

NUREG/CP-0062  
ORNL/TM-9585

Proceedings of the

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# Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment

Held at  
Oak Ridge, Tennessee  
October 2-5, 1984

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Edited by: G. K. Jacobs and S. K. Whatley

Sponsored by  
Office of Nuclear Material Safety and Safeguards  
U.S. Nuclear Regulatory Commission

Oak Ridge National Laboratory

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B506130505 B50531  
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CP-0062 R PDR

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Manuscript Completed: February 1985  
Date Published: May 1985

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**U.S. Nuclear Regulatory Commission**  
**Washington, D.C. 20555**

**Oak Ridge National Laboratory**  
**Oak Ridge, TN 37831**

Proceedings prepared by  
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## ABSTRACT

A conference on the application of geochemical models in the assessment of high-level nuclear waste repositories was held to discuss the current status of geochemical code development, thermodynamic data bases, reaction kinetics, and coupled-process models as applied to site characterization and performance assessment activities. These proceedings include extended abstracts of the technical presentations given at the conference, a discussion of the role of geochemical modeling in predicting the performance of repositories, and a set of recommendations that identify the key developments needed in order for geochemical models to become more applicable for quantitative evaluations of repositories. Detailed recommendations relevant to the following subjects are discussed: (1) improved simulation of repository performance through inclusion of additional important geochemical processes and parameters into current geochemical models, (2) more careful attention to uncertainties associated with geochemical model calculations, (3) assigning priorities to (through sensitivity studies and critical evaluations) and then improving and/or obtaining important thermodynamic data, and (4) addressing the importance of kinetics in simulating repository behavior.

## PREFACE

Geochemical models (e.g., solubility/speciation, reaction path, coupled reaction/transport, hydrothermal chemistry) will be useful in determining if high-level radioactive waste can be safely isolated in deep geologic formations, and if such a repository can be shown to meet or exceed all the technical criteria and performance objectives set forth in current regulations. Therefore, a conference was sponsored by the Oak Ridge National Laboratory and the U.S. Nuclear Regulatory Commission to discuss the application of geochemical models in the assessment of the safety and performance of repositories. The purpose of this conference was to summarize and discuss the status of geochemical code development, thermodynamic data bases, reaction kinetics, coupled-process models, and the application of geochemical models in high-level nuclear waste repository site characterization and performance assessment activities. The goal of this conference was to develop a consensus, to the extent possible, on the capabilities and limitations of geochemical models.

The conference consisted of five sessions, each devoted to a topic of importance to geochemical modeling. The sessions and corresponding chairpersons are listed below:

- Session I:       Solution Chemistry: Theory, Code Development, and Non-Repository Applications - H. L. Barnes, The Pennsylvania State University
- Session II:       Thermodynamic Data - G. R. Choppin, Florida State University and R. J. Silva, Lawrence Berkeley Laboratory
- Session III:      Kinetics and Coupled Processes - P. Ortoleva, Indiana University and Geochem Research Associates, Inc.
- Session IV:       Applications of Geochemical Models - A. C. Lasaga, Yale University
- Session V:        Summary and Conclusions - G. K. Jacobs, Oak Ridge National Laboratory

Chapter 1 of these proceedings introduces the problem of high-level nuclear waste (HLW) isolation and then provides a brief discussion of disposal concepts, regulations, and geochemical models. Chapters 2 and 3 summarize the results of debate during the conference, especially during Session V, and are based on the presentation and discussion of ideas related to two questions posed at the beginning of the conference. The recommendations in these two chapters were prepared by the editors, with the invaluable help of the chairpersons. The speakers reviewed the recommendations to help ensure that the views expressed during the conference are fairly represented. Chapter 2 presents a discussion of the

role that geochemical models should play in evaluating the geochemical processes important to the performance of a HLW repository. Chapter 3 presents recommendations concerning the application and development of geochemical models, thermodynamic data, and kinetics and coupled processes. Chapter 3 also presents some general recommendations related to the implementation of the technical recommendations.

Chapters 4 through 7 include extended abstracts of presentations given during the conference. The purpose of Session I (Chapter 4) was to discuss currently available geochemical codes and some theoretical aspects of thermodynamic calculations. The codes PHREEQE, MINTEQ, and EQ3/EQ6 were chosen for detailed discussion because they are presently most widely used for high-level waste applications within the repository projects of the Department of Energy. Session II (Chapter 5) emphasized the state of thermodynamic data bases used to support geochemical calculations. Session III (Chapter 6) addressed the increasingly important consideration of coupling thermodynamics, fluid flow, and reaction kinetics in order to more appropriately model the geochemical processes important to repository systems. Session IV (Chapter 7) provided the opportunity for individuals from repository projects of the United States and Canada to give examples of, and plans for, the use of geochemical models in characterizing the geology, geochemistry, and hydrology of candidate repository sites, evaluating geochemical processes within the repository system, and assessing the potential performance of the disposal system.

We hope that the reader finds these proceedings a useful overview of the role geochemical modeling could play in evaluating the safety and performance of high-level radioactive waste repositories. Although a single set of recommendations are presented, it should be noted that with approximately 75 scientists in attendance at the conference, complete consensus was achieved on few topics. Diverse viewpoints in many of the technical recommendations is to be expected from the geochemical community, because rarely is there only one correct solution to any problem with a degree of complexity similar to that of waste disposal. Therefore, the technical recommendations discussed in these proceedings represent an initial step in the development of a technical consensus among scientific experts.

Technical problems involved in waste disposal are complex, and the potential for inadvertent errors is great. The repercussions from such errors are not entirely known at this time. Therefore, care should be taken to not overlook or avoid tough technical questions just because data are not available, time is short, or it is not perceived (currently) as a problem. The development and application of geochemical models to repository assessments is a basic issue which must be properly addressed prior to the permanent disposal of high-level radioactive waste.

Gary K. Jacobs  
Susan K. Whatley

## ACKNOWLEDGMENTS

We would like to express our thanks to the chairpersons H. L. Barnes, G. R. Choppin, A. C. Lasaga, P. Ortoleva, and R. J. Silva, who helped run the conference and pull together the recommendations resulting from the discussions during the week. We thank the speakers who graciously took the time to present information at the conference and prepare written summaries for the proceedings. Special thanks go to L. N. Plummer and J. L. Haas, Jr. of the U.S. Geological Survey who, although not able to attend the conference, nevertheless kindly prepared written papers. The chairpersons, speakers, and participants are thanked for their contributions to the conference through stimulating discussion and debate — without this, the conference would have been of little consequence. The chairpersons and speakers provided reviews of the proceedings to help ensure that the recommendations are consistent and fair in presenting views expressed during the conference; however, the editors assume full responsibility for the final version. M. J. Apted and D. Melchior provided particularly thorough and helpful reviews and we thank them for their efforts. K. J. Kitts, A. R. Calhoun, and B. S. Reesor were indispensable in helping with organizational details of the conference. K. J. Kitts patiently helped with the preparation of the proceedings and C. H. Shappert provided editorial assistance.

## CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	iii
PREFACE . . . . .	v
ACKNOWLEDGMENTS . . . . .	vii
1. INTRODUCTION . . . . .	1
1.1 BACKGROUND . . . . .	1
1.2 PURPOSE . . . . .	4
1.3 REFERENCES . . . . .	5
2. ROLE OF GEOCHEMICAL MODELS . . . . .	6
2.1 APPLICATIONS OF GEOCHEMICAL MODELS . . . . .	7
2.1.1 Sensitivity Studies . . . . .	8
2.1.2 Data Interpretations . . . . .	9
2.1.3 Predictions of Performance . . . . .	9
2.2 REFERENCES . . . . .	9
3. RECOMMENDATIONS . . . . .	13
3.1 APPLICATIONS AND PROCESSES . . . . .	13
3.2 THEORY AND CODE DEVELOPMENT . . . . .	14
3.3 THERMODYNAMIC DATA . . . . .	19
3.4 KINETICS AND COUPLED PROCESSES . . . . .	20
3.5 GENERAL RECOMMENDATIONS . . . . .	22
3.6 REFERENCES . . . . .	23

### CONFERENCE PROCEEDINGS

4. SOLUTION CHEMISTRY: THEORY, CODE DEVELOPMENT, AND NON-REPOSITORY APPLICATIONS . . . . .	27
Thermodynamic Problems in Speciation Modeling . . . . . H. L. Barnes	29
Prediction of Mineral Solubilities and Diagenesis in Rock/Water Association at High-Temperature . . . . . N. Møller, J. H. Weare, and J. Greenberg	31
PHREEQE: Status and Applications . . . . . L. N. Plummer and D. L. Parkhurst	37
MINTEQ Geochemical Reaction Code: Status and Applications . . . . . K. M. Krupka and J. R. Morrey	46

	<u>Page</u>
EQ3/6: Status and Applications . . . . .	54
T. J. Wolery, D. J. Isherwood, K. J. Jackson, J. M. Delany, and I. Puigdomenech	
5. THERMODYNAMIC DATA . . . . .	67
Complexes of Actinides with Naturally Occurring Organic Compounds . . . . .	69
G. R. Choppin	
Determination of Stability Constants of the Carbonate Complexes of Uranium and Neptunium . . . . .	72
L. Maya	
Temperature Dependence of Actinide Solubilities and Speciation . . . . .	74
R. J. Silva	
Neptunium and Technetium Behavior in Geologic Systems . .	77
R. E. Meyer, A. D. Kelmers, W. D. Arnold, J. S. Johnson, J. H. Kessler, R. J. Clark, G. C. Young, F. I. Case, and C. G. Westmoreland	
Thermodynamic Properties of Geologic Materials: Status and Future . . . . .	81
J. L. Haas, Jr.	
6.0 KINETICS AND COUPLED PROCESSES . . . . .	85
Modeling Water/Rock Interactions . . . . .	87
P. Ortoleva	
Coupled Geochemical and Solute Transport Code Development . . . . .	90
J. R. Morrey and C. J. Hostetler	
Flow/Reaction Models of Natural Systems . . . . .	93
C. H. Moore	
Dissolution and Precipitation Kinetics of Minerals . . . . .	96
A. C. Lasaga	

	<u>Page</u>
7. APPLICATIONS OF GEOCHEMICAL MODELS . . . . .	99
CANADIAN PROGRAM:	
Applications of Geochemical Modeling in the Canadian Program . . . . .	101
N. C. Garisto	
BASALT WASTE ISOLATION PROJECT:	
Applications of Geochemical Modeling to High-Level Nuclear Waste Disposal at the Hanford Site, Washington. . . . .	104
T. O. Early, J. Myers, and E. A. Jenne	
NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS PROJECT:	
Matrix Diffusion Coefficients for the NNWSI Waste Package Environment . . . . .	109
K. G. Eggert and M. A. Revelli	
Applications of Geochemical Modeling to Site Characterization and Radionuclide Transport in the NNWSI Project . . . . .	111
J. F. Kerrisk	
OFFICE OF NUCLEAR WASTE ISOLATION PROJECT:	
Chemical Modeling of Nuclear Waste Repositories in the Salt Repository Project . . . . .	113
G. Jansen, G. E. Raines, J. F. Kircher, and N. Hubbard	
Ion-Interaction Modeling of Deep Brines, Palo Duro Basin . . . . .	115
D. Melchior and N. Hubbard	
8. LIST OF PARTICIPANTS . . . . .	117

PROCEEDINGS OF THE CONFERENCE ON THE APPLICATION OF GEOCHEMICAL  
MODELS TO HIGH-LEVEL NUCLEAR WASTE REPOSITORY ASSESSMENT

G. K. Jacobs  
S. K. Whatley

1. INTRODUCTION

1.1 BACKGROUND

The disposal of high-level radioactive waste is a complex issue involving science, engineering, economics, and sociology. The waste products from past and future activities must be properly isolated from the environment to protect the health and welfare of the human population as well as our natural habitats. The option of "no action" is clearly not acceptable because the temporary storage techniques in use today are not feasible for continued long-term containment and isolation. More sophisticated surface storage techniques could be developed that could isolate the waste for time periods of 50 to 100 years. Thus, the current situation is not so desperate that an accelerated program designed to meet arbitrary deadlines, in some cases established by legislation, is the only solution. It is an unavoidable fact that a premature decision could be regrettable for thousands of years. Therefore, the information necessary to properly evaluate and predict the safety and performance of a waste repository should be developed by addressing technical and social problems in a manner such that issues of unproven or unknown impact will not be overlooked simply because data may not exist or may be difficult to obtain.

The current concept for the disposal of high-level radioactive waste (HLW)\* in the United States is that of containment and isolation in deep geologic formations, utilizing a combination of natural and engineered barriers. A typical repository system may include a waste form contained within one or more metallic or ceramic canisters, packing material (crushed rock, clay) around the canister, and backfill (crushed rock) and seal materials (cement, compacted clay) to fill and seal off the drifts and shafts created during the construction and operation of the repository. These engineered barriers are placed within a geologic setting that may possess several barriers itself (e.g., location above deep water table, impermeable rock layers, favorable geochemistry for precipitation and/or sorption of radionuclides, slow groundwater velocities). The concept of a deep geologic repository, and some of its variations, has been previously described (1-5), and the reader is referred to these articles for additional details.

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\*For the purpose of these proceedings, HLW is intended to include both spent fuel and the high-level radioactive waste from the reprocessing of spent fuel.

The philosophy of the multiple-barrier approach is to have a system in which each barrier contributes significantly to the overall performance of the repository in an independent manner. In this way, the likelihood of a catastrophic failure of the repository system will be reduced, because if one barrier fails, others of a different type could still function to some degree. Because of the long time (thousands of years) required to reduce the hazards from HLW to an acceptable level, predictions of performance will be somewhat uncertain. Therefore, utilizing several different barriers can provide for added confidence in the performance of the system. Two examples of how natural geologic barriers and engineered components may be combined to achieve a desirable allocation of performance are discussed by Deju et al. (6) and Smith et al. (7).

Ultimately, a repository must limit the rate, concentration, and accumulation of radionuclides released to the accessible environment to an acceptable level, because absolute containment for thousands of years cannot be guaranteed. Although many complex interactions are involved, hydrologic and geochemical processes will dominate the control of the timing, rate, and quantity of radionuclides released from a repository. Bird and Fyfe (2) describe some of the geologic considerations involved in assessing the behavior of a repository system. Geochemical factors are important in the selection of materials for waste forms, canisters, packing, and backfill, and in selecting a site for a repository. Confident predictions of the long-term performance of a repository, including the corrosion of canisters, the dissolution of waste forms, and the interactions of radionuclide-contaminated groundwater with engineered materials and host rocks, require a significant understanding of geochemical processes and conditions in this system.

The National Waste Policy Act of 1982 (Public Law 97-425) specifies that the U.S. Department of Energy (DOE), the U.S. Nuclear Regulatory Commission (NRC), and the U.S. Environmental Protection Agency (EPA) are responsible for conducting the activities necessary to implement the siting, construction, and eventual operation of a HLW repository in the United States by the year 1998. The EPA has established a set of draft environmental standards (8) that define limits for the cumulative release of radionuclides to the accessible environment for a period of 10,000 years. The NRC is responsible for ensuring that the EPA standards are met. To help provide confidence that a repository system will meet the EPA standards, the NRC has established additional performance objectives for a repository (9). These objectives are (for precise wording and definition of terms, see reference 9): (1) substantial containment of radionuclides within the waste packages for a period of time no less than 300 to 1,000 years, (2) a rate of release of individual radionuclides from engineered barrier system no greater than  $10^{-5}$  per year of the inventory of the radionuclide calculated to be present at 1,000 years after disposal, and (3) a pre-waste-emplacement groundwater travel time from the disturbed zone around a repository to the accessible environment of at least 1,000 years. The DOE has the responsibility to develop the information and technology necessary to site, license, construct, and operate the repository. The schedule set forth

in the National Waste Policy Act requires that most research and development (R&D) be completed by approximately 1988 so that an application for a license can be submitted to the NRC. Complete information may not be required at this time because the initial authorization will only be to begin construction of a repository; another authorization from the NRC will be required to begin actual operation of the repository and the emplacement of waste.

To focus on more specific technical items related to the performance objectives listed above, the NRC has developed a set of "issues" that, when resolved, will help ensure that the performance objectives are met and that a repository can be licensed. Three geochemical issues have been identified that relate to the nature of geochemical processes and conditions in and around the repository during three periods of repository history:

1. What are the present geochemical conditions?
2. What are the changes in the geochemical conditions/processes as a result of waste emplacement?
3. What are the future geochemical processes/conditions that will affect release and transport of radionuclides to the accessible environment?

Geochemical processes can represent a significant barrier to the release of radionuclides. Thus, it is desirable to establish an understanding of geochemical conditions prior to, during, and after waste emplacement. This information will be helpful in evaluating the effects of repository construction, operation, and waste emplacement on the geochemical conditions. An assessment can be made of the containment, release, and transport of radionuclides from the waste packages through the repository host rock to the accessible environment.

Geochemical models can be used to interpret and predict chemical relationships in geologic systems and, therefore, will be of substantial use in analyzing the geochemical processes important to the performance of HLW repositories. Many types of geochemical models are available which have the ability to calculate some or all of the following: (1) aqueous speciation, (2) saturation indices, (3) mass transfer, (4) reaction paths, (5) sorption reactions, (6) reaction kinetics, and (7) groundwater flow, coupled with one or more of the above geochemical processes. Specific geochemical models have individual capabilities that make them useful for one application or another. For a brief review of geochemical models and some of their applications and limitations, see Jenne (10, 11).

The term "geochemical model" has been generally adopted to refer to computer codes that perform the geochemical calculations listed above. However, "geochemical model" is a somewhat misleading term. A geochemical model is really composed of three parts: (1) a model, (2) a computer

code, and (3) a data base. The model consists of mathematical representations of the physical, chemical, geological, thermodynamic, and kinetic concepts that provide the basis for the calculations. Each computer code contains algorithms required to obtain quantitative solutions to the model. A data base for a geochemical model can include several types of data depending on the nature of the model: fundamental thermodynamic properties, kinetic rate law expressions and constants, empirical relationships, chemical information about the system of interest, and hydrologic parameters. Because the term "geochemical model" is currently in wide use, and by precedent refers to calculations utilizing the three components discussed above, "geochemical model" continues to be used throughout these proceedings referring to any calculational methodology involved in the simulation of physical and chemical processes important to the evaluation of a geologic system.

