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EQ3/6 GEOCHEMICAL MODELING TASK PLAN FOR NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS (NNWSI)

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APRIL 10, 1984

Lawrence Livermore National Laboratory

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ABSTRACT

This task plan outlines work needed to upgrade the EQ3/6 geochemical code and expand the supporting data bases to allow the Nevada Nuclear Waste Storage Investigations (NNWSI) to model chemical processes important to the storage of nuclear waste in a tuff repository in the unsaturated zone. The plan covers the fiscal years 1984 to 1988. The scope of work includes the development of sub-models in the EQ3/6 code package for studying the effects of sorption, precipitation kinetics, redox disequilibrium, and radiolysis on radionuclide speciation and solubility. The work also includes a glass/water interactions model and a geochemical flow model which will allow us to study waste form leaching and reactions involving the waste package. A special emphasis is placed on verification of new capabilities as they are developed and code documentation to meet NRC requirements. Data base expansion includes the addition of elements and associated aqueous species and solid phases that are specific to nuclear waste (e.g., actinides and fission products) and the upgrading and documentation of the thermodynamic data for other species of interest.

INTRODUCTION

EQ3/6 is a set of related computer codes which represents the state-of-the-art in geochemical modeling. EQ3NR calculates from water sample analyses the distribution of ions, ion-pairs, and complexes and determines whether the water sample is saturated with various minerals (Wolery, 1983). EQ6 calculates dynamic models of rock/water interactions, that is, minerals and other phases can be added to a chemical system such that the state of a new system is predicted (Wolery, 1978, 1979). Both codes assume that chemical equilibrium controls most reactions. At the present time, the EQ6 code has a limited ability to handle kinetics, however this ability is insufficient for dealing with the complexities that will likely be encountered in a waste repository. EQ3NR and EQ6 can tell us whether a system is at equilibrium, but in most cases, cannot tell us how long it will take for equilibrium to occur. For example, the codes cannot predict how long it will take for specific mineral phases to precipitate or how long it will take for the system to return to equilibrium when new reactants are added to a system already in equilibrium (e.g., the introduction of the waste package into the tuff/water system).

To run EQ3NR, the code user defines the model for a given application by entering a water analysis and system description. A thermodynamic file is needed that contains the equilibrium constants for the various species and mineral phases as a function of temperature for reactions involving oxidation-reduction, ion-pairing and complexation, and mineral dissolution/precipitation. As part of the output, EQ3NR generates part of an input file for EQ6. This input file is then edited to represent the dynamic system the user wishes to study. A successful application of the code's abilities requires that all the necessary species (aqueous and solid) are represented on the data file and that the equilibrium constants are correct.

The work listed for FY84 in this document is underway. The scope of work for FY84 was decided based on the immediate needs of the NNWSI. Tasks include documentation of EQ6 and MCRT (the thermodynamic data processor), completion of the graphics capability needed for interpreting the verification and applications studies, development and upgrading of the data base, completion

of the model for systems open to gas exchange, and development of the capability to model basic precipitation kinetics. FY84 work for NNWSI focuses on developing the capability to understand processes occurring in the rock/water interactions tests now ongoing at LLNL, on modeling the conditions in the unsaturated zone which will affect these processes, and on providing the data base necessary to model mineral reactions specific to tuff and the radionuclides contained in the waste.

Documentation of the codes and verification/validation studies are equally important to the geochemical modeling effort. Documentation of the codes is needed to fulfill NRC documentation requirements (Silling, 1983). A code that is not adequately documented and verified cannot be part of a performance assessment code package used to support a licensing application. Although the current version of EQ3/6 used in NNWSI modeling applications work is verified, both verification studies related to new capabilities and validation studies are necessary to prove the value of EQ3/6's predictive capabilities.

NEED

The goal of our geochemical modeling task is to upgrade the EQ3/6 code package and supporting data base which will allow the NNWSI to model chemical processes to determine the relative contribution of these processes to the potential transport of radionuclides in ground water from a nuclear waste repository in tuff at Yucca Mountain. Implicit in this goal is the need to interpret the results of laboratory and field tests which form the basis for the evaluation of the geochemical characteristics of the tuff site. To meet this need, a computerized approach is necessary given the complexity of the interactions between the ground water, the tuff and, in the case of the laboratory experiments, the radionuclides. This approach recognizes that geochemical interactions are not a single process, but a set of simultaneous, linked processes, whose mathematical descriptions must be evaluated by a computer code.

The best use of the capabilities in the EQ3/6 codes will require close cooperation between the experimentalists and modelers. Geochemical modeling allows the experimentalists to sort out the contribution of individual processes or mechanisms that dominate the experimental results. In the absence of modeling, the experimentalist is driven--given the complexity of the systems being studied--toward a "lumped-effect" approach, that is, the observations are lumped together and considered the result of a single, overall process. Geochemical modeling also allows the experimentalist to create a numerical description of his or her results for use in the performance assessment models. Original experimental data is rarely in a useful form for use by performance assessment modelers.

Geochemical modeling is also useful for testing the thermodynamic feasibility of proposed mechanisms and for establishing whether a certain equilibrium reaction is controlling a given process. For example, we can test whether a given redox reaction is controlling the solubility of a solid phase. If so, we can then determine--knowing the uncertainty in the redox potential measurement for the tuff ground-water system--the uncertainty in the calculated solubility limits for the radionuclide contained within that solid phase.

The need to make predictions of site stability and radionuclide release from a nuclear waste repository will require the licensing agency, the Nuclear Regulatory Commission, to rely on computer model simulations (Davis, 1983). This is the only technically feasible approach given the limited time scale of field and laboratory experiments, however justified these limits may be. For long-term predictions involving tens of thousands of years, the geochemical codes used to support the licensing application must be capable of modeling processes already identified as major contributors to radionuclide retardation, such as sorption and precipitation. The plan described in this document is designed to meet the immediate geochemical modeling needs of the NNWSI on a time schedule responsive to that of the Civilian Radioactive Waste Management Program given the resources available to us. The plan is also designed to address the NRC recommendations for research and future work outlined in Guzowski et al. (1983) and Apps et al. (1982).

It is important to recognize that the data base expansion and the development of supporting data bases for models such as radiolysis, sorption, redox disequilibrium, and others that are described in this document refer only to the gathering and evaluation of existing experimental data and do NOT include experimental tasks to provide data that is missing, incomplete, or inadequate. It may be that the lack of existing data will defeat our efforts to develop these models. Unfortunately, we cannot evaluate the seriousness of this problem until the work begins.

BACKGROUND

The EQ3/6 code package was first created by T. J. Wolery in the period 1975-1977 at the Department of Geological Sciences, Northwestern University. It was built to study the interactions of sea water with basalt in mid-ocean ridge hydrothermal systems (Wolery, 1978). The general modeling approach followed that laid down by H. C. Helgeson and others in the late sixties and early seventies. This emphasized the concepts of thermodynamic equilibrium and arbitrary kinetics. In its simplest form, this was equivalent to a titration model, that is, where a reactant is added stepwise in a set quantity to a system and the system is adjusted to equilibrium at each step. The numerical approaches in EQ3/6 are original and represent a major improvement over the predecessor code, PATHI (Helgeson, 1968). Figure 1 shows the parts of the code package and how they are related.

From FY78 through mid FY80, EQ3/6 development activities took place at LLNL with support from DOE's Office of Basic Energy Sciences, the Geothermal Energy Program, and the LLNL Nuclear Regulatory Commission (NRC) Waste Management Program. From FY80 through FY82, support at LLNL for continued upgrading of the code's capabilities came from WISAP and other Programs at Pacific Northwest Laboratory. In FY83, funding was received from ONWI at Battelle Columbus for code development capabilities uniquely designed for modeling processes in a salt repository (see Program Interface section). Also, in FY83, work began to upgrade and document EQ3/6 in support of the NNWSI to develop a repository in tuff at Yucca Mountain, NTS.

These earlier periods of code development for the various sponsors resulted in a number of significant improvements. EQ3NR, a completely new version of the original EQ3 code was developed. EQ3NR uses a highly efficient algorithm originally developed for EQ6 and is considerably faster than the old EQ3 code. EQ3NR features a number of user-controlled options which allows the user to customize the code input to fit a wide range of applications. Diagnostics include an informative set of error messages for analyzing code failures and debugging bad input. EQ3NR is also user-friendly in that, unlike EQ3, minerals and aqueous species are identified by their name or chemical formula rather than an index number that is tied to its position in the data base.

EQ6 code improvements from 1978 to 1982 included the capability to model dissolution kinetics, an improved numerical algorithm to handle redox reactions which involve large shifts in oxidation-reduction potentials, changes similar to those incorporated into EQ3NR to identify minerals and aqueous species by name or formula, and new user-controlled options for selecting how and what is printed in the output files. Recognizing that portability is an essential aspect of any code developed for wide distribution, the codes were designed for use on a number of computers including the CDC 7600, the CRAY, the VAX, and the IBM.

From 1978 to the present time, there have been a number of significant improvements in how the data base is processed for use by EQ3NR and EQ6. The data base was completely reformatted to make it easier to expand and revise and to allow for self-documentation (i.e., the data are labeled according to what they represent, the source of the thermodynamic data given for each mineral or aqueous species is referenced, and the quality of the data is stated if known). In 1981, a code called MCRT was created to aid in data revision and expansion. MCRT is a data base building program which uses the Gibbs free energy, enthalpy and/or entropy of each individual species to calculate a grid of stability constants as a function of temperature. MCRT writes individual data blocks for minerals or species which can then be edited into the main data base as they are developed. EQTL, a companion code to MCRT, processes the main data base and creates especially formatted data bases for use either by EQ3NR or EQ6.

