from the site, one well was drilled into the explosion cavity and a satellite well was drilled 91 meters away in the direction of the flow path. Continued pumping of the satellite well led to the breakthrough of ruthenium about the same time as tritium, indicating little retardation of the ruthenium. This was not expected, because batch Kd (distribution coefficient) studies of sorption implied high retardation, thus ruthenium should have migrated only a few centimeters.

Recently a modeling study (31), using the results of an exhaustive review of the thermodynamics of ruthemium (32), has shed some light on this problem. EQ3NR, using this new data set, predicts a dissolved Ru concentration in the chimney [2.4×10^{-11} molal, assuming saturation with $RuO_{2(s)}$] that, considering the uncertainties involved, is nearly identical to the measured value of 4.5×10^{-11} molal. The calculations indicate that the species RuO_4^- makes up over 99% of the total dissolved Ru. An anionic species such as this would be expected to exhibit little retardation. On the other hand, the data also show that the field of dominance of this ion in Eh-pH space is small and surrounded by fields for $Ru(OH)_2^{2+}$, $Ru_4(OH)_{12}^{4+}$, and RuO_4^{2-}. Although RuO_4^{2-} should also be a poor sorber, the two cationic species would be expected to be good sorbers. It seems likely that the aqueous form of the ruthenium in the Kd experiments was actually one of these. The sorption experiments were insufficiently characterized to allow any stronger conclusions.

URANIUM SOLUBILITY IN THE PRESENCE OF CONCRETE

A question which was asked in conjunction with the NNWSI project was, "What happens to the solubility limit on dissolved uranium under oxidizing conditions at 25°C if concrete is present in the system?" Concrete may be represented by its principal component, portlandite [$Ca(OH)_{2(s)}$]. Under these conditions, the phase limiting uranium concentration is expected to be schoepite ($UO_3 \cdot 2H_2O$).

A simple calculation suggests that the uranium solubility should be greatly reduced. Schoepite solubility is pH dependent. In the normal groundwater (pH 6.9), the uranium solubility limit is 3.1×10^{-3} molal. However, if the groundwater is in equilibrium with portlandite, its pH is driven up to 12.3, at which the uranium solubility limit is only 9.3×10^{-7} molal.

Taking into account the reservoir of CO_2 gas in the surrounding void space changes this result, however. Reaction path calculations using EQ6 with the fugacity of CO_2 fixed at $10^{-3.5}$ bar (using the capability described by Ref. 21), predict that portlandite and CO_2 react to make calcite [$CaCO_{3(s)}$], and consequently, the pH increases to only 8.3. The uranium solubility limit, in turn, is 4.2×10^{-3} molal, a slight increase over the case where concrete is not present. Thus, concrete actually appears to have little effect on uranium solubility in the NNWSI waste package environment.

MODELING OF LABORATORY EXPERIMENTS

Laboratory experiments (especially autoclave experiments) comprise a key methodology to attacking the problem of predicting performance in a waste repository. Here modeling is useful in several ways: 1) helping to find out what did and didn't happen; 2) testing the consistency of assumptions about controlling factors; 3) extrapolating with respect to such factors as rock/water ratio, open vs. closed systems, different compositions of starting solids and waters, temperature, pressure, and time; 4) designing new experiments, and 5) resolving differences between laboratory results and field observations. Modeling can also serve as an important check to detect bad analyses (esp. via charge balance calculations) and undesired experimental artifacts. Modeling can not make up for deficiencies in characterizing experiments, and indeed the "modelability" of an experiment is a strong function of the degree of characterization.

Two parallel approaches can be taken to the modeling of laboratory experiments. The first we will call the analytical approach. Here one can make speciation-solublity calculations using fluid samples taken with increasing time or distance along a flow path, and look for trends, especially changes in saturation indices. The EQ3NR code alone might be sufficient for this purpose. If, for example, an experiment is conducted at 150°C and the pH is measured at 25°C, this quench pH can be used as an input to EQ3NR, and a one-step temperature correction can then be made by feeding the resulting model into EQ6. Usage of this technique on fluid samples taken from tuff-groundwater experiments shows that the calculated pH at 150°C is usually less than 0.2 units higher than the measured quench value.

The analytical approach is helpful, but it is limited in that it is not extrapolatable or even interpolatable. This kind of power can only be gained by the synthetic approach, which involves actual process modeling. Here one chooses the governing equations (rate laws, equilibria, etc.) and a set of initial conditions, and lets the code predict what will happen. In the first attempts to model tuff-groundwater autoclave experiments (33,34), we found that a purely black box approach is unworkable. One must look to the experiments themselves for certain information critical to the success of the model. Much of this aspect has to do with supersaturation metastabilities and whether or not various thermodynamically possible secondary minerals will actually form in the time of the experiment.

For example, the devitrified tuff in the NNWSI repository horizon consists mostly of quartz (SiO_2), cristobalite (a less stable form of SiO_2), sanidine [$(Na,K)AlSi_3O_8$], and plagioclase [$(NaSi,CaAl)AlSi_2O_8$]. Its reaction with tuff groundwater at 150°C achieves a near steady-state condition after several days. However, the water is then about saturated with respect to the latter three minerals, which are not the most thermodynamically stable. The water is supersaturated with respect to quartz and a host of possible secondary minerals. Some possible secondary minerals form close to saturation, some form under obvious kinetic control, and some apparently do not form at all. There is no a priori way to predict this sort of behavior, except perhaps by the development of "rules of thumb." Thus, kinetic modeling must be closely tied to trends in solution chemistry and careful characterization (SEM, EMP, STEM, XRD, etc.) of secondary phases. It is useful in synthetic modeling to consider a series of models which vary with regard to the exact assumptions of this kind. This "multiple hypotheses" approach is even more critical if one is attempting to extrapolate to longer times.

Work to date appears to demonstrate the feasibility of synthetic, kinetic modeling, at least for tuff-groundwater experiments. This should also be true if granite is substituted for tuff. Kinetic modeling of basalt may be more difficult. If systems of repository rock and water can be modeled in this way, then the next step is to attempt the addition of other repository components, such as canister metals, backfill components, and waste forms. The extent to which this rather detailed modeling will be actually carried out will depend on some balance between the feasibility of the modeling itself and the extent to which the waste disposal programs require it. We should expect to find some of the these answers along the way.

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