## 1.2 PURPOSE

It is sometimes stated that the disposal of HLW is not a technical problem, but rather a sociopolitical issue, and that adequate technology to dispose of the waste currently exists. There is no question that the technology exists to manufacture waste packages and to emplace them in deep geologic formations. However, a more pressing issue is whether the information and technology exists to predict, with reasonable assurance, that the emplaced waste will be contained and isolated to an acceptable level after operation of the repository is completed. The National Academy of Sciences (1) has concluded that current technology is sufficient to proceed with the program of geologic repositories for HLW. Even though it is likely that a geologic repository for HLW will be successful, the Academy states that final decisions must await at-depth characterization and testing of actual sites.

Predicting the behavior of a complex system of geologic and engineered materials for 10,000 years is unprecedented. In the past few years considerable progress has been made in addressing some of the geochemical processes important to the long-term performance of HLW repositories through experimental and theoretical studies. However, it is not clear that the current U.S. schedule will successfully provide all the necessary information in a timely manner. The recommendations from this conference are intended to be used to help elucidate some key geochemical items that may require more careful consideration than previously given.

The focus of the conference was confined to the application of geochemical models to HLW repository assessments. The scope of the resulting recommendations is purposely limited, and there are R&D areas (e.g., tectonics, hydrology, meteorology, climatology, and metallurgy) important to HLW isolation that are not addressed. These omissions are regrettable but, hopefully, can be addressed by other conferences. Priorities were not assigned to the recommendations because this was beyond the scope of the conference. General recommendations related to the management and funding of the technical recommendations are included because, within the directives of current programs in the

U.S., there appears to be little fiscal support of the type of studies required. Implementation of some of the more important recommendations contained in these proceedings should aid in establishing an understanding of geochemical processes important to the performance of a repository. Such an understanding is essential to reduce uncertainties and increase the level of confidence in the predictions of safety for a repository.

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## 2. ROLE OF GEOCHEMICAL MODELS

**What role should geochemical modeling play in characterizing and understanding the nature and performance of high-level radioactive waste repositories?**

There was a general consensus at the conference that modeling the geochemical behavior of a HLW repository is an essential part of estimating the overall safety and performance of the system as a function of time. This conclusion resulted from the recognition that there is no viable alternative to numerical simulation of geochemical processes important to repository performance. It is not possible to adequately assess the geochemical behavior of a repository system through laboratory and/or field techniques alone. In attempting to scale down mass transport processes important to a repository, there is an unavoidable loss of similitude between a system of geologic proportions in space and time and short-term laboratory, bench, or field tests. Parameters such as porosity, thermal gradients, permeability, grain size, thermal conductivity, and, perhaps most importantly, time, are not always amenable to changes in scale that would allow processes to be accelerated so that meaningful results can be obtained within a reasonable period of time (e.g., weeks to months). Therefore, numerical simulation of geochemical and mass transport processes, in conjunction with careful experimental and field observations, is probably the only means available to estimate the geochemical behavior of a repository system for time periods of thousands of years.

In the preceding paragraph the phrase "to estimate" was used rather than "to establish." This distinction is important because uncertainties will always be present in assessing geochemical processes important to a repository. It is not possible to explicitly account for all facets of geochemical behavior. Rather, it is necessary to accept a philosophy of trying to achieve a "best-guess" estimate that can be shown to be reasonable and not overly optimistic. The oft-cited philosophy of using "conservative" estimates does not necessarily relax requirements on the amount and/or quality of information necessary to describe the geochemistry, because establishing conservatism presumes a certain level of understanding of the processes and mechanisms involved. Otherwise, one would not know whether a value is conservative or not.

Modeling geochemical processes important to the performance of a HLW repository involves extrapolation from small-scale, short-term laboratory and field tests to full-scale, long-term geologic behavior. Extrapolation outside the limits of existing data can be unpredictable and uncertain, as well as completely meaningless in physical terms, unless the method and assumptions of the extrapolation are fundamentally sound.

For example, arbitrary polynomials, useful for interpolating P-V-T data of gases, can be unreliable for extrapolating beyond the range of measured values because of their lack of a fundamental thermodynamic basis (1). Acceptable extrapolations involve establishing a conceptual framework for the parameter or process of interest and obtaining enough

data so that the fundamentals of the theory can be validated. For example, an arbitrary five-term polynomial can provide an excellent fit to high-temperature (>25°C) heat capacity data, thereby retaining the accuracy and precision of calorimetric methods in the equation (2 and 3). However, using this equation beyond available heat capacity data can result in extrapolations that violate fundamental thermodynamic principles. Therefore, a more appropriate approach might be to use the five-term polynomial only within the region where data exists, and to use an equation that can be constrained to obey thermodynamic precepts governing the behavior of heat capacity as a function of temperature (4) for extrapolations beyond the limit of existing data (5). In an analogous manner, geochemical processes and parameters important to a HLW repository need to be described by fundamental concepts appropriate for reproducing data as well as for making physically meaningful extrapolations constrained by some estimated amount of uncertainty.

There are many examples in the geologic literature of studies that have successfully combined fundamental data and modeling calculations to evaluate the behavior of natural systems (e.g., 6-11). Although all parameters and mechanisms are not always explicitly established, significant information can be obtained through careful data collection, experimentation, theoretical calculations, and comparison to natural systems. An obvious difference between most geologic studies such as these and the problem of HLW isolation is that there is no repository in existence today that model predictions can be tested against. Therefore, pure prediction, as opposed to interpretation and comparison, will be required for repository simulations. Because of the necessary reliance on predictions and long-term extrapolations, the importance of establishing sound conceptual models and theoretical frameworks for the evaluation of geochemical processes important to HLW repositories cannot be stressed strongly enough.

## 2.1 APPLICATIONS OF GEOCHEMICAL MODELS

Geochemical models can be useful in addressing each of the three issues listed previously in the Introduction. For example, geochemical models can aid in elucidating the nature of, and possible controls on, the geochemical conditions in the undisturbed geologic setting. Parameters and characteristics that can be included in such evaluations include: temperature, pressure, groundwater chemistry, pH, redox potential, and mineralogy of the host rocks. Examples of such studies (not limited to waste isolation) include reference (8) and references (12) through (20).

Emplacement of HLW into a geologic repository can substantially affect the pre-emplacment geochemical conditions. Therefore, the use of geochemical models to help evaluate these potential changes seems imperative because a comprehensive set of experiments is not possible. Important considerations include: (1) physicochemical interactions between heated groundwaters, host rocks, and engineered materials; (2) radiation damage to solids; (3) radiolysis of groundwaters; and (4) residual effects of repository construction (e.g., introduction of air, bacteria, organic material, etc.). Studies in this area are not abundant, as much of the work is just under way. Wolery and Delaney (21)

have modeled high-temperature (90 to 150°C) water-rock interactions pertinent to the candidate repository site at the Nevada Test Site. Neretnieks (22) has addressed the possible movement of a redox front as a result of migrating  $H_2O_2$  formed via alpha radiolysis. Modeling of rock-water systems at elevated temperatures is common within the geologic literature (6, 23-26).

The eventual release and transport of radionuclides is also amenable to geochemical modeling calculations, provided that the necessary supporting data are available. Consideration needs to be given to the alteration (corrosion) of engineered materials (packing, backfill, and metals) and the mobility of radionuclides during and after the time period of release of radionuclides from the failed waste packages. Simulations of processes such as these have been rather simplistic to date and have concentrated primarily on calculating possible solubility controls for radionuclides (e.g., 27-31), although Wolery (32) has modeled the co-dissolution of  $UO_2$  and copper (as an analog for copper canisters). Calculations such as these serve to illustrate the utility of geochemical models.

#### 2.1.1 Sensitivity Studies

When operated in a sensitivity mode, geochemical models can be used to help identify deficiencies in conceptual models, data, and analytical techniques. For example, the impact of uncertainties in the stability constants for aqueous complexes of radionuclides on the solubility of a radionuclide-bearing phase can be investigated (33). This is not to say, however, that sensitivity studies can replace scoping experiments. It is important to recognize that, for a sensitivity study to have any meaning at all, there must at least be estimated data available for all potentially important complexes. Sensitivity studies can also be used to help identify areas of improvement for site characterization activities. For example, if low concentrations of a complexing agent can significantly increase the solubility of some radionuclide-bearing phase, then research into improved detection limits, precision, and accuracy of analytical techniques for measuring the presence of this chemical constituent would be warranted (33). Early et al. (34) discuss how modeling studies aid in identifying solid phases that could require special attention during the characterization of host rocks, because they are calculated to be possible solubility controls for the groundwater and could be important for the sorption of radionuclides. The importance of relative rates of dissolution, precipitation, and sorption can be evaluated and used to help establish priorities for detailed experimentation. Sensitivity studies can also be used to evaluate alternative conceptual models and, thus, avoid problems that stem from preconceived notions about the behavior and performance of a repository system. Sensitivity studies can also be useful for evaluating potential effects of coupled processes which may require additional attention. For example, Ortoleva (35) has pointed out that potential chemical instabilities, which are found in laboratory experiments and natural occurrences, may be inadvertently missed if sensitivity studies using coupled chemical reaction/transport models are not performed.

### 2.1.2 Data Interpretations

Data interpretation is probably the most widely used application of geochemical models. Models can be used to help establish a qualitative understanding of mechanisms and to develop guidelines for future directions of work in topics including: field tests, corrosion tests, waste/barrier/rock/water interactions, conceptual groundwater flow models, and waste form dissolution. For example, models can be used to evaluate the relative saturation state of groundwaters with respect to phases present in the host rocks (e.g., 8). This type of information can be used to help assess the validity of conceptual groundwater flow models by comparing the chemical trends and likely flow directions. Analyses such as this can be helpful in evaluating the importance of kinetic constraints in the evolution of the groundwater system, an important factor when attempting to assess the impact waste emplacement (i.e., elevated temperature - thus, accelerated chemical processes) will have on the ambient characteristics. One application of geochemical models to the interpretation of hydrothermal experiments is the determination of whether a final assemblage of phases is stable or metastable (34), an important consideration if test results are to be used for extrapolations.

### 2.1.3 Predictions of Performance

Numerical simulation of geochemical processes is the only viable approach for predicting the long-term performance of repositories. Unfortunately, the processes and parameters to be considered are numerous and make the problem complex. Currently, there is no single model consisting of a conceptual framework and necessary supporting data available that can be used for such predictions. However, there is a significant amount of effort being expended in model development. The next chapter contains recommendations relevant to model development and data collection. These recommendations are intended to complement the current on-going activities. If implemented, they will result in a comprehensive model that can be used to reliably estimate geochemical and mass transport characteristics important to the performance of a repository.

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### 3. RECOMMENDATIONS

What are some of the key developments that could enhance the role of geochemical modeling in repository assessments?

The consensus at the conference was that (1) geochemical modeling will have to play a significant role in showing that HLW can be safely isolated in deep geologic formations, and (2) current models are inadequate to properly account for all potentially important processes and parameters. To progress to the point where simulations will provide reliable predictions, significant advances will have to occur in the areas of: (1) Applications and Processes, (2) Theory and Code Development, (3) Thermodynamic Data, and (4) Kinetics and Coupled Processes. Specific recommendations in these four topical areas are discussed in the following sections. No attempt has been made to establish priorities for the recommendations, because priorities will be somewhat dependent on the site and design characteristics of a given repository (e.g., temperature, pressure, ionic strength of groundwaters, and hydrologic regime). In addition to the specific technical recommendations, there is some discussion of general recommendations that relate to the reasons for, and implementation of, the technical recommendations. These general recommendations are intended to illustrate some of the problems in the current HLW programs and to stimulate discussion and action that might help to promote the resolution of these problems.

#### 3.1 APPLICATIONS AND PROCESSES

Outlined below are a set of applications and processes that are regarded crucial for inclusion into models appropriate for predicting the geochemical behavior of HLW repositories. Neglecting one or more processes that could lead to conservatism may be acceptable in certain instances, although care must be taken so as to not overlook potential synergisms that could ultimately result in incorrect and possibly overly optimistic estimates of performance.

(1) Transport. The transport of materials to, through, and away from an HLW repository is an essential component of its performance. Geochemical mass transport models that properly account for this movement should include (as appropriate for a particular site and sale) the following: (a) advection, (b) diffusion, (c) dispersion, (d) unsaturated flow processes (e) vapor transport, and (f) brine migration through salt. These processes represent the major physical and chemical mechanisms that contribute to the transport of material in most repository settings, although all the processes are not applicable to all the candidate rock types or at all scales of mass transport.

(2) Geochemical Conditions. The geochemical conditions in and around a repository will significantly influence the containment of radionuclides within the waste packages and the eventual release and transport of

radionuclides away from the repository. In treating such processes, geochemical models should account for the following parameters and characteristics: (a) temperature, (b) pressure, (c) groundwater chemistry, (d) pH, (e) redox potential, and (f) solid phases pertinent to the geologic setting and engineered materials. Many of these parameters are directly correlated with each other or with other repository characteristics (e.g., pH-temperature-chemistry, and redox-temperature-radiation). These correlations should be included in models of geochemical conditions for repositories.

(3) Chemical Reaction. The chemical reactions that can occur in a repository are numerous. This complexity makes it difficult to identify and properly account for the important reactions. A reaction should not be neglected unless it can be shown to not affect, or to affect in a conservative manner, the results of simulations. This determination of conservatism should include an analysis of potential synergisms between processes. Reactions that should be addressed include: (a) dissolution/precipitation [includes the behavior of waste forms, metals, packing and backfill materials, minerals, and glass (waste form and/or rock)], (b) aqueous speciation/complexing, (c) sorption (physical and chemical), (d) colloid and particulate formation, aggregation, and filtration, and (e) isotopic exchange (e.g.,  $^{14}\text{C}$  may be an important radionuclide for some repositories).

(4) Radiation. Radiation effects have received little attention to date, generally because of the cost and time involved with performing experiments to obtain data for modeling. Nevertheless, radiation may significantly alter geochemical processes important to a repository in ways not yet anticipated. Geochemical processes should be coupled with possible radiation effects, including: (a) radiation damage to solids, (b) radiolysis of aqueous solutions, and (c) radioactive decay. These processes have not yet been adequately coupled with important geochemical processes and parameters (e.g., redox reactions, waste form dissolution, and corrosion of metals), although radioactive decay is a mechanism commonly included in contaminant transport codes. Mills and Vogt (1) and Coffman et al. (2) discuss some attempts to include radionuclide inventory and radiation dose calculations into codes describing the behavior of waste packages. Most of the work to date on the coupling of geochemical processes with radiation effects is incomplete, and much work is needed in this important area.

### 3.2 THEORY AND CODE DEVELOPMENT

To properly describe the geochemical processes discussed earlier, some general and specific deficiencies in many geochemical models need to be corrected. Most of these deficiencies are relevant (either directly or indirectly) to all the geochemical processes and need to be addressed to properly simulate the mass transport processes important to HLW isolation.

(1) Uncertainty. Predictions of performance will be inherently uncertain, and the degree of uncertainty needs to be incorporated into all

analyses. Four areas of uncertainty should be considered: (a) computational precision, (b) uncertainty in analytical parameters, (c) uncertainty in thermodynamic and kinetic parameters, and (d) documentation of uncertainty. Each of these is discussed below.

(a) Computational precision: It is essential that the degree of computational uncertainty (e.g., round-off errors, convergence problems) in a computer code be established and minimized to an acceptable level as part of any code development activity. An accounting of this uncertainty must be included with code documentation.

(b) Uncertainty in analytical parameters: Analytical parameters that have associated uncertainties important to the results of mass transport calculations include: (1) physicochemical parameters (e.g., temperature, pressure, pH, redox potential, groundwater chemistry, properties of solid phases), (2) hydrologic parameters (e.g., porosity, permeability, hydraulic heads), and (3) physical parameters (e.g., thermal conductivity, stratigraphic relationships, boundary conditions). Uncertainties in these parameters need to be carried through calculations to determine their impact on predicted results.

(c) Uncertainty in thermodynamic and kinetic parameters: Probably the largest source of uncertainty in geochemical-model calculations results from uncertainties associated with fundamental thermodynamic and kinetic parameters. These uncertain parameters can include:  $\log(K)$  values, entropy, heat capacity, rate constants, and activation energies. The choice of methods for uncertainty analyses will depend to some extent on the type, quantity, and quality of data available. Methods such as simple addition of errors may be appropriate in some cases, although care must be taken to properly account for correlated errors.

(d) Documentation of uncertainty: Of equal importance to the actual analysis of uncertainties is the proper documentation of the data base (including both analytical parameters and fundamental thermodynamic and kinetic parameters). Documentation of a data base should include: the identification of the most sensitive and/or uncertain values, the precision and accuracy of the value, the method of derivation, a discussion of internal consistency among fundamental thermodynamic and kinetic parameters, and the source and a short history of the value.

(2) Properties of Solid Phases. The treatment of solid phases, their compositional effects, surface and defect characteristics, and the presence of non-crystalline solids is incomplete in most geochemical models. Assuming end-member, stoichiometric compositions for the calculation of the thermodynamic free energies of solids is not appropriate for most repository applications, where many materials will exhibit a wide range of composition, as well as a degree of crystallinity. In addition, the presence of radiation, elevated temperatures, and other repository induced effects may alter the surface and structural characteristics of solids such that the thermodynamic properties are affected.

Therefore, to simulate repository systems that will include assemblages of solid phases having complex chemistry and structure, improvements in

the following areas are warranted: (a) calculation of free energies for amorphous solid and crystalline solutions, (b) effects of radiation, surface properties, and defect structures on the free energies of solids, and (c) calculation of free energies for complex solids with variable degrees of crystallinity such as glasses, zeolites, and clays.

(3) Metastability and Kinetics. The assumption that complete thermodynamic equilibrium occurs in geochemical systems is clearly invalid. Metastability at both low and high temperatures among redox couples (3, 4), aqueous species, and the formation of solids (5) can exhibit a significant influence on the geochemical behavior of the system. Because the assumption of complete equilibrium may not be valid for some important geochemical processes within a repository (e.g., dissolution, precipitation, oxidation/reduction, sorption, and speciation), it is essential that the ability to account for (a) metastability and (b) kinetic relationships be developed and incorporated into geochemical models. Further details are discussed in the section on Kinetics and Coupled Processes.