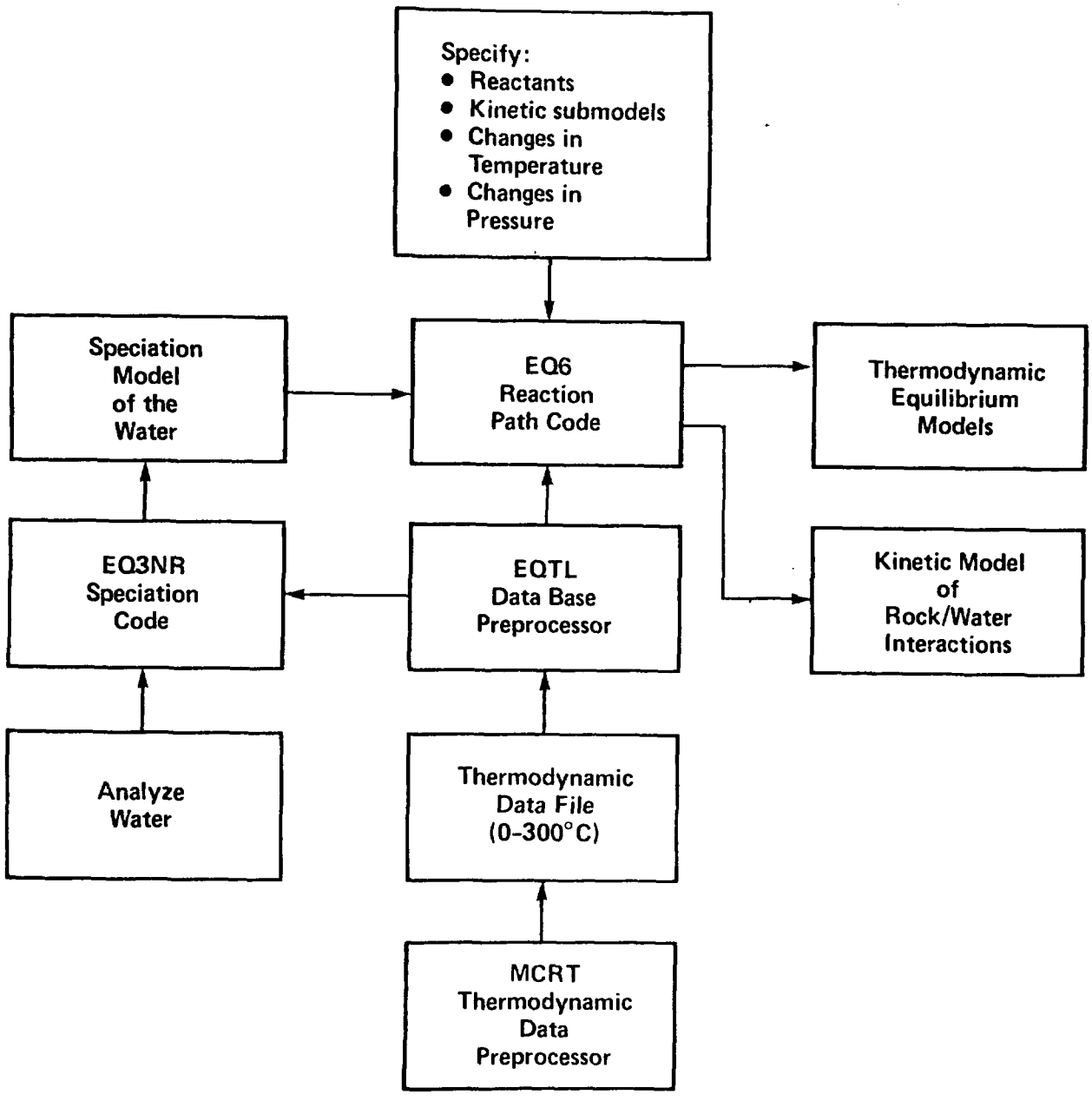


Figure 1. Flow of information between computer codes EQ3NR, EQ6, MCRT, and EQTL (from Wolery, 1983). The EQLIB library (not shown) contains routines that support all of these codes.

With this long history of code development, verification and use, the EQ3/6 code package represents a tested geochemical modeling tool. In addition to interested government agencies, the code is widely distributed to both the industrial and academic world. Applications using the code include studies of geothermal systems (Taylor, et al., 1978), recovery of ore minerals by leaching processes, ore genesis (Brimhall, 1980; Garven, 1982; Sverjensky, 1984), and the chemical evolution of sea water and other fluids (Janecky, 1982; Bowers et al., 1983; Bowers and Taylor, 1983).

Within the nuclear waste management programs, the codes are used to interpret the results of rock/water interaction tests (Wolery and Delany, 1983; Knauss et al., 1984), to evaluate ground-water analyses to determine whether equilibrium conditions exist, to identify potential errors in the analytical data, to determine solubility limits for radionuclides for use in mass transport codes, to aid in the design of laboratory experiments by identifying what needs to be measured to understand the chemical processes which drive the experimental system, and to study the evolution of ground-water chemistry (Kerrisk, 1984a).

MODELING SUB-TASKS

This section describes the geochemical modeling sub-tasks to be accomplished during the five year period covered by this plan (FY84-FY88). Each sub-task is briefly described. For sub-tasks where the scope of work is clearly defined, the technical approach is outlined. Since some sub-tasks are dependent on the successful completion of prerequisite sub-tasks and the information gained from subsequent verification studies, the technical approach may not be obvious at this time. Updates of this plan will be needed as the work progresses. A Network Chart showing the various activities as a function of time is located in a later section.

The geochemical modeling task is designated part of the NNWSI Work Breakdown Structure (WBS) Category 1.3 (Site) and has been assigned the WBS number 1.3.1.9. Within that task designation, we have broken down the activities into the following three groups of sub-tasks.

Code Improvement
Code Documentation
Code and Data Base Maintenance

Activities related to code improvement and code documentation are listed below according to the year they are planned. The sub-task referred to as code documentation is limited to major documents called user's manuals which will be written to meet the NRC documentation requirements described in Silling (1983). Documents written to describe or report on new improvements as they are added to the code are considered deliverables for that activity rather than code documentation and are listed in the Deliverables section. Since code and data base maintenance and quality assurance activities are on-going throughout the five years covered in this plan, they are described in a separate section called Other Sub-tasks. Code improvement sub-tasks funded by ONWI that are also required for the NNWSI geochemical modeling work are described in the Work For Others section.

FY 1984 Activities

Code Improvement

Complete Model for Systems Open to Gases

Work started in FY83 on developing the capability to model systems open to gases (i.e., a fixed fugacity model). This capability will allow us to model the unsaturated zone (vadose zone) in Yucca Mountain where the void space of the unsaturated zone is conceptualized as a large external reservoir containing O_2 and CO_2 at fixed fugacities. (Fugacity is a thermodynamic quantity very nearly equal to the partial pressure of a gas.) As these gases are consumed by reactions in the waste package environment, they may be replenished from this reservoir. Because it is so difficult to collect undisturbed samples directly from the vadose zone in the field, geochemical modeling may provide us with the most realistic approximation to the vadose zone water chemistry that we can expect to obtain.

Add Precipitation Kinetics to EQ6 Code

In FY84, we will begin work on adding basic precipitation kinetics to EQ6. This will allow us to model precipitation growth kinetics according to fairly simple rate laws. It will not allow for the treatment of complex factors such as the kinetic effects of nucleation or poisoning of the system by substances which inhibit precipitation. (See FY 1985 Activities.)

The precipitation kinetics model will only be as useful as the data base which supports it. Relatively good data are available for determining the rate laws governing precipitation of quartz and its polymorphs (e.g., cristobalite), carbonate minerals (especially for calcite), and some sulfates and phosphates. Fortunately, in a number of important cases, we can reasonably extrapolate dissolution data to handle precipitation growth kinetics. This has been demonstrated by Rimstidt and Barnes (1980) to work for quartz and its polymorphs. A preliminary evaluation suggests the method can be expanded to include other silicates. Fortunately, dissolution rate data for the major silicate minerals is more abundant, although there are remaining uncertainties to be worked out before using the data to model precipitation kinetics.

Add a Graphics Post-Processor to EQ6

A graphics post-processor will allow the output from EQ6 runs to be displayed graphically on demand. This capability will aid in the interpretation of the calculated results and will increase the code user's efficiency. EQ3/6 generates a large amount of output depending on the options used in a particular run. At the present time, this output is plotted by hand. When numerous runs are required for parameter sensitivity studies or to refine a problem (e.g., to determine the model constraints that give the most satisfactory results), plotting of the output becomes burdensome.

Examples of the kinds of plots that will be available with the graphics post-processor are graphs of ion concentrations versus reaction progress or time or some other variable that can be related to reaction progress such as pH or oxidation potential. Work has already begun on development of this capability using DISSPLA, a library of FORTRAN routines designed for engineers

and scientists which is already available at most computer facilities. DISSPLA is computer independent which fits in well with our commitment to portability of the code package.

