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GEOCHEMICAL MODELING (EQ3/6) PLAN OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT PROGRAM

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TABLE OF CONTENTS

GEOCHEMICAL MODELING (EQ3/6) PLAN:
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT PROGRAM

ABSTRACT

This plan replaces an earlier plan (Isherwood and Wolery, 1984) for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. It includes activities for all repository projects in the Office of Geologic Repositories (OGR): NNWSI, the Basalt Waste Isolation Project (BWIP), the Salt Repository Project (SRP), and the Crystalline Project (CPO). Each of these projects is part of the Office of Civilian Radioactive Waste Management (OCRWM) Program. The scope of work for fiscal years 1986 to 1992 includes the work required to upgrade the geochemical codes and supporting data bases, to permit modeling of chemical processes associated with nuclear waste repositories in four geological environments: tuff, salt, basalt, and crystalline rock. Planned tasks include theoretical studies and code development to take account of the effects of precipitation kinetics, sorption, solid solutions, glass/water interactions, variable gas fugacities, and simple mass transport.

Recent progress has been made in the ability of the codes to account for precipitation kinetics, highly-saline solutions, and solid solutions. Transition state theory was re-examined resulting in new insights that will provide the foundation for further improvements necessary to model chemical kinetics. Currently there is an increased effort that is concentrated on the supporting data base. For aqueous species and solid phases, specific to nuclear waste, requisite thermodynamic values reported in the literature are being evaluated and for cases where essential data is lacking, laboratory measurements will be carried out. Significant modifications and expansions have been made to the data base. During FY86, the total number of species in the data base has almost doubled and many improvements have been made

with regard to consistency, organization, user applications, and documentation. Two Ridge computers using a RISC implementation of UNIX were installed and they are completely dedicated EQ3/6 machines. All codes have been re-written in FORTRAN 77 resulting in a more portable and efficient software package.

PREFACE

The critical need for the safe disposal of high-level radioactive waste material (HLW) was recognized by Congress in 1982 with the passage of the Nuclear Waste Policy Act (NWPA), which subsequently was signed into law by the President in January 1983. This act stated that it is the responsibility of the Federal government to dispose of HLW from both the civilian and military sectors. Most of the civilian HLW results from fissioning of nuclear fuel in reactors operated by electrical utilities. Radioactive products are contained in spent fuel. Utilities presently have about 13,000 tonnes of spent fuel in short-term storage facilities near the reactor sites, and about 2000 tonnes of additional spent fuel is being generated yearly. Presently, commercially generated spent fuel is not reprocessed for recovery of unfissioned uranium and plutonium. Most of radioactive material from previous reprocessing activities is liquid waste that is stored in tanks at West Valley, New York.

The NWPA established a fee of one mil/KWH on utilities that generate electricity generated from nuclear reactors to pay for the disposal and associated Federal management of HLW . The NWPA also established formal procedures for the evaluation and selection of repository sites, dictating that mined repositories should receive the primary emphasis. In addition, regulations regarding the construction, operation, and closure of repositories were to be issued and a timetable was provided for Federal agencies to meet in carrying out the program. The Department of Energy (DOE) is charged with the responsibility to provide for waste disposal and is scheduled to begin receiving wastes in 1998 at the first repository. In February 1985, the President approved that high-level defense wastes, created by military activities would be disposed of with the civilian waste.

Technical criteria to be used in the evaluation of license applications for a repository have been published by the Nuclear Regulatory Commission (NRC) (10 CFR 60, July 21, 1983). The DOE has issued guidelines for the recommendation of sites (10 CFR 960, December 6, 1984). Applicable environmental standards for HLW repositories have been established by the Environmental Protection Agency (40 CFR 191, August 15, 1985). Licensing procedures require the DOE to submit site-characterization reports to the NRC prior to characterizing sites that may be suitable for the disposal of HLW. The NRC is to analyze these reports and make appropriate comments to the DOE. However, the formal licensing process will begin with the submission of a license application to the NRC for a site that has been characterized by the DOE and recommended by the President for approval by Congress.

DOE rules for selecting sites for a first and a second repository are presented in 10 CFR 960 with the overall guidance provided in the NWPA. At present, the candidates for the first repository site include three rock types: tuff, basalt, and salt. Candidates for the second repository, which has been indefinitely postponed, (DOE News release, May 28, 1986) will likely include the addition of granite and shale to the three rock types being considered for the first repository. Each of the potential repository localities have different geologic settings and hydrological characteristics as well as rock type. Therefore, the assessment of hazards associated with HLW disposal at each site will require different studies.

The NRC (10 CFR 60) "...anticipates that licensing decisions will be complicated by the uncertainties that are associated with predicting the behavior of a geologic repository over the thousands of years during which HLW may present hazards to public health and safety." In order to address this difficulty, the NRC required the DOE to incorporate multiple barriers in their repository design. An engineered barrier system consists of the waste package (waste form, containers, and any materials immediately surrounding the containers) and the underground facility (excluding shafts, boreholes and their seals). The engineered barrier is required to compensate for the geological uncertainties, whereas the geological setting must be able to contribute significantly to isolation in order to compensate for uncertainties in the performance of the engineered barrier.

The requirement to predict materials performance and the geological environment over long periods of time is unprecedented. Field and laboratory experiments are carried out for only short periods of time relative to the period over which a repository must maintain integrity. Consequently, the prediction of radionuclide migration as part of the evaluation of potential repository sites must be made by models that extrapolate the data to longer times. The EQ3/6 software package is being modified and improved for the purpose of modeling the complex geochemical processes that result from interactions among the host rock, groundwater, air, and the engineered barrier.

1.0 REQUIREMENTS RESTRICTING RADIONUCLIDE MIGRATION

The goal to attain in geochemical modeling is the capability to simulate the processes of radionuclide release followed by migration away from the repository site. Requirements set by the NRC and the EPA restrict the potential migration of certain radionuclides to specific levels over defined periods of time. The EQ3/6 geochemical modeling codes must be developed, and the requisite thermochemical data obtained, to the extent that is necessary to address these regulatory requirements. An understanding of the necessary regulations is required to focus the development of the codes and the supporting data base.

1.1 NRC Performance Objectives for a HLW Repository

The NRC (10 CFR 60) has detailed four performance objectives for a repository. Two of the performance objectives are concerned with the engineered barrier system (EBS) in a repository and the rule states in part that

> "...the engineered barrier system shall be designed, assuming anticipated processes and events, so that... (A) Containment of HLW within the waste packages will be substantially complete for a period to be determined by the Commission taking into account the factors specified in 60.113(b) provided that such period shall not be less than 300 years nor more than 1,000 years after permanent closure of the geologic repository; and (B) The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure or such other fraction of the inventory as may be approved or specified by the Commission: provided that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste originally emplaced in the underground facility that remains after 1,000 years of radioactive decay" (10 CFR 60, section 60.113 (a) (1) (ii)).

The first performance objective for the EBS is the containment period, for which there will be a thermal pulse (from radioactive decay of HLW) that will cause an increase in temperature of the surrounding rock, water, and gas. This temperature increase will cause changes in both the fluid and rock compositions. When simulated by geochemical models, these changes will provide the characteristics of the fluid that may interact with and potentially cause a breach in the waste package.

The second performance objective for the EBS encompasses the radionuclide release rate. Geochemical modeling should be able to predict the release of radionuclides from the EBS following a breach of the container and/or any interactions involving the waste package, aqueous fluids, gases, and surrounding rock. These calculations will not only determine if the requirements set by the NRC will be met, but can also serve as guidance for optimizing design characteristics and aid in choosing a safe repository site.

The third performance objective is for the undisturbed site. The NRC states: "The geologic repository shall be located so that pre-waste-emplacement groundwater travel time along the fastest path of likely radionuclide travel from the disturbed zone to the accessible environment shall be at least 1,000 years or such other travel time as may be approved or specified by the Commission" (60.113 (a) (2)). Geochemical modeling will not be required for this performance assessment. However post-emplacement groundwater travel times will be coupled with geochemical modeling to address performance assessment for the total repository system.

The fourth performance objective is for the overall system and geochemical modeling is required for the performance assessment. The NRC states in part "...that releases of radioactive materials to the accessible environment following permanent closure conform to such generally applicable environmental standards for radioactivity as may have been established by the Environmental Protection Agency with respect to both anticipated processes and events and unanticipated processes and events" (60.112).

1.2 EPA Final Rule for Health and Safety for HLW Repositories

The EPA has issued requirements for environmental containment, individual protection, and groundwater protection. This final rule, 40 CFR 191, contains the standards referred to by the fourth performance objective set by the NRC.

The containment requirement limits the total quantities of radionuclides that are predicted to be released to the accessible environment over a period of 10,000 years. Cumulative releases from all significant processes and events must "have a likelihood of less than one chance in 10 of exceeding the quantities calculated according to Table 1" of 40 CFR 191 and "less than one chance in 1,000 of exceeding ten times the quantities calculated according to Table 1". Geochemical modeling will provide input to performance assessment to the overall system. In other words: the fate of radionuclides will be determined as the containers are breached, and the HLW interacts with any aqueous fluids present, gases, and the surrounding rock as radionuclides migrate towards the accessible environment.

Oversby (1986) has identified the most important radionuclides to be considered by using a comparison of the NRC performance objectives for the EBS and the EPA requirements as the basis for the evaluation. The maximum allowed release rates were integrated over time for PWR spent fuel. These release rates were then compared to the EPA cumulative release rate limits, and with reasonable assumptions americium and plutonium were by far the most important. Thus, it is critical that the thermochemical properties of americium and plutonium be obtained so that modeling of the behavior these radionuclides under relevant repository conditions can be done.

1.3 Issues and Information Needs Addressed (7/10/86 Version)

The EQ3/6 Geochemical Modeling NNWSI Work Breakdown Structure (WBS) 1.2.3.8.L activities do not directly address particular issues or information needs. Rather, it provides techniques and data needed to resolve them. The issues and information needs related to WBS 1.2.3.8.L as well as the BWIP and Office of Nuclear Waste Isolation (ONWI, a division of Battelle Memorial Institute, serves as project manager for SRPO) activities are:

KEY ISSUE 1: Will the mined geologic disposal system at Yucca Mountain isolate the radioactive waste from the accessible environment after closure in accordance with the requirements set forth in 40 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960?

PERFORMANCE ISSUES AND INFORMATION NEEDS

ISSUE 1.1: Will the mined geologic disposal system meet the system performance objective for radionuclide releases to the accessible environment as required by 10 CFR 60.112 and 40 CFR 191.13?

1.1.1 Site information needed to calculate the releases of radionuclides to the accessible environment.

1.1.4 Calculational models to predict radionuclide releases to the accessible environment.

ISSUE 1.4: Will the waste package meet the performance objective for containment as required by 10 CFR 60.113?

1.4.3 Scenarios and models needed to predict the time to loss of containment and the ensuing degradation of the containment barrier.

1.4.4 Estimates of the rates and mechanisms of containment barrier degradation in the repository environment for anticipated and unanticipated processes and events.

1.4.5 Determination of the time to loss of substantially complete containment of the waste packages for anticipated and unanticipated processes and events.

ISSUE 1.5: Will the waste package and repository engineered barriers meet the performance objective for radionuclide release rates as required by 10 CFR 60.113?

1.5.3 Scenarios and models needed to predict the rate of radionuclide release from the waste package and engineered barrier system.

1.5.4 Determination of the release rates of radionuclides from the engineered barrier systems for anticipated and unanticipated processes and events.

1.5.5 Determination of the amount of the radionuclides leaving the near-field environment of the waste package.

2.0 GEOCHEMICAL MODELING

2.1 Relation to Regulatory Requirements

Geochemical and transport models will play a critical role in determining migration rates for radionuclides away from a repository, and thereby determine whether HLW can be safely disposed of in geologic repositories for very long periods of time. The NRC considers estimates of aqueous concentrations of radionuclides under site specific conditions as being fundamental for predicting the release rates of radionuclides (U.S. Nuclear Regulatory Commission, 1984). Because of the complexity of the problem, the physical scale, and the long time period being considered for the release limit, 10,000 years, numerical simulations of the various processes are the only viable approach to the prediction of long-term performance. In a report prepared for the NRC (Coffman et al., 1984, p. 1-2) it has been pointed out that "in discharging its responsibility, the NRC must review DOE performance assessments and independently evaluate the likely performance assessments of each repository and waste package the DOE seeks to license. Computer models provide a framework for simulating the important processes expected to be active in a repository, thereby allowing assessment and prediction of the behavior of a waste isolation system. The

NRC is supporting the development of computer codes to be used to evaluate its HLW regulations and review of proposed nuclear waste management systems. Independently, the DOE is also developing and using computer codes for the assessment of repository sites and designs".