(4) Radiolysis. Radiolysis may alter significantly some chemical characteristics of the groundwater (e.g., pH, redox potential, and solute speciation). During the first few hundred years of repository history, while the waste packages are likely to remain intact, the potential effects of gamma radiolysis will predominate over those of alpha radiolysis because the canister shields the system from the low-energy alpha radiation. By the time the waste packages are breached (>300 to 1000 years), the high-energy gamma-emitting radionuclides will be mostly decayed. Therefore, the effects of alpha radiolysis, although likely to be important only on a local scale (i.e., formation of micro redox environments), will be of potentially greater significance than those of gamma radiolysis. Areas related to radiolysis needing development include: (a) experimental determination of constants necessary for radiolysis calculations (e.g., G-values and rate constants for reactions), (b) incorporation of radiolysis effects into geochemical models, and (c) validation tests of radiolysis calculations. For further information on radiolysis effects, see references (6) through (8).

(5) Sorption. Distribution coefficients ( $K_d$ ), though a useful measure for relative comparisons, have no underlying mechanistic theory and are not recommended for predicting radionuclide sorption where predictions and extrapolations of high confidence are needed as in HLW isolation. Areas requiring improvements include: (a) more realistic models of sorption, and (b) better experimental design of sorption experiments to obtain sound data for interpreting important mechanisms involved in the sorption process. For example, many sorption experiments utilizing samples of bulk rocks crushed to an arbitrary grain size may not represent the actual processes and retardation effects expected during transport in anisotropic fractured, porous media. Predictions of migration rates for radionuclides based on this type of data will be highly uncertain because similitude between the natural and experimental systems is not maintained in these types of tests. Sorption experiments should be designed to produce meaningful data that can be incorporated

into fundamentally sound conceptual models appropriate for simulating mass transport processes. Otherwise, extrapolations of performance cannot be constrained within reasonable bounds of uncertainty.

(6) Thermodynamic Data Needs. There is a critical need for basic thermodynamic data relevant to the behavior of radionuclides in a geologic system. This subject is discussed in more detail in the section on Thermodynamic Data. Discussions during the conference suggested that the key elements requiring more emphasis include the actinides and technetium, although sensitivity studies may suggest others of equal priority.

(7) Activity Coefficients for Aqueous Species. Among the considerations in calculating mineral/solution equilibria pertinent to HLW isolation are that aqueous solutions need to be modeled over wide ranges of ionic strength and temperature. Information on ion pairs in solution can be essential for the meaningful interpretation of kinetic and thermodynamic experiments. Two approaches for calculating activity coefficients currently in use are the "ion interaction" approach (9-13) and the "ion association" approach, which is based on extensions of the Debye-Huckel theory (12-15). Neither of the two approaches has a clear advantage for all applications. To extrapolate calculations to high temperature and to interpret data from kinetic experiments, the ion association approach provides greater utility. In addition, further research may provide methods for extending the useful range of the ion-association approach to ionic strengths beyond 1 to 2 molal. On the other hand, the ion-interaction approach can currently be used for solutions of ionic strengths from zero to 20 (11). Its greatest utility is in the accurate representation of experimental data. However, reliable extrapolations with the ion-interaction approach are difficult, especially for systems with a somewhat different bulk chemistry. The opinions at the conference were mixed as to the best direction to take in developing methods to calculate activity coefficients, although there appeared to be a slight preference for the ion interaction approach. Because of the divided opinions, and because the specific-ion and ion-pairing approaches both have their appropriate place for a given set of circumstances, it would seem most prudent at this time to continue to improve and develop information in this area utilizing both approaches.

(8) Temperature Corrections. Because of the elevated temperatures expected in a repository system (up to 300°C), improved methods for extrapolating thermodynamic functions to elevated temperatures must be incorporated into geochemical models. As a general rule of thumb (13), calculations at elevated temperatures can be approached through the following assumptions: (1)  $\Delta C_p = 0$ , (up to 100°C); (2)  $\Delta C_p = \text{constant}$ , (up to 200°C); and (3)  $\Delta C_p = f(T)$ , (up to 300°C). As Barnes (13) points out, data for the application of assumption (3) are not always available. Therefore, it may be desirable to use the "isocoulombic approach," where reactions are written such that ionic charges cancel out (13). Because ions are generally the dominant contributors to  $C_p$ , this technique tends to cancel out the effects of changes in thermodynamic properties as a function of temperature, thereby forcing  $\Delta C_p$  toward zero and extending the useful temperature range of extrapolations using assumption (1) to approximately 200°C.

(9) Pressure Corrections. Although calculations of homogenous aqueous solution equilibria, in general, are rather insensitive to pressure at temperatures <300°C (14), calculations of mineral-fluid and gas-fluid equilibria can be significantly affected. Therefore, to avoid unnecessary errors, geochemical models should incorporate pressure corrections for all appropriate thermodynamic parameters. To avoid confusion and inadvertent errors, explicit reference states should be chosen and rigidly adhered to.

(10) Documentation, Verification, Benchmarking, and Validation.

Geochemical models may eventually be developed that contain a complete and sophisticated algorithm for describing the mass-transport phenomena that may occur in an HLW repository. However, for a model to be considered reliable, the following code management requirements are needed: (a) documentation, (b) verification, (c) benchmarking, and (d) validation.

(a) Documentation: Some aspects of code documentation are discussed in Silling (16). In general, proper documentation includes: (1) a summary of the software, (2) a description of the conceptual, mathematical, and numerical models, (3) a user's manual, and (4) a discussion of code verification.

(b) Verification: This process essentially tests a model for its "mathematical correctness" and includes: (1) evaluating the algorithms used to solve the conceptual model and its mathematical representations, (2) comparison of results with analytical solutions to sample problems or previously verified solutions, and (3) establishing limiting boundary conditions and assumptions where application of the model may be inappropriate.

(c) Benchmarking: Benchmarking involves making code-to-code comparisons using sample problems that are appropriate for the model and its intended applications. For some geochemical models there may not be other codes in existence similar enough to allow comparison. These models may have to be benchmarked through sample problems that test only portions of the entire model.

(d) Validation: Validation confirms model calculations through comparisons with observed conditions in laboratory experiments or field studies (16, 17). The use of field studies (i.e., natural analogs) for the validation of geochemical models seems most appropriate, given the long time periods involved in HLW isolation. Experiments carefully designed to test specific geochemical mechanisms can be of help in attempting to validate conceptual models important to predictions of mass transport (e.g., kinetic versus equilibrium control of sorption reactions). Krupka et al. (18) specifically discuss the validation of the thermodynamic data base for uranium in the geochemical model WATEQ4. Further information on validation can be found in ANS (19). As Plummer and Parkhurst (20) point out, validation, in addition to obtaining key thermodynamic and kinetic data, is one of the most critical areas to be addressed in geochemical modeling.

### 3.3 THERMODYNAMIC DATA

A great variety of thermodynamic data bases is available. Many address only geologic materials, while others include elements representative of radionuclides to be emplaced in HLW repositories. Some data bases are associated with a specific geochemical model, while others are not. This variety may appear to be advantageous in that, for a specific application, one has the option of choosing the most appropriate data base from among those available. However, most of the data bases contain values taken from similar sources and compilations, and most of the data bases currently in use for the assessment of HLW repositories have not been critically evaluated. Therefore, an informed decision to choose among data bases is not easily accomplished — in some instances any choice may be poor. To help resolve this situation, four recommendations are offered: (a) establish a critically evaluated compilation of thermodynamic data, (b) perform sensitivity studies to identify key areas for future data development, (c) obtain key thermodynamic data, and (d) establish a procedure for the review, revision, and updating of data bases.

(1) Compilation of Thermodynamic Data: It is essential that a critically evaluated data base for elements, aqueous species, gases, and solids be compiled. The critical evaluation must be representative of the key radionuclides anticipated to be present in HLW repositories as well as the geologic materials important to the sites currently being investigated. The compilation should include, in addition to a set of internally consistent thermodynamic data: (a) uncertainties, (b) a discussion of the reliability of the value, and (c) a short history of the source and method of determination. Internal consistency and documentation of how a value was chosen are particularly important because they establish the validity of a data set and, thus, the reliability of calculations (21).

(2) Sensitivity Studies: A sensitivity study evaluating the impact of uncertainties in thermodynamic data on the calculated results should be undertaken concurrently, to the extent possible, with the compilation of a critically evaluated thermodynamic data base. In this way, key parameters can be identified that require additional experimental determinations to check, and/or improve, their reliability. Experimental sensitivity/scoping studies should be initiated in order to identify solid phases and potential aqueous complexes for which there are no data, because the importance of missing values cannot be addressed through sensitivity studies unless the solid or complex is known to exist and an estimate of the thermodynamic parameters has been made. These scoping tests are particularly important because a large variety of as yet unidentified aqueous complexes and solids may result from waste/barrier/rock/water interactions in a repository.

(3) Data Development: Detailed recommendations on the key areas needing immediate attention in obtaining thermodynamic data should await results of the sensitivity analyses. However, a few general areas were identified during the conference: (a) organic complexes with radionuclides, (b) actinide elements, (c) technetium behavior, (d) data for elevated

temperature, (e) amorphous solid and crystalline solution series, (f) data for clays, zeolites, glasses, and (g) strong electrolyte interactions.

(4) Procedures for Review, Revision, and Updating Data Bases: As items (1) through (3) are accomplished, many "bookkeeping" items will be required to be tracked. Therefore, procedures to ensure traceability are needed. These procedures do not need to be newly developed. Haas (21) briefly discusses systems and organizations that are experienced at this task and should be included in the development of data bases for geochemical calculations.

### 3.4 KINETICS AND COUPLED PROCESSES

The closely related nature of geochemical, mass transport, and fluid flow processes suggests that some degree of coupling may be necessary to adequately assess some aspects of the performance of repositories (22, 23). Coupled-process models do not necessarily imply direct coupling of geochemical and fluid-flow processes or the creation of "megacodes" (22, 24). Rather, several approaches may be appropriate for a given set of circumstances, including: direct coupling, iterative calculations, or the simple sharing of relevant data and conceptual models. Kinetic effects may also be important in the prediction of the geochemical behavior of a repository, although it is possible that the assumption of equilibrium can be conservative relative to a kinetic approach under some circumstances. During the conference, three general topics were identified as requiring further attention in the area of kinetic and coupled-process models. The reader is also referred to the following reports dealing specifically with needs related to coupled-process models: OECD (22) and Tsang and Mangold (23).

(1) Coupled Chemical Reaction/Flow Models. Predicting the release and transport of radionuclides from a repository located in a geologic medium involves addressing both the geochemical and hydrologic aspects of the system. Pearson (24), Ortoleva (25), and Moore (26) point out some of the important relationships between the chemistry and fluid flow characteristics of a given system (e.g., the chemistry can influence the flow regime, and vice versa). In coupling chemical reaction and flow, there are two end-member bounding assumptions - equilibrium control versus kinetic control. It is apparent that neither approach is completely satisfactory for all applications because there is typically a mixture of control by equilibrium and kinetic processes. The assumption that equilibrium processes, rather than kinetic, control some aspects of repository performance can be conservative and make performance assessment analyses somewhat simpler. This is an important option to maintain, but it must be recognized that some information on the kinetic aspects of the process in question will have to be obtained in order to validate that the assumption of equilibrium is truly conservative.

For most low-temperature systems, kinetics is clearly the dominant factor, and efforts in both model development and experimental studies that are directed toward evaluating the effects of coupling kinetic relationships and mass transport need to be intensified.

(2) Sensitivity Studies. Three areas of sensitivity analyses were identified: (a) delineate where equilibrium-vs-kinetic control applies, (b) investigate areas of "unexpected" performance, and (c) identify basic kinetic data needs. For any given application of coupled-process models, sensitivity studies are needed to determine whether a conceptual model based on equilibrium control or kinetic control of geochemical and mass transport processes is necessary and sufficient to describe the behavior of the system. Repositories will go through a thermal cycle that will influence the relative importance of kinetic-vs-equilibrium control of geochemical and mass transport processes. For example, during the high-temperature period of repository history (approximately the first 50 years after closure), redox reactions may occur rapidly enough to justify the assumption of equilibrium. However, as the temperature decreases to 50 to 150°C, these same redox reactions may become sluggish, thus requiring a kinetic treatment for the relatively short (<10,000 years) geologic time scale mandated by regulatory criteria, unless it can be shown that the assumption of equilibrium is conservative.

As another example, the formation of metastable alteration phases during the high-temperature period may be able to be treated with thermodynamics (27). However, as the temperature decreases and these phases become unstable with respect to other more thermodynamically favored phases, the dissolution/precipitation kinetics of these phases becomes important if they contribute significantly to the retention of radionuclides released from the waste packages. Because the selection of appropriate techniques for simulating mass transport behavior will be somewhat dependent on whether a particular process is controlled by equilibrium or kinetic constraints, it is important to attempt to identify the transition temperature from kinetic to equilibrium control for the different geochemical processes that are important to the performance of a repository (e.g., redox equilibria, dissolution, precipitation, speciation reactions). Sensitivity studies can also help to identify areas of "unexpected" behavior (25), which is crucial in attempting to reliably predict the performance of a complex system for thousands of years. Sensitivity analyses may also aid in identifying basic data needs for applying kinetic and coupled-process models (26).

(3) Kinetic Data. There is a paucity of basic kinetic data applicable to both geologic and repository systems. This circumstance is unfortunate because kinetics may play a significant role in predicting repository behavior. The importance of kinetics derives from the fact that geochemical processes in a repository system, involving complex waste/barrier/rock/water interactions, must be predicted over a geologic time scale (10,000 years). Therefore, kinetics, which addresses physical and chemical changes as a function of time, must be an essential part of any assessment. Experimental scoping studies are needed to identify key processes that require more detailed kinetic analyses. In addition, results of sensitivity studies as discussed above may prove useful in identifying areas needing development. The following broad categories were identified during the conference as needing attention: (a) dissolution, nucleation and growth kinetics for materials such as minerals, glasses, metals, alteration phases, colloids, and surface coating; (b) kinetics of redox equilibria involving both homogenous

aqueous solution reactions and heterogenous water-rock reactions including the effects of temperature and radiolysis); and (c) kinetics of aqueous speciation reactions. One specific item that was identified as requiring special attention is the proper characterization of effective surface area in kinetic experiments. Rather than a bulk rock/water ratio, it is desirable to establish the surface area/volume ratio (28). In addition to detailed experimental and theoretical analyses, there is also a need for "feedback" studies addressing the potential mediating effects of the natural chemistry of a system. For example, minor and trace components in a groundwater may have a significant poisoning or promotive effect on the dissolution or precipitation of phases.

### 3.5 GENERAL RECOMMENDATIONS

A significant number of technical recommendations have been made as a result of the conference. There are no easy solutions to the assessment of geochemical and mass transport processes important to the performance of HLW repositories. Improving our capability to simulate geochemical processes in an HLW repository in a time scale useful to the licensing process will require intense cooperation among the current site projects as well as between DOE and NRC. Based on the technical recommendations presented in previous sections, there are many areas of mutual need in the development of models and basic data. It seems apparent that the current site projects should cooperate more closely in identifying and developing models and obtaining data that would be mutually beneficial. But first, a conceptual model should be developed that describes all geochemical processes and interactions that could potentially impact the performance of a repository from the initiation of construction through the period of containment and isolation (approximately 10,000 years). Such a model, which apparently has not yet been developed and/or documented for any of the candidate sites, could be the basis for the DOE to establish levels of detail and understanding required to adequately describe the geochemical and mass transport characteristics of a repository.

Throughout these proceedings there is an underlying theme that a certain level of understanding is necessary to make reliable predictions and extrapolations of geochemical and mass transport processes relevant to the performance of a repository. Although it is recognized that the DOE site projects need to obtain basic geologic, hydrologic, and geochemical data, the characterization of a site should also include establishing at least a qualitative understanding of the important processes and mechanisms. Many of these processes, although somewhat site-specific, have many more similarities among sites than there are differences (e.g., groundwater interactions with waste forms and canisters, and sorption reactions with secondary minerals). A qualitative understanding of important processes will also contribute to engineering-decision studies by allowing the impact of alternative designs on the performance of a repository to be evaluated with some degree of certainty, because conservative analyses may mask important differences in performance among alternatives.

It is strongly recommended that technical considerations related to these proceedings receive the necessary attention in the scheduling and funding of research, development, and testing activities within the DOE. The technical community has the right and responsibility to provide input on technical matters so that there is an opportunity for DOE and NRC to make informed and rational decisions. This is the primary purpose of this report -- to provide the DOE and NRC with some preliminary recommendations from the geochemical community concerning the simulation of geochemical and mass transport processes important to the performance of a HLW repository.

Because of the potential consequences of improperly disposing of radioactive waste, arbitrary legislative deadlines should not override technical considerations in the planning and carrying out of research, development, and testing programs. Significant improvement in the ability to model geochemical and mass transport processes can be made in a timely manner (<15 years), providing that a focused program with adequate fiscal support is implemented -- history has shown that such success is possible (e.g., Apollo and Space Shuttle programs). To develop successful models of repository performance will require some consolidated, separate programs to address common needs (e.g., model development, compilation and maintenance of a proper thermodynamic and kinetic data base, and investigation of synergistic effects). Implementing the recommendations presented in these proceedings will ensure that programs in repository development will obtain the geochemical information necessary and sufficient to guarantee the safe disposal of nuclear waste.

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4. SESSION I

SOLUTION CHEMISTRY: THEORY, CODE DEVELOPMENT, AND  
NON-REPOSITORY APPLICATIONS

Chairman: H. L. Barnes  
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## THERMODYNAMIC PROBLEMS IN SPECIATION MODELING

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The principal goal of geochemical modeling is to provide a rigorous evaluation of mass transport in nuclear waste repositories. Either experimental or numerical models could be used. However, experimental modeling cannot provide an exact model because the thermal and physical characteristics of the repository solids and solutions, including heat capacities, porosities, permeabilities, and viscosities, require that the scale ratio be 1:1 and equivalent only to full scale operation of a repository. Consequently, numerical models, in principle and if carefully constructed, should provide the most accurate basis for understanding in advance the behavior of a repository.

Numerical modeling depends upon both kinetic and thermodynamic methods for realistic evaluation of mass flow rates. The purpose of this paper is to emphasize some thermodynamic methods that have not yet been exploited or that need further development to achieve the necessary resolution of our models. Kinetic and sorption phenomena are to be considered by other papers in this Workshop.

Good scientific method implies that the uncertainties in the accuracies, not precision, of the thermodynamic data base be evaluated and compiled. Such uncertainties are additive except where they have common ancestries. Where gaps in the data base are filled by estimated values, these deserve an identifying notation. These uncertainties should also be carried through as error bands about curves on diagrams resulting from such thermodynamic calculations.

Improved thermodynamic characterization of solids is very necessary. This can be accomplished by including in activity coefficients the effects of radiolysis, of solid solution, of excess surface energy or strain or defect concentrations, and of the inclusion of components in the glassy phases of host volcanic rocks.