Expand and Revise Data Base

In FY84, we began what will be a two year effort to expand and revise the data base. This is a separate data base centered activity from that described in the next section (see Other Sub-Tasks). We are adding a number of elements to the data base that are not now included (e.g., tin, neptunium, thorium, boron, and many others). This requires surveying the literature for the best compilations of solids and aqueous species for each of the elements of interest. The choice of elements to be added is dictated by the needs of the NNWSI, for example, elements important to the ground-water interpretation, rock/water interactions tests, sorption experiments, and corrosion tests. We will share the thermodynamic data base expansion activity with the geochemistry task group at Los Alamos National Laboratory (LANL) . For example, an americium data set (Kerrisk, 1984b) which was supplied by LANL has been incorporated into our data base.

We also plan to revise the data base in FY84 by replacing previously undocumented thermodynamic data for aqueous species in the system Na-K-H-Mg-Ca-Al-OH-CL-SO_4-HCO_3-CO_3. This activity is necessary to meet Quality Assurance requirements. However, it is important to note that this activity is not covered by NNWSI funding. It is an activity funded by LLNL's Base Technology Program in recognition of EQ3/6's potential contribution to geochemistry projects both within and outside LLNL. This data revision is very important to the code's predictive capabilities. If we had not received support from Base Technology, funds from NNWSI would have been necessary. Verification studies using the revised data are included in this activity.

As stated earlier in this document, we are expanding the existing EQ3/6 data base using data currently available in the literature. The completeness of the final product will depend on experimental work accomplished in the past by others. There are no provisions in this geochemical modeling plan for experimental work to solve the problem of missing or inadequate thermodynamic data. The need to expand our thermodynamic data base beyond what is in the

literature is a need that exceeds the specific goals of the individual projects such as NNWSI or ONWI. Eventually this need must be met by funding experimentalists directly from the National Program or from research agencies such as the National Science Foundation or Basic Energy Sciences.

Code Documentation

Complete EQ6 User's Manual

The EQ6 User's Manual will satisfy NRC's documentation requirements for computer codes (Silling, 1983). It will contain a description of the code, examples of input and output files and example problems. The EQ3NR User's Manual has been published (Wolery, 1983). The EQ6 User's Manual is the second in a series of user's manuals which are designed not only to teach the user how to use the code, but also to describe the underlying geochemical theory and the numerical and computational methods by which the theory is implemented in the code. With this background information, the code user can decide whether the code's capabilities are adequate for modeling a particular system.

Complete MCRT User's Manual

Like the EQ6 User's Manual, the MCRT User's Manual will satisfy NRC's documentation requirements for computer codes (Silling, 1983). It will contain a description of the code's capabilities and include examples of the data base files which contain the thermodynamic data and references. The MCRT User's Manual is the third in the EQ3/6 report series designed both to document the code and to provide a teaching tool for the code user.

The MCRT code is a data base building program which uses thermodynamic data (e.g., Gibbs free energy, enthalpy, entropy and heat capacity) of individual species and minerals to calculate stability constants for reactions involving those species and minerals. EQTL, a companion code to MCRT takes the data base (DATA0) developed by MCRT and creates especially formatted data bases (DATA1, DATA2, and DATA3) for use by EQ3NR and EQ6. EQTL is described in the EQ3NR User's Manual (Wolery, 1983).

FY 1985 Activities

Code Improvement

Extend Precipitation Kinetics Model in EQ6

In FY84, we limited the precipitation kinetics model to fairly simple rate laws. In FY85, we will expand this model to include poisoning effects and nucleation phenomena as required to meet the needs of the applications work. The extent to which we can extend the precipitation model will depend on the amount and kind of information available on substances which control or inhibit precipitation and on nucleation kinetics. Part of this task will be to determine whether sufficient information is available, and, if so, whether it is applicable to NNWSI studies.

Upgrade MCRT and EQTL, the Data Base Management Programs

Unification of the many MCRT data files that support MCRT is the key to continued growth of the EQ3/6 data base. At the present time, each element has a separate MCRT data file. With so many new elements being added, these files are quickly becoming unmanageable. By adding a random access file capability to MCRT, we will avoid a number of potential QA problems related to file management and documentation. This upgrade will add the capability to check for duplicate data entries (a rapidly growing problem as the data base increases in size) and to extract subsets of data on command. This will improve our ability to meet QA documentation retrieval requirements. At the same time, MCRT's capabilities will be expanded to include one or two new temperature extrapolation algorithms to generate high temperature equilibrium constants depending on the current modeling needs. Following the upgrading of MCRT, we will upgrade EQTL, the program which creates the specially formatted data bases for EQ3NR and EQ6. This upgrade will allow EQTL to carry out similar data base management tasks.

Add Equilibrium Sorption Model and Supporting Data Base to EQ3/6

Sorption is often considered the single most important process affecting radionuclide retardation. The current mass transport models are limited to the use of a simple distribution coefficient, K_d, to represent sorption. This K_d is a constant for a particular set of experimental conditions and fails to adequately account for sorption when the chemistry of the system changes (Reardon, 1981). For example, a large volume of experimental data tells us that sorption is a function of rock or mineral type, temperature, concentration, and charges of the species present. A constant K_d fails to take into account changes in ground-water chemistry which determine the competition for available sorption sites or the oxidation potential of the system which determines the oxidation state or charge of the radionuclide species. In many cases, the K_d used in the transport model also includes processes other than sorption, such as precipitation, which is described by different mathematics.

In FY85, we will begin a three-year activity to add the capability to model sorption processes using EQ3/6. In the first year, we will focus on an equilibrium sorption model and build a supporting data base. The types of equilibrium sorption models (e.g., a simple Langmuir isotherm versus the complex electrical double layer model) added to EQ3/6 will depend on which models LANL recommends for NNWSI geochemical modeling studies as the result of their scoping study planned for FY84. The sorption sub-model is needed to identify the sorption mechanisms which dominate the retardation process (e.g., precipitation versus physical adsorption on mineral surfaces) and to predict the sorption behavior of the various radionuclides as a function of the environmental parameters (e.g., ground-water composition, pH, Eh, etc.). This will aid us in interpreting the sorption experiments already conducted and provide information needed to design future experiments.

At first, LLNL will incorporate the simplest of models, the linear isotherm model, and write the coding changes necessary for implementation. It is important to remember that even the addition of the least complicated of the sorption models will require major changes in the codes. If we are successful in modeling systems using the linear isotherm approach, we will then attempt to add one of the models suggested by LANL. Depending on the

complexity of this model, this task may extend into FY86. Insertion of new and, in the future, additional sorption models will be facilitated by modular programming, that is, by sub-models which can be called upon by the code user as needed. However, a generalized capability that can accept any possible sorption model is not likely. Sorption models which rely on a rigorous definition of the physical and chemical structure of the interface may not be what we want if the uncertainties in the many parameters used to define them is greater than the uncertainties inherent in a simpler, but better understood model. Simple sorption models may be adequate in many cases as long as we provide separately for the effects of aqueous speciation, including redox state, and such competing processes as precipitation of secondary solids.

LANL will also supply the supporting data base from their NNWSI sorption experiments. We will take this data base and format it for use by the sub-models. Our goal for FY85 will be limited to building the general sorption superstructure for the sub-models and for including the linear isotherm model, and if time permits, one of the models suggested by LANL. Additional work related to sorption which is part of this activity are discussed under FY86 and FY87 Activities.

Begin Glass/Water Interactions Model

Currently, all reactants in EQ6 simulations dissolve homogeneously as do many minerals under natural conditions. Siliceous glasses do not react exclusively this way. Instead, some glass components may diffuse out toward the surface of the glass and some aqueous components may diffuse into the glass, thus forming a gradient in the concentration of the various elements which is quite different from that of the original glass. The surface of the glass may then dissolve homogeneously and secondary phases may form.

In FY85, we will evaluate the models currently used to describe waste glass leaching (e.g., White, 1983; White and Claassen, 1980) and identify the most appropriate technical approach for developing a sub-model for glass/water interactions which takes into account the role of diffusion and dissolution kinetics. Consideration will be given to modeling the alteration of the glass surface via hydration (caused by steam in the vicinity of the waste package).

Extend Solid Solutions to Include Site-Mixing Concept

Solid solutions are now represented in EQ3/6 as percentages of end-member components and can be thought of as molecular-mixing models. A simple example would be in the olivine family where chrysolite can be represented as 80% forsterite (Mg_2SiO_4) and 20% fayalite (Fe_2SiO_4). The half-dozen or so specific types of molecular mixing models now in EQ3/6 are only marginally useful. These models were originally designed for high temperature systems above 500°C. For low temperature systems, the data base is limited. More importantly, there are no data for the clays and zeolites that are important to the NNWSI modeling work.

An alternate and more sophisticated approach would be to include a site-mixing model in EQ3/6. The site-mixing concept recognizes that cations substitute for one another on well-defined sites in crystal lattices. Interestingly, molecular-mixing models tend to work well only when they are equivalent to a site-mixing model, that is, when there is only one site over which two or more ions of the same charge may substitute. Site-mixing models will allow us to represent individual compositions as separate and distinct solids including those where radionuclide ions have substituted into the crystal structures provided the supporting thermodynamic data is available. LANL is currently working on site-mixing models for some zeolites and there is now available a site-mixing model for illites (Stoessell, 1981) and the epidote family (Bird and Helgeson, 1980).