The NRC has taken the position that the results of computer model simulations by themselves will not be acceptable for demonstrating compliance with HLW regulations (NRC, 1985, p. 15). The NRC has stated that all predictive capabilities of computer codes will have to be validated with a substantial body of independent experimental data.

2.2 Geochemical Modeling

Geochemical modeling is an integrated approach that uses physicochemical principles of hydrogeochemical systems in order to interpret geologic processes such as water/rock interactions. Models are constructed utilizing theoretical concepts cast in mathematical representations. The computations grow increasingly complex for systems comprised of many components, as will be the case for any HLW geologic repository. Computers are necessary to solve the large number of coupled equations by numerical methods.

The first calculation of the distribution of major dissolved species in sea water was done in 1962 by Garrels and Thompson. This study pointed out the fact that the entire system must be considered when studying water/rock interactions. For example, the precipitation of calcium carbonate is dependent on the magnesium and sodium content of sea water as well as the calcium and carbonate concentrations. Magnesium forms an aqueous complex with carbonate, which is then unavailable to combine with the calcium ion needed for precipitation of calcite (calcium carbonate). Sodium chloride is the major component of salinity or ionic strength. This in turn affects the activity of all ions including both calcium and carbonate. It is the activity product (and not the analytical concentrations) of calcium and carbonate that determines whether precipitation or dissolution will occur. Only by considering all components in a system simultaneously can one address the distribution of species in solution and whether or not equilibrium with various solid phases exists.

Lack of thermochemical data was the limiting factor in early speciation calculations. Calculations were limited to natural waters no more concentrated than sea water and to approximately room temperature (Garrels and Christ, 1965). Helgeson (1964) was the first to estimate thermodynamic data for higher temperatures and used these estimates to calculate complexing involved in hydrothermal ore deposition. Nordstrom et al., (1979) reviewed more recent chemical models that have been developed for solving equilibrium calculations in aqueous systems. These models are all equivalent to the way that Garrels and Thompson set up the seawater problem, but may use different techniques for finding a mathematical solution.

Helgeson (1968, 1970) initiated computerized geochemical modeling for water/rock reactions and allowed the user to observe the series of changes in the chemical composition of a solution as well as the identification of solid phases being precipitated and dissolved from a given set of initial conditions (composition of water, composition of rock, temperature, pressure, etc.).

The geochemical modeling codes that are the most general and have the widest application are EQ3/6 developed by Wolery (1978) with later improvements by Wolery and others (e.g., Wolery, 1983; Wolery et al., 1984; Jackson and Wolery, 1985; Delany and Wolery, 1984; Delany, et al., 1986) at Lawrence Livermore National Laboratory (LLNL). This software package is operational and has successfully simulated many field and laboratory processes directly related to HLW repositories. Although a broad framework has been constructed for the geochemical models, much remains to be done to account for all potentially important processes associated with a HLW repository. These include advances in theory and code development, thermodynamic data, and kinetics and other coupled processes. Planned developments will broaden the capabilities of the codes to respond confidently to the necessary evaluation of radionuclide migration.

In addition to the three candidate repository site projects' planned utilization of EQ3/6 codes in performance assessment, Oak Ridge National Laboratory has recently brought the EQ3/6 software package on-line to provide the NRC with the ability to do independent evaluations of geochemical modeling done by the DOE (Kelmers et al., 1986).

2.3 EQ3NR, A Computer Program for Speciation-Solubility Calculations

EQ3NR (Wolery, 1983) calculates the thermodynamic state of an aqueous solution, which includes the degree of formation of ion pairs and complex aqueous species. Determination of the thermodynamic activities (concentrations corrected for non-ideality) of the species in solution, and a quantitative measure (saturation index or affinity) of the thermodynamic state of the solution (undersaturated, in equilibrium, or supersaturated) with respect to solid phases is made. This speciation-solubility calculation is useful as a method to test if a solution is in equilibrium with a particular solid phase. EQ3NR also serves to initialize the solution composition for reaction-path calculations made by the EQ6 code (EQ6 is discussed in the following section).

An example of calculations involving the determination of equilibrium would be the study of a sequence of water samples drawn at successive times from an autoclave in a rock/water interactions experiment. The state of over- or under-saturation with the minerals present in the original rock and/or those that may form as secondary phases can be computed. This can be used to check the consistency of reaction results with the supporting thermodynamic data, to determine whether or not an observed short term steady state is thermodynamically stable, and to identify new phases that may form (useful in guiding microprobe and other solids characterization work).

Speciation-solubility calculations of a fluid progressing along a known flow path can be used to construct models of chemical changes in aquifers, and allowing for inference of possible subsurface mineral-water interactions (see Parkhurst, Plummer, and Thorstenson, 1982). Speciation-solubility calculations using EQ3NR are being done by the Basalt Waste Isolation Program to investigate the direction of groundwater flow in an area where the hydraulic gradient is too low to establish the flow direction by conventional hydrologic tests (G. C. Solomon, personal commun. 1986).

EQ3NR is also used to calculate the electrical imbalance of a fluid. This provides a useful check on the completeness and correctness of analytical measurements. At LLNL, electrical imbalance calculations using EQ3NR led to the replacement of a procedure for determining dissolved carbonate by alkalinity titration. A new technique that measures evolved carbon dioxide by absorption of an infrared beam is now used. EQ3NR can calculate the pH if one assumes electrical balance. This is usually not appropriate for complex solutions such as natural waters, because of uncertainties in the solution analysis. This type of calculation is useful for designing pH buffer solutions to be used in laboratory experiments (Knauss and Wolery, 1986). For example, the composition of buffer solution with a pH of 8.0 at 70°C contains 0.005 H_3BO_3 and a small amount of NaOH. EQ3NR can calculate the concentration of NaOH required.

A planned application of EQ3NR is to calculate the pH in brines and other concentrated salt solutions from coupled specific-ion electrode measurements. By replacing the reference electrode used in making pH measurements in dilute solutions with a chloride electrode, it is possible to measure pHCl (= pH + pCl). Liquid junction effects, which prevent the usual pH measurement technique from being used in concentrated solutions, are avoided by eliminating the usual reference electrode. Measurement of chloride concentration, along with the other usual components of solution analysis, allows pHCl to be split into pH and pCl. A speciation calculation is required to make the split and any pH scale can be chosen. The pH electrode could be paired off with a specific ion electrode other than chloride, say sodium, which would give the parameter pH/Na (= pH - pNa). This approach in concentrated solutions has yet to be proven and standard procedures remain to be developed, although it appears to be the only potential method for routinely determining pH in brines.

Reaction rates depend on the degree to which a reaction is out of equilibrium (see Wolery, 1986a, and references therein). Constructing rate laws and obtaining values for the necessary constants from experimental data require speciation-solubility calculations to evaluate this degree, usually expressed as a saturation index or thermodynamic affinity. Although the thermodynamic affinity depends on the activities of the species participating in the reaction, the reaction rate may depend on the activities of certain species through another factor appearing in the rate equation. The pH represents the activity of the hydrogen ion, and the activities of many other ions as well can be measured by single ion electrodes. At present, measurements using specific ion electrodes are limited to temperatures less than 100°C. Activities at temperatures greater than 100°C can only be determined by speciation calculations (EQ3NR).

EQ3NR can also calculate the concentration of a dissolved component, assuming that solubility equilibrium exists with a specific solid phase (i.e., that the saturation index is zero). This type of calculation yields the equilibrium concentration of a component if other solution parameters, such as pH, are known. Care must be taken to ensure that these types of calculations are properly interpreted. For example, if one knows the concentration of uranium in a solution, one could use the code to determine the saturation index of a specific uranium mineral. One might then ask the question, what would the concentration of uranium be if the solution were in equilibrium with this mineral. If the results of these calculations depend on, say pH, the question asked of EQ3NR is not necessarily the same as what would be the concentration of uranium if the mineral were allowed to equilibrate with the solution. The reason is that one would need to know the pH after equilibration, and this might change as a consequence of mineral/water interaction, just as the concentration of uranium would. EQ3NR can not calculate both the new uranium concentration and the new pH; it can only calculate the equilibrium concentration of uranium assuming that the old pH still holds. It is necessary to use EQ6 to calculate the reaction of a mineral with an aqueous solution.

2.4 EQ6, A Computer Program for Reaction-Path Modeling

EQ6 (Wolery, 1979, 1986b) calculates reaction paths and mass transfer in dynamically reacting systems by considering consecutive stages of partial equilibrium as equilibrium is approached and then attained. These calculations include such effects as changes in pH and redox potential, and changes in solute concentrations caused by the creation or consumption of the solvent (H_2O). EQ6 operates in more than one physical mode, but the basic one is the closed system (see section "Physical Systems and the Coupling of Geochemistry with Transport"). For example, during the dissolution of a mineral, there commonly occurs a sequential precipitation and dissolution of other solid phases before equilibrium is reached. EQ6 tracks that type of succession by noting both mineralogical composition and the aqueous phase speciation.

The approach in EQ6 is to dissolve an increment of a mineral into a "thermodynamically homogeneous" system composed of aqueous solution plus solids with which it is in equilibrium. The code recalculates the composition of the phases in this system and checks to see if any saturation relationships have changed. If so, the set of phases present may be changed. For example, if the solution becomes supersaturated with a mineral that is not present, it may be added to the system (precipitated). Usually the code adjusts the size of the reaction increment so as to accurately locate the position at which the new phase appears. The incrementing then continues. The reaction path ends when either all original reactant minerals have equilibrated or been totally consumed, or when a preset limit in terms of reaction progress, time, or number of increments is reached.

To make reaction-path calculations in a time framework, a rate law must be provided for each reaction that is not at equilibrium. In most calculations, these reactions represent mineral dissolution. Mineral precipitation is primarily modeled by assuming instantaneous precipitation upon reaching saturation. However, the code can also model precipitation according to specific rate laws (Delany, et al., 1986). When reaction-path calculations are made without a time framework, the process is similar to a titration and is reported in terms of a reaction progress variable. This parameter describes how much mass transfer has occurred, as opposed to how much time has elapsed.

EQ6 uses the same speciation model as EQ3NR. Each code has its own speciation coding, although some routines are shared through the EQLIB library. The two codes also share a common thermodynamic data base. EQ3NR initializes EQ6 by providing a model for the aqueous solution at the start of the reaction path. EQ3NR only calculates the thermodynamic state of an aqueous solution. EQ6 must be used to calculate how that solution changes when it is reacted with other phases.

3.0 THEORY AND CODE DEVELOPMENT

The development of the EQ3/6 geochemical models involves incorporating conceptual models with a theoretical framework. These models simulate processes that may contribute to the potential transport of radionuclides from a HLW repository. There is an obvious need to interpret laboratory and field tests, which together with the predictive capabilities of the geochemical models, will provide the basis for the evaluation of potential repository sites.

3.1 Activity Coefficients

3.1.1 Background. In order to model many of the geochemical processes that may occur in and around HLW repositories and to interpret experimental studies over wide ranges of temperatures and solution compositions, it is essential to be able to calculate activity coefficients for aqueous solutes. Activity coefficients relate the concentrations of species in solution to their thermodynamic activities used in geochemical calculations. Activity coefficients are routinely calculated in EQ3/6 using Helgeson's (1969) B-dot equation. The B-dot equation is based on a simple, one-term extension of the Debye and Huckel model for dilute electrolytes combined with an ion association or "true speciation" concept. This equation can be used to calculate activity coefficients for aqueous species in solutions up to relatively high temperatures, but it is generally useful only for solutions with ionic strengths less than about 1 molal. This constraint severely limits the utility of EQ3/6 in modeling chemical reactions, and precludes those conditions that might occur in and around a proposed salt repository. Consequently, recent and planned efforts sponsored by SRP, through the Office of Nuclear Waste Isolation (ONWI), have concentrated on extending the capability of the EQ3/6 codes to model the geochemistry of high ionic strength solutions.