The choices made in evaluating the activity coefficients of aqueous species need careful documentation. For ionic species, the usual alternatives are (1) the stoichiometric  $\gamma$ 's, calculated by an adaptation of Pitzer's semi-empirical, five-parameter regression equation after assuming complete solute ionization, or (2) the non-stoichiometric or "true"  $\gamma$ 's where an extended Debye-Hückel or the Davies equations are used for the calculations which include all pertinent ion-association reaction constants. Method (1) is advantageous where exact speciation is not important and at low temperatures and to high concentrations where ion-association is not dominant. Method (2) is preferred where exact speciation is needed for kinetic or mechanistic arguments and especially at higher temperatures and at analytical concentrations exceeding the solute ionization constant where ion-pairing is dominant. For neutral species, the usual assumptions that  $\gamma = 1.0$  or  $\gamma = \gamma_{\text{CO}_2(\text{aq})}$  are apparently inaccurate. Instead, our recent research indicates that because the dipole moment of the neutral species causes an electrostatic field similar to that of weak ions, it has a corresponding effect on  $\gamma$ . Further development of this concept is needed.

In modeling, the standard states used in the thermodynamic calculations are often either inconsistent or inexplicit. Rigorous treatment means that these be fixed at a constant pressure rather than drifting along the L + V curve of pure water. This correction becomes more important at higher temperatures and for reactions with large changes in molar volumes. Preferred is a 1 bar standard state, hypothetical at higher temperatures.

An improved procedure for extrapolating or correlating thermodynamic data to higher temperatures should also be adopted for thermal modeling. It has been conventional to assume that  $(\Delta C_p^\circ)_R$  is equal to zero (van'T Hoff equation), to a constant, or to a function of temperature, such as Criss and Cobble's entropy correspondence method. By writing reactions so that they are charge-balanced with an equal number of species with identical charges and of neutral species on each side of the reaction, then  $(\Delta C_p^\circ)_R$  is effectively = 0. To about 200°C, this conclusion remains sufficiently accurate where the total charge of a differing number of species on each side of the reaction is the same and even if the number of neutral species involved is not balanced.

The remaining improvement in numerical modeling of concern here is for a means to be found to treat reactions that proceed in neither direction, or in one direction only, rather than assuming that all are reversible. Examples include many redox reactions, such as sulfide oxidation to form sulfate, irreversible below 200°C, and of either oxidation or reduction of carbon to  $\text{CO}_2$  or  $\text{CH}_4$ , both of which are of importance to solubilities in repositories.

The adaptation of the above procedures must increase the complexity of computer codes considerably but with major benefits in the accuracies of the resulting numerical geochemical results.

PREDICTION OF MINERAL SOLUBILITIES AND DIAGENESIS IN ROCK/WATER  
ASSOCIATION AT HIGH TEMPERATURE

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To make qualitatively correct predictions of the solubility of minerals in natural brines above 1 km, it is necessary to use thermodynamic models of high accuracy (5% in the log of the activity coefficients). This requirement results from the fact that in complex systems small errors in the calculated solution phase free energy often drastically change the predicted equilibrium solid phase assemblage. An example of the need for high accuracy is shown in the successful modeling of the complex changes which occur in the seawater equilibrium mineral assemblage during evaporation (Harvie, Weare, Hardie and Eugster (1980)). Accurate chemical models are also required for reliable application to nuclear waste management programs. Examples of uses of such models in these programs are given in Table 1.

Table 1. Some Uses of a Chemical Model for Nuclear Waste Management Programs

- Calculation of the thermodynamic characteristics of aquifer brine/mineral association under a variety of field conditions (temperature, pressure, and composition).
- Prediction of aquifer (or site) integrity upon introduction of waste material (e.g., after mixing, calculate new brine/mineral equilibrium configuration and determine extent of significant mineral solubility changes).
- Description of optimal disposal site chemical characteristics for containment of specific waste material.
- Testing of strategies to improve chemical containment characteristics of specific disposal sites.
- Support laboratory simulation experiments.
- Prediction of chemical evolution of liquid waste material during storage.

Harvie and Weare (1980) and Harvie, Møller and Weare (1984) have recently demonstrated that chemical models of complex rock-water systems can be developed to the required accuracy from the phenomenological approach of Pitzer (1973). These specific interaction models are based on a virial expansion of the free energy. When strong association between species is evident from the data these ion pairs are included in the model. *Our calculations have shown that it is necessary to include both ion association and specific interaction to model natural waters to the desired accuracy.* We have shown that that it is necessary to include only up to third order specific interaction coefficients (virial coefficients) to obtain the accuracy required for most geochemical predictions. Consequently, all model parameters may be evaluated from binary and ternary experimental data, and reliable predictions can be made for much more complicated systems (Harvie, Møller and Weare (1984)).

Ion pair species are modeled explicitly only for very strong ion associations (e.g.,  $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$ ). For intermediate ion association strengths, we have found (Harvie, Møller and Weare (1984)) that the specific interaction model provides a more accurate description than approaches emphasizing ion pairing. This is true even at high temperature ( $T < 300^\circ\text{C}$ ; Møller and Weare, in preparation). Although ion pairing becomes more important at high temperature, it is still necessary to include specific interactions to allow for changes in ion association as the solution concentration increases. As an example of the accuracy that can be obtained from our models, we show in Fig. 1. the predicted solubility of gypsum vs.  $\text{Na}_2\text{SO}_4$  at  $25^\circ\text{C}$ .

Also shown in the figure are the predictions of two other available models. Recently, Kerrisk (1981), has extensively tested current chemical models. In Fig. 2, taken from Kerrisk, we show the level of accuracy that can be expected from these models. As can be seen, predictions become less accurate as the temperature increases.

Recently, we extended our seawater models to  $300^\circ\text{C}$  (carbonate not included) (Møller and Weare, in preparation). That our modeling capability may be successfully extended to high temperature is illustrated in Fig. 3, which shows  $\text{CaSO}_4$  solubility in  $\text{Na}_2\text{SO}_4$  aqueous solution at  $100^\circ\text{C}$ . As in the case of our  $25^\circ\text{C}$ -seawater models, the high temperature model's agreement with the data is within experimental error. When high temperature data in certain binary and ternary systems are scarce, the model's predictions for these interactions will reflect this lack of data. We are now collaborating with experimental groups to take the necessary high temperature data.

The aqueous solution models of Weare and co-workers have been applied to a variety of geochemical problems at  $25^\circ\text{C}$ : The Permian Zechstein of Germany (Harvie, Weare, Hardie and Eugster (1980)); the Great Salt Lake (Spencer

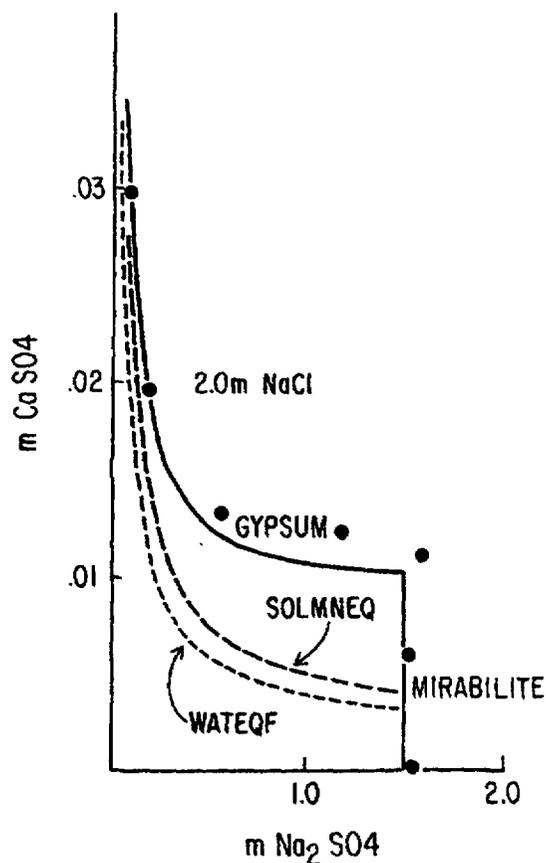


Fig. 1.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  solubility in the Na-Cl- $\text{SO}_4$ - $\text{H}_2\text{O}$  system at  $25^\circ\text{C}$ . The data are represented by solid circles, the solid lines are predictions of the Harvie-Weare model and the broken lines are predictions of two other models.

(1980)); the Peruvian estuary, Bocana de Virrila, (Brantley, Møller, Crerar and Weare (1984)); and salt pan evolution, as measured by Herrmann, Knake, Schneider and Peters (1973) (Møller, Greenberg and Weare, in preparation). In all these examples, the appearance of minerals in the sediments is accurately predicted by the water chemistry utilizing the Harvie-Weare model. The accuracy of these predictions suggests that equilibrium modeling can provide detailed information about mineral formation, and diagenesis in natural rock/water systems.

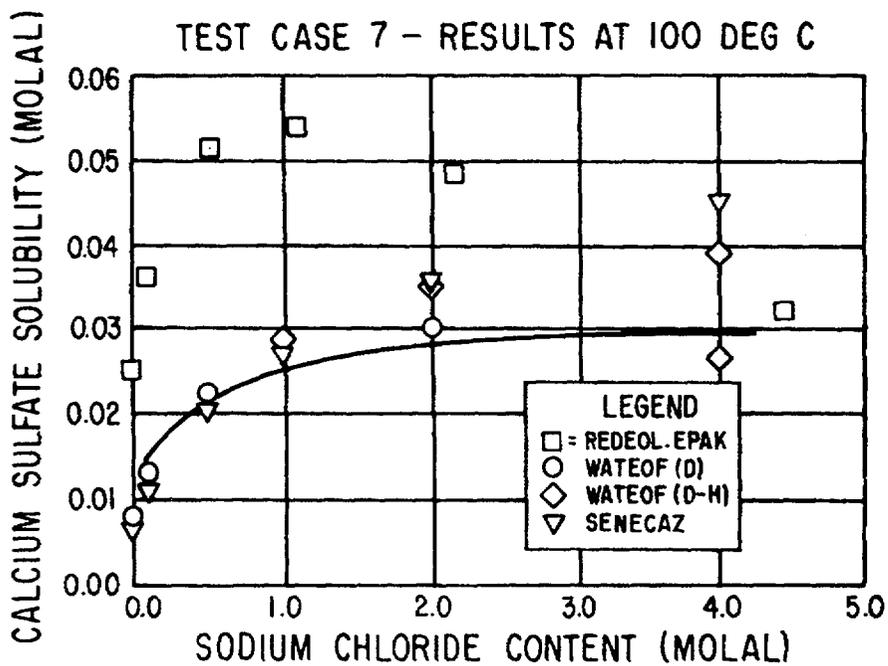
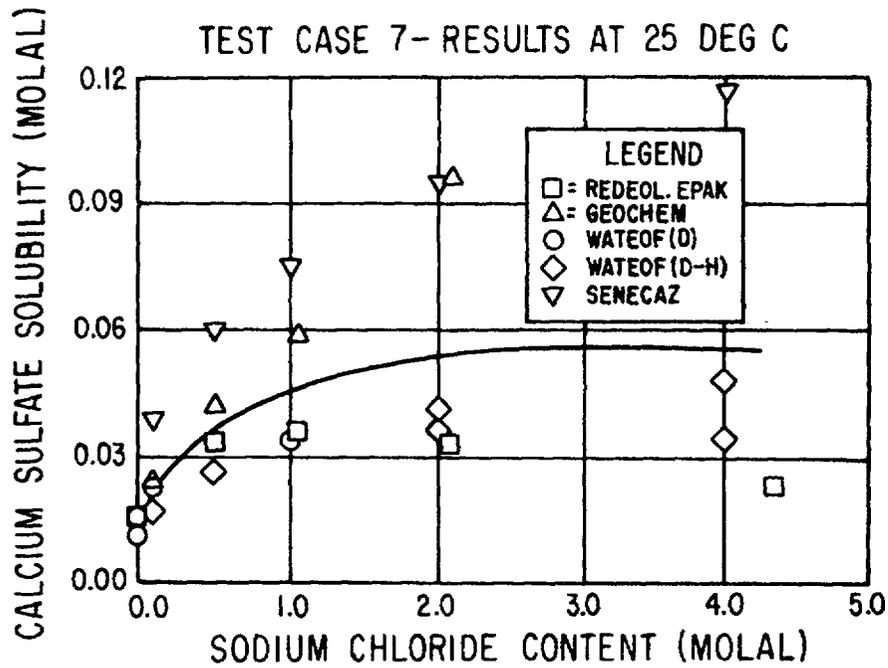


Fig. 2a and 2b. Results of test calculations for various chemical models compared to experimental results (solid lines). Taken from Kerrisk (1981).

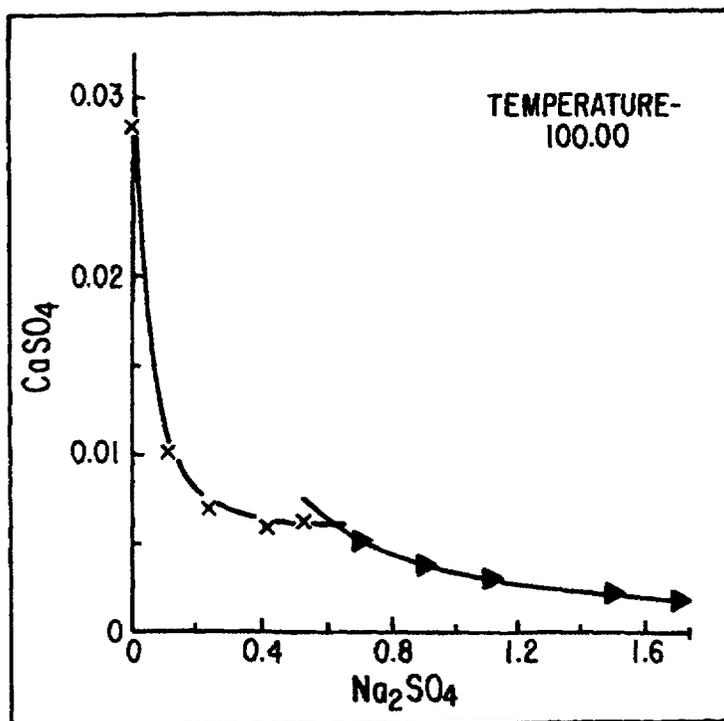


Fig. 3. Predicted (solid line) solubilities in the  $\text{CaSO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  system at  $100^\circ\text{C}$ . Data for anhydrite (x) and glauberite (▴) are shown.

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## PHREEQE: STATUS AND APPLICATIONS

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## INTRODUCTION

PHREEQE (PH-REdox-EQuilibrium-Equations) is a generalized aqueous speciation, solubility, mass transfer simulation code. The program was written with groundwater modeling applications in mind; but with appropriate modifications to the data base, PHREEQE can be applied to a wide variety of environments. This paper reviews the capabilities, limitations, applications, and current status of PHREEQE. As an application of PHREEQE, results of a sensitivity analysis are presented in which PHREEQE was used to model the composition of Madison Limestone groundwater in the Northern Great Plains, U.S.A. Additional information on PHREEQE and its applications may be found in (1) and (2).

## CAPABILITIES

The initial condition (pH, pe, solution composition, and temperature) is defined by the user. The code then makes adjustments to the initial solution to assure charge balance either by changing pH or the total concentration of one of the elements in the starting solution, or alternatively, by carrying the initial charge imbalance through subsequent calculations as "inert charge". Once the thermodynamic distribution of species is defined in the initial solution, PHREEQE can calculate new values of pH, pe, solution composition, and mineral mass transfer for the following cases: 1) mixing or titration of two solutions, 2) adding (removing) user defined amounts of an overall stoichiometric reaction to (from) solution (an irreversible reaction), 3) equilibration with one or more minerals and/or gases, 4) finding the amount of a specified irreversible reaction required to bring an initial solution to equilibrium with a particular mineral, i.e., locating a phase boundary along an

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irreversible reaction path, and 5) varying temperature. These cases can be combined in a variety of ways within a single problem. Some of the more useful applications of PHREEQE are 1) predicting the theoretical chemical composition of hypothetical equilibrium systems, 2) modeling mass transfer in partial equilibrium systems, 3) modeling reaction paths, 4) mixing waters in partial equilibrium systems, 5) modeling evaporation, 6) solving geochemical problems at constant pH or constant pe (pH-stat or pe-stat), and 7) evaluating effects such as changing temperature, open or closed systems, and varying the relative rates of irreversible reactions in determining sensitivity to uncertainties in thermodynamic and/or kinetic data.

The numerical method combines a continued fraction approach (3) to solve the mass balance and mass action equations in the aqueous model and a modified Newton-Raphson technique to estimate changes in solution composition, pH, pe, and mass transfer.

#### DATA BASE

PHREEQE uses an ion-pairing model. The current data base for the model is adopted from WATEQ2 (4, 5) for the elements Ca, Mg, Na, K, Fe, Mn, Al, Ba, Sr, Si, Cl, C, S, N, B, P, F, Li and Br. The aqueous model currently contains 121 aqueous species of these elements and is regarded as a preliminary data base provided with the code for testing purposes. Activity coefficients of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  are those of (6). Of these, the cations are based on mean activity coefficient data for chloride salts to several molal. All other activity coefficients of charged species are calculated either from the extended Debye-Hückel equation or the Davies formula. Thermodynamic data are provided for twenty-four minerals only. Equilibrium constants are adjusted for temperature changes either through empirical formulas of the form  $\log K = a + bT + c/T + d \log T + e/T^2$ , or via the van't Hoff equation assuming a constant  $\Delta H_r^\circ$ . The species and mineral data base is constructed external to the code so that changing the existing data base or adding new elements and species is relatively simple. Provided the ion-pairing concept and general formulation of activity coefficients is maintained, the data base may be modified extensively without requiring changes to the source code.

#### STRONG POINTS: WEAK POINTS

There is a growing number of codes available today with capabilities comparable (and in some aspects superior) to PHREEQE, but a comparison is beyond the scope of this paper. Summarized below are some of the attributes and limitations of PHREEQE that may be of interest.

Because PHREEQE solves mass transfer problems only at requested points in reaction progress, there is a relatively short execution time. For example, on an Amdahl 470 V/7 computer, Parkhurst *et al.* (1) give CPU timings for five extensive test cases. These test cases required 750

iterations and 10.88 CPU sec. If the solution to a single problem typically requires 10-20 iterations, it is estimated that 0.15 to 0.30 CPU seconds are required per problem on the Amdahl computer. This may be advantageous to future coupling attempts with flow models (7). Within the stability limits of water, redox reactions are handled rigorously in PHREEQE through both oxidizing and reducing environments. Other attributes include the modular nature of the input problem sets using keywords, the user definable data base external to the source code, and the extensive documentation (1). The source code contains 2300 lines including comments.