In FY85, we propose to scope out the difficulties of incorporating site-mixing models into EQ3/6. Using the models for illite and epidote mentioned above, we will determine whether the coding can be generalized to accommodate wide classes of solid solutions or whether each one will require its own coding. Site-mixing models are mathematically much more complex than the molecular-mixing models now in the codes. We must be able to identify the number of distinct sites available for substitution, the cations that may substitute at each site, and the equilibrium constants for each phase. If the results of our scoping study allow it, we will add either an illite or zeolite site-mixing model following LANL's recommendations.

Expand and Revise Data Base

This task represents a continuation of the data base expansion and revision started in FY84. Elements identified as important to the NNWSI geochemical modeling applications and newly identified species of elements already in the data base will be added as the data become available.

FY 1986 Activities

Code Improvement

Complete Model for Gas Phase in a Closed System

This task expands EQ6's capability to deal with reactions involving gases. In FY84, we added a fixed fugacity model to handle open systems containing gases such as the unsaturated zone. In FY86, we will add a variable fugacity model which will allow us to model closed systems containing varying amounts of gases such as those often encountered in experimental systems (e.g., rock/water hydrothermal experiments).

Complete Glass/Water Interactions Model

Using the technical approach selected in FY85, we will develop a glass/water interactions model for EQ6. Depending on the model chosen, we may need to modify EQ6 to take into account the diffusion process, the changing thickness of the altered layer, and the changing composition at the interface where the glass is dissolving. More extensive bookkeeping routines will be necessary to keep track of mass transfers from the reactants to the solution and transfers involved in the formation of the secondary minerals. This will allow us to handle reactants such as glasses that are non-uniform in composition (before and/or after reaction). This capability is important for modeling both waste glass dissolution and interactions involving tuff units containing amorphous glass that has not devitrified.

Complete Equilibrium Sorption Model

In FY86, we will complete work started in FY85 on the addition of one of the more complex sorption isotherms recommended by LANL. If successful, we will include additional sub-models. Modifications of the models may be necessary if the data base provided by LANL and used to support the model calculations is insufficient in that it does not contain all of the information needed by the models. Much of what we learn in FY85 will guide our approach and progress in FY86. It may be that the experience gained in the past year will suggest a new approach is needed in both the modeling efforts and the laboratory work done to collect the data for the models. The scope of our work will depend on how difficult it is to find an approach that is "good enough", that is, an approach both scientifically defendable and one that allows us to model sorption using the data and models currently available.

Complete Solid Solutions Model

In FY86, we will continue the work started in FY85. The work on the site-mixing models is similar to that on the sorption models in that much of what we learn in FY85 will guide our approach and progress in FY86. Our attempts to model illites or zeolites in FY85 will determine the level of effort needed to complete this task. Success in adding an illite or zeolite site-mixing model to EQ3/6 will allow us to add other phases of interest such as the montmorillonites. Given the complexity and sophistication of the coding for any site-mixing model, our time schedule must be flexible. In FY86, we will evaluate our position and make adjustments in the scope of work, if necessary.

FY 1987 Activities

Given the prerequisite work that must be accomplished in the three years prior to FY87 which will greatly influence the need for and the approach to be taken in any of the tasks listed below, we have provided only a brief description of the type of work that is planned at that time. An updated plan will be written when appropriate that will better describe the approach and extent of each activity.

Code Improvement

Extend Geochemical Flow Model

At the present time, EQ6 models ground-water flow by conceptualizing a single packet of ground water which moves along the flow path. The ground-water composition in this packet changes as the water interacts with the rock and as precipitates form. EQ6 simulates the movement of this packet along the flow path by leaving the precipitates behind, that is by removing the precipitates so that they are no longer part of the reacting system. This simulation works well for some geothermal systems or for the precipitation of secondary minerals along fracture surfaces, however, it is inadequate for modeling waste form leaching where the waste form and its precipitates remain stationary in contact with flowing ground water. In FY87, we plan to add to the existing flow model the ability to retain the precipitates, flush the ground water (whose composition has presumably changed) from the waste form and bring in "new" ground water to react with the waste form, its alteration products and the rock. This adaptation will permit us to model flow-through leaching, a commonly used experimental configuration (Weed and Jackson, 1979; Knauss and Wolery, 1984). This extension of EQ6 is similar in concept, but with greatly expanded capabilities, to the flow model offered in the PROTOCOL code being developed at LLNL for the Materials Characterization Center at Pacific Northwest Laboratory (D. Jackson, LLNL, private communication).

Add Isotopic Fractionation Model to EQ3/6

Isotopic fractionation refers to the preferential substitution of one isotope for another of the same element in a solid or aqueous phase. Examples are changes in the ratio of sulfur-34 to sulfur-32 in the formation of sulfate from the oxidation of sulfide minerals (Fritz and Fontes, 1980) and the fractionation of carbon isotopes when calcite is precipitated from solution--carbonate will have an isotopic composition heavier than the dissolved carbonate from which it is derived (Bender, 1972).

At the present time, it is not known whether the capability to model isotopic fractionation will be important to the NNWSI work. As it is too early in our modeling work to decide the merits of this sub-task, this task is not shown on the Network Chart or assigned a deliverable date. It is included in the plan (and in the budget) as a reminder to evaluate the need for such a capability prior to FY87 when the work would otherwise begin. If needed, modifications to EQ3/6 will include the ability to maintain separate mass balances for the different isotopes. We will require a data base of fractionation factors, the ratio of two isotopes for a given environmental condition, that is sufficient for modeling a tuff repository (e.g., the ratio of ^{13}C to ^{12}C expected in calcite precipitated from ground water in contact with atmospheric CO_2). We are fortunate in that two researchers at the California Institute of Technology, T. Bowers and H. Taylor, have already modified a version of EQ6 to study isotopic fractionation of oxygen during the evolution of sea water near hydrothermal vents in the ocean crust. The existence of this technique should focus interest in other applications that are more applicable to waste disposal. We will benefit by their work.

Sorption Kinetics Coding and Data Base

In FY87 we will complete the three-year effort involving the upgrading of EQ6 to handle sorption processes. The progress made in FY87 will be highly dependent on our experiences in the previous two years. Our current plan is to add the capability to model sorption kinetics in order to predict the time needed for equilibrium to occur in both experimental and natural systems. The coding used to handle redox disequilibrium and redox kinetics will be used as a starting point. A kinetics data base to be supplied by LANL from the results of their experimental program will provide the rate laws for reactions expected in a tuff repository. Cases involving non-equilibrium sorption where the rate of sorption does not equal the rate of desorption will be included if there is sufficient data.

FY 1988 Activities

Code Documentation

Revision and Release of Updated EQ3/6 User's Manual

At the end of this four year period (FY84-FY87) of EQ3/6 code modifications and improvements we plan to assemble a final package of documents, to be released as a single report. This report will describe in detail the capabilities now included in the EQ3/6 code package. It will include chapters representing updated versions of older documents as well as new chapters describing more recent improvements. This report will constitute the final version of the User's Manual for NNWSI geochemical modeling studies and will contain the necessary documentation needed to meet NRC code documentation requirements.

OTHER SUB-TASKS

Throughout the five-year period covered by this plan certain activities will be ongoing which, unless specifically called out as separate activities, can easily be forgotten although they are critical to the success of the program.

Code and Data Base Maintenance

Code maintenance involves not only fixing bugs discovered by ourselves and other users, it also includes communicating to others information on those bugs, responding to requests for help, distributing new versions of the code to NNWSI participants and others (upon request), organizing periodic meetings of NNWSI personnel to discuss their future needs, applications, and new capabilities, addressing the impact of new information generated in the U. S. and elsewhere, and coordination of code and data base improvements done by others.

Data base maintenance involves keeping the data base up-to-date as data becomes available in the literature and replacing data found to be deficient. For example, the SUPCRT data base from H. C. Helgeson's group at the University of California at Berkeley is a major part of our data base and it is periodically revised by them. In FY84, we will write a utility routine to update the data base file (DATAO) with the latest version of SUPCRT.

In FY84, we will remove the inconsistencies in the phosphate thermodynamic data. These inconsistencies are the result of the failure of different researchers to use the same chemical form of phosphorus as the elemental reference state. We have discovered that the Gibbs energies for some phosphate compounds were based on red phosphorus as the reference form while others were based on white phosphorus, the reference form more commonly used. The problem with using two reference forms for a single group of compounds is that they cannot be combined without first making a correction in the Gibbs free energy for those based on red phosphorus. Unfortunately, our phosphate data was pulled together from a wide variety of sources. No check has been made on the extent to which these data are inconsistent.

Quality Assurance Activities

The Quality Assurance (QA) requirements of NNWSI have increased the level of documentation and planning activities for the geochemical modeling task. Files are kept, updated and indexed, each individual working on the geochemical modeling tasks keeps a notebook describing day-to-day activities involving the code or data base, memos documenting code bugs and how they were fixed are written and distributed, and procedures for dealing with various aspects of the program (e.g., data base revision and verification runs) are created and discussed. The number of verification runs required as the code is upgraded and new capabilities added has increased. These verification runs require documentation in memos and reports. We also prepare for and participate in QA reviews and respond to any findings. Time is also spent keeping the QA Engineer and support staff informed so they can better understand what aspects of the geochemical modeling require their special attention.