3.1.2 Recent Progress. One approach for calculating activity coefficients in brines is based on a set of equations developed by Pitzer (e.g. 1973, 1975, 1979) which can be used for calculations in both dilute and very concentrated solutions. Pitzer's equations together with the empirical fit coefficients, which are necessary to evaluate these equations, have been incorporated in EQ3/6 (Jackson and Wolery, 1985). The fit coefficients required for Pitzer's equations, however, are scarce for most electrolytes at elevated temperatures and have not been determined at all for many of the actinide and lanthanide species. The reason for this is that the Pitzer method can be applied easily only to systems of strongly dissociated electrolytes. It is much more difficult to apply it to strongly associated electrolytes due to increased data requirements that involve a higher level of sophistication required to regress the data. An alternate approach to activity coefficients is based on hydration theory, a concept first advanced by Stokes and Robinson (1948). These equations have been extensively modified by Wolery and Jackson (1986), and have also been added to EQ3/6 as an option. It is hoped that this set of equations will accurately estimate activity coefficients at both high ionic strength as well as elevated temperatures. The hydration theory equations require use of two adjustable parameters: a hydration number and an ion size parameter. These parameters must be regressed from experimental data. In contrast to the parameters in Pitzer's equations, it appears that the parameters in the hydration theory equations may exhibit systematic variations among various solute species which will make it possible to estimate them using various correlation algorithms or from a variety of experimentally determined parameters.

3.1.3 Planned Work. An internally consistent set of hydration numbers and ion sizes, which can be used to approximate the compositional dependence of activity coefficients in compositionally complicated solutions, will be compiled. These efforts should greatly expand the capability of EQ3/6 to include the modeling of solutions with high ionic strengths over a range of temperatures and for a variety of solute components. Presently it is planned to retain each of the different options for calculating activity coefficients (B-dot equation, Pitzer's equations and hydration-theory equations) because each approach is useful for a certain range of conditions. In addition, it is planned to develop an EQ3/6 capability to use the equations of Helgeson et al. (1981) as modified by Wolery and Jackson (1986). This activity-coefficient model development has a special significance to the program-wide effort. This improvement will bridge the gap that exists between laboratory experiments conducted in dilute and concentrated solutions.

3.2 Solid Solutions

3.2.1 Background. Solid solutions are common in minerals. They have varying compositions but retain the same overall structure. For example, the mineral calcite ($CaCO_3$) contains primarily calcium ions bound in six-fold coordination with small amounts of strontium, barium, and magnesium ions replacing calcium on those sites without significantly changing the structure of the phase. Some degree of solid-solution behavior is universal in minerals found in nature. The mutual solubility of two end-member minerals in a solid-solution phase may be complete, or may be severely restricted. Regions of immiscibility exist where two phases of different composition coexist rather than there being a single homogenous phase.

Solid-solution phases occur both as primary and secondary phases. Consequently, in order to compute chemical equilibrium and simulate reaction path models of rock/water interactions, it is necessary to take account of phases with variable compositions. The thermodynamic properties for many solid solutions can be calculated from the properties of its end members.

3.2.2 Recent Progress. Bourcier (1985) has improved the treatment of solid solutions in EQ3/6 by incorporating a new algorithm for molecular mixing. This model is mathematically equivalent to a single-site mixing model. The equations needed for modeling ideal random multiple-site mixing of solid solutions are being derived and incorporated into the codes. These equations are generally applicable to all randomly-mixed solid solutions. Also, the data base has been expanded to include calcite-structured solid solutions based on the model of Sverjensky (1985).

3.2.3 Planned Work. Most multiple-site solid solutions do not mix randomly. For those cases, ions on different types of crystallographic sites interact with each other and give rise to a preferential ordering of ions in the solid. An example of this is the "aluminum avoidance" behavior in the plagioclase solid solution, where aluminum ions avoid being nearest neighbors on the tetrahedral sites. For those non-random solid solutions, a separate set of equations must be derived, solved, and added to the code for each solid solution case. In order to build a comprehensive data base for solid solutions, a continuous effort must be made to obtain thermodynamic data for solid solutions and incorporate it into the code. Our emphasis will be on alteration minerals important in the waste environment: clays, micas, and zeolites. Mineral solid solutions may also be important sinks for trace elements in rock/water systems. Trace element substitution in solid solutions will be incorporated into the code using recent experimental data on partition coefficients and by using theoretical models, such as those of Sverjensky (1984, 1985). Incorporation of radionuclides as trace components in solid solutions may be an process that may be solubility limiting for some elements.

3.3 Kinetics

3.3.1 Background. Thermodynamic calculation of the equilibrium assemblage gives some indication of whether a given process (or reaction) will proceed. The equilibrium assumption is reasonable when geological time scales are considered, which are on the order of hundreds of thousands and millions of years. This has been supported by field observations of equilibrium minerals assemblages found in many rocks. However, for periods of shorter duration, where temperatures are relatively low, equilibrium may not be reached, if reaction kinetics are sluggish. Both experimental and field data support cases where equilibrium is not reached (Lasaga and Kirkpatrick, 1981). There is thus a need to apply kinetics in cases where thermodynamics is of limited applicability. Time frames of interest for HLW repositories are from hundreds to thousands of years where equilibrium will not always be attained. It is also important to be able to model the laboratory experiments in real time in order to understand the factors that affect extrapolation to longer time intervals.

3.3.2 Recent Progress. A precipitation-kinetics option for the EQ6 geochemical reaction path code is available (Delany, et al., 1986). This option complements the pre-existing capability to model dissolution kinetics. Several precipitation rate laws have been programmed into EQ6 as well as options for transition state theory and "activity term" expressions. More realistic simulation of water/rock interactions are now possible. This is especially useful for comparison with short-term laboratory experiments. In addition, Wolery (1986a) re-examined transition state theory, which resulted in new theoretical insights. This work will provide the foundation for further improvements necessary to model chemical kinetics.

3.3.3 Planned Work. Presently data are available for the rates of precipitation for only a few few minerals (e.g., silica polymorphs, carbonates and some sulfates and phosphates). It appears possible to extract precipitation information from dissolution data (Rimstidt and Barnes, 1980), which is more abundant than precipitation rate data for silicate minerals. Efforts will be undertaken to evaluate this approach. Additionally, reconnaissance studies will be initiated to explore the effects of nucleation phenomena and poisoning by substances that inhibit precipitation.

3.4 Gas Phases

3.4.1 Background. Gases may be produced or consumed in aqueous geochemical systems during reactions involving the solid and fluid phases. As some quantities of various gases (e.g., oxygen, carbon dioxide, methane and hydrogen sulfide) are expected to be present in all potential repository sites, it is imperative that geochemical models attain the capability to include gases in the systems under consideration. Gas phase equilibrium is expressed in terms of fugacity ("thermodynamic partial pressure"). If a species is more concentrated in the gas phase than the aqueous phase, the fugacity of the gas phase can be assumed to control the fugacity of the aqueous phase. The paths and rates of chemical reactions in the aqueous phase can be altered by such constraints.

3.4.2 Recent Progress. A fixed-fugacity option has been added to the EQ6 geochemical reaction path code (Delany and Wolery, 1984). By permitting the fugacity of any gas to be set to a fixed value, the effect of rapid chemical exchange with a large external gas reservoir can be simulated. Groundwater systems that are both open and closed to the atmosphere as well as buffered laboratory experiments can be modeled.

3.4.3 Planned Work. A variable-fugacity model will be added to allow modeling of closed systems containing varying amounts of gases, such as unbuffered hydrothermal experiments. It will also be possible to treat a gas phase of finite mass.

3.5 Pressure Corrections

3.5.1 Background. Previously, all calculations were made at pressures along the liquid-vapor curve for pure water. The approach for incorporating pressure corrections into the codes is to use the present equilibrium constants along the liquid-vapor curve and to extrapolate these values up in pressure using molar volume data for the reaction and the relationship:

$$\ln K_{T,P} = \ln K_{Tr,Pr} - \frac{\Delta V^\circ_R}{RT} (P - P_r)$$

where Tr and Pr are the reference temperature and pressure (i.e. along the l-v curve) and ΔV_r° is the calculated molar volume change for the reaction. The molar volume of the reaction is determined from the molar volumes of all the constituents of the reaction.

3.5.2 Recent Progress. This effort has just begun.

3.5.3 Planned Work. In order to make these changes, the program MCRT must be modified so that it computes molar volume changes for reactions and writes this data into the file DATA0. The molar volume data are then read and used by EQTL to compute a polynomial to fit the equilibrium constants as a function of both temperature and pressure. Finally, EQNR and EQ6 must be modified to read the revised DATA1, DATA2, and DATA3 files and obtain pressure-corrected equilibrium constants from the revised fitting polynomial.

Work is in the progress to make the necessary modifications to the MCRT program. The MCRT program itself, and the subroutines DECOMP, DLTAQ1, DLTSOL, DLPSOL, AND DLPAQ1 must be modified to compute molar volume properties of reactions. The routines GRSOL and GRAQS must also be modified to correctly read in molar volume data from the MDA data file.

For computation of aqueous equilibria at elevated temperatures, the current activity coefficient subroutines must be modified to use the proper high-pressure Debye-Hückel parameters. These data are available in the program SUPCRT, and we are currently adding the necessary routines from SUPCRT into the MCRT code. This addition will also provide the capability for calculating high-temperature thermodynamic properties of ions and minerals internally in the MCRT code. Previously, they were obtained from running the SUPCRT program and placing them into the DATA0 file using an editor.

3.6 Sorption

3.6.1 Background. Trace components are usually observed in precipitated, dissolved, or sorbed forms. Precipitation and dissolution reactions may be hindered by sluggish kinetics, thus leaving sorption an important process to consider for reducing the concentrations of trace components or contaminants in solution. Sorption is thought to be particularly important when considering the transport of radionuclides in groundwater. Radionuclides may sorb onto surfaces of aquifers or colloids and retard radionuclide transport.

Sorption is one of several processes that affect the movement of dissolved radionuclides in ground waters. Several processes have been identified that retard their transport in solution: adsorption, ion exchange, membrane filtration, diffusion into pores, and chemical precipitation (Neretnieks, 1980). Sorption is a term that can include physical adsorption, chemisorption, and ion exchange processes. Modeling of sorption phenomena generally assumes that adsorption of trace quantities of radionuclides obey first-order reversible kinetics (Krishnaswami et al., 1982). Two principal models commonly used to explain reversible ion sorption reactions on natural surfaces are constant charge and constant potential models. At low concentration in a liquid, Henry's law is obeyed and the activity in solution is directly proportional to its concentration.

Langmuir (1918) was the first to develop a quantitative model for adsorption. He related the amount of a substance adsorbed on a surface in a fixed number of independent sites to the concentration. This model is called the Langmuir adsorption isotherm. Since that time, many sorption models have been developed, based on both theory and empirical observations. Some models also relate parameters such as pH, Eh, ionic strength, and valence state in solution to sorbed concentrations.

3.6.2 Recent Progress. This effort has just recently started.

3.6.3 Planned Work. Sorption is being considered for addition to the EQ3/6 code during FY86. The main objectives during this year are to investigate the fundamental principles that are involved in understanding adsorption column dynamics, to model batch adsorption systems, sorption kinetics, and equilibria, and provide a framework for the interpretation of experimental data. The addition of a sorption capability to the EQ6 code will follow next year. This capability will be similar to the precipitation kinetics capability recently added to EQ6, and will consist of a representative sampling of sorption isotherms based both on theory and empirical observations. The actual isotherm to be used in a EQ6 run will be chosen by the user and indicated on the INPUT file. Also planned for inclusion are any site-specific sorption models developed for NNWSI. LANL is currently studying sorption characteristics of Topopah Spring Tuff.

3.7 Physical Systems and the Coupling of Geochemistry with Transport

3.7.1 Background. Geochemical interactions take place in physical systems where it is significant whether or not the system is open to any components, and if so, which ones. The EQ6 code now operates in more than one physical mode and additional modes are planned. The relation of these modes to the broader needs of the program will be discussed below.

The simplest physical system to treat using EQ6 is a thermodynamically homogeneous closed system. Thermodynamic homogeneity is defined as a static system without gradients in either temperature, pressure, or chemical potentials. The composition of the aqueous phase must be uniform. Other phases may be present, but they must be in equilibrium with the aqueous phase. EQ6 can solve parameters for these systems given the temperature, pressure, and bulk composition. It can identify the phases present and their compositions. By themselves, systems of this kind are of limited usefulness, but the ability to model them is a computational prerequisite to making more interesting calculations in more complex physical systems.