By assuming a constant mass of water, an approximation is introduced in PHREEQE which can lead to errors in modeling reactions involving hydration and dehydration of minerals and for redox conditions near or beyond the stability of water. Reactions of these types are usually not important in the geochemical environment and the efficiency in computing gained from the approximation outweighs any loss in accuracy by not including mass balance equations for hydrogen and oxygen. As with most codes which utilize the Newton-Raphson method, convergence is not guaranteed and adjustments to the source code may be required. Ion-exchange reactions are considered only in the sense of an infinite exchange capacity, i.e., the ratio of the activities of two ions may be fixed in solution and accompanying ion-exchange mass transfer computed. General sorption models are not included nor does the program provide a capability for including kinetic rate laws for any reaction. Although the code can calculate reaction paths, it does not automatically include appropriate minerals once a phase boundary is reached. The user is required to solve the reaction path manually by deciding which phase boundaries are to be included and manipulating the problem data set accordingly. In complex systems in which many phase boundaries are encountered, the path capability of PHREEQE makes problem solving cumbersome. At the same time this extra effort forces the user to grasp a firm understanding of the phase relations and, in general, of the problem being solved.

#### VERIFICATION AND VALIDATION

A code-to-code verification of PHREEQE and EQ3/6 (8, 9, 10, 11) was performed by F. J. Pearson, Jr. in examining the suitability of these codes for nuclear waste performance assessment (12, 13, 14). According to these reports PHREEQE and EQ3/6 gave virtually identical results when using the same aqueous model and thermodynamic data. This is of interest because the two programs satisfy the required master equations in different ways. Both programs include the charge balance condition, but EQ6 includes mass balance equations for hydrogen and oxygen, while PHREEQE substitutes an electron balance equation and performs all calculations relative to an assumed constant mass of water (1 kg).

In general, the PHREEQE data base has not been validated. In fact, several studies have shown that parts of the data base are invalid at high ionic strengths (15, 16).

Because the Pitzer model of Harvie *et al.* (17) is perhaps the most completely validated, a comparison of modeled results using the ion-pairing model of PHREEQE with those calculated using the Harvie *et al.* (17) as implemented in a preliminary USGS code are of interest. Table 1 summarizes the compositions of nine natural waters that vary from dilute calcium bicarbonate water to brines with ionic strengths of 10 or more.

Table 1. Composition of Selected Waters<sup>a</sup>

	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	C <sub>T</sub>	pH
Jones Sp., SD	1.77	0.91	0.06	0.02	0.01	0.06	6.42	7.2
Keg Coulee, MT	8.78	2.19	65.63	3.09	56.74	13.61	6.78	6.5
Seawater	10.73	55.16	486.95	10.63	568.17	29.39	2.14	8.31
Harris Co., TX	113.6	42.15	2040.	4.1	2402.	2.5	4.75	6.5
Red Sea	174.7	42.1	5425.	65.4	5926.	11.8	—	5.
Sweetwater, WY	0.13	0.26	4656.	5.2	760.	2.2	2056.	10.
Dead Sea	426.	2034.	1809.	222.	6910.	4.7	1.52	6.2
Angora-Lena	2700.	809.	385.	111.	7421.	2.6	8.8	4.
Eddy Co., NM	3.6	2332.	2827.	80.	702.	3422.	36.3	6.

<sup>a</sup>Concentrations in mmol/kg H<sub>2</sub>O. All temperatures taken as 25°C.

Table 2 compares the computed activity of water, ionic strength, log P<sub>CO<sub>2</sub></sub> and saturation indices of calcite, dolomite, gypsum, and halite from PHREEQE (1) and the Harvie *et al.* model (17). Because the equilibrium constants are model dependent, it is not appropriate to compare ion activity products. Table 2 shows reasonable agreement between the two models to sea water concentrations and in a number of cases to much higher concentrations.

The aqueous model of PHREEQE with its origin from WATEQ (6, 18) and WATEQ2 (4, 5) is best suited for relatively dilute waters. Extensive testing has been carried out in low ionic strength natural waters nationwide by USGS personnel. For example, the origin of waters from the Mississippian Madison Limestone aquifer of the Northern Great Plains have been shown in a recent geochemical modeling study (Plummer, unpub. data) to be due to the dedolomitization reaction (precipitation of calcite and dissolution of dolomite driven by the irreversible dissolution of anhydrite). The Madison Limestone waters evolve from Ca-Mg-HCO<sub>3</sub> to Ca-Mg-HCO<sub>3</sub>-SO<sub>4</sub> to Na-Cl-HCO<sub>3</sub>-SO<sub>4</sub> predominance over a a temperature range of 5 to 90°C and ionic strengths reaching a maximum of 0.11. For these waters the aqueous model of PHREEQE consistently shows slight oversaturation with calcite (apparent equilibrium with aragonite), equilibrium

Table 2. Comparison of Modeled Results<sup>a</sup>

Name	H <sub>2</sub> O <sup>a</sup>	Ionic Strength	Log PCO <sub>2</sub>	Saturation Index <sup>b</sup>			
				Calcite	Dolomite	Gypsum	Halite
Jones Sp., SD	0.999	0.0081	-1.67	0.12	0.09	-2.81	-10.89
	0.999	0.0084	-1.71	0.12	0.21	-2.78	-10.88
Keg Coulee, MT	0.997	0.102	-1.16	-0.41	-1.27	-0.42	-4.25
	0.998	0.114	-1.23	-0.33	-0.97	-0.42	-4.23
Seawater	0.981	0.68	-3.49	0.82	2.55	-0.59	-2.50
	0.981	0.72	-3.58	0.85	2.73	-0.64	-2.49
Harris Co., TX	0.922	2.53	-1.52	0.34	0.53	-0.87	-1.21
	0.919	2.54	-1.25	0.26	0.45	-1.03	-1.20
Red Sea	0.802	6.14	---	---	---	0.13	-0.15
	0.763	6.17	---	---	---	-0.04	-0.07
Sweetwater, WY	0.900	3.41	-3.17	1.66	3.99	-4.93	-1.48
	0.899	6.57	-3.76	1.04	2.72	-5.94	-1.51
Dead Sea	0.806	9.38	-2.83	-0.05	1.12	-0.38	-0.30
	0.687	9.40	-1.03	-0.29	0.71	0.02	-0.07
Angora-Lena	0.806	10.96	-0.73	-1.30	-2.76	0.33	-0.81
	0.661	10.98	-0.01	-2.82	-5.61	0.45	-0.57
Eddy Co., NM	0.881	4.73	-0.29	-1.28	0.48	0.09	-1.54
	0.836	13.34	-0.01	-1.87	-0.26	-0.22	-1.25

<sup>a</sup> Upper value calculated using PHREEQE. Lower value based on model of (17). All results at 25°C.

<sup>b</sup> Saturation index =  $\log(IAP/K)$  where IAP is ion activity product and K the equilibrium constant.

with dolomite and waters approaching gypsum equilibrium from undersaturation as more distant points downgradient are approached. This constitutes a partial field validation of the PHREEQE model.

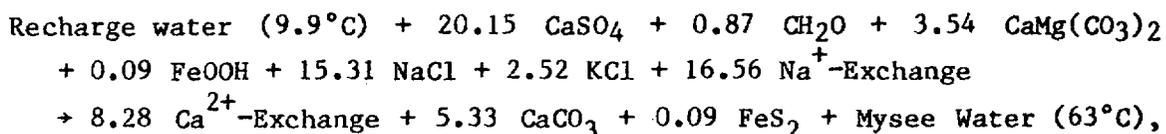
In laboratory studies of the carbonate system, PHREEQE has been used extensively to design experimental solutions in the  $KHCO_3$ - $Na_2SO_4$ - $NaCl$ - $CaCl_2$ - $Ca(HCO_3)_2$ - $Sr(HCO_3)_2$ - $CO_2$ - $H_2O$  system for conducting kinetic and thermodynamic studies. A partial validation is again provided by the close agreement in predicted and measured pH of these solutions ( $\pm 0.02$  pH at 25°C).

#### CURRENT DEVELOPMENTS

Since release of PHREEQE in 1980, there have been very few changes made to the USGS version of the source code. The data base has been modified to incorporate new carbonate data (19). An interactive program (PHRQINPT) was written to aid in constructing input data sets to PHREEQE (20). Currently two versions of PHREEQE are being tested: one utilizing the PHREEQE aqueous model but with improved convergence criteria, and another utilizing the improved convergence criteria and the model (17).

## APPLICATION: A MODELING EXAMPLE

An example is given using PHREEQE to predict the composition of Madison Limestone ground waters from knowledge of 1) the composition of the starting (recharge) water, 2) likely reactants and products, 3) known temperature variation (modeled to 80°C), and 4) reasonable estimates of relative rates of reactions derived from mass balance calculations. The mass balance calculations, based on observed compositions of the recharge water and water from the Mysse Well (130 miles downgradient in south-central Montana), are consistent with the measured carbon and sulfur isotope data indicating the following net mass balance reaction:



where the stoichiometric coefficients are in mmol/kg H<sub>2</sub>O. Using initial estimates of relative rates of reaction computed from the above stoichiometric reaction coefficients, and maintaining partial equilibrium with calcite, dolomite, FeOOH and pyrite, a range of water compositions is calculated for variations of a factor of 2-3 in relative rates of anhydrite dissolution, sulfate reduction, and Na-Ca ion exchange (treated as an irreversible reaction) as a function of temperature variation.

Table 3 compares calculated and observed ranges in dissolved calcium, magnesium, inorganic carbon concentrations, pH, log PCO<sub>2</sub> and net calcite mass transfer for the modeled Madison Limestone waters at various temperatures. The exercise was generally successful in predicting observed trends and ranges of groundwater compositions in the Northern Great Plains as a function of temperature and irreversible reactions. But even though very realistic estimates of relative rates of reactions (derived from the mass balance calculations) were used, there is no close match in computed and observed water composition for any particular well. Much larger uncertainties in mass transfer/reaction path modeling can be expected without prior knowledge of reasonable estimates of relative rates of reactions.

## CONCLUDING REMARKS

As general comments on the usefulness and suitability of mass transfer/reaction path modeling to high-level nuclear waste repository assessment we offer the following:

1. More attention should be dedicated to measuring and evaluating reliable thermodynamic and kinetic data than to model development. Much work remains to be done in model validation, and considerable caution should be exercised guarding against over-interpretation of modeled results. The coupling with flow models may further obscure the usefulness of modeled results.

Table 3. Comparison of Range of Madison Water Compositions Modeled

Parameter	40°C		60°C		80°C		63°C	Observed <sup>a</sup> Range for Madison Waters	
	Min.	Max.	Min.	Max.	Min.	Max.	Mysse Well Obs.	Min.	Max.
mmol Ca <sub>T</sub>	2.8	14.1	7.5	19.9	9.1	17.4	11.3	1.2	13.8
mmol Mg <sub>T</sub>	0.7	7.2	0.6	9.2	0.7	10.4	4.5	0.9	5.0
mmol C <sub>T</sub>	3.8	4.8	3.5	5.1	3.3	5.3	6.9	1.9	6.9
pH	6.6	7.2	6.4	7.0	6.2	6.9	6.6	6.4	7.6
log PCO <sub>2</sub>	-1.7	-1.3	-1.4	-1.0	-1.2	-0.7	-0.9	-2.6	-0.7
α <sub>calcite</sub> <sup>b</sup>	-12.5	+0.9	-17.4	+0.9	-19.7	+0.6	-5.3 <sup>c</sup>	-0.2 <sup>c</sup>	-22.5 <sup>c</sup>

<sup>a</sup> (21).

<sup>b</sup> α<sub>calcite</sub> is the net calcite mass transfer (mmol/kg H<sub>2</sub>O), positive for dissolution, negative for precipitation.

<sup>c</sup> Derived from mass balance calculations.

2. The mass transfer/reaction path calculations are best suited for performing sensitivity analyses using an accepted range of uncertainties in thermodynamic data and relative rates of reactions. This exercise leads to predicted trends and ranges in water composition and may guide the experimentalist to areas where more accurate data are required.

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MINTEQ GEOCHEMICAL REACTION CODE:  
STATUS AND APPLICATIONS

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INTRODUCTION

MINTEQ (1,2) is a geochemical reaction code that calculates complex chemical equilibria among aqueous species, gases, and solids, and between dissolved and adsorbed states. At present, the documented version of MINTEQ is dimensioned to equilibrate a maximum of 40 elements between a total of 450 aqueous species, gases, and solids. The code has been constructed by combining the mathematical structure of the MINEQL code (3) with the thermodynamic database and geochemical attributes of the WATEQ3 code (4). MINTEQ includes the capability to transfer mass between phases and to model adsorption via several algorithms (i.e., activity  $K_d$ , activity Langmuir isotherm, activity Freundlich isotherm, simple ion exchange model, and the constant capacitance and triple-layer surface complexation models). MINTEQ incorporates a Newton-Raphson iteration scheme to solve the set of mass-action and mass-balance expressions, and uses the Davies and extended Debye-Hückel equations to calculate activity coefficients for aqueous ions.

The MINTEQ thermodynamic database has been upgraded using critical reviews and recently published studies of thermodynamic data for the aqueous species and solids of Cr, Cu(II), Pu, Tc, and U. Preliminary compilations of thermodynamic data for Co, Mo, Ra, Se, Th, and V have been added to the developmental versions of MINTEQ to provide an initial modeling capability for these elements. Future efforts will require that these preliminary data bases be critically reviewed and documented.

MINTEQ is currently being used to interpret possible geochemical equilibria that may control the compositions of waters in aquifer systems and the leachates resulting from interactions with sediments and industrial

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\* This presentation is supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory (PNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute.

wastes. Site-specific reaction models have been developed in conjunction with MINTEQ code calculations in order to simulate chemical processes observed in the laboratory and expected to occur in geologic systems. To establish the accuracy and reliability of geochemical reaction code calculations, MINTEQ and its thermodynamic database have been used in three partial validation studies of aqueous systems that contain Cu(II), Pu, and U, respectively.

#### CODE DEVELOPMENT

Extensive modifications are now under way to increase the versatility and to correct some deficiencies of the MINTEQ code package. An interactive preprocessor code, called PRODEF and written by J. R. Morrey, has been developed to help users to formulate the input data sets for solution by MINTEQ. PRODEF incorporates complex logic to detect logical errors in the formulated chemical equilibria problems and to allow users to create data sets without having to rely on the coding scheme used to identify aqueous species, gases and solids in the code's thermodynamic database. Another code of less complexity has been written by C. E. Cowan and R. A. Peloquin (PNL) to facilitate the entry of water analyses to MINTEQ.

A new version of MINTEQ, to be known as MINTEQ2, is currently being developed by J. R. Morrey and is scheduled to be verified, documented and released one year from now. Modifications will include 1) an improved convergence algorithm, 2) addition of Pitzer's equations to calculate activity coefficients of concentrated aqueous solutions, 3) more complete diagnostics, 4) revised output formats, and 5) an improved method to calculate mass transfer problems for minerals that are initially present in finite quantities.

MINTEQ relies on Newton-Raphson iteration method for calculating chemical equilibria. To increase the speed and ability of MINTEQ to reach convergence, a user can include estimates for the starting values of the activities of the independent aqueous species. If these activity estimates are too far from the true value, the Newton-Raphson algorithm may fail to converge. MINTEQ2 does not require any initial estimates for activities. It avoids the difficulties attendant with erroneous activity guesses by initially determining the deDonder parameter for each mass-action equation, thus allowing the simultaneous correction of each component rather than only that of the derived component. For the initial iterations, MINTEQ2 also incorporates a back-substitution method to permit more rapid convergence when activity estimates are far from equilibrium.

The Davies and extended Debye-Hückel equations are at best inadequate and at worst ill-behaved in solutions of high ionic strength. The Pitzer formulation has been shown to be applicable to very concentrated brines (5,6). To model high-ionic strength solutions, the Pitzer equations have been added to MINTEQ2, but have not yet been verified. Additional efforts are also needed to improve computational times when the Pitzer option is used.

Finally, MINTEQ often fails for problems where extremely soluble salts are present in small finite quantities, because, as an intermediate step, the code must calculate the equilibrium concentration of resulting aqueous species by assuming that the mineral is in infinite supply. If this calculation results in too large concentrations, the activity coefficient algorithms will be ill-behaved and the code will fail to converge. MINTEQ2 avoids this problem by using the deDonder formulation to transfer solid mass between phases.

#### THERMODYNAMIC DATABASE

The thermodynamic database for MINTEQ continues to be expanded and documented. The MCRT code, which is part of the EQ3/EQ6 geochemical code package developed by T.J. Wolery (Lawrence Livermore National Laboratory) (7), has been modified for use with MINTEQ. MCRT is being used to systematically check the internal consistency of the MINTEQ thermodynamic database and to provide documentation for the supporting files of thermodynamic data. The aqueous speciation and solubility reactions and their associated  $\log K_{r,298}^{\circ}$  and  $\Delta H_{r,298}^{\circ}$  values in the MINTEQ database are also being formulated and calculated with MCRT.

Critical reviews of thermodynamic data for aqueous species and solids of selected elements are being conducted in support of several research programs at PNL. Thermodynamic data for inorganic aqueous species and solids of Cr have been critically reviewed by R. L. Schmidt (PNL) (8) and added to the MINTEQ database. A. P. Schwab (Kansas State University) and K. M. Krupka are in the process of completing (FY85) a critical review of thermodynamic data for Np. To support a Ph.D. dissertation study on the toxicity of dissolved Cu, C. E. Cowan (PNL) has critically reviewed the thermodynamic data for Cu(II) aqueous species and solids (9,10). Data taken from recently published critical reviews (11,12) and laboratory studies are also being used to upgrade the MINTEQ thermodynamic database with respect to U, Pu, and Tc.

S. R. Peterson and others at PNL have completed preliminary compilations of thermodynamic data for the aqueous species and solids of Co, Mo, Ra, Se, Th, and V, and for reduced sulfur species. These compilations are based primarily on accepted tabulations of thermodynamic data from the Committee on Data from Science and Technology (CODATA) (13) of the International Council of Scientific Unions, the U.S. National Bureau of Standards (14), and the U.S. Geological Survey (15). Depending on the future goals and available funding for PNL research programs, some of these preliminary compilations will be expanded to include critical reviews and documentation for thermodynamic data accepted for these elements. Plans for FY85 also include the compilation of a preliminary thermodynamic database for organic complexes.