WORK FOR OTHERS

This section describes work planned for FY1985 to FY1988 to be funded by ONWI which is also needed by the NNWSI for modeling geochemical systems in a tuff repository. Other LLNL geochemical modeling work done for ONWI is specifically related to code development and site specific modeling associated with a salt repository (e.g., systems involving high ionic strength brines, Jackson, 1984 and Wolery, 1984) and is not described in this document. This sharing of geochemical code work between NNWSI and ONWI benefits both the salt and tuff programs in that the use of a single geochemical code reduces duplication of effort and makes the comparison of geochemical modeling results from different candidate repository sites easier to interpret. Because of the importance of the ONWI work to the NNWSI geochemical modeling effort, the two tasks described below are included both in the Network Chart (Figure 2) and the Deliverables Section.

Add Redox Disequilibrium and Kinetics to EQ6

The EQ6 code now carries one mass balance equation for each chemical element and divides the mass balance of the element's oxidation states according to a redox parameter (i.e., oxygen fugacity, Eh or pe). EQ3NR allows separate mass balances for the different oxidation states and can therefore handle systems where one redox couple (e.g., Fe^{2+}/Fe^{3+}) is out of equilibrium with another (e.g., SO_4^{2-}/S^{2-})--a common condition in natural systems which is due to kinetic effects. EQ6 should be updated to match EQ3NR's capabilities so that both codes are able to model the same systems. This is one of the few cases where EQ3NR can model a system and EQ6 cannot. The codes should be compatible in their capabilities. This activity will begin in FY86 as a prerequisite to adding radiolysis effects to EQ6. It is also needed for modeling corrosion experiments and for other related applications work involving cannister and overpack materials.

Once EQ6 can deal with non-equilibrium redox systems, redox kinetics can be added so that predictions of equilibrium times can be made both for natural systems and experimental ones. This will aid us both in experimental design and performance assessment. This activity also includes compilation and evaluation of the existing data on redox kinetics to determine its adequacy for modeling aqueous redox kinetics of systems of interest to NNWSI.

Add Coding to Handle "Stiff" Kinetics

Stiff kinetics refers to the complexity of the ordinary differential equations that need to be solved. At the present time we can only handle equations which can be solved by integrating numerically in a series of simple steps. A more sophisticated method will be necessary to handle the complex kinetic equations we are likely to run into in the future such as the work involving sorption kinetics, redox disequilibrium, and radiolysis effects.

Radiolysis Coding and Data Base

The addition of redox kinetics to EQ6 planned for FY86 will allow us to add a provision to study the relative importance of radiolysis effects on the near-field environment. This capability will be useful for evaluating the waste package design and for interpreting corrosion experiments done in a radiation field. We will use a data base of G-factors to evaluate rate expressions for the production of radiolytic species. (G-factors are the parameters that relate radiation flux to the production of radiolysis products.) We expect these rate expressions to be sufficiently complex that the coding added in FY86 to handle "stiff" kinetics will be necessary to solve them. Ordinary chemical rate laws will describe the subsequent decay of the radiolysis products.

VALIDATION ISSUES

Before discussing validation issues, we should define what we mean by validation and how validation studies differ from the verification studies which are included in the code improvement activities outlined earlier. Silling (1983) defines validation as "assurance that a model as embodied in a computer code is a correct representation of the (natural) process or system for which it is intended". Ross et al. (1983) added to this definition the statement that model validation is a test of how well "theory" describes actual system behavior, that is, how well do the model calculations match the actual measured data. In contrast, verification is not concerned with whether the model is a correct representation of the real world, but is concerned with

whether the code correctly performs the operations specified in the numerical model. To verify a model, we must check the accuracy of the algorithm used to solve the equations and assure ourselves that the code is fully operational. We can verify a model by comparing code-to-code and code-to-hand calculations, however, we can only validate a model by studying a real system where there are sufficient data to clearly describe that system without having to resort to estimates for the system's parameters. In other words, our validation studies should not require "tweaking" of the code to get the desired results.

The EQ3/6 codes are verified. Verification studies of an earlier version of the codes are documented in ONWI-472 (Intera Environmental Consultants, 1983). Since each new version of the codes is successfully verified against the old version before release, verification of the codes remains current. When new capabilities are added to the codes, verification studies specifically designed to test these capabilities are done. They are documented either in the user's manuals and/or in the task's QA records.

Validation studies of EQ3/6 remain to be done. Validation requires selecting suitably well-constrained sets of experimental or field data against which the EQ3/6 calculations can be compared. We have not yet identified specific geochemical systems where there are sufficient data for use in validation studies. Beginning in FY84 and continuing throughout the life of the task, we will be evaluating the geochemical literature for candidate systems. Validation studies will be run and documented whenever possible. Because of the uncertainty in finding suitable sets of data that represent well-defined geochemical systems, validation is not listed as a separate activity. Some validation studies will be done by researchers outside the waste management community who use EQ3/6 for their geochemical modeling studies and publish their results in the literature. To that end, copies of the code have been distributed to graduate students interested in using EQ3/6 in thesis related research and to university professors interested in using the codes as a teaching tool.

NETWORK CHART

The Network Chart shown in Figure 2 is a work-flow diagram which identifies the activities, the time period during which those activities will take place, the points at which information from other participants (e.g., LANL) will feed into the activities, and the interrelationship of activities. It is important to emphasize that this Network Chart is a plan, in every sense of the word. Because of the uncertainty associated with any research activity, a plan must have flexibility. The time periods shown are estimates of the time required to begin and complete an activity. As we gain more experience, we expect to revise the Network Chart to reflect that experience and any change in priorities or program direction that may occur over the next four years.

In developing the Network Chart, we assumed that:

(1) Funds needed to accomplish the work described in this document will be made available according to the budget established for this plan.

(2) Any peer reviews of the project will be timely and will not result in extensive modifications of the plan.

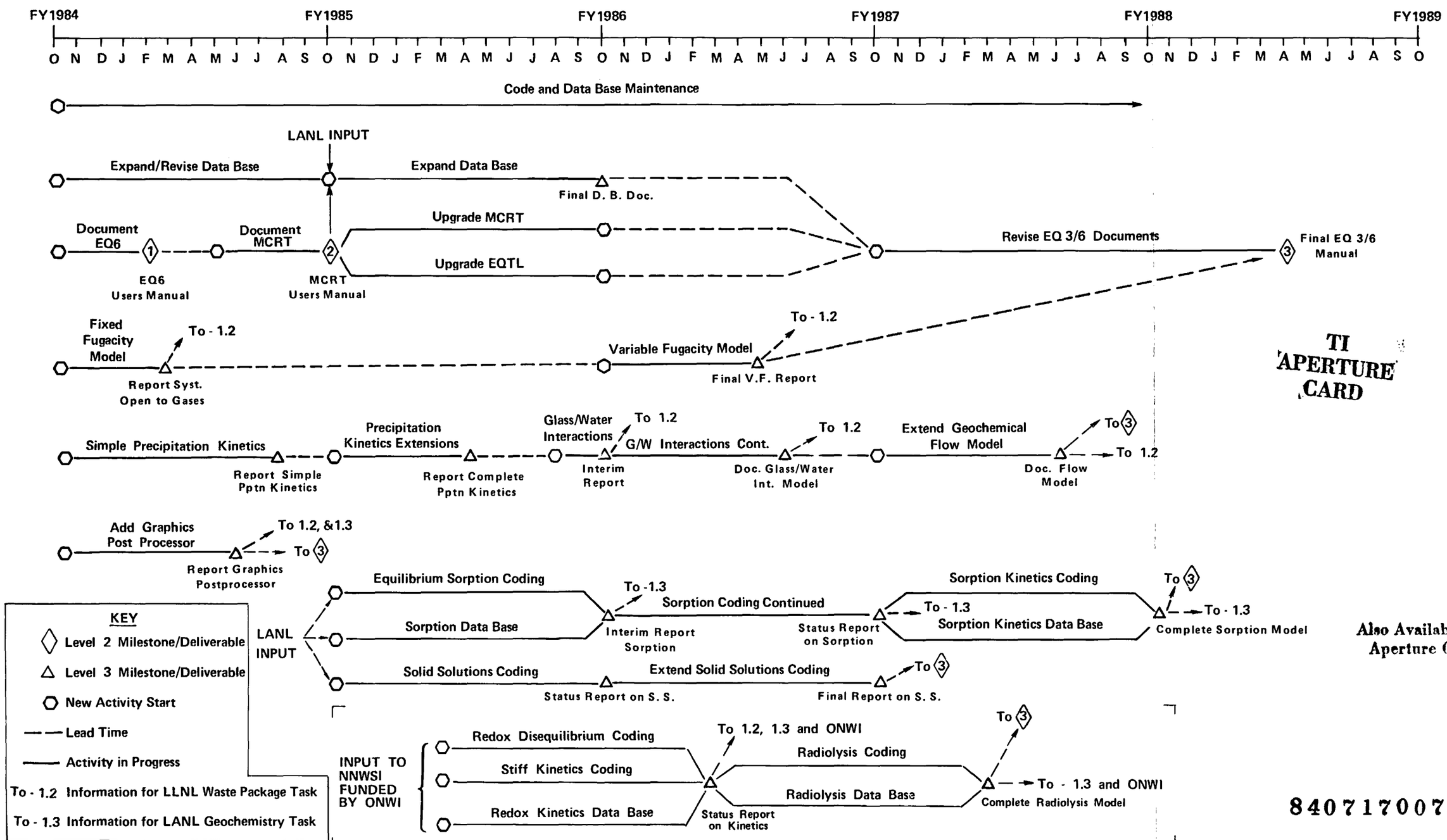
(3) Extensive revision of the documents identified in the Schedule of Deliverables will not be required.