A more important mode is a closed system in which the phases are physically homogeneous but some reactions are out of equilibrium. Temperature and pressure are initially specified and uniform within the system, although they need not be constant with time or reaction progress. Driving forces are present to cause reactions that proceed toward equilibrium. It is possible to conceptualize such a system as consisting of a thermodynamically homogeneous subsystem, including an aqueous solution and one or more phases with which it is not in equilibrium. Progress toward equilibrium can then be viewed as a titration process in which increments of the non-equilibrium phases are added to, or in some cases subtracted from, the thermodynamically homogeneous subsystem. Composition of the aqueous solution is then adjusted to satisfy internal equilibrium. Calculations of this kind can be used to model mineral/water reaction in closed systems, actual titration processes, and, by "reverse titrating" of water, processes of evaporation and boiling. Such calculations may or may not be directly related to a time framework, depending upon the availability of rate laws to describe the incrementing process in terms of time.

The closed system is an excellent representation of many experimental systems, such as Dickson rocking autoclaves. Much of the laboratory work being carried out in support of the OCRWM Program is being carried out in such systems. EQ6 can be used to model these experiments; the results can be related to basic thermodynamic data that can yield prediction of longer-term behavior with some degree of confidence. For example, short-term experiments may achieve apparent steady states that persist until the experiments are terminated. Geochemical modeling has shown that in a number of instances, these steady state conditions are thermodynamically metastable and probably cannot be expected to persist over the long time intervals required for repository performance assessment (Delany, 1986).

In contrast to closed systems, open systems imply some degree of transport, that is, movement of matter across system boundaries. Several kinds of open systems are possible, and it is useful to relate these to the closed system. The latter can be thought of as a model system at a positional node or box in a spatial framework, with the fluxes into or out of the box temporarily suspended or infinitesimal. A flow path, for example, could be represented by a series of boxes.

One type of open system is a box that is open to a large external gas reservoir, for example a beaker or flask open to the air. In such a system, as a dissolved gas such as CO_2 or O_2 is consumed or produced by chemical reaction in the box, an equivalent amount enters or leaves the box. The fugacity of such a gas is held constant. The reaction path representing the geochemical interactions taking place within the box may be significantly changed by such an effect. This type of model is not only applicable to a simple benchtop experiment open to the atmosphere (or controlled by a constant source), but also to surficial weathering processes and processes in the unsaturated zone. The fraction of open space not occupied by water contains chemically reactive gas that appears to be much like air. EQ6 was recently modified to be able to model such systems (Delany and Wolery, 1984). With this code option, it is possible to calculate the affect of the presence of a gas reservoir. An important EQ6 application may be to use experimental data from laboratory experiments (conducted to characterize geochemical behavior in and about the proposed repository) to model the effects of a gas reservoir often not present in the laboratory systems.

It is possible to conceptualize a fully one-dimensional geochemical transport model by considering water moving through a sequence of boxes representing a flow path. The closed system calculational modeling capability would be used to solve for the chemistry in each box at each time step. Gas fugacities may be fixed, if desired. In the simplest case, fluid flow would be fixed, ignoring possible changes in flow due to mineral precipitation or dissolution. A temperature or pressure gradient could also be imposed.

At present, EQ6 does not have a full one-dimensional modeling capability. It only has a pseudo one-dimensional physical mode. A pseudo one-dimensional mode here refers to a model that focuses on a single packet of water or a single box. This mode in EQ6 tracks the evolution of a single package of water as it flows through a uniform reactant medium. System parameters such as temperature gradients and gas fugacities may be fixed, and product minerals removed from the system as they are formed. A full one-dimensional model would be required to allow precipitates to back react with the fluid or react with following packets of water.

An additional pseudo one-dimensional mode is planned. It focuses on the evolution of the contents of a box containing water and solids. Fluid of constant composition flows into the box and displaces fluid whose composition has been modified by geochemical interactions in the box. Gas fugacities may be held constant. Part of the problem is to calculate the composition of the exiting fluid. The box can be thought of as the first box in a sequence. Alternatively, it can be conceptualized as a flow through leaching cell, an apparatus that is used in laboratory studies as part of the OCRWM Program. Thus, this capability will be useful in geochemical modeling of an additional important class of experiments.

These two pseudo one-dimensional modes allow a partial link of transport (fluid advection) with detailed geochemical models. By linking a sequence of boxes, a full one-dimensional model could be developed. The decision of whether or not to build such a model into EQ6 has not yet been made. EQ6 is a highly sophisticated tool for modeling geochemical interactions and is already a substantial code package, larger than many transport codes.

Solving the necessary chemistry equations in a single box may already involve simultaneous solution of hundreds of equations. A full one-dimensional model probably would represent the upper limit to transport development for the EQ6 code. Even with this treatment, the transport mechanism would be rudimentary compared to that which exists in current transport codes. These codes tend to treat geochemistry in a complementary rudimentary fashion.

The need for coupled geochemistry and transport models in the OCRWM Program is well established (e.g. Garven, 1984; Pearson, 1984; Cederberg, 1985; Lichtner, 1985). Geochemical interactions can be significantly affected by transport phenomena and vice versa. In the near field during the thermal-pulse period, dissolution and precipitation effects could have a significant effect on fluid flow. In the far field, geochemical interactions will probably have very little effect on fluid flow. Transport of radionuclides through both the near and far fields could be significantly affected by geochemical interactions such as sorption and precipitation.

The principle role of EQ3/6 is presently in the design and interpretation of laboratory experiments and in the interpretation of site geochemistry. The former involves both purely thermodynamic as well as kinetic modeling, and serves the important function of relating observations in complex systems to known basic data, such as solubility product constants. This is important for the identification of possible metastable assemblages in short-term experiments. The use of EQ3/6 in interpreting site geochemistry largely involves purely thermodynamic modeling and simulating rock/water interactions.

Although many effects may be included in a geochemical modeling calculation, it usually turns out that in any geochemical system only a small fraction of these effects dominate the results. Unfortunately, the identities of all of the dominant effects can usually be determined only after the calculation has been done with all of the possible effects included. For example, the mass balance of a dissolved component is usually 99% composed of only one to five species. The number of species included in the calculation may be quite large - for example, there are already dozens of aqueous species of uranium in the EQ3/6 data base. The set of dominant effects is not necessarily fixed, but may vary with such parameters as temperature, pressure, and fluid composition. If these change too much, the set of dominant effects may be changed. The possible effects of transport on these parameters and hence the set of dominant geochemical effects can be evaluated. It is expected that this can be accomplished primarily by reference to EQ6 calculations using the pseudo-one dimensional modes, and possibly the fully one dimensional mode. These should represent the transport effects sufficiently well to evaluate their effect on the identities of the dominant geochemical factors. If necessary, further justification for eliminating certain geochemical effects can be obtained by including a few that are thought unnecessary in a complete geochemistry-transport calculation.

3.7.2 <u>Recent Progress</u>. This effort has not started.

3.7.3 Planned Work. Modeling the behavior of the near-field environment will require a more sophisticated treatment of coupled geochemistry and transport. As planned, EQ3/6 will play an important role in interpreting the results of laboratory experiments and provide guidance for predicting long-term scenarios. This is viewed as necessary but not sufficient, because we do not plan to expand EQ3/6 into a sophisticated transport code. If EQ3/6 is not to be expanded to treat transport in more than a rudimentary fashion, the question arises as to what code will be used to make calculations in which both geochemistry and transport must be treated in more than a rudimentary way. It is anticipated that the need for such software will be met outside the EQ3/6 subtask by incorporating the improved descriptions of geochemistry generated by the subtask and by others using EQ3/6 into existing transport codes. Two approaches are possible. One is to carry out the geochemistry calculations utilizing subroutines. In this way, a scaled down version (in terms of reduced array dimensions and elimination of unnecessary supporting data and submodels) of EQ6 could be employed. The other approach would be to take the chemical equations and substitute them into the transport equations. Preliminary attempts of both approaches currently exist.

There are advantages in developing subroutines for geochemistry calculations. The geochemistry part of the model need not be extensively duplicated. New developments in modeling geochemical processes would quickly and more assuredly be included in the combined geochemistry-transport model. Most of the equations that describe geochemical interactions are fundamentally algebraic in nature. Substituting them into transport equations turns them into differential equations, and different numerical methods must then be employed. Errors in numerical integration of differential equations can be more devastating to chemistry equations than to transport equations. EQ3/6 is written to treat algebraic equations by algebraic methods. Only kinetic rate laws, which are inherently differential equations, are treated by numerical integration. Thus, duplication or partial duplication of the geochemistry submodels in EQ3/6 in a combined geochemistry - transport code would require not only parallel coding, but coding using different numerical methods.

4.0 THERMODYNAMIC DATA BASE

4.1 PURPOSE

The thermodynamic data base is a summary of the available thermodynamic data for aqueous species, solids, and gases in tabular form that are necessary to serve as input to the geochemical modeling codes EQ3NR and EQ6. The data base will be evaluated by testing predictions of host-rock phases, secondary phases, solution species, and total solution concentrations against the results of laboratory measurements made over a range of identified parameters that include: temperature, ionic strength, redox conditions, and solution composition. The user is responsible for determining the acceptability of the data base for its intended application.

The data base is structured to allow a convenient means for expansion, revision, and documentation as new data become available. The primary EQ3/6 data base is comprised of two data files. A master data file (MDAR) contains all species and data sources that have been considered by the EQ3/6 group. This data file is in direct access format and contains extensive comments and documentation. The second data file (DATAO) is generated in part from MDAR and contains thermodynamic values that have been selected for use by the EQ3/6 codes for actual calculations. A portion of DATAO that represents rock/forming minerals is taken from SUPCRT, a data base maintained at the University of California, Berkeley.

4.2 BACKGROUND

The two data files contain the standard thermodynamic data that are reported in the literature for solids, aqueous species, and gases. These values have been gathered from the available literature and inserted into the EQ3/6 data base format as an ongoing effort over several years. In general, the data base work has lagged behind code development. During FY85, a significant amount of time was spent reviewing and revising the thermodynamic data for the actinides. As a result of this work, an experimental plan was developed to fill in thermodynamic values that are either lacking and to resolve inconsistentcies. This plan is designed to span a 5-year period.

Significant modifications with regard to consistency, organization, user information, and documentation are in progress. These changes affect the on-line maintenance of all the data base files, related data base manager codes, and thermodynamic codes. Recent revisions of the thermodynamic data for several of the aqueous and solid species of U, Am, and Pu have demonstrated the need for an experimental data base activity that would be able to provide data that is currently lacking for solubility limiting solid phases and/or solution species. Measurements will be made as a function of temperature, ionic strength, and oxidation state as required. The activity, which commenced in mid-FY86, has been divided into three sections: sensitivity analysis, development of thermodynamic data, and validation.

Two members of the EQ3/6 data base staff are participants on critical review teams for the International Thermodynamic Data Base, sponsored by the Nuclear Energy Agency (NEA). As a result of this work, the following principles have been accepted for the EQ3/6 data base.

1. Incorporate results of peer reviewed data. This will provide compatibility with CODATA (Committee on Data for Science and Technology) task group recommended key values and with NEA (Nuclear Energy Agency) as their data values are released.

2. Implement EQ3/6 data base methodology for new and existing data.

3. Create and maintain a data base library on the computer for all documented sources of thermodynamic data.

4.3 DATA BASE DEVELOPMENT

Sensitivity Analysis

A necessary part of this task is to meet the programmatic time constraints imposed by the NWPA. As a consequence of this, it is important that the number of experiments be limited by assigning priorities. Sensitivity analysis will: (1) identify reactions that can be neglected and (2) recommend additional experiments for improving and/or obtaining important thermodynamic data. The master EQ3/6 data base file now contains more than 1200 species. This program will evaluate the degree of importance various solution species have under different solution conditions. The precision needed for thermodynamic quantities will be determined for these species. The ranges of system parameters for which all thermodynamic data would be needed will also be determined.

All sensitivity analysis tasks have been postponed until thermodynamic data for all important radionuclides have been entered into the data base from the available literature. During FY86, the thermodynamic data for neptunium solids and aqueous species are being reviewed and compiled to be incorporated into the EQ3/6 data base. Major emphasis is being given to species that may be significant in geochemical applications for radioactive waste disposal. Solids considered so far include oxides, hydroxides, phosphates, and carbonates; aqueous species include ions, anions, and complexes with the halides, phosphate, carbonate, and sulfate.