## APPLICATION STUDIES

The MINTEQ code is routinely being used in a number of PNL research programs\* to assist the interpretation of geochemical equilibria associated with aquifer systems, laboratory solubility and sediment-interaction studies, and leachates resulting from the reaction of waters with industrial wastes. In order to analyze the geochemical equilibria that may control ground-water compositions, aqueous speciation and permissible solubility controls were calculated with MINTEQ for ground-water samples from basalt aquifers of the Columbia Plateau in eastern Washington (16), the Chalk River aquifer in Canada, and a Texas aquifer being mined for U by in situ leaching methods. MINTEQ has also been used to calculate possible solubility controls for the compositions of surface waters associated with a disposal site for low-level nuclear wastes (17,18) and waters prior to and after migrating through spent oil shale at a retort site in Colorado.

Results from laboratory column and batch studies of interactions between synthetic ground waters and sediment have been combined with aqueous speciation, solubility, and adsorption calculations using MINTEQ to derive site-specific reaction models. These reaction models use geochemical equilibria to simulate the observed experimental results and provide a possible method for extrapolating laboratory results to natural geochemical systems. Site-specific reaction models have been developed for the simulation of oxidative leaching of uraninite ore, equilibria associated with the restoration of an aquifer used for in situ U mining (19), interactions of ground water with spent oil shale and coal combustion by-products, dissolution of nuclear waste glass (20), and reactions between acidic U mill tailings and clay liner materials and natural sediments (21,22).

To analyze possible consequences of the disposal of nuclear waste in geologic media, maximum possible concentrations of radionuclides (e.g., U) in certain ground-water systems (23,24) have been determined from solubility equilibria calculated with MINTEQ. MINTEQ has additionally been used to 1) evaluate the solubilities of U(VI) hydroxide solids, 2) compare calculated and analytically-determined (from exchange resins) charge-form distributions of radionuclides dissolved in contaminated ground water, 3) calculate aqueous speciation for solutions used in experimental adsorption studies of Cr, Np, Se and Tc on soils and sediments, and 4) determine equilibration periods required for sediments contacted with synthetic ground water to attain permissible equilibrium with particular solid phases.

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\* Because many of the modeling studies mentioned in this abstract are still in progress, references to published reports that describe each study are not available.

## MODEL VALIDATION

Validation studies provide integrated tests of the accuracy with which a geochemical computer code and its associated thermodynamic database simulate actual chemical processes. However, because all geochemical model validation efforts are only pertinent to the range of chemical conditions used in the calculations, such studies constitute partial validations. The MINTEQ code and its thermodynamic database have been used in partial validation studies of aqueous systems that contain Cu(II), Pu, and U. The validation effort contained in the Cu(II) toxicity modeling study of C. E. Cowan and others (9,10) resulted in coherence between MINTEQ calculations and experimental solubility data for CuO, malachite, brochantite, and azurite, and resolved contradictory thermodynamic data for three Cu(II) aqueous species. A validation study of MINTEQ for Pu has also been initiated at PNL using published data from Pu solubility studies. A charge-form distribution study (i.e., determination of relative quantities of anionic versus cationic plus neutral species) provided a partial validation for MINTEQ with respect to U dissolved in two natural water samples. Results showed that the calculated speciation of U was within the accuracy of the U charge-form distributions determined analytically with exchange resins (25). The partial validation of the WATEQ4 model for U (26) is also expected to be applicable to MINTEQ, because the MINTEQ thermodynamic database was taken from WATEQ3 (predecessor to WATEQ4) and the MINTEQ code was verified during its development by comparison calculations against WATEQ4 (1,2). Future efforts will attempt to extend our knowledge of the accuracy and reliability of geochemical reaction codes, used in conjunction with site-specific reaction models, by integrating, where possible, validation efforts with ongoing critical reviews of thermodynamic data and experimental solubility and sediment-interaction studies.

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## EQ3/6: STATUS AND APPLICATIONS

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## INTRODUCTION

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

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

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

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

#### RECENT IMPROVEMENTS

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

EQ3/6 prior to FY83 had no capability for modeling brines, because the approximations for calculating the thermodynamic activity of water and the activity coefficients of the solute species were restricted to low ionic strengths ( $<1.0$  molal). Under ONWI sponsorship, we have added an option (4,7) to use Pitzer's equations (8-11) for such calculations. These equations, based on a semi-empirical approach using virial coefficients, represent a proven methodology for modeling the thermodynamics of brines. Fig. 1 shows an example of this option, in which Pitzer's equations have been used to calculate the solubility of gypsum as a function of NaCl concentration in the system  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  at 25°C.

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

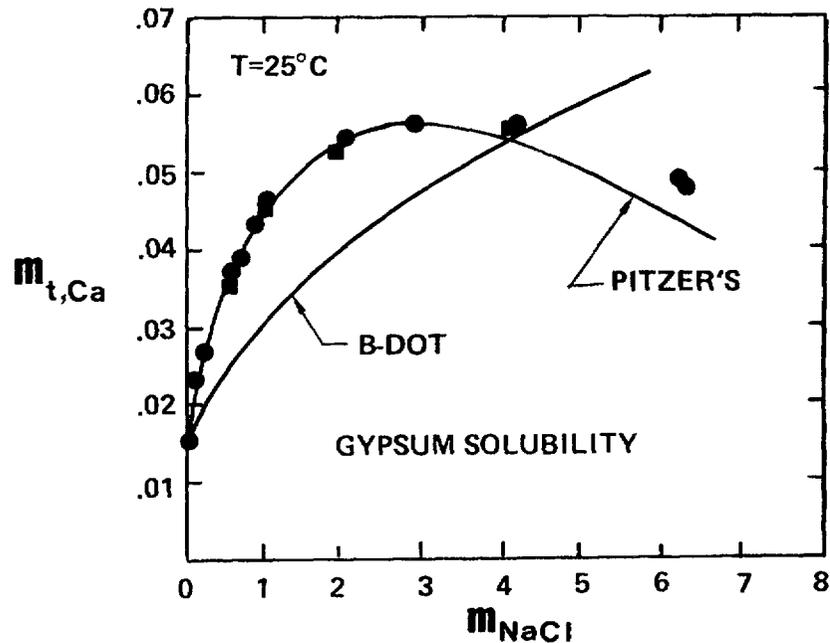


Fig. 1. The solubility of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in NaCl solution at 25°C, calculated using the Pitzer option in the EQ6 code (solid line marked "PITZER'S"). Small squares represent the experimental data of Block and Waters (14); circles those of Marshall and Slusher (15). The Pitzer coefficients were taken from Harvie et al. (11). The second line shows the solubility calculated using the B-dot equation, which was formerly the only activity coefficient model in EQ3/6.

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

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

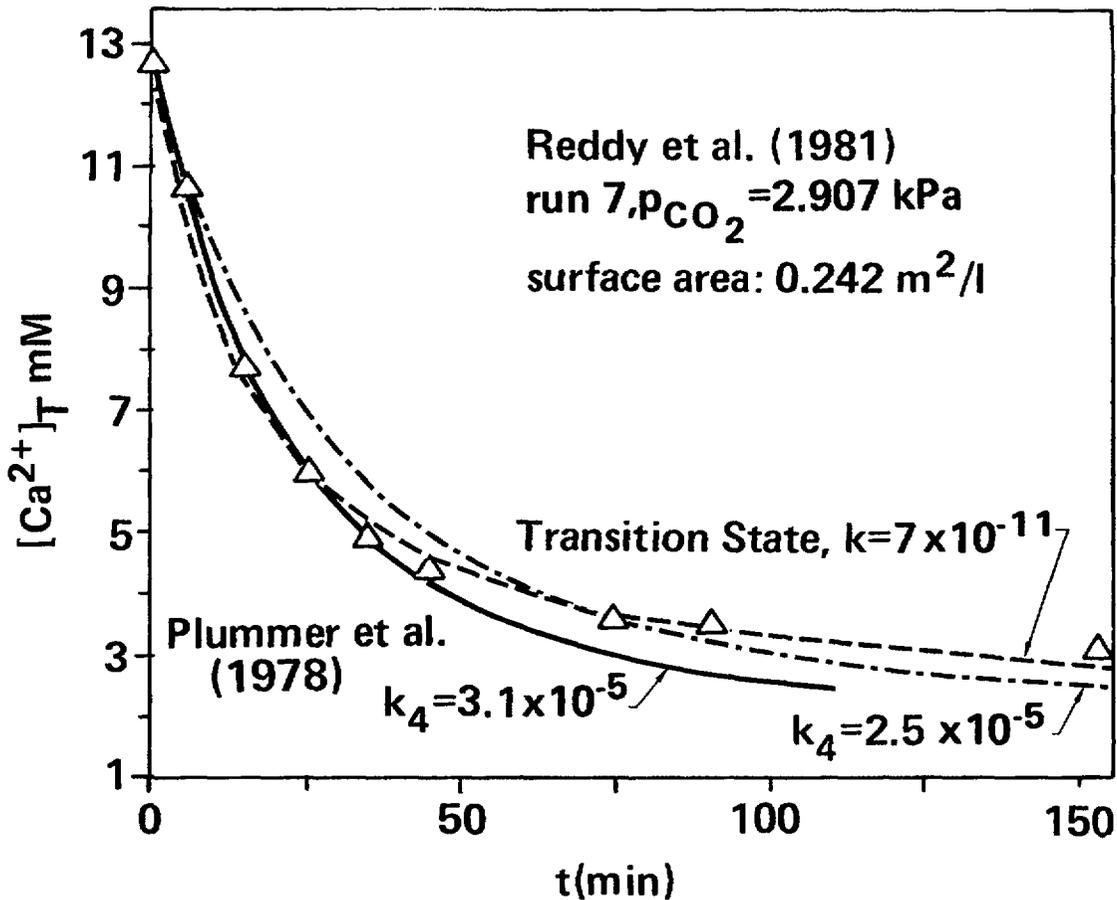


Fig. 2. The precipitation kinetics of calcite, modeled using the new capability in EQ6 (16). Symbols represent the experimental data reported by Reddy et al. (19). Two of the lines were generated using the four term rate law of Plummer et al. (20), using different values for the  $k_4$  constant.

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

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

Several improvements have been made to the EQ6 code. Prior to FY83, the code could run models of mineral dissolution kinetics, but could not calculate models of precipitation kinetics. This problem has recently been overcome by additional code development (16). Fig. 2 shows the results of some attempts of modeling calcite  $[\text{CaCO}_3(\text{s})]$  precipitation using this capability. For a general review of kinetics in geochemistry, see Lasaga and Kirkpatrick (17).

The speed of non-kinetic EQ6 calculations has recently been enhanced by the creation of two new calculational modes, economy mode and super economy mode. Economy mode gives essentially the same information

density as before. In super economy mode, however, the code skips over phase boundaries (points where minerals appear and disappear along the reaction path), and consequently gives somewhat less information. The ability to analyze the output of EQ6 has been greatly improved by the addition of a graphics postprocessor (18).

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

#### PLANNED DEVELOPMENT

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

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

Other planned tasks include:

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

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

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

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

#### RATIONALE FOR CODE DEVELOPMENT

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

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

#### APPLICATIONS

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

#### RUTHENIUM MIGRATION AT THE CAMBRIC SITE

Although ruthenium is not a prominent element of concern in high-level nuclear waste management, this example is nevertheless a good illustration of the application of geochemical modeling using EQ3/6 to shed

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

Recently a modeling study (31), using the results of an exhaustive review of the thermodynamics of ruthenium (32), has shed some light on this problem. EQ3NR, using this new data set, predicts a dissolved Ru concentration in the chimney [ $2.4 \times 10^{-11}$  molal, assuming saturation with  $\text{RuO}_{2(s)}$ ] that, considering the uncertainties involved, is nearly identical to the measured value of  $4.5 \times 10^{-11}$  molal. The calculations indicate that the species  $\text{RuO}_4^-$  makes up over 99% of the total dissolved Ru. An anionic species such as this would be expected to exhibit little retardation. On the other hand, the data also show that the field of dominance of this ion in Eh-pH space is small and surrounded by fields for  $\text{Ru}(\text{OH})_2^{2+}$ ,  $\text{Ru}_4(\text{OH})_{12}^{4+}$ , and  $\text{RuO}_4^{2-}$ . Although  $\text{RuO}_4^{2-}$  should also be a poor sorber, the two cationic species would be expected to be good sorbers. It seems likely that the aqueous form of the ruthenium in the  $K_d$  experiments was actually one of these. The sorption experiments were insufficiently characterized to allow any stronger conclusions.

#### URANIUM SOLUBILITY IN THE PRESENCE OF CONCRETE

A question which was asked in conjunction with the NNWSI project was, "What happens to the solubility limit on dissolved uranium under oxidizing conditions at 25°C if concrete is present in the system?" Concrete may be represented by its principal component, portlandite [ $\text{Ca}(\text{OH})_2(s)$ ]. Under these conditions, the phase limiting uranium concentration is expected to be schoepite ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ).

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

Taking into account the reservoir of CO<sub>2</sub> gas in the surrounding void space changes this result, however. Reaction path calculations using EQ6 with the fugacity of CO<sub>2</sub> fixed at 10<sup>-3.5</sup> bar (using the capability described by Ref. 21), predict that portlandite and CO<sub>2</sub> react to make calcite [CaCO<sub>3(s)</sub>], and consequently, the pH increases to only 8.3. The uranium solubility limit, in turn, is 4.2 x 10<sup>-3</sup> molal, a slight increase over the case where concrete is not present. Thus, concrete actually appears to have little effect on uranium solubility in the NNWSI waste package environment.

### MODELING OF LABORATORY EXPERIMENTS

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

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

The analytical approach is helpful, but it is limited in that it is not extrapolatable or even interpolatable. This kind of power can only be gained by the synthetic approach, which involves actual process modeling. Here one chooses the governing equations (rate laws, equilibria, etc.) and a set of initial conditions, and lets the code predict what will happen. In the first attempts to model tuff-groundwater autoclave experiments (33,34), we found that a purely black box approach is unworkable. One must look to the experiments

themselves for certain information critical to the success of the model. Much of this aspect has to do with supersaturation metastabilities and whether or not various thermodynamically possible secondary minerals will actually form in the time of the experiment.

For example, the devitrified tuff in the NNWSI repository horizon consists mostly of quartz ( $\text{SiO}_2$ ), cristobalite (a less stable form of  $\text{SiO}_2$ ), sanidine  $[(\text{Na,K})\text{AlSi}_3\text{O}_8]$ , and plagioclase  $[(\text{NaSi,CaAl})\text{AlSi}_2\text{O}_8]$ . Its reaction with tuff groundwater at  $150^\circ\text{C}$  achieves a near steady-state condition after several days. However, the water is then about saturated with respect to the latter three minerals, which are not the most thermodynamically stable. The water is supersaturated with respect to quartz and a host of possible secondary minerals. Some possible secondary minerals form close to saturation, some form under obvious kinetic control, and some apparently do not form at all. There is no a priori way to predict this sort of behavior, except perhaps by the development of "rules of thumb." Thus, kinetic modeling must be closely tied to trends in solution chemistry and careful characterization (SEM, EMP, STEM, XRD, etc.) of secondary phases. It is useful in synthetic modeling to consider a series of models which vary with regard to the exact assumptions of this kind. This "multiple hypotheses" approach is even more critical if one is attempting to extrapolate to longer times.

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

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

We wish to acknowledge in particular the support of EQ3/6 work by the Nevada Nuclear Waste Storage Investigations (NNWSI) and the Office of Nuclear Waste Isolation (ONWI).

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5. SESSION II

THERMODYNAMIC DATA

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## COMPLEXES OF ACTINIDES WITH NATURALLY OCCURRING COMPOUNDS

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Among the variables of major influence on the chemical behavior of actinides in natural systems are redox potential, pH, complexation by inorganic ligands (particularly carbonate and hydroxide), complexation and/or reduction by organic ligands, sorption to solids and residence time.  $E_h$  - pH diagrams for surface waters in equilibrium with atmospheric  $CO_2$  and including the effects of hydrolysis and carbonate complexation indicate that the III and IV states of plutonium would be likely in most anoxic waters and the IV state in most oxic systems (1). This assumes the  $E_h$  in anoxic, reducing subsurface waters is determined by the Fe(II)-hematite, magnetite equilibrium while in oxic waters, the oxygen-peroxide equilibrium establishes the  $E_h$ . However, much evidence exists that such  $E_h$  values are meaningless as redox equilibrium is rarely present (2). Moreover, the effects of complexation and/or redox reactions with organic compounds may be very important.

In fresh waters, the concentrations of dissolved organic material (expressed as DOC in terms of the weight of carbon) vary considerably, ranging in 100 sample sites in the U.S. from 0.1 mg/l to 15 mg/l with 85% below 2 mg/l. In deep (100 - 700 m) groundwaters in crystalline rock in Sweden, the DOC values were between 0.1 and 8 mg/l. A wide variety of compounds have been identified in the DOC among which are proteins, lipids, carbohydrates, amino acids, fatty acids, and humic and fulvic acids. The latter polymeric substances have frequently been associated with geochemical accumulation of heavy metals.

Calculations with known or estimated stability constants indicate that monomeric organic ligands at natural concentrations would not be important as actinide complexing agents in competition with the complexing properties of organic macromolecules, hydroxide and carbonate. However, the presence of carboxylic acids, amines, organic phosphates etc. in various categories of waste from the nuclear industry could have a very large, or even a dominating effect on the actinide speciation and solubility.

Laboratory experiments have demonstrated that humic materials do bind actinides strongly in the III, IV, and VI states.

The role of such polymeric organics can be summarized as follows.

- a) They could dominate the solution chemistry of trivalent actinides even at moderately low concentrations and even in the presence of carbonate.
- b) Humic material is unlikely to be of importance for the solution chemistry of the tetravalent actinides even at high concentrations since hydrolysis would be dominant in most natural water systems.
- c) Pentavalent actinides form complexes with these compounds but carbonate complexation may be more significant in most environments. The presence of organics could lead to a slow reduction to lower oxidation states (3).
- d) Carbonate complexation is likely to dominate over that with organic macromolecules for the hexavalent actinides. However, the organic complexation can cause a reduction of Np(VI) and Pu(VI) to lower oxidation states which in the case of (IV) would be the path for removal of the actinide from the solution phase (3).