(4) The QA Administrative Procedure for Software Control being developed by LLNL for computer code tasks will not result in significant increases in the scope of our QA activities.

(5) Information identified on the Network Chart as coming from other NNWSI participants will be available when needed.

Failure of these assumptions will result in added cost and time.

FIGURE 2: NETWORK CHART FOR GEOCHEMICAL MODELING – EQ 3/6



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DELIVERABLES

We have identified the following deliverables as a way of measuring our progress towards meeting the task goals outlined earlier in this document. The dates we expect them to be completed are estimates based on the assumptions listed for the Network Chart and on our evaluation of the level of effort needed to complete each task. We expect that as new capabilities are added to the code package, the time needed for code maintenance and QA will increase. Criteria for each deliverable is provided to give a clear understanding of what constitutes a completed activity. We have listed deliverables that originate at LLNL. Input needed by a specific time from other participants such as LANL's input to the sorption data base are not included as we assume they will be included in the deliverables shown by others.

Deliverable	Date
FY1984	
(1) Complete Model for Systems Open to Gases	3/01/84

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will describe the code's capability to model systems open to gases (i.e., a fixed fugacity model) such as the unsaturated zone at NTS.

(2) Complete Draft "EQ6 User's Manual"	3/30/84

Criteria: This deliverable will be met with submission of a draft copy to the WMPO-NV. The user's manual will satisfy NRC's documentation requirements for computer codes. It will contain a description of the code, examples of input and output files and example problems.

Deliverable	Date
(3) Add a Graphics Post-Processor to the EQ6 Code	5/15/84

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will describe the code's capability to graph output from EQ6 runs which will aid in the interpretation of the calculated results. Examples will be included in the report.

(4) Add Precipitation Kinetics to EQ6 Code	7/01/84

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will describe the code's capability to model precipitation growth kinetics using simple rate laws. An example of modeling tuff/water interactions using this capability will be included in the report.

(5) Complete Draft "MCRT User's Manual"	9/28/84

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will describe MCRT, the data processing routine used in the EQ3/6 code package, and the data base files which contain the thermodynamic data and their sources. This report is needed to meet NRC documentation requirements.

FY1985

(1) Complete Precipitation Kinetics Addition to EQ6	4/01/85

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will describe the code's capability to model precipitation kinetics in a more complex system, that is, where nucleation and/or poisoning affects the system's kinetics.

Deliverable	Date
(2) Interim Report on Modeling Sorption with EQ3/6	9/30/85

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. The report will document progress made in FY85 towards adding the capability to model sorption with EQ3/6. In FY85, we expect to add an equilibrium sorption model and develop a supporting data base. Verification runs will be documented.

(3) Interim Report on Modeling Solid Solutions	9/30/85

Criteria: This deliverable will be documented in the quarterly report to WMPO-NV. Progress made during FY85 will depend on the level of sophistication required for NNWSI applications and on the availability of supporting data.

(4) Final Report on Data Base Expansion	9/30/85

Criteria: This deliverable will be documented in the quarterly report to WMPO-NV. Completion of this activity in FY85 will depend on the availability of the thermodynamic data. As new elements are added to the data base, informal LLNL reports will be released documenting the data files for that element.

(5) Interim Report on Glass/Water Interactions Model	9/30/85

Criteria: This deliverable will be documented in the quarterly report to WMPO-NV. We will evaluate the role of diffusion in waste form leaching based on the diffusion models currently available and describe the approach to be used in developing a glass/water interactions model for EQ6.

Deliverable	Date

FY1986

(1) Report on Redox Disequilibrium Kinetics 3/01/86

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV and ONWI. This report will document the redox kinetics data base, the coding changes in EQ6 needed to model redox disequilibrium, and the methods used to handle the complex kinetic equations ("stiff") kinetics we can be expected to solve in more sophisticated systems.

(2) Report on Model for Gas Phase in a Closed System 4/15/86

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. This report will document the variable fugacity model which will allow us to model closed systems containing varying amounts of gases such as those encountered in some experimental systems.

(3) Report on Glass/Water Interactions Model 6/01/86

Criteria: This deliverable will be met by submission of a draft final report to the WMPO-NV. This report will document modifications in EQ6 needed to model glass/water interactions by taking into account diffusion processes and the development of an altered layer on the surface of the glass.

(4) Status Report on Equilibrium Sorption Model 9/30/86

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. This report will document the progress made in FY86 on the development of an equilibrium sorption model for EQ6 and the status of the supporting data base.

Deliverable	Date
(5) Final Report on Solid Solutions Model	9/30/86

Criteria: This deliverable will be met with submission of a draft final report to the WMPO-NV. This report will document any changes necessary in the solid solutions model created in FY85 to incorporate new site-mixing models of interest to NNWSI work.

FY1987

(1) Complete Radiolysis Model	3/01/87

Criteria: This deliverable will be documented in the quarterly report to the WMPO-NV. We will briefly describe the approach used to add the radiolysis model to EQ6. A detailed description of this model will be incorporated into the final EQ3/6 User's Manual to be released in FY88.

(2) Final Report on Flow Model Extension	7/01/87

Criteria: This deliverable will be met with submission of a draft report to the WMPO-NV. This report will document coding changes in EQ6 made to allow us to model waste form leaching in a flowing ground-water system and will include an example problem demonstrating the model capabilities.

(3) Complete Sorption Kinetics Model	9/30/87

Criteria: This deliverable will be documented in the quarterly report to the WMPO-NV. We will briefly describe the capability to model sorption kinetics and the status of the supporting data base. A detailed description of this model will be incorporated into the final EQ3/6 User's Manual to be released in FY88.

Deliverable	Date
FY1988	
(1) Draft of Final EQ3/6 User's Manual	4/1/88

Criteria: This deliverable will be met by submission of a draft Final EQ3/6 User's Manual to the WMPO-NV. The user's manual will include chapters representing updated versions of older user's manuals plus more recent improvements and will satisfy NRC's documentation requirements.

PROGRAM INTERFACES

The code improvements described in this document were selected on the basis of their importance to the needs of the NNWSI. EQ3/6 is currently being used by LLNL for the Waste Package experimental program to define the package environment (WBS 1.2.1) and by LANL in support of the geochemistry tasks defined in the NNWSI WBS 1.3.1. In addition, EQ3/6 is needed in the Subsystem Analysis Task (WBS 1.1.2) at Sandia National Laboratory (SNL) involving both the analysis of the geologic-system and the engineered-system. EQ3/6 will provide information on geochemical parameters such as radionuclide solubility, radionuclide speciation, precipitation products, and ground-water chemistry as a function of temperature and rock mineralogy. It is expected that EQ3/6 will not be used directly in the systems analysis codes, but will be used to verify and provide input to a computationally simplier geochemical sub-model used in the system analysis.

We have encouraged close cooperation between LLNL and the other two Laboratories to ensure that the geochemical modeling needs of each one are represented in our code improvement activities. We believe this plan addresses both the needs of the Laboratories and the overall requirements of the NNWSI to use codes which are sufficiently documented and verified in accordance with NRC guidelines.

Within the Civilian Radioactive Waste Management (CRWM) Program , LLNL is also funded by the Office of Nuclear Waste Isolation (ONWI) for code improvements designed for geochemical modeling studies related to a salt repository. This work began in FY83 and is focused on activity coefficient corrections needed to model natural brines and interactions between the brines and salt minerals, including those at high temperatures. Some of this work is specific to brines and will not directly benefit NNWSI, however ONWI is responsible for supporting the work described in the Work For Others section plus a share of the data base development, maintenance, and QA costs.

The use of a single geochemical code within the CRWM Program benefits both NNWSI and ONWI in that is eliminates duplication of effort in data base development and code improvement where the new capabilities are of use to both Projects (e.g., disequilibrium kinetics). It is hoped that the Basalt Waste Isolation Project (BWIP) and the Office of Crystalline Rock Repository Development (OCRD) will join with the other two projects in making EQ3/6 their choice for geochemical modeling. If this occurs, then support for the EQ3/6 geochemical modeling work could be considered the responsibility of CRWM rather than the individual projects.

BUDGET

The budget showing operating and capital equipment costs of the task described in this plan is broken down by fiscal years in Table 1. The budget is based on our best estimate of the level of effort required to complete the activities for code improvement, code documentation, and code and data base maintenance. We believe that the activities described in this plan are needed to allow the NNWSI to model chemical processes important to the storage of nuclear waste in a tuff repository in the unsaturated zone. Given the uncertainties of the budgeting process, there is no guarantee that the funds needed to upgrade the code, expand the data base, and maintain the code will be available in the amounts specified in Table 1. If funds for geochemical code work are below those requested in Table 1, the work will not be accomplished in the time currently allotted and it will be necessary to revise the schedule outlined in the Network Chart (Figure 2).

All of the assumptions used in developing the Network Chart apply to the development of the budget. For example, increased levels in QA activities, delayed peer reviews, and failure to receive guidance or input from other NNWSI participants as identified on the Network Chart will impact the schedule and the budget.

The capital equipment funds are for upgrading computer terminals and related hardware. Funds for code and data base maintenance may be required beyond FY88 to provide support for the applications work (e.g., code debugging, minor data base changes, etc.).