Compatibility with CODATA

CODATA values have been published for 125 chemical species (CODATA, 1978) and a preprint of a revision has been received that includes a number of additional compounds. The current EQ3/6 data base is consistent with most of the CODATA values although full compatibility has not been obtained.

To date, reports have been prepared comparing the 1978 CODATA values with the 1985 CODATA values and comparing these values (especially 1985) with the values found in MDAR.

Compatibility with International Thermodynamic Data Base

Aqueous and solid species for I, Pb, Tc, Cs, Sr, Ra, U, Np, Pu, and Am are being considered by NEA panels at this time. Most of this work is in the critical review process and has not yet been completed and released. NEA has also published standards on extrapolation to zero ionic strength, format for compilation and review processes, selected values for reference phases, treatment of uncertainties, and conventions with regard to notation, solution description, etc. (Muller, 1985). In order to incorporate these data into the EQ3/6 data base, the master data file will be reformatted to include additional species information that is required by the NEA format.

Data Evaluation and Maintenance

Several elements that are not currently in the data base, but which will be needed for modeling nuclear waste glass dissolution behavior, include Mo, Ti, Y, Zr, Te, Ce, Nb, Pd, Cm, and several lanthanide elements. Compilations of thermodynamic data exist for some of these elements (Eu, Mo) but additional evaluations and laboratory experiments are expected to be necessary for these elements. Critical reviews are also needed for values that have been entered into the data base but are yet to be evaluated, for example, thermodynamic values for species of C, Sn, Cr, Co, Se, Cs, I, Th, and Ra. Literature search and data collection tasks still need to be conducted for Sm and Pb before species of these elements can be inserted into the data base and a sensitivity analysis made. In some cases, the basic chemistry will have to be clarified before a thermodynamic assessment can be made.

The thermodynamic data for the rock-forming minerals has been taken from the SUPCRT compilation (Helgeson et al., 1978). SUPCRT is a FORTRAN code and supporting data base that calculates the thermodynamic properties of minerals, aqueous species, and gases at high temperatures. The SUPCRT data base stores the standard modal entropies, heat capacity power function coefficients, molar volumes, and enthalpy and Gibbs energy of formation for each mineral phase.

These thermodynamic values were extracted with high temperature/pressure phase equilibria constraints. The SUPCRT code generates a log K grid as a function of temperature for the dissociation reaction of each phase from 25-300°C. The log K values are then used as input to a SUPCRT formatter code (written at LLNL for the EQ3/6 data base by T. Wolery) to generate portions of EQ3/6 data blocks for the thermodynamic data file (DATA0).

The SUPCRT data base has been an integral part of the thermodynamic data base for minerals since 1978. The data has been updated with corrections as released by H. C. Helgeson at the University of California, Berkeley. The EQ3/6 thermodynamic data file contains thermodynamic data for many other solids and minerals in addition to that reported in SUPCRT. These data are generally documented and entered through the master data file (MDAR).

The work currently planned is to update SUPCRT by (1) updating values for molar heat capacities and calorimetric entropies with new experimental data that has been reported in the literature; (2) expanding the heat capacity fit equation ($H_T^\circ - H_{298}^\circ = A + BT + CT^2 + D/T + ET^{1/2} + FT_3$) to include more recent calorimetric data; and (3) evaluate the impact of CODATA values on the SUPCRT thermodynamic values.

Under consideration is replacing the SUPCRT data base with a new data base for rock-forming minerals. Berman et al. (1985) have reported data for 71 minerals, this new data base already contains many of the updated values we outlined above. They use linear programming techniques to ensure internal consistency between phase equilibrium, calorimetric, and volumetric data. This approach is similar to SUPCRT in that it uses constraints from phase equilibria data to derive thermodynamic properties of minerals. The authors also use a predictive Cp function (Berman and Brown, 1985) that is compatible with the high-temperature heat capacity limit predicted by lattice vibrational theory.

A continuing effort will be required to keep the data base current as new data become available. This will involve maintaining an archive of literature used to generate the data base and to continue to document the selection of values chosen for the data base.

4.4 Laboratory Measurements

The objective of this activity is to correct gaps or conflicts in the master EQ3/6 data file by making the necessary experimental measurements. Laboratory measurements will supply thermodynamic data on solids and solution species that are critical to the reliable prediction of radionuclide solution concentrations in waste repository settings where there are no reliable data, where serious discrepancies exist in published data, or where data of sufficient accuracy do not exist. The quality level assignment for data introduced from this activity will be identified in the data base.

Solubility Measurements

We propose to generate a resource body of data on possible controlling solid phases and to determine the free energies of solubility reactions needed by EQ3/6. Some redeterminations of existing data may be necessary because several values in the published literature are taken from experimental studies where the solid phases were not characterized. Additional data may be needed in some cases for amorphous and crystalline counterparts, especially if short-term solubility experiments are to be modeled successfully. To accomplish this activity, all solids must be well characterized both structurally and compositionally. This will be accomplished through the use of x-ray, infrared, and surface spectroscopy techniques for both synthetic and natural materials when possible.

The complete set of solution species and solid phases to be investigated over the life-time of the program is not as yet known since their identification is the object of the critical review, sensitivity analysis and validation of the EQ3/6 calculations. Our initial review of thermodynamic data for U, Pu and Am, and initial modeling studies of these elements in J-13 water in FY85-86 led to the following proposed research on these elements for FY86-88.

Uranium

The free energies for the solubility reactions of several uranyl silicate compounds that appear likely to form in dilute groundwater in the presence of spent fuel will be determined. These phases may be solubility limiting, but no experimental data presently exist. These solids are: soddyite, uranophane, Na-boltwoodite, and Ca-haiweeite.

Americium

We plan to determine the free energy of the solubility reactions of amorphous and crystalline $Am(OH)_3$. Also, we will investigate the nature of the solid phase that forms for pH values greater than about 9.

Plutonium

A number of important thermodynamic constants in the data base are highly unreliable, e.g. the Ksp values for $PuO_2(OH)_2(s)$ and $PuO_2(OH)(am)$. We propose to prepare and characterize the structure of $PuO_2(OH)_2$ and to measure the solubility product constant. Also, we plan to determine the solubility product constant of $PuO_2(OH)(am)$.

Speciation Experiments

Solubility product constants are not usually sufficient to predict accurate solution concentrations. This is because the formation of hydrolysis products and other complexes can increase apparent solubilities. Therefore, reliable formation constants for the major solution species that are likely to form under site-specific ground water conditions are needed to make accurate EQ3/6 calculations. A number of gaps and inconsistencies were identified for carbonate formation constants, particularly for Am(III) and Pu(IV). This is primarily because indirect methods that do not provide information on the nature of the solution species have commonly been used (e.g. nuclear counting methods). UV-visible near-IR spectroscopy can supply information for characterizing solution species and concentration levels. Initially, we will be using standard absorption spectroscopy methods to investigate both oxidation state distributions and the nature of solution complexes. Attempts will be made to apply more sensitive laser techniques to these measurements. Carbonate complexation of americium will be studied in FY87 and plutonium in FY87-88.

Americium

We plan to investigate the carbonate complexation of Am^{+++} to verify the existence of bicarbonate and hydroxycarbonate complexes and to determine the relative importance of these complexes to the normal carbonates. If possible, formation constants will be obtained.

Plutonium

We will investigate the carbonate complexes of PuO_2^+ and attempt to obtain formation constants and plan to measure the first hydrolysis constant for PuO_2^+.

Laser-Induced Pulsed Photo-Acoustic Spectroscopy

The determination of waste radionuclide solubilities and speciation (i.e., oxidation state distributions, solution complexes, and ionic or colloidal forms) involves measurements that must be made in aqueous solutions of pH 7-9 (common to groundwaters). Many important waste radionuclides, particularly the actinides, are only sparingly soluble under these conditions and submicromolar concentrations are frequently encountered. While the nuclear counting methods usually provide the necessary sensitivity for the measurement of total concentrations, they provide no information on the nature of the solution species. Conventional UV-visible-near-infrared absorption spectroscopy can supply some information on solution species characterization, but generally lacks the necessary sensitivity. Thus, methods for the adequate characterization of solution species at submicromolar concentrations are not available. This limitation has led to serious gaps and conflicts in available thermodynamic data on many of the waste radionuclides. The inadequacies of present techniques and the need for new, more sensitive methods for identifying solution species has been a subject for discussion at two recent workshops sponsored by DOE and NRC.

Within the last few years, a new laser technique has been developed for measuring very weak sample absorbance. The approach is to measure directly the deposited energy resulting from the absorption process rather than the more conventional method of measuring the attenuation in a light beam. This technique, pulsed photoacoustic spectroscopy, has been shown to be several orders of magnitude more sensitive than the conventional approach. Although applied to the study of gases and solids rather extensively, little has been reported on measurements involving aqueous solutions. Recently, a West German group has demonstrated that this technique can be applied to measurements of actinide speciation at submicromolar concentrations (Stumpe et al, 1984).

We are developing a pulsed photoacoustic (PA) spectroscopy system using the existing Nd-YAG pumped dye laser and associated computer-control instrumentation at LBL and will investigate the capabilities and sensitivity limitations of this system for characterizing waste radionuclide species in aqueous solutions. Since the application of PA spectroscopy to the study of aqueous solution species is still in the early stages of development, PA cells and associated preamplifiers tailored to the purpose are not yet commercially available. Therefore, our initial efforts would involve (1) experiments to determine optimum cell geometry and construction materials for efficient coupling of the cell liquid to the transducer for maximum signal to noise; (2) design and construction of PA cells based on the test results; and (3) design and construction of low-noise, high-impedance, high-frequency response preamplifiers tailored for use with the PA cells.

With the completed system, measurements of signal strength versus concentration of U, Np, and Pu in the submicromolar region would be made to determine usable detection limits. The final phase would involve tests to determine the capability of the system to distinguish ionic (complexed and uncomplexed), polynuclear, and colloidal forms of Pu at submicromolar levels.

Vibrational Spectroscopy

Frequently, a positive identification or characterization of the controlling solid phase in experimental measurements is lacking. This causes a serious problem when comparing the results of modeling studies with experimental measurements. The amount of solid material is often present in submilligram quantities (sometimes only surface layers) and it is frequently amorphous in nature. While x-ray spectroscopy can often be used to characterize submilligram amounts of crystalline material, multimilligram amounts are usually required for a chemical analysis of amorphous material.

We are generating a spectral library using Fourier transform infrared techniques to characterize phases that may be the controlling concentration in site-specific ground waters. Library spectra can be used to identify spectra of unknown solids from spent fuel and waste form dissolution experiments from their characteristic "finger prints." We plan to use this spectroscopic data, along with structural and elastic data to predict thermodynamic functions using a spectral-averaging model developed by Kieffer (1979a, b, c; 1980). This model is a FORTRAN code based on the theory of lattice vibrational properties of minerals, and observed trends in the high-temperature thermodynamic properties of silicates. These parameters are determined by the position and relative numbers of high-frequency modes. The entropy on the other hand is most sensitive to the low-frequency optic modes, generally observed in the far-infrared region. Model values of heat capacities and third law entropies have been shown to be in good agreement with experimental values at 298-1000°C for over 30 minerals. This method has been successful in predicting experimentally documented phase relations for a number of silicate and oxide systems. These data can then be used to calculate molar heat capacities and third law entropies. These quantities are needed to make thermodynamic calculations at temperatures above 25°C, and are stored directly in the EQ3/6 data base. At this time, quantitative spectral techniques are proposed for several uranyl silicate phases mentioned above.

4.5 User Guidelines for Validation of Data Base

The user has the responsibility for determining the acceptability of the data base for its intended application. This section outlines activities that serve as a guideline for users in that evaluation. This activity will involve both theoretical calculations using EQ3/6 and additional laboratory and field measurements aimed at confirming the validity of code predictions. Measurements of solution concentrations of the waste radionuclides as well as the identification and characterization of solid phases and solution species will be made over the range of system parameters expected in the proposed repository sites. Validation of rock-water systems at elevated temperatures can be conducted by comparison with existing literature. The majority of the inorganic components that form insoluble compounds and solution complexes in dilute ground waters are presently included in the data base. Many of these species have been qualitatively documented from previous EQ3/6 runs and presumably need only to pass the validation procedure. Additional complexes may need to be added to the data base as studies are completed with waste radionuclides that may be important depending on specific site characteristics. If any of these species are lacking thermodynamic characterization and need to be considered for the development portion of the data base, it will be critical that the validation staff work closely with the experimentalists to ensure that the necessary measurements are made. Because of the large number of solid phases and solution complexes that can conceivably form in groundwater-host rock interactions, this task must be sufficiently flexible to fill any gaps or conflicts in thermodynamic values on an as-needed basis. At this time, the site-specific solubility measurements of individual solid phases is being funded directly by each of the three project site tasks. The final data base will need to be validated by testing predictions of host-rock phases, secondary phases solution species, and total solution concentrations against the results of laboratory measurements made over a range of identified parameters that include: temperature, ionic strength, redox conditions, and solution composition. This validation work should complement measurements that are currently being made by the site tasks on specific systems.