A major path of removal of actinides from the solution phase is sorption or precipitation on solids. This is particularly true for  $\text{Pu}(\text{OH})_4$ . The sorption behavior of actinides in the presence of natural organic polyelectrolytes is affected through several mechanisms as follows.

- a) Changes in actinide complexation and/or oxidation state speciation would lead to changes in solubility as well as in the sorption behavior with respect to solid sorbing phases.
- b) Solid or particulate organics may serve as agents for sorption (physical adsorption as well as ion exchange and chemisorption).
- c) Inorganic solid phases can be associated with organic materials which may lead to an enhanced uptake of the actinide.

A detailed and sophisticated treatment of complexation reactions (probably equilibrium controlled) as well as of the redox and sorption reactions (probably kinetic controlled) is required for development of satisfactory models of actinide behavior in natural systems. It is obvious that in both the equilibrium and kinetic aspects of actinide behavior in many natural systems, organic material and, in particular, the polyelectrolytes, are important.

This research was supported by the U.S.D.O.E. Office of Health and Environmental Research.

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DETERMINATION OF STABILITY CONSTANTS OF THE CARBONATE COMPLEXES  
OF URANIUM AND NEPTUNIUM\*

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This contribution attempts to convey the difficulties and limitations encountered in obtaining stability constants of complex ions in solution. This information, I believe, is of importance to the people involved in developing mathematical models describing the migration of a given element in the geosphere. The difficulties in obtaining speciation schemes and therefore reliable models of migration are particularly accentuated in dealing with the actinide elements. The aqueous chemistry of these elements, under conditions similar to those found in groundwaters, is subject to a series of competing reactions, aside of adsorption phenomena which is a complex subject on its own right. The actinides undergo redox reactions, hydrolysis and complexation; mainly by carbonate, sulfate, phosphate and fluoride. Under certain circumstances, the solubilities of some of these species are exceeded and solid phases precipitate.

Speciation schemes for the actinides are difficult to obtain because of the multiplicity of species that might be present at any given pH and ligand concentration. Thus an accurate representation requires consideration of all possible species and reliable stability constants for each one.

The determination of stability constants involves for the most part the observation of a continuous response as a function of ligand concentration. This response might be a potential, a distribution coefficient, optical absorptivity at one or more wave lengths or similar phenomena. Computational and analytical tools have been developed to analyze the response curve vs ligand concentration in order to extract the contribution and therefore stability constant of each species

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\*Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

involved. The procedures are not foolproof and the possibility exists for the incorporation of non-existing species or disregarding the existence of a species that is present. The way out of these problems is through the use of an extensive data base of high accuracy which is not always accessible because of material availability and experimental difficulties and/or through the validation of the observations by means of additional physicochemical techniques. This approach is illustrated with examples taken from my own work in the determination of the hydrolysis and carbonate complexation constants of U(VI), Np(V) and Np(VI). Raman spectroscopy,  $^{13}\text{C}$  NMR and differential pulse polarography were used to complement the potentiometric titration data in establishing the existence of  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ,  $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$ . Similarly equilibrium potential measurements of the Np(V)/Np(VI) couple served to validate the corresponding hydrolytic and carbonate complexation schemes for each oxidation state of neptunium.

It is seen that in order to develop a reliable speciation scheme it is necessary to have accurate and validated stability constants which should show some degree of consistency when tested by different physicochemical techniques. Consistency of values in following trends among the actinides is also a measure of reliability but this sort of extrapolation should be used with caution.

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## TEMPERATURE DEPENDENCE OF ACTINIDE SOLUBILITIES AND SPECIATION

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## INTRODUCTION

Most of the available thermodynamic data on the nature and solubilities of compounds, as well as solution species, of the actinides U, Np, Pu and Am come from measurements made at or near 25°C. Elevated temperatures are, however, expected in a nuclear waste repository(1). Since oxidation state distributions, solubility product constants and formation constants for solution complexes are in general a function of temperature, one would expect the solubilities, and perhaps even the nature of stable compounds and solution species, of the actinides to change with increasing temperature in a complex way. Unfortunately, not nearly enough thermodynamic data are available at temperatures above 25°C to accurately predict solubilities as a function of temperature. However, using available data and estimates of the temperature dependence of reaction constants, one can perform equilibrium calculations that may provide information on the trends in solubilities and speciation and delineate the important parameters. This was done for U, Np, Pu and Am.

## CALCULATIONS

Of the many inorganic components in groundwaters, hydroxide and carbonate anions are expected to play a dominant role in the formation of insoluble compounds and solution complexes of the actinides in groundwaters of low salt content (2, 3). Therefore, to reduce the magnitude of the task, only oxide, hydroxide and carbonate compounds and only hydrolysis and carbonate complexation of U, Np, Pu and Am were considered in the calculations. Reactions involving the tri, tetra, penta and hexavalent oxidation states of the four actinides were considered.

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Research supported by the Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, under contract FIN No. B-3040-0.

Equilibrium constants relating the four oxidation states for each actinide at 25°C were calculated from free energy data given by Fuger and Oetting (4). In cases where a value had not been reported for a solubility product, hydrolysis or carbonate complexation constant, an estimate for the constant was obtained from correlations in the reported value or values of one or more of the other four actinides in the same oxidation state (5, 6).

For only a few reactions, primarily involving uranium, have experimental data on the variation of equilibrium constants with temperature been reported. However, the equilibrium constant for a reaction at a given temperature, T, can be approximated if the entropy change for the reaction at 25°C and the average value of the heat capacity change for the reaction between T and 25°C are known or can be estimated (7, 8). Since few entropies or heat capacities are known for the compounds or solution species of interest, several methods were used to estimate the required values (5, 6, 8, 9, 10, 11).

A data base was generated which contained the various solubility product, hydrolysis, carbonate complexation and redox constants for the four actinides at 25°, 60°, 100° and 150°C. The stable solid phases and solution species form by U, Np, Pu and Am were calculated as a function of pH (6, 7, 8, 9) and Eh (-0.22, 0.0, + 0.22 volts) at 0.01M ionic strength and a total carbonate concentration of  $2 \times 10^{-3} \text{M}$  for the four temperature using the computer code MINEQL (12).

## RESULTS

The following trends were observed in the results of the calculations:

- (1) Increasing T tends to favor the formation of the higher oxidation states.
- (2) Solubility product constants for all compounds decrease with increasing T.
- (3) Hydrolysis and most carbonate complexation constants increase with increasing T.
- (4) The solubility of U, Np, Pu and Am tend to increase with increasing T (factors of 10-1000 depending on the element and solution conditions), except Am and Pu (at the low pH values) where the trend reverses. The increase is due primarily to the increase in the formation constants of the higher and more complex hydrolysis products.
- (5) Except for Am, where there are no changes, the solubilities tend to increase with increasing Eh as the 5+ and 6+ oxidation states become more important.

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NEPTUNIUM AND TECHNETIUM BEHAVIOR IN GEOLOGICAL SYSTEMS<sup>†</sup>

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## ABSTRACT

Technetium, if present in groundwaters as the  $TcO_4^-$  ion, will not adsorb significantly on the minerals normally encountered in geological formations (1,2). Neptunium(V) has been reported to adsorb to some extent (2-4), but reported sorption ratios are sometimes as low as 0.5 L/kg (2). A number of investigators have suggested that if Tc(VII) and Np(V) are reduced, then the expected lower solubilities of the lower valence states might significantly reduce the potential rate of migration of these nuclides (5,6,7). There is also evidence that the lower valence forms of these elements may tend to be more highly adsorbed on geological components than the oxidized valence states (8). Thus, performance of these two nuclides in high level waste repositories may be dependent on whether reduction to a lower valence state actually occurs under repository geochemical conditions and whether the solubilities of the reduced species are as low and sorption as high as expected.

Repository performance assessment calculations of Tc migration in a reducing environment rely on a value for the solubility of the reduced state of Tc, presumably  $TcO_2$  or a hydrated form of  $TcO_2$ . Solubilities have been calculated from the literature (6,9), but the data supporting these calculations are sparse and have not been adequately verified. Furthermore, there is considerable uncertainty concerning whether Tc(IV) exists in solution as a true equilibrium monomeric species, a polymeric

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<sup>†</sup>Research sponsored by the Office of Nuclear Materials Safety and Safeguards and Office of Research, U. S. Nuclear Regulatory Commission under Interagency Agreements 40-549-75 and 40-550-75 with the U. S. Department on Energy under contract No. DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

species, or a colloidal or pseudocolloidal form. Even at pH 1-3, there is disagreement (10,11). However, there appears to be some agreement that below a concentration of about  $10^{-5}$  to  $10^{-6}$  mol/L, at least a metastable monomeric species might exist. Above this concentration, there is fairly strong evidence that polymeric species exist (11,12). Investigations of solubility and hydrolysis must address the problem of polymer and colloid formation if the measurements are to be considered sufficiently valid for inclusion in data bases.

Technetium, present initially as  $TcO_4^-$ , is moderately adsorbed by basalt under highly anoxic conditions, but the extent of sorption is very sensitive to the composition of the groundwater and the surface preparation of the basalt. Valence analysis shows that much of the sorbed technetium is reduced, and most of the technetium is very difficult to resolubilize (8,13-15).

Neptunium can exist in aqueous solution as Np(III), Np(IV), Np(V), and Np(VII). The oxidation states of environmental interest are (V) and (IV). In acid and neutral solution, there is little doubt that Np(V) exists as the singly charged  $NpO_2^+$  ion. However, as the pH is increased to the neutral or alkaline pH of many groundwaters, a number of competing reactions can occur which will affect the speciation of Np(V). Above about pH 8, hydrolysis will begin but hydrolysis will compete with formation of carbonate complexes in groundwaters containing sufficient carbonate species (16). Thus, at pH levels above 8, it is possible that negatively charged carbonate species might be formed which would probably be poorly adsorbed. On the other hand, hydrolysed forms of Np(V) might be strongly adsorbed. Reducing geologic environments, particularly those which contain accessible ferrous ions, are likely to reduce Np(V) to Np(IV). Np(IV) is expected to be strongly hydrolysed to form a number of Np(IV) species (17,18).

Np(V) is strongly adsorbed by some hydrous oxides from neutral and alkaline solutions. There is experimental evidence that Np(IV) species are strongly adsorbed by some minerals (8). Np(V) is adsorbed by basalt to varying degrees, and the extent of sorption is dependent upon the type of basalt and the composition of the groundwater. Valence state analysis shows that under some conditions the neptunium basalt is reduced to Np(IV) (8,13-15).

Great care should be taken in the use of values from the literature which have not been adequately verified. An example of the use of suspect or uncertain values is a case where free energies of formation are given for oxides of Tc which have only been postulated to exist (19). An example of this is the oxide  $Tc_3O_4$ . We have not seen any reports of the characterization of this oxide, and its existence has only been inferred from some very indirect electrochemical measurements. Despite the lack of evidence for the existence of this oxide, it has appeared in some Eh-pH diagrams and data bases. A critical examination of the electrochemical evidence for the existence of  $Tc_3O_4$  shows that its existence is only hypothetical.

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## THERMODYNAMIC PROPERTIES OF GEOLOGIC MATERIALS: STATUS AND FUTURE

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Chemical and physical modelling of geological processes through numerical methods is based on thermodynamic principles and thermodynamic descriptions of the properties of the phases in the environment being modelled. Such modelling is used because direct experimental investigations are impossible for many problems. For chemical and physical modelling to be effective, the thermodynamic data used must be accurate, internally consistent, and complete for the environment being studied. At present, there is in existence no compilation of thermodynamic data for minerals that can be used in such modelling and yield satisfactory results! Furthermore, no complete compilation will exist in the foreseeable future if the present lack of interest in aggressively seeking and supporting a coordinated evaluation effort continues.

The current compilations reflect the interest of the independent compilers and evaluators. With a properly coordinated effort, data for more phases could be included in the compilations and the quality of the data could be improved. The costs of compilation and critical evaluation of thermodynamic properties represent less than five percent of the costs of the original research. When the wider utility of the evaluated thermodynamic properties is considered, these additional costs are minor.

Compilations of thermodynamic data presently available for use in geological problem solving may lack either thermophysical consistency or thermochemical consistency. All data sets are incomplete; that is, they do not cover all phases in the chemical systems being considered. The most critical need is for an evaluation of solid solutions. Many minerals are complex solid solutions where elements were incorporated because the elements had the right size, charge, and abundance, relative to other candidates for the crystal site. No one exchange model has been described to date that is applicable to most equilibria for such solid solutions. At present, the approach is to treat each such equilibrium separately. Besides the problems related to solid solution, we have the incomplete data for chemical end-member phases. For phases such as spinels, illites

and other clay minerals, chlorites, micas, amphiboles, and pyroxenes, evaluated data for many of the end-member compositions are lacking. Data for the many minor phases in rocks, particularly the sulfides, are not properly evaluated, yet some of these phases control the oxidation state of the environment.

Until recently, tabulations of thermochemical data were built up by a stepwise process. Beginning with the data for a few reference phases, a scientist would add data for one phase at a time by examining some well-documented study or studies relating that phase to the reference phases. The new phase became a secondary reference phase and the process was repeated. In such an approach, an error in a reaction relating two phases can lead to a change in the reference state for an element. This change may then be propagated to other phases subsequently added to the data set.

Some tabulations lack thermophysical consistency in that one function is used to fit one property and another, unrelated function is used to fit a second, related property. Inconsistency is common for data on water because different functions have been used to describe heat capacity and Gibbs energy (or fugacity).

All tabulations published prior to about 1975 contain the problems described above. Beginning in the early 1970's, two methods for the evaluation of experimental data were developed that have the potential for producing thermophysically and thermochemically consistent data for minerals. The methods are the linear-program approach of Gordon (1) and the multiple-regression approach of Haas and Fisher (2).

Experimental data are reduced to a set of equalities and inequalities in the linear-programming approach. These are then used to solve for the set of entropies, enthalpies, and Gibbs energies that supply a permissible solution to the chemical observations. Advantages of the linear-programming method are 1) the entire range of permissible thermodynamic parameters is accessible for inspection by the appropriate choice of objective criteria, 2) any constraints such as calorimetric data may be added to the problem, 3) constraints may be examined with or without additional assumptions, 4) the solution cannot violate any experimental or thermodynamic constraint, and 5) the decision-making process can be documented.

In the multiple-regression approach, the available experimental data are fit simultaneously by least-squares techniques with functions for the molar volume and heat capacity and the appropriate constants of integration to provide consistent functions for entropy, enthalpy, and Gibbs energy. The experimental data are weighted proportional to the precision of the measurement. The approach returns the best set of constants that permit the calculations of the observed properties with a minimum relative error. Advantages are 1) the entire spectrum of experimental data types can be simultaneously evaluated, 2) copious data can be evaluated, 3) the experimental data can be in minor conflict, 4) the variance-covariance matrix enables one to prepare tables of

thermodynamic properties with the associated precisions, and 5) the decision-making process can be documented also.

The compilation of an extensive data base of thermophysically and thermochemically consistent properties for mineral phases is possible with procedures and technology currently available. However, the necessary long-term funding commitments and a coordinated evaluation program are lacking. An effort to resolve these problems should be focused through an agency that has historical perspective and technical competence in programs in thermodynamics. The Office of Standard Reference Data of the U.S. National Bureau of Standards would be a candidate. The advantages of working within the National Standard Reference Data System are 1) the significance, reliability, internal consistency, and verifiability of the product can be maintained, 2) the feasibility of the approach in the evaluation can be examined, 3) the investigators can be required to provide evidence of technical qualifications, experience, and support facilities, 4) the compatibility of the mineral data with the remainder of the information in the National Standard Reference Data System can be maintained, and 5) the agency already serves as a focus for grants, contracts, and standards.

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6. SESSION III

KINETICS AND COUPLED PROCESSES

Chairman: P. Ortoleva  
Indiana University and Geochem Research Associates, Inc.

## MODELING WATER-ROCK INTERACTIONS

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## ABSTRACT

The passage of waters through a rock involves a number of coupled reaction and transport processes. This coupling can lead to qualitatively and quantitatively different long time behavior than can be predicted based on equilibrium considerations. The approach suggested here involves chemical kinetics and transport equations solved both partially analytically and via a series of numerical algorithms that take special advantage of the geological constraints placed on the equations. The overall approach allows for the description of a host of instability and related nonlinear phenomena not accessible to equilibrium models. Here we outline our methods and cite selected applications that demonstrate the power of the approach and the pitfalls involved in other models and methods.

In our model the transport of fluids through a rock is driven by gradients of pressure and temperature (buoyancy) while the flux of solute species is due to diffusion as well. The diffusion coefficients and permeability are related to the porosity and connectivity of the pores. The latter are determined by the texture and hence by the size and shape of the various mineral grains. Since the growth or dissolution of mineral grains can thus effect permeability and hence the flow of the very waters that cause these texture changes, it is clear that the grain growth-flow coupling accounted for in our model is a potentially important facet of water-rock systems.

The rate of change of volume of a mineral grain is proportional to its surface area. Consider a mineral  $M$  dissolved according to the process  $x_1X_1 + x_2X_2 + \dots + M \rightleftharpoons y_1Y_1 + y_2Y_2 + \dots$  with stoichiometric coefficients  $x_1, x_2, \dots, y_1, y_2, \dots$  for the aqueous species  $X_1, X_2, \dots$  and  $Y_1, Y_2, \dots$ . Mass action kinetics yields a growth law of the form  $\partial R/\partial t =$

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\*includes C. Moore, E. Merino, J. Chadam, E. Ripley, J. Hettmer, J. Elzea

$k\{X_1^{x_1} X_2^{x_2} \dots - K Y_1^{y_1} Y_2^{y_2} \dots\}$  where  $k$  is a rate coefficient and  $K$  is the equilibrium constant;  $R$  is the radius of the assumed spherical  $M$  grain. Rate laws yielding more accurate equilibria are obtained by replacing the concentrations  $X_1, X_2, \dots, Y_1, Y_2, \dots$  by activities. When available, more realistic rate laws may easily be incorporated in our simulation program.

A complete description must allow for the nucleation of grains not already present in the system. Nucleation takes place in different ways. It may be as a coating on selected grains or as occasional crystallites at selected surface sites on preexisting grains. These and other detailed models are handled in a similar way in our program. For example in the case of grain coating we introduce a thickness  $\tau$  of the coating;  $\tau$  obeys an equation similar to that for  $R$  in the previous paragraph except that the rate constant  $k$  is replaced by a nucleation factor  $q$  defined as

follows. Let  $E = X_1^{x_1} X_2^{x_2} \dots / Y_1^{y_1} Y_2^{y_2} \dots$ . Then if  $K_n (>K)$  is the nucleation threshold for the above mentioned dissolution reactions, we have  $q = k$  when  $E > K_n$  or  $\tau \neq 0$  and  $q = 0$  otherwise.