TABLE 1: Estimated Budget for Geochemical Modeling Task FY84-FY88 (in thousands)

Operating Funds	FY1984	FY1985	FY1986	FY1987	FY1988
Code Improvement	185	405	442	468	-
Code Documentation	85	-	-	52	75
Code and Data Base Maintenance	95	125	163	190	150
Sub-Total	365	530	605	710	225
Capital Equipment Funds	-	15	15	-	-
Total	365	545	620	710	225

REFERENCES

Apps, J., C. Carnahan, P. Lichtner, M. Michel, D. Perry, R. Silva, D. Weres and A. White, 1982, Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, 1982, Lawrence Berkeley Laboratory, LBL-15103.

Bender, M., 1972, Carbon Isotope Fractionation, in The Encyclopedia of Geochemistry and Environmental Sciences, R. Fairbridge, ed., Van Nostrand Reinhold Co., New York.

Bird, D., and H. Helgeson, 1980, Chemical Interactions of Aqueous Solutions with Epidote-Feldspar Mineral Assemblages in Geologic Systems--(1). Thermodynamic Analysis of Phase Relations in the System $CaO-FeO-Fe_2O_3-Al_2O_3-SiO_2-H_2O-CO_2$, American Journal of Science, vol. 280, p. 907-941.

Bowers, T., and H. Taylor, 1983, Chemical and Isotope Mass Transfer Calculations Pertaining to Seafloor Hydrothermal Systems, Abstract, Geol. Soc. Amer. Abstracts with Programs, p. 727.

Bowers, T., K. von Damm and J. Edmond, 1983, Chemical Evolution of Hot Springs on the East Pacific Rise and in the Guaymas Basin, Abstract EOS, vol. 45, p. 723.

Brimhall, G. H., Jr., 1980, Deep Hypogene Oxidation of Porphyry Copper Potassium-Silicate Protore at Butte, Montana: A Theoretical Evaluation of the Copper Remobilization Hypotheses, Economic Geology, vol. 75, pp. 384-409.

Davis, J., 1983, NRC's Policy and Strategy on High-Level Waste, paper presented at the Civilian Radioactive Waste Management Information Meeting, Washington, D. C., December 13-15, 1983, proceedings to be published.

Fritz, P., and J. Ch. Fontes, 1980, Handbook of Environmental Isotope Geochemistry, Elsevier Scientific Publishing Co., New York.

Garven, G., 1982, The Role of Groundwater Flow in the Genesis of Stratabound Ore Deposits: A Quantitative Analysis, University of British Columbia, unpublished Ph.D. thesis.

Guzowski, R., N. Nimick, N. Siegel, and N. Finley, 1983, Repository Site Data Report for Tuff: Yucca Mountain, Nevada, Nuclear Regulatory Commission, NUREG/CR-2937, SAND82-2105.

Helgeson, H. C., 1968, Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solutions--I. Thermodynamic Relations, Geochim. Cosmochim. Acta., vol. 32, p. 853-857.

Intera Environmental Consultants, 1983, EQ3/6Q6: A Geochemical Speciation and Reaction Path Code Package Suitable for Nuclear Waste Performance Assessment, Office of Nuclear Waste Isolation Report, ONWI-472.

Jackson, K., 1984, Verification and Validation Studies of the EQ3/6 Brine Model, Lawrence Livermore National Laboratory, UCRL-in press.

Janecky, D., 1982, Serpentinization of Peridotite within the Oceanic Crust: Experimental and Theoretical Investigations of Seawater-Peridotite Interaction at 200°C and 300°C, 500 Bars, The University of Minnesota, Minneapolis, MN, unpublished Ph.D. thesis.

Kerrisk, J. 1984a, Reaction-Path Calculations of Ground-Water Chemistry and Mineral Formation of Rainer Mesa, Nevada, Los Alamos National Laboratory Report, LA-9912-MS.

Kerrisk, J., 1984b, Americium Thermodynamic Data for the EQ3/6 Data Base, Los Alamos National Laboratory draft report to be published.

Knauss, K., and T. Wolery, 1984, Dependence of Albite Dissolution Kinetics on pH and Time at 25°C and 70°C, to be submitted for publication to Geochim. Cosmochim. Acta.

Knauss, K., V. Oversby and T. Wolery, 1984, Post Emplacement Environment of Waste Packages, paper presented at Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, November, 1983, proceedings to be published.

Reardon, E., 1981, K_d's--Can They Be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration?, Ground Water, vol. 19, pp. 279-286.

Rimstidt, J. and H. Barnes, 1980, The Kinetics of Silica-Water Reactions, Geochim. Cosmochim. Acta., vol. 44, pp. 1683-1699.

Ross, B., J. Mercer, S. Thomas, and B. Lester, 1983, Benchmark Problems for Repository Siting Models, U. S. Nuclear Regulatory Commission, NUREG/CR-3097.

Silling, S., 1983, Final Technical Position on Documentation of Computer Codes for High-Level Waste Management, U. S. Nuclear Regulatory Commission, NUREG-0856.

Stoessell, R., 1981, Refinements in a Site-Mixing Model for Illites: Local Electrostatic Balance and the Quasi-Chemical Approximation, Geochim. et Cosmochim. Acta, vol. 45, pp. 1733-1741.

Sverjensky, D., 1984, Oil Field Brines as Ore-Forming Solutions, Economic Geology, vol. 79, pp. 23-37.

Taylor, R., D. Jackson, T. Wolery, and J. Apps, 1978, Geothermal Resource and Reservoir Investigation of U.S. Bureau of Reclamation Leaseholds at East Mesa, Imperial Valley, California, Section 5, Lawrence Berkeley Laboratory, LBL-7094, p. 165-233.

Weed, H., and D. Jackson, 1979, Design of a Variable Flow-Rate, Single Pass Leaching System, Lawrence Livermore National Laboratory, UCRL-52785.

White, A., 1983, Surface Chemistry and Dissolution Kinetics of Glassy Rocks at 25°C, Geochim. Cosmochim. Acta., vol. 47, pp. 805-815.

White A. and C. Claassen, 1980, Kinetic Model for Short-Term Dissolution of a Rhyolitic Glass, Chemical Geology, vol. 28, pp. 91-109.

Wolery, T., 1978, Some Chemical Aspects of Hydrothermal Processes at Mid-Ocean Ridges--A Theoretical Study, unpublished Ph.D. thesis, Northwestern University, Evanston, Illinois.

Wolery, T., 1979, Calculation of Chemical Equilibrium Between Aqueous Solutions and Minerals: The EQ3/6 Software Package, Lawrence Livermore National Laboratory, UCRL-52658.

Wolery, T., 1983, EQ3NR--A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation, Lawrence Livermore National Laboratory, UCRL-53414.

Wolery, T., 1984, EQ3/6 Modifications for Geochemical Modeling of Brines, Lawrence Livermore National Laboratory, UCRL-in press.

Wolery, J. and J. Delany, 1983, The Reaction of Bullfrog Tuff with J-13 Ground Water at 150°C and 90° C. II. Geochemical Modeling, G.S.A. Abstracts with Programs, No. 20919, p. 722.

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051-075	10.00	376-400	29.50
076-100	11.50	401-426	31.00
101-125	13.00	427-450	32.50
126-150	14.50	451-475	34.00
151-175	16.00	476-500	35.50
176-200	17.50	501-525	37.00
201-225	19.00	526-550	38.50
226-250	20.50	551-575	40.00
251-275	22.00	576-600	41.50
276-300	23.50	601-up[1]	
301-325	25.00		

[1]Add 1.50 for each additional 25 page increment, or portion thereof from 601 pages up.

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WHAT LLNL'S GEOCHEMICAL MODELING CODE EQ3/5 CAN DO

INPUT

CHEMICAL COMPOSITION OF SOLUTION AND SOLIDS IN THE SYSTEM AND A DESCRIPTION OF THEIR PHYSICAL/CHEMICAL ENVIRONMENT (TEMPERATURE, pH, OXIDATION POTENTIAL)

OUTPUT

1. PROVIDES SOLUBILITY LIMITS FOR RADIONUCLIDES IN A SPECIFIC ENVIRONMENT.

2. PREDICTS THE FORMATION OF SECONDARY SOLIDS WHICH MAY EFFECT SORPTION CAPABILITY (E.G., THE FORMATION OF CLAYS).

3. ESTIMATES pH, EH AT HIGH TEMPERATURES FROM VALUES MEASURED AT LOW TEMPERATURES.

4. SIMULATES LONG TERM AUTOCLAVE AND OTHER LAB EXPERIMENTS.

5. EXTRAPOLATES EXISTING DATA AND/OR UNDERSTANDING TO NEW CONDITIONS (E.G., SIMULATES THE ADDITION OF WASTE PACKAGE MATERIALS INTO THE NATURAL ENVIRONMENT).

6. DETERMINES WHETHER THERMODYNAMIC EQUILIBRIUM CONDITIONS ARE PRESENT IN A LABORATORY EXPERIMENT.

1/13/83

WHAT EQ3/6 CAN NOT DO --

CODE DEVELOPMENT NEEDS

THE ABILITY TO HANDLE

- SORPTION PROCESSES (EQUILIBRIUM AND NON-EQUILIBRIUM) - BEGIN IN FY85
- PRECIPITATION KINETICS TO DETERMINE THE RELATIVE IMPORTANCE OF SOLUBILITY LIMITS - BEGIN IN FY84
- RADIOLYSIS EFFECTS - BEGIN IN FY85
- REDOX KINETICS - BEGIN IN FY85

OTHER NEEDS

- EXPANDED DATA BASE (A CONTINUING PROCESS)
- CODE MAINTENANCE
- USER'S GUIDES TO UPGRADED VERSIONS - FINISH IN FY84
- DOCUMENTATION TO MEET NRC REQUIREMENTS

APPLICATIONS OF EQ3/6 IN GEOLOGIC DISPOSAL OF NUCLEAR WASTE

- Site characterization — determining what controls the natural groundwater chemistry
- Predicting the behavior of radionuclides in the groundwater system in and far from the repository
- Modeling hydrothermal laboratory experiments
- Conducting computerized thought experiments
- Introducing a scientific basis for long-term (1,000–10,000 year) predictions by
  - Aiding in getting mechanistic understanding, not just using it after we have it
  - Showing the general predictive approach works when applied to nature's analogous long term experiments (formation/alteration of U, Th ore bodies, contact metamorphism, etc.)