5.0 MAINTENANCE, DOCUMENTATION, AND SUPPORT FUNCTIONS

5.1 Code Maintenance

Complex computer codes inevitably contain bugs. Bugs may be divided into four categories according to the nature of the effects they produce:

A The program crashes. For example upon attempting to divide by zero. Program termination is abnormal from the point of view of the operating system.

B The program fails. For example because an iterative calculation fails to converge. Program termination is normal from the point of view of the operating system.

C The program produces output that is normal in format, but the results are erroneous and are readily recognized as such by a knowledgeable user. For example, a result that should have a value within an order of magnitude of unity has a value of 1.e+30.

D The program produces erroneous data that appears to be normal. There is a high probability that the user will not catch the error, at least not right away.

A large portion of any code development effort normally is spent in fixing bugs, particularly types A and B. The discussion here will focus on the appearance of bugs in a version of a code that has been released by the developers for applications work. This program plan assumes that, as EQ3/6 is used in applications here at LLNL and elsewhere, bugs will be discovered and corrective action will be required. Fixing bugs takes time and money, because significant effort is usually required not only to change the code, but to diagnose the problem before changes are made and afterward to test the modified code. The EQ3/6 Software Quality Assurance Plan defines a procedure for resolving errors in released code (see "Software Quality Assurance, Section 6.0"). Bugs sometimes arise in the transfer of a code to a new machine, due to differences in either the hardware or the operating system software. Even a change in the operating system software on a given machine may cause new bugs to appear. Increasing standardization of languages and operating systems is beginning to reduce the frequency of such problems, or at least offer the possibility of writing code in some manner that will reduce portability problems. Not all portability-related bugs can be caught prior to release of a code by the developers. Portability standards have been adopted for EQ3/6 development to help reduce the incidence of such problems.

Verification and validation activities are required as part of the EQ3/6 Software Quality Assurance Plan. However, testing, verification, and validation activities are necessarily finite. If a code is simple, or only solves a limited range of problems, a high degree of confidence may be achieved that all bugs have been eliminated. In the EQ3/6 package, this situation can be realized with the data base management code, MCRT. Less confidence is possible with codes that are more complex or solve a broader range of problems. The codes EQ3NR and EQ6 fall into this category. Part of our response to this problem in EQ3/6 development is the creation of verification libraries. As codes such as EQ6 are developed by the addition of new capabilities, test cases from these libraries will be periodically re-run to assure that new development has not compromised previous capabilities. Another method of bug detection is to encourage others to use the code and report problems that they may encounter.

Type C and D bugs may result from coding errors. However, they may also result from erroneous data on supporting data files. In the EQ3/6 Software Quality Assurance Plan, supporting data files and codes are both treated as "controlled items." Error resolution pertaining to such data files is handled much like that for coding errors.

Bugs of all types may result from errors in numerical integration or iterative procedures. Because these procedures are inherently inexact, special attention must be paid to the sizes of the errors. When such procedures are used in EQ3/6, problems of this kind are avoided in two ways. First, convergence tolerances, which are changeable by the user, are assigned default values that are on the tight side. Second, if the error can be quantified in more than one way, each way is tested. For example, Newton-Raphson iteration is employed in both EQ3NR and other speciation-solubility codes. Most such codes test for convergence only the magnitudes of the residual functions; we also test the magnitudes of the correction terms.

5.2 Programming Improvements

A code may produce correct results, but still be deficient in terms of portability, efficiency, modularity, clarity, or new language or coding standards. EQ3/6 was originally written in extended FORTRAN 66 on CDC 6400, 6600, and 7600 computers, and was not especially portable to different kinds of machines. In recent years, there has been a considerable effort to increase portability and clarity, and adopt new programming standards. Some of these standards presaged adoption of the FORTRAN 77 language. EQ3/6 has recently been moved from CDC 7600 and Cray-1 computers, which have, respectively, 60- and 64-bit word sizes, to two dedicated Ridge computers, which are 32-bit UNIX machines. The big LLNL machines did not support a full FORTRAN 77. Hence, moving to the Ridge machines has permitted a move to full FORTRAN 77. FORTRAN 77, among other things, offers programming structures of the IF-THEN-ELSE-ENDIF type, which are clearer and less error prone than equivalent conditional GO TO structures. Another reason for moving EQ3/6 development to a 32-bit UNIX machine with FORTRAN 77 is that it increases portability as other users of EQ3/6 are now likely to run it on compatible (e.g., Ridge, VAX, PRIME, Sun).

Programming improvements can be separated into those which are mandatory and those which are enchacements. Some of the FORTRAN language changes were necessary to make EQ3/6 run on the new machines. Whether or not some other changes are truly necessary is less clear. Although there has been an effort in recent years to cut down the size of individual subroutines, a trend toward greater modularity, some internal pressure has developed to cut them even further on grounds of easier documentation and future modification. Many conditional GO TO structures remain in the codes, and there is pressure to rewrite them on similar grounds, even though the structures are valid (but discouraged) under FORTRAN 77.

Other than language changes, there is also a clear need to increase the speed of the computations. The Ridge computers and similar machines are considerably slower than the CDC 7600 or the Cray-1, and activities are presently underway to reduce the execution times of the MCRT, EQ3NR, and EQ6 codes. As the codes have grown, there have also resulted pressures to change the ways that information is stored. For example, reaction coefficients in EQ3NR and EQ6 have been stored in arrays that contain a space for each master species on the data file. This scheme has an advantage in execution speed in that the coefficient for a given master species could be found without having to calculate its location in the array. When the number of master species was small, it also represented a not too inefficient means of storage. However, the number of master species is now large and the storage arrays are not only very large, but also sparse. The balance has shifted and it would now be more efficient overall to shift to a different storage scheme, one represented by a pair of smaller arrays: an element of one array would hold the coefficient, the corresponding element in the other would identify the corresponding master species.

An increase in storage efficiency is also possible for EQ3NR and EQ6. Some arrays, for example those that hold reaction coefficients, have only a few significant figures. Such arrays are currently double precision (REAL*8) on the Ridge machines, to match the single precision of the Cray-1 (equivalent to REAL*16). With some programming care, it should be possible to reduce these to REAL*4.

5.3 Installation of New Computing and Graphics Equipment

At the start of fiscal year 1985, the two codes EQ3NR and EQ6 would no longer fit into the small core memory of a CDC 7600, and all further development had to be done on the Cray-1. An expansion of computing needs by

LLNL's weapons programs reduced the allowable use of the LLNL Crays for EQ3/6 development and application to nearly zero. Thus, at this time the hardware resource necessary to work with the two largest codes in the package had vanished, the codes were written in a form of FORTRAN that was rapidly becoming archaic, the new form of FORTRAN was only partially available, and the codes were primarily written for long word length machines at a time when most users were working with short word length machines.

During 1985, the EQ3/6 group established, with NNWSI support, its own local computing system, based on a Ridge 32C and a Ridge 32S. The Ridge 32C was obtained second-hand, and significantly upgraded in memory, operating system, and disk space upon arrival at LLNL. These machines are being linked to an Ethernet system with other machines that belong to the Seismology group in the LLNL Earth Sciences Department. The purpose of this linking is to facilitate sharing of resources in local utilities development and peripheral hardware, to allow optimal usage of all machines, and to provide an insurance policy so work can continue if one or more computers go down. The EQ3/6 group has obtained, in addition to the two Ridge computers, a plotter and two laser printers. The system that has been put together can grow as necessary by the addition of more machines as needed.

It is anticipated that in two or three years the scope of EQ3/6 and related waste program calculation needs will require significantly more power to carry out all the applications calculations that are anticipated. A computer with the necessary power and within a reasonable price range now exists (the Convex C-1, described as "1/5 of a Cray," now costing about $600,000). Thus, it is reasonable to expect that in two years a machine of at least this power will be available, probably for less money, and that it will meet the necessary programmatic requirements. It is currently planned to add such a machine to the local network at about that time.

5.4 Code Manuals: Preparation and Updating

Code manuals published by LLNL are written to satisfy the requirements of NUREG-0856 and various DOE Project requirements, such as NNWSI SOP-03-02.

A main user manual is presently or will soon be available for each scientific/engineering code in the EQ3/6 package (Wolery, 1983, 1986b). Auxiliary user manuals, such as the report of Delany and Wolery (1984) on the fixed-fugacity option in EQ6, are used to cover special topics in greater detail and to document new improvements. Present plans call for putting all existing and future user manuals on the Ridge system, and making use of electronic publishing capabilities to maintain these manuals and keep them up to date.

5.5 Distribution of Codes, Manuals, and Publications

Distribution of codes is handled under existing DOE and LLNL regulations pertaining to unclassified software. When a new version of EQ3/6 is publicaly released, a copy of the software package and the documentation is deposited in the LLNL QA archive and the DOE's National Energy Software Center under the Center's "as is" release policy. The Center is the primary means of public distribution of EQ3/6. Copies are transmitted directly from LLNL to sponsoring agencies, sponsors' subcontractors, participating agencies and other national laboratories, and informal collaborators at universities and other public institutions who share relevant information or provide other feedback or services that enhance the success of the mission. In addition, pre-release copies of software may be transmitted to sponsors or others for review purposes.

An EQ3/6 Mailing List is maintained for the purpose of making announcements, updates, and distribution of EQ3/6 manuals and related reports that are published by LLNL. Distribution of manuals and other relevant LLNL reports is also carried out using various distribution lists that are required by DOE, LLNL, or the sponsoring Projects (NNWSI, SRP, BWIP). Additional copies of all documents may be obtained directly from LLNL, subject to availability, or from the National Energy Software Center and the National Technical Information Service.

5.6 General Assistance and Consulting

Current and anticipated use of EQ3/6 for the entire OCRWM Program (outside LLNL) encourages us to provide some effort directed toward general assistance and consulting activities. The most common assistance needed is hardware portability problems, advice on code options and use to solve specific problems, critiquing the results of specific calculations, and providing information on current developmental work that may affect future ability to perform desired calculations. Additional assistance is provided for examining reported code failures to determine whether the cause is due to code bugs or improper usage. If the problem lies in the latter, advice on the correct usage is given. If a bug is found, changes are made to the current development versions of both the codes and/or supporting data bases, (see section "Correcting Programming Bugs"). Temporary fixes may be recommended to allow work elsewhere to proceed, or LLNL may provide corrected software.

5.7 Peer Reviews

A formal peer review is provided for in the EQ3/6 Software Quality Assurance Plan as a means of approval for a public release (see below). No other examples of formal peer reviews are planned regarding EQ3/6 work. Informally EQ3/6 is subjected to the peer review of the geochemical community by outside use. This includes other programs at LLNL and in the academic community for applications to ore deposits, rock water interaction in mid-ocean ridges, and interactions in geothermal systems. Feedback is particularly encouraged by "informal collaborators" in universities.

6.0 SOFTWARE QUALITY ASSURANCE

EQ3/6 activities are governed by a quality assurance plan (LLNL, 1986) that is consistent with sponsor' requirements. This plan includes the development and maintenance of the EQ3/6 package, the application of software to critical calculations, export and import of software, and documentation of all activities. Development and maintenance of the package contains guidelines for producing the necessary code documentation, coding standards, and error reporting and resolution. The plan also calls for formal peer review prior to release. Some elements dealing with system file maintenance, archival storage, and backup procedures have yet to be added to the plan.

The first plan element, "Requirements for Development and Use of Scientific and Engineering Software, (R19.1)," is a master requirements document. It contains an analysis of quality assurance problems that relate to scientific and engineering software, and an outline of the requirements documents and procedures that make up the rest of the plan. This document examines the most important problems that arise in the development of scientific software. This approach differs from that often employed in working level quality assurance plans for software development, which is to focus on the content of the "higher level" documents (such as NNWSI SOP-03-02). This type of "upward focus" approach, although more likely to require less work, would not provide a workable and efficient plan. Higher level requirements documents often neglect or do not emphasize the most important factors of software quality.