The description of the water-rock system in our model consists of the spatio-temporal dynamics of the pressure, temperature, aqueous species concentrations and the texture. The texture consists of the local particle radius of mineral grains or the coating thickness of the minerals that are thus distributed. The modeling proceeds by coupling the mineral grain growth or nucleation equations with conservation equations for the mobile species concentrations. Let  $c_i$  be the concentration of species  $i$  per pore fluid volume. Then we write

$$\frac{\partial \phi c_i}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i + F_i + \sum_{\alpha=1}^m v_{i\alpha} \rho_{\alpha} n_{\alpha} \frac{\partial V_{\alpha}}{\partial t} \quad (1)$$

where  $\phi$  is the porosity (volume fraction of the rock that is pore space);  $\vec{J}_i$  is the flux of species  $i$ ,  $F_i$  is the rate of aqueous reactions and surface attachment processes;  $v_{i\alpha}$  is a stoichiometric coefficient for the dissolution/growth of  $\alpha$ ; and  $V_{\alpha}$ ,  $n_{\alpha}$  and  $\rho_{\alpha}$  are the volume, grain number density and molar density of  $\alpha$ -mineral in the rock. For example  $V_{\alpha} = 4\pi R_{\alpha}^3/3$  for spherical  $\alpha$ -grains;  $m$  is the number of minerals. The flux  $\vec{J}_i$  accounts for diffusion and percolation. For example in an isothermal system  $\vec{J}_i = -\phi D_i \vec{\nabla} c_i - \phi \kappa c_i \vec{\nabla} p$  where  $D_i$  is the diffusion coefficient of mobile species  $i$  in the rock and  $p$  is the pressure. The permeability  $\kappa$  depends on texture and underlies the coupling between texture and flow. The dependence of  $\kappa$  on texture can be approximated by the Fair-Hatch law.

The above description seems straightforward enough. However it presents some very difficult problems when standard numerical techniques are applied. To see the origin of the difficulties it is useful to transform to dimensionless variables. Let  $\bar{c}_i$  be a typical value of  $c_i$  so that  $\bar{c}_i = c_i \gamma_i$ , thus  $\gamma_i$  varies between zero and one. Then we see the emergence of a characteristic large parameter  $\rho_{\alpha} / \bar{c}_i$  in front of the  $\partial V_{\alpha} / \partial t$  terms in Eqn. (1) when rewritten in as an evolution equation for  $\gamma_i$ . Typically

this ratio can be on the order of  $10^3$  to  $10^9$  or even higher for weakly soluble minerals. Thus straightforward numerical computations are essentially impossible. One result of this "stiffness" in the equations is the presence of sharply defined mineral zones - i.e. quasi-discontinuous variations in texture. In our approach we turn this difficulty into an advantage by using analytical methods to partially solve the continuity equations exactly and incorporate the partial solutions into our computer codes.

Another difficulty with a straightforward integration of (1) is that many of the reactions contributing to the rate term  $F_1$  are very fast on a geological time scale. Thus a viable approach must be flexible enough to allow selected aqueous processes to be maintained at equilibrium while others are kinetically limited. In our computer codes we have implemented an "equilibrium subdynamics projector" technique that allows us to maintain selectable reactions at equilibrium.

Combining these approaches with methods for accelerating the calculations with improved projection techniques for getting accurate first guesses for various iteration loops in the numerical algorithm, we have an overall computer simulation approach that makes realistic computer modeling of water-rock interactions possible. To test our approach we have attacked some simple problems as follows.

Consider an aquifer containing an insoluble matrix and a soluble component. As undersaturated waters flow through it a dissolution front advances. If there is a region on the front jutting slightly ahead of the rest of an otherwise planar front, the flow will tend to be directed towards the protrusion. This focused flow of undersaturated waters further extends the protrusion since a higher degree of local dissolution yields a higher local permeability. This leads to dissolution fingers of augmented permeability that propagate at a speed much greater than that of the planar alteration front.

The coupling of nucleation, growth and soluble species transport can lead to the periodic deposition of certain minerals as a reaction zone advances across the system. Such periodic precipitation are discussed in more detail in the abstract by C. Moore in this volume.

These and other instability phenomena are sensitive tests of the viability of our techniques. These water-rock instabilities are apparently possible in a great variety of systems. They are often qualitatively different in behavior from what might be expected and is predicted by simpler models not incorporating reaction-percolation feedback, nucleation and other effects. Because one purpose of mathematical models is to point out the possibilities for "unexpected" behavior, any acceptable approach must take account of the full range of water-rock reaction and transport phenomena.

## COUPLED GEOCHEMICAL AND SOLUTE TRANSPORT CODE DEVELOPMENT

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## INTRODUCTION

A number of coupled geochemical hydrologic codes have been reported in the literature (Table 1). Some of these codes have directly coupled the source-sink term to the solute transport equation (1-3). The current consensus seems to be that directly coupling hydrologic transport and chemical models through a series of interdependent differential equations is not feasible for multicomponent problems with complex geochemical processes (e.g., precipitation/dissolution reactions). A two-step process appears to be the required method of coupling codes for problems where a large suite of chemical reactions must be monitored. Two-step structure requires that the source-sink term in the transport equation is supplied by a geochemical code rather than by an analytical expression (4-7). Because an equilibrium geochemical code is used to supply the source-sink term, kinetic processes are assumed not to be important. The validity of this assumption depends on the relative rates of chemical reactions and fluid flow rate.

## COMPUTER CODES

We have developed a one-dimensional two-step coupled model designed to calculate relatively complex geochemical equilibria (CTMID). Our geochemical module implements a Newton-Raphson algorithm to solve heterogeneous geochemical equilibria, involving up to 40 chemical components and 400 aqueous species. The geochemical module was designed to be efficient and compact. A revised version of the MINTEQ Code (8) is used as a parent geochemical code. The parent code is used as a scoping tool to define the smallest conceptual model needed to describe the geochemical

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\* This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory (PNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute.

system. The conceptual model is solved iteratively by the geochemical module using concentrations determined by the transport module. Geochemical processes considered include aqueous speciation, ion exchange, adsorption (triple-layer model), and precipitation/dissolution reactions. A Markov approach is used in the transport module to model advection, hydrodynamic dispersion, and molecular diffusion. The Markov model is easily parameterized from column data (e.g., a breakthrough curve of a conservative tracer) and is an extremely rapid method for calculating transport. At the present time, the computer code is undergoing verification tests and a user's guide is being prepared.

Table 1. Summary of Geochemical-Transport Coupled Codes

Model	Coupling Method	Dimension	# of Comp.	Aqu. Spec.	Sorp- tion	Precip- itation	Activity Coeff.
Rubin & James(1)	Direct	1	3	no	IE	no	no
Valocchi et al. (2)	Direct	2	3	no	IE	no	no
Miller & Benson (3)	Direct	1	4	yes	IE	no	Davies
Grove & Wood (4)	2-step	1	4	yes	IE	yes	D-H
Walsh et al. (5)	2-step	1	7	yes	Lan.	yes	Davies
Theis et al. (6)	2-step	1	6	yes	Lan.	no	Davies
Felmy et al. (7)	2-step	1	10	yes	Lan.	yes	Davies and D-H
This Work	2-step	1	40	yes	TL IE	yes	Davies and D-H

NOTE: D-H = Extended Debye-Huckel; IE = ion exchange; Lan. = Langmuir Isotherm; TL = Triple- Layer Model

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## FLOW/REACTION MODELS OF NATURAL SYSTEMS

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Because of the complexities of natural systems, coupled reaction/transport simulations are requisite for modeling them. Examples of computer simulated time-space evolution for two systems are given in the following discussion. For both examples the reaction/transport equations were solved using methods described in Ortoleva, this volume.

Every species in the simulation can be modeled using the continuity equation

$$\frac{\partial X}{\partial t} = \nabla \cdot (D_x \nabla X - \vec{v} X) + R_x \quad (1)$$

where  $X$  is the concentration of  $x$ ,  $t$  is time,  $D_x$  is the diffusion coefficient of  $X$ ,  $\vec{v}$  is the flow velocity,  $R_x$  is the amount of  $X$  produced by reaction and  $\nabla$  is the del operator.  $R_x$  is the sum of rates for all reactions  $r$ , multiplied by the stoichiometric coefficient of  $X$  in  $r$ ,

$$R_x = \sum_{i=1}^r \nu_i^r W_i \quad (2)$$

where  $\nu$ 's are stoichiometric coefficients and  $W$ 's are rates. For all reactions in these systems we have chosen to write the rate equation as

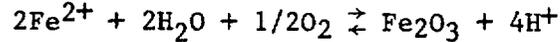
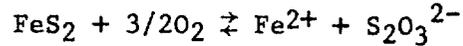
$$W_r = k_r (A_r + a_r) (K_r \Xi_e^R - \Xi_r^P) \quad (3)$$

where  $k_r$  is a rate constant,  $A$  the surface area of the solid (if present) in the reaction,  $a_r$  a nucleation parameter,  $K_r$  an equilibrium constant,  $\Xi_r^P$  the product or reaction products raised to their stoichiometric coefficients and  $\Xi_r^R$  the same for the reactants.

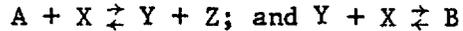
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\*includes P. Ortoleva, E. Merino, J. Chadam, E. Ripley, J. Hettmer, J. Elzea

As a first example consider the six species, two-reaction system



For simplicity here, make all stoichiometric coefficients 1 and assume pH is buffered to give two reactions of the form



This is a model for a simple redox front. Three different evolutions of the solids in this system are shown in Fig. 1. A nucleation threshold is crucial for the occurrence of banding.

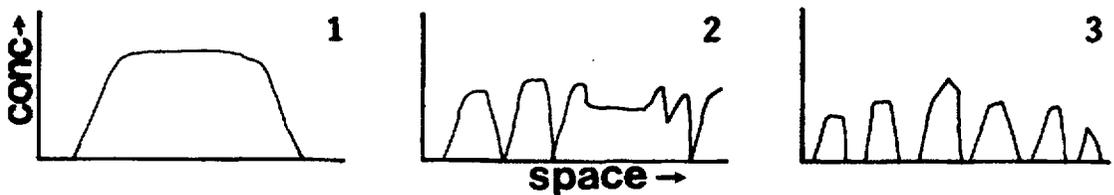
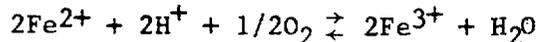
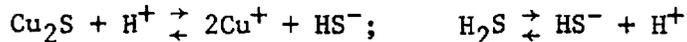
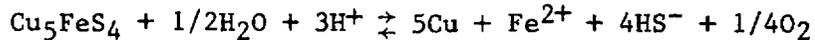
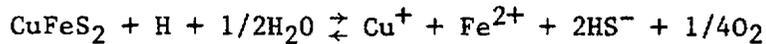
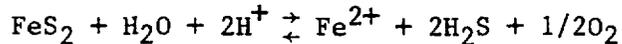


Fig. 1. Goethite concentration vs. space. 2) can be derived from 1) by increasing initial pyrite concentration and lowering input oxygen; 3) can be derived from 1) by decreasing input oxygen and slightly increasing the activity product required for nucleation.

Now consider a somewhat more complex system of species and reactions:



This system is a rudimentary model of a 'red bed' copper deposit. The initial configuration is a pyrite-bearing, inert (e.g. quartz) matrix through which copper-bearing fluid not in equilibrium with pyrite flows. As the pyrite dissolves, sulfur and iron are added to the fluid and hydrogen is removed resulting in precipitation of copper-iron sulfides and a concomitant increase in the Cu:Fe and Cu:S ratios at space points where the precipitation takes place. Because the initially undersaturated fluid relentlessly impinges on the solid bearing zones the Cu-Fe sulfides also dissolve and the process is repeated. The sequence of minerals as well as the number produced is a function of many variables. Two examples are shown in Fig. 2.

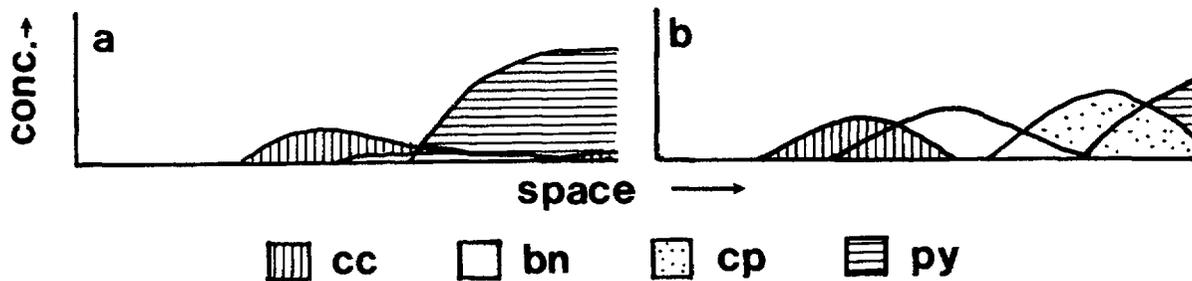


Fig. 2. Disposition of Fe-Cu-S minerals for a) velocity = 10 and b) velocity = 1. All other parameters are the same.

An interesting and important aspect of this type of modeling is sensitivity analysis. In the copper system above we find relative insensitivity to the concentration of iron and sulfur in the incoming fluids but high sensitivity to copper, oxygen and hydrogen. Figure 3 shows the sensitivity to variations in the equilibrium constants for the pyrite dissolution reaction. Such investigations are useful in determining to what degree of accuracy various parameters need be determined.

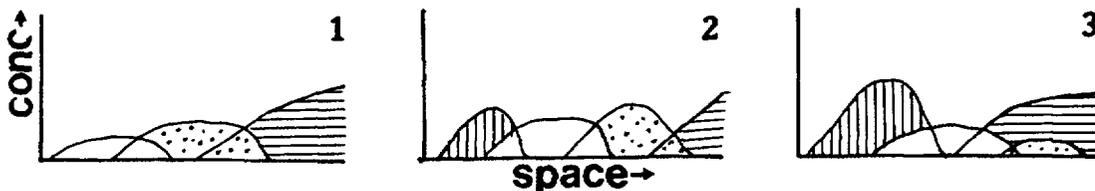


Fig. 3. Disposition of Cu-Fe-S minerals for 1)  $K_{\text{pyr}} = -1 \times 10^{-36}$ , 2)  $K_{\text{pyr}} = 1 \times 10^{-37}$ , 3)  $K_{\text{pyr}} = 1 \times 10^{-38}$ . Other parameters are the same as 2b.

The agreement of prediction from our models with naturally occurring deposits substantiates our approach.

## DISSOLUTION AND PRECIPITATION KINETICS OF MINERALS

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The chemical evolution of repository sites will necessarily involve the response of minerals to interactions with natural fluids. This water-rock interaction will lead to both the growth and the breakdown of a number of important mineral phases. These heterogeneous chemical reactions induce a strong and important coupling between the fluid flow dynamics and the minerals present in the geologic environment. The time-dependent dissolution or precipitation of solid phases in a repository environment will have direct effects on the porosity and permeability, on the mineralogy in the near field, and on the solution chemistry including the sorption and adsorption of radionuclides in the host rock. Therefore, to understand and accurately predict the long-term dissolution-precipitation behavior of phases in potential host rocks, a knowledge of a full rate law (that is, the rate law for both dissolution and precipitation) for individual phases is required. This rate law would include the possibility of attaining equilibrium (zero net rate) as a special case. In particular, kinetic data are urgently needed for dissolution-precipitation of individual phases such as smectites, zeolites, natural glasses, silica phases (quartz, cristobalite, and tridymite), feldspars, and evaporative minerals (especially halite). The kinetic data on individual phases will then be combined with whole-rock experiments to provide a critical link and validation of the kinetic models that will be used to predict the chemical behavior of host rocks in the evolution of a repository site.

The rocks in areas that are being actively considered as hosts for high-level radioactive waste repositories (including basalts, tuffs, and granitic rocks) are complex multiphase mixtures. The long-term chemical and physical integrity of these rocks is one of the many considerations in the ultimate selection of a repository site. This has led to numerous "whole-rock" dissolution experiments that have attempted to characterize the interactions between these rocks and the solutions that might come in contact with them. Interpretation of the results from these dissolution experiments and extrapolation to the behavior of various repository sites is an extremely complex task, primarily because the factors that regulate the reaction rates of the individual minerals are poorly understood at present.

To develop a solid and defensible understanding of the interactions that are occurring, it is essential that we undertake experiments in which the rates and mechanisms of dissolution and precipitation of well characterized minerals are determined. The dissolution-precipitation experiments must be done under conditions that can be used to model the response of the repository to changing environmental conditions. The factors that should be considered in such a study include temperature, pH, starting solution compositions, progress of fluid modification dissolution, stoichiometry (and, if needed, secondary-mineral precipitate characterization), the speciation of aqueous components, and reaction site characterization.

Minerals in the host rocks will be exposed to temperatures ranging from ambient groundwater temperatures (approximately 20°C) to, in the most extreme case, values close to that generated by the waste canisters (approx. 250°C). The dissolution experiments should span some or all of this range. Two major types of information should result.

1. The variations of rates with temperature will yield activation energies for the dissolution reaction. This will allow accurate prediction of reaction rates over a wide range of conditions.
2. It will be possible to determine whether there are changes in the reaction mechanism as a function of temperature.

Similarly, the pH-dependence of the reaction rates (and mechanisms) must be detailed. Here the primary efforts should be concentrated on a range of pH values of groundwaters in the area. The pH range of 4 to 10 should encompass most fluids of interest.

To date, little is known about the effect of solution composition (aside from pH) on the rates of mineral dissolution. Studies should be undertaken to determine how reaction characteristics of the various minerals respond to changes in the ionic composition of the fluid. Because fluid compositions vary from site to site, the range of experimental conditions must be adjusted on a site-specific basis, although a more general understanding of the reaction processes is central to development of a generalized reaction-path model.

Another critical task that has not been uniformly undertaken in the past is a determination of the complete reaction stoichiometry. This includes, to the extent possible, a complete time-series determination of the major mineral-forming elements (for example, Si, Al, Na, K, Mg, Ca, and Fe) and, where applicable, the minor components (for example, Sr and Mn) of the mineral. These analyses should be completed on both the solutions that evolve from the reactions and, if secondary precipitates are forming, on those solids. Care must be taken in these measurements to differentiate