A PARTIAL LIST OF EQ3/6 USERS INCLUDES

- LLNL (Climax Stock RNM, NNWSI Waste Package, U.S.-Canadian Technical Exchange)
- LANL (NNWSI Site Geochemistry)
- ONWI (Salt Waste Package)
- KBS (Swedish nuclear waste disposal)
- Chevron Oil Field Research Co.
- Exxon Production Research
- Arco Oil and Gas Co.
- University of California, Berkeley
- University of Minnesota
- University of Wisconsin
- University of Washington

NNWSI PROJECT

GEOCHEMICAL MODELING CODE EQ3/6
(FY84 ACCOMPLISHMENTS AND PLANS)

ACCOMPLISHMENTS

- EQ6 USER'S MANUAL CONTAINING A COMPLETE DESCRIPTION OF THE CODE AND ITS CURRENT CAPABILITIES RELEASED IN DRAFT FORM. IT MEETS NRC CODE DOCUMENTATION REQUIREMENTS OUTLINED IN NUREG-0856.

- MODEL FOR SYSTEMS OPEN TO GASES COMPLETED AND TESTED. IT WILL BE USED TO MODEL REACTIONS INVOLVING OXYGEN AND CARBON DIOXIDE GASES IN THE UNSATURATED ZONE AT YUCCA MOUNTAIN.

PLANNED ACTIVITIES

- THE USER'S MANUAL FOR MCRT, THE CODE WHICH PROCESSES THE THERMODYNAMIC DATA BASE, WILL BE RELEASED THIS WILL COMPLETE THE DOCUMENTATION OF THE CODES WHICH MAKE UP THE EQ3/6 CODE PACKAGE.

GEOCHEMICAL MODELING CODE EQ3/6
(PLANS FOR FY 1985 AND FY 1986)

FY 1985

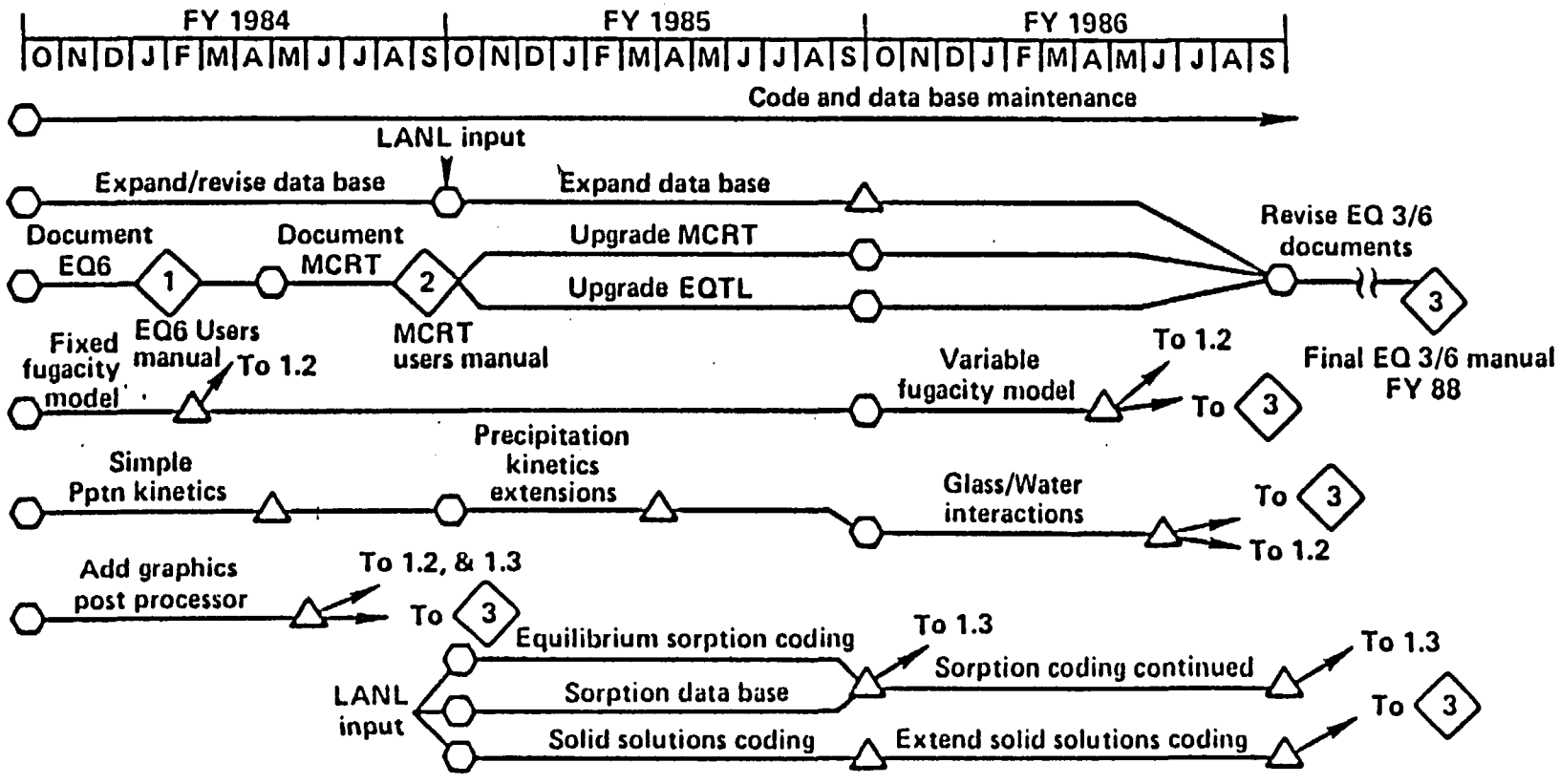
- ADD SIMPLE SORPTION PROCESS MODELS AND ACCOMPANYING DATA BASE.
- UPGRADE MCRT AND EQTL, THE THERMODYNAMIC DATA BASE PROCESSORS.
- COMPLETE WORK ON ADDING PRECIPITATION KINETICS IN ORDER TO MAKE LONG-TERM PREDICTIONS ON THE ROLE OF SOLUBILITY LIMITS.

FY 1986

- IMPROVE SORPTION MODEL BY INCLUDING MORE COMPLEX ISOTHERMS.
- BEGIN WORK ON A GLASS/WATER INTERACTIONS MODEL THAT WILL ALLOW US TO EVALUATE WASTE GLASS LEACHING EXPERIMENTS.
- EXPAND CAPABILITY TO MODEL REACTIONS INVOLVING GASES IN A CLOSED SYSTEM (E.G., ROCK/WASTE/WATER HYDROTHERMAL EXPERIMENTS).

WBS 2.3.1.9

EQ 3/6–geochemical modeling summary network



FY83 WORK FOR THE SALT PROGRAM (ONWI)

- ADDED TO THE THERMODYNAMIC DATA BASE
  - SELECTED ACTINIDE DATA (ESP. NEW DATA ON PLUTONIUM SPECIES)
  - DATA FOR SALT MINERALS
- PUT INTO EQ3/6 ACTIVITY COEFFICIENT APPROXIMATIONS VALID IN BRINES (HAVING IONIC STRENGTHS UP TO ABOUT 6 MOLAL)
  - THE OLD TREATMENT IN EQ3/6 WAS NOT VALID IN BRINES
  - TWO NEW TREATMENTS WERE CHOSEN TO PUT INTO EQ3/6
    - PITZER'S EQUATIONS, WITH THE OPTION TO INCLUDE ASSOCIATION PRODUCTS AS SPECIES)
    - HYDRATION THEORY, MODIFIED TO INCLUDE ASSOCIATION PRODUCTS AS SPECIES

FY84 WORK FOR THE SALT PROGRAM (ONWI)

- COMPLETE DRAFT REPORT ON MODEL VERIFICATION STUDIES FOR CONCENTRATED SOLUTIONS - DONE
- EXTEND EQ3/6 PITZER EQUATIONS TO HIGH TEMPERATURES - DONE
- TRANSMIT EQ3/6 PACKAGE WITH BRINE MODIFICATIONS TO ONWI - DONE
- COMPLETE DRAFT REPORT ON VERIFICATION OF HYDRATION THEORY EQUATIONS - IN PROGRESS
- BEGIN WORK ON NEAR FIELD SITE SPECIFIC SALT/BRINE INTERACTION MODELING - WAITING FOR ONWI INPUT

FY85/86 WORK FOR THE SALT PROGRAM (ONWI)

- INCLUDE PROVISION IN EQ3/6 FOR REDOX DISEQUILIBRIUM AND REDOX KINETICS
- INCORPORATE THE CAPABILITY TO CALCULATE THE EFFECTS OF RADIOLYSIS ON GEOCHEMICAL REACTIONS