The EQ3/6 plan has identified the two greatest problems in scientific software development: the lack of adequate documentation and the lack of adequate coding standards. The NRC (U.S. Nuclear Regulatory Commission, 1983) has called attention to the former in a very effective way, stimulating much attention to this problem in nearly all higher level requirements documents pertaining to software development in the Civilian Radioactive Waste Management (CRWM) Program. In contrast, very little attention has been paid to the issue of coding standards. The presence or adequacy of such standards can critically affect the portability of computer codes, the ability to efficiently continue development, and the frequency of errors. Adequate coding standards can also make documentation much easier.

We do not believe that a single very detailed set of standards is necessary for the entire CRWM Program. Although it may be useful to require adherence to some of the currently existing national or international language standards (e.g., FORTRAN 77). It is important to attain a level of standardization within each code or code package to achieve desirable goals of portability, efficient ongoing development, and programming error reduction. Each development group should have its own set of more detailed standards. Plan element, R19.2, specifies the coding standards to be used for the development of EQ3/6. It requires adherence to the FORTRAN 77 language standards and specifies additional standards.

The EQ3/6 Software Quality Assurance Plan provides for a matrix system of controlling and documenting code development. One "axis" of this matrix is the configuration management system, the other is the "File Folder" (FF) system. The former is built around the concept of the "controlled item," which is a computer file subject to a configuration management tracking procedure. All source codes (including auxiliary library routines), primary versions of supporting data bases, and verification libraries are treated as controlled items. A controlled item is identified by a label consisting of a name, release number, machine letter, and stage number. If a controlled item is changed by so much as one byte, the configuration management system requires that it be reflected by changing either the machine letter (appropriate only under certain conditions) or by incrementing the stage number (appropriate for the vast majority of changes). An example of a full label is "eq6.3245R22," where eq6 is the code name, 3245 is a release number, R is a machine letter, and 22 is the stage number. Computer files are normally given by a shortened label in which the period is omitted and the release number is implied as the current development version (e.g., "eq6R22").

To modify a controlled item, a developer must have both "development rights" obtained by signing out the latest exact version from a development log and "authority" obtained from a "code development file folder". Development rights are held on a very short-term basis, between signing out the most recent version and signing back in a successor. They are also exclusive- only one developer may work on a controlled item at a time. Thus, development is linear and traceable. The plan allows for branch development, but generally discourages it.

A code development file folder (CDFF) is created for each development task affecting a code or code package. This system is designed to generate a records package to complement the development logs maintained for the controlled items. These logs are created by the Task Leader, who assigns associated "authority" to one or more developers. This authority may cover more than one controlled item in a package, and is held open until the FFs are closed (i.e., the work is thought to be complete). Requirements for the CDFF include a description of pertinent requirements, designs, and changes, as well as records pertaining to verification or validation.

The plan assumes that a sequence of consecutive development efforts will be undertaken, under a given release number (release numbers in the plan, following previous tradition, are four digit and increase monotonically but not by a constant increment). A set of CDFFs is opened for each line of development, and all must be closed prior to release of that line. After closure of all ordinary CDFFs, a special CDFF called "Release Package Integration" is opened to allow coordination of final testing and closing of any loose ends. When this FF is closed, a formal peer review is to be held. If the peer review turns up any problems that must be fixed before the code package is approved for release another special CDFF called "Review Response" may be opened to authorize the needed changes. The code package is then "approved," and distributed as described above.

In addition to "Release Package Integration" and "Review Response," a number of other special CDFFs exist for each development line. A "Maintenance" FF covers routine maintenance activities during the normal time of development. A "Post-Release Maintenance" FF covers such activities after the release of an "approved" code. After release of an "approved" code, an "Error Resolution" FF is opened, which remains open until the software development task is shut down.

The FF system is designed to be highly flexible. It presumes that most scientific software is developed by the approach that is formally known as "prototyping," as opposed to that which is referred to as "structured programming." Structured programming presumes that the situation is one in which the requirements can be laid down at the start in essentially final form and the approach to meeting the requirements can be laid out largely in advance of doing the actual coding. The traditional QA approach is automatically to think of this approach when asked to deal with the software quality assurance problems of the CRWM Program. Unfortunately, it does not work well when the problem to be dealt with by the software is not very cut and dried, in terms of model/submodel adequacy, numerical methods adequacy, or both. The development of scientific software is usually much better addressed by prototyping, because it is usually the case that both model/submodel adequacy and often also numerical methods adequacy must be tested during code development, and it is often necessary for both the requirements of the work and the approach to meeting them to evolve as actual software development proceeds.

The EQ3/6 Software Quality Assurance Plan extends the FF system to cover other activities in addition to development. "Code Applications File Folders" (CAFFs) are used to document applications involving "critical calculations" that are to be used in direct support of a licensing application. Acquisition of outside codes are dealt with by "Acquisition" FFs, and subsequent evaluation by an "Evaluation" FFs. Code transfer (export) is not treated by formal FFs, although similar records packages are created. The EQ3/6 Software Quality Assurance Plan is a "form" driven system. Each entry to a FF or other records package is either on a specific form, or must be accompanied by a specific form. The system design is twofold to ensure standardization and help enforce the system.

The Task Leader is the FF manager. He is responsible for all procedures, approval of contributions, and setting priorities for code development work.

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8.0 MILESTONES AND DELIVERABLES

8.1 BWIP: In Support of WBS 1.1.3 and 1.1.2 (FY86)

Increased Pressure Capability for EQ3/6

The deliverable will be met with submission of a letter report to BWIP. This project is the modification of the EQ3/6 geochemical modeling software package for application to aqueous systems involving basalt at the BWIP site. The first activity is to modify the EQ3/6 codes and data base to incorporate pressure-corrections to the thermodynamic data. The modification will enable BWIP to model fluid speciation and fluid/rock interactions at any pressure between 1.013 and 300 bar, at temperatures between 0° and 300°C.

8.2 NNWSI: WBS 1.2.3.8.L (FY86-90)

Level II

M343 Complete Draft MCRT User's Manual

This deliverable will be met with submission of a draft manual report to WMPO-NV. The user's manual will satisfy NRC's documentation requirements for computer codes. It will contain a description of the data processing routine used in the EQ3/6 code package, and the data base files which contain the thermodynamic data and their sources.

P331 Status Report on Data Base

This deliverable will be met with submission of a letter report to WMPO-NV. This report will include progress on data base activities for FY86, and all changes and additions made to selected species will be documented. Topics that will be included are; the addition of neptunium to the EQ3/6 data base, recommendations for experimental work as a result of evaluation of data for uranium, americium and neptunium.

P330 EQ3/6 Code Release

This deliverable will be met with a formal release of the EQ3/6 Software Package. The codes and supporting data bases will satisfy NUREG-0856, NNWSI SOP-03-02, and OGR Guidance on Computer software Control requirements. The release will be by magnetic tape to WMPO-NV and the National Software Distribution Center at Argonne.

P332 Issue Revised Data Base and User's Manual

This report will be met by a formal release of the EQ3/6 Data Base. The release will be by magnetic tape with distribution to WMPO-NV and the National Software Distribution Center at Argonne. This release will be CODATA compatible and contain significant format changes. A draft data base user's manual will also be submitted that describes EQ3/6 data base procedures and methods of evaluation, and use of the direct access data base manager codes.

P333 Draft EQ3/6 User's Manual

This deliverable will be met by submission of a draft summary report to the WMPO-NV. This report will include summarizing all code options from the EQ3/6 User's Manual and supplementary reports. This report will be written for EQ3/6

P334 Issue Final Data Base

This deliverable will be met by a magnetic tape release to WMPO-NV. The data base release will include all the supporting data files and documentation.

P399 Complete Final EQ3/6 User's Manual

This deliverable will be met by submission of a summary report to the WMPO-NV. This report will include summarizing all code options from the EQ3/6 User's Manual and supplementary reports. This report will be written for EQ3/6 applications users.

Level III

C317 Complete Precipitation Kinetics Addition to EQ6

This deliverable will be met by submission of a draft report to the WMPO-NV. The report include an added code capability to model precipitation kinetics in complex systems that include nucleation. A description of the code option, input and output file modifications, and sample test cases will be included. Supplemental documentation will be included.

C319 Interim Report on Modeling Sorption with EQ3/6

This deliverable will be met by a letter report. This report will contain background data on equilibrium sorption mechanisms, the necessary theory and recommendations on the addition of selected mechanisms to the EQ6 code.

C800 Final Report on Uranium - EQ3/6 Data Base

This deliverable will be met with submission of a draft report to the WMPO-NV. The report will be prepared for UCRL distribution and will contain a critical review of the chemistry and thermodynamics of both aqueous and solid species of uranium. All species data will be compatible with the NEA critical compilation on uranium (currently in draft form). This report will summarize the final data values based on existing results and those from the EQ3/6 laboratory and sensitivity analysis program.

C395 Report on Equilibrium Sorption Modeling

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will describe the EQ6 capability to model various sorption mechanisms. A description of the code option, supporting equations and supporting data base will be included along with input and output file changes and sample problems. This document will be a supplementary EQ6 manual.

D301 Final Report on Solid Solutions Model

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will describe the EQ3/6 capabilities to handle complex mineral solid solutions. It will contain a brief outline of selected solution models that have been incorporated into the codes, examples of input and output files and sample problems. This document will be a supplementary EQ6 manual.

C393 Final Report on Variable Fugacity Model

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will describe the codes capability to model systems open to gases with variable fugacities. This capability will allow modeling of systems that contain varying amounts of gases such as unbuffered hydrothermal experiments. It will contain an outline of code changes, examples of input and output files, and example problems. This document will represent a supplementary EQ6 manual.

C801 Final Report on Americium - EQ3/6 Data Base

This deliverable will be met with submission of a draft report to the WMPO-NV. The report will be prepared for UCRL distribution and will contain a critical review of the chemistry and thermodynamics of both aqueous and solid species of americium. All data base values will be compatible with the NEA critical compilation on americium (currently in draft form). This report will summarize the final data values based existing results and those from the EQ3/6 laboratory and sensitivity analysis program.

C394 Final Report on Flow Model Extension

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will describe an extension to the EQ6 reaction path code that will allow the code to trace the chemical evolution of a packet of fluid in a dynamic system. It will contain an outline of code changes, examples of input and output files, and sample problems. This document will be a supplementary EQ6 manual.

C809 Complete Sorption Modeling

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will describe the EQ6 capability to model kinetics as well as equilibrium sorption mechanisms. A description of the code options, supporting equations and supporting data base will be included along with input and output file changes and sample problems. This document will be a supplementary EQ6 manual.

C802 Final Report on Plutonium -EQ3/6 Data Base

This deliverable will be met with submission of a draft report to the WMPO-NV. The report will be prepared for UCRL distribution and will contain a critical review of the chemistry and thermodynamics of both aqueous and solid species of plutonium. All data base values will be documented. This report will summarize the final data values based on existing results and those from the EQ3/6 laboratory and sensitivity analysis program.

C806 Interim Report on Results of Validation Studies

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will outline the experimental program that has been set up for the EQ3/6 Data Base Expansion Program. It will detail the techniques and procedures used to determine thermodynamic values. This report will mainly concern experiments in progress on the actinides, U, Am, Pu, Np.

C302 Ridge Computer system Fully Operational

Completed.

C307 Software QA Procedures

Completed.

C303 All Codes Running on the Ridge

Completed.

C304 EQ3/6 Code Release

This deliverable will be met by a letter documenting to WMPO-NV the submission of magnetic tapes to the National Software Distribution Center at Argonne and programmatic users. This release will include the Pitzer Activity Coefficient Option, the Precipitation Kinetics Option, and an improved Solid Solution Option.

C803 Final Report on Neptunium and Technetium - EQ3/6 Data Base

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will update the critical review of the chemistry and thermodynamics of technetium completed by J.A. Rard (UCRL-53440), and the NEA compilation on neptunium (currently in draft form). This report will summarize the final data values based on the above reports and those from the EQ3/6 laboratory and sensitivity analysis program.

C804 Canister Materials - EQ3/6 Data Base Report

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will outline the experimental results that have been obtained for metals important to the OCRWM Waste Package activities at the first repository projects. Experiments on these materials are designed to follow the program set up for the actinides in the EQ3/6 Data Base Expansion Program. It will detail the techniques and procedures used to determine thermodynamic values. This content of this report will depend on the canister specifications currently being formulated.

C807 *Report on Rock-Water Validation Studies*

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will contain results of EQ3/6 runs in rock-water systems. It will summarize the validation of common rock-water systems from peer reviewed experimental systems existing in the literature. Most rock-water systems can be validated without additional experimental measurements. Any gaps or inconsistencies will be recommended for investigation by the EQ3/6 Data Base Laboratory Program. All results will be summarized in the Final Report on Validation Studies.

C805 Complete Laboratory Measurements on Less Abundant Radionuclides

This deliverable will be met with submission of a draft report to the WMPO-NV. This report will outline the experimental results that have been obtained for radionuclides with allowed release rates set by 0.1% of the calculated release rate limit (see Oversby, 1986). It will use the same techniques and procedures used to determine thermodynamic values set up for the actinides in the EQ3/6 Data Base Expansion Program.

C808 Final Report on Validation Studies

This deliverable will be met by submission of a draft report to the WMPO-NV. This report will summarize the validation of the EQ3/6 code for the actinides, less abundant radionuclides, canister materials and rock-water systems. It will contain sample input and output files and satisfy requirements set forth in the EQ3/6 QA Plan (Draft date 2/14/86).

8.3 ONWI: In Support of WBS 1.2.3 (FY86-87)

Activity Coefficients I(2)

A paper has been submitted to the American Journal of Science entitled: "Activity Coefficients in Aqueous Salt Solutions. I. The Ion Size Problem." The primary purpose of this paper was to document the ion size averaging technique which we have already built into the hydration theory equations and to compare this technique with the treatment of ion size parameters in other activity coefficient equations. A discussion of the requirements of thermodynamic consistency was included as was an introduction to improvements on the equations of Helgeson et al. (1981)* in ternary (as well as more compositionally complex) aqueous solutions.

Pitzer Coefficient Data Update(3)

The versions of the Pitzer data files currently used by EQ3/6 need to be updated to include data which have become available subsequent to Pitzer's (1979) compilation on which they are based. The updated versions of the Pitzer data files contain both updated values for aqueous species in previous released versions of the data files and data for species not previously included in them.

Code Release(4)

A magnetic tape containing a new version of the EQ3/6 package released. This release includes all the codes in the package and features the capability to do calculations using Pitzer's equations at 25°C. The code release is accompanied by current versions of the appropriate data files.

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* The equations used by Helgeson et al. (1981) to calculate the activity coefficients of dissolved species in aqueous solutions are collectively referred to in this report as the "Part IV" equations.

Thermodynamics of Solutions(5)

An article submitted to the American Journal of Science tentatively entitled "On the Thermodynamics of Solutions." This paper develops many of the fundamental thermodynamic equations, definitions and relationships which will be used in the subsequent papers in this series (e.g., Milestones #2, 17, 18 and 19).

Pitzer Term Tabulation Option(6)

This project entails modification of the subroutine in EQLIB which reads the Pitzer interaction coefficients from the DATA1 and DATA2 files. The modification is designed to tally the number of interaction coefficients loaded into the EQ3NR and EQ6 codes from the data files for each of the aqueous species present in the model. The modified subroutine will generate information to be written onto the OUTPUT file and will be activated by turning on a print option switch. The principle use of this new option will be to help in evaluating whether or not a particular species is adequately represented by the interaction coefficients in the data files. It should serve to prevent accidental misuse of the Pitzer activity coefficient option. The culmination of this project will be documented in a letter report submitted to ONWI.

pH in Brines(7)

A letter report entitled "Approaches to Dealing with pH in Brines." This letter report covers two milestones delayed from FY85. One covers the methodology for measuring pH in brines (the pHCl and mineral saturometry methods). The other takes care of activity coefficient scale conversions (equivalent to pH scales).

Construction of EQ3/6 Subroutines to Evaluate the Part IV Activity Coefficient Expressions(8)

The Part IV activity coefficient expression offers an alternative to the hydration theory option and Pitzer's equations for calculating activity coefficients in relatively concentrated aqueous solutions. In addition, the Part IV equations can be used at elevated temperatures for a wide variety of aqueous species. The new subroutines will take advantage of the Part IV equations corrected to account for variable ion sizes as described in the "ion size paper" (Milestone #2). A progress report on the new subroutines written to evaluate the Part IV expressions will document the completion of this milestone.

Brine Modifications II(9)

A draft version of a UCRL report which will be forwarded to ONWI is tentatively entitled "EQ3/6 Modifications for Geochemical Modeling of Brines. II. Hydration Theory Equations." This code document will represent an extension of a portion of the information contained in an earlier letter report to ONWI by K. Jackson and T. Wolery entitled "Hydration Theory Modifications to the EQ3/6 Geochemical Modeling Code: Verification and Validation Studies." This will be a supplementary user's guide for the EQ3/6 codes.

Activity Coefficients II(10)

A journal article entitled "Activity Coefficients in Aqueous Salt Solutions. II. Hydration Theory Models for Electrolyte Solutions" will be submitted to document this milestone. The scope of this paper will be to evaluate the hydration theory model for aqueous activity coefficients at 25°C. This report will expand on some of the principles mentioned briefly in an earlier letter report to ONWI ("Hydration Theory Modifications to the EQ3/6 Geochemical Modeling Code: Verification and Validation Studies") by K. Jackson and T. Wolery.

Compilation of Data Files for the Part IV Equations(11)

This project is comprised of two steps. The first is the assembly of data files containing the appropriate coefficients for use in evaluating the Part IV activity coefficient equations. (These data will have to be manipulated to make it compatible with the form of the equations which will be used by the EQ3/6 codes.) The second step involves modifications to the EQ3/6 codes so they can read these data.

Data Base Update(12)

A magnetic tape release containing updated versions of all of the thermodynamic data files which support EQ3/6 calculations and the new data base pre-processing codes will be forwarded to ONWI. This data base update will be consistent with the work of the EQ3/6 data base effort funded by the Nevada Nuclear Waste Storage Investigation (NNWSI) and will represent a major upgrade of the current data base. Included in this effort is a plan to ensure CODATA compatibility and internal consistency for the thermodynamic parameters.

pH Options in EQ3/6(13)

A code document ("EQ3/6 Options for Dealing with pH and Related Quantities") will be submitted to ONWI which will detail the installation and use of the various pH options available in the EQ3/6 code package. This document is closely related to (and dependant upon) the more theoretically oriented paper which comprises Milestone #5, but concentrates more on the ways in which pH is computed by EQ3NR and EQ6 and details how each of these options is evoked.

Preliminary Analysis of Salton Sea Data Package from University of California, Riverside (UCR)(14)

Contingent on receiving a set of data from UCR, and in conjunction with P. Cloke of ONWI and A. Williams of UCR, the suitability of the Salton Sea Geothermal Field data for use in validation exercises for the EQ3/6 geochemical modeling codes and as natural analog for waste disposal in a salt repository will be evaluated. Completion of this milestone will be documented in a letter report submitted to ONWI.

Code Release(15)

A magnetic tape release containing a new version of the EQ3/6 code package which will have the capability to calculate activity coefficients in high ionic strength solutions at elevated temperatures (up to about 300°C) using the hydration theory option. This code release will be accompanied by current versions of the EQ3/6 data files which will contain a preliminary hydration theory data set.

Installation of the Part IV Routines into EQ3/6(16)

The subroutines described in the letter report which constitutes Milestone #6 will be installed in the EQ3NR and EQ6 codes. This progress report will document the code modifications necessary to install the Part IV capabilities and outline how to use this EQ3/6 activity coefficient option. Preliminary results of runs used to verify this activity coefficient option will be included as will an analysis of how results from these equations compare with results calculated using other EQ3/6 activity coefficient options.

Activity Coefficients III(17)*

A draft version of a journal article tentatively entitled "Activity Coefficients in Aqueous Salt Solutions. III. Extension of Hydration Theory Models to High Temperatures," by K. Jackson and T. Wolery will be submitted to ONWI to document this milestone. This paper represents the culmination of a series of articles detailing the theoretical development of the hydration theory equations for calculating aqueous activity coefficients and documents the ability of these equations to be extended to high temperatures along the liquid vapor saturation curve for water.

Analysis of Salton Sea Data Package from University of California, Riverside (UCR)(18)

This milestone represents the second of two scheduled studies of data collected by the UCR group at the Salton Sea Geothermal Field. As with the first analysis in this series, the work will be performed in conjuction with P. Cloke of ONWI and A. Williams of UCR and will concentrate on the potential use of Salton Sea data for validation of the EQ3/6 ability to model geochemical reactions involving brines at elevated temperatures. This deliverable will be documented in a letter report to ONWI.

Part IV Verification and Validation(19)

A letter report submitted to ONWI will document verification studies for the Part IV activity coefficient option in EQ3/6. Discussion of modeling runs intended to partially validate this option will also be included.

Brine Modification III(20)

A supplementary user's guide for the addition of the Part IV equations to EQ3/6 will be submitted to ONWI in the form of a draft version of a UCRL report. This report will contain detailed instructions for the use of the Part IV activity coefficient option in EQ3/6 as well as documentation for the code changes involved in their implementation.

Part IV Code Release(21)

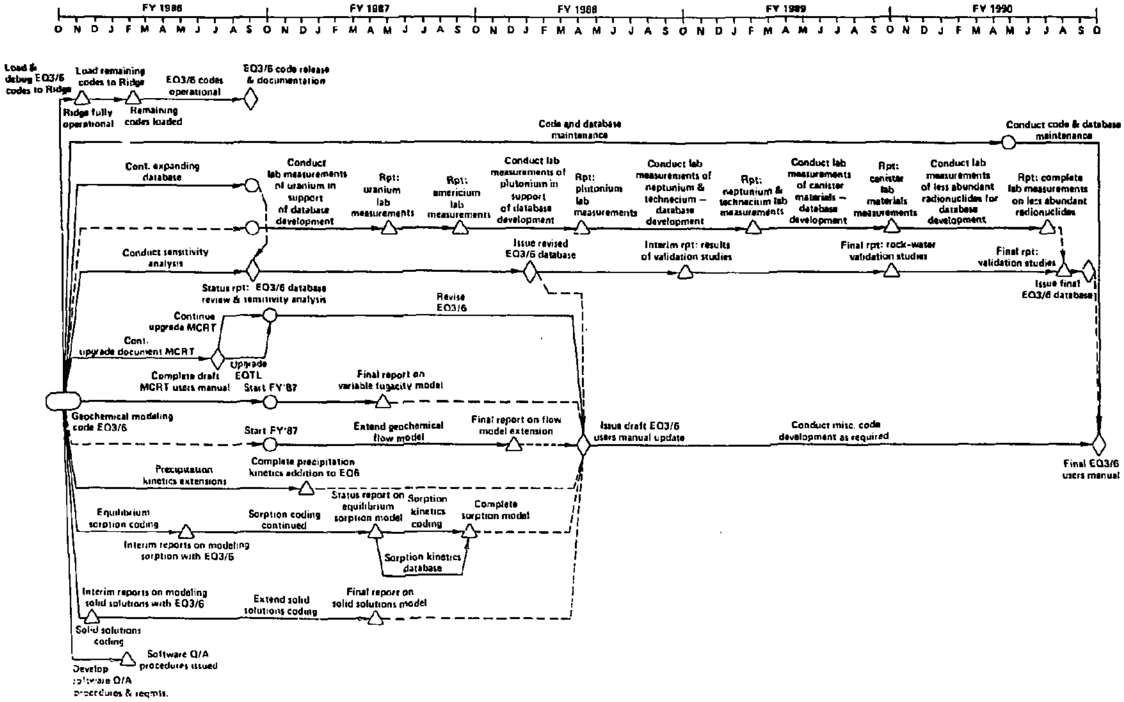
A magnetic tape containing a new version of the EQ3NR and EQ6 codes will be forwarded to ONWI. These code versions will include the capability to use the Part IV equations to calculate activity coefficients and will be accompanied by the appropriate date files.

Redox Disequilibria(22)

A letter report will document the code modifications necessary to allow EQ6 to maintain the redox pairs in solution in a disequilibrium state. These code modifications will be consistent with the EQ3NR capabilities to model aqueous solutions which are not in chemical equilibrium with respect to redox reactions.

APPENDIX A1 NETWORK CHART

NNWSI NETWORK FOR WBS 1.2.3.8.L



ONWI NETWORK FOR FY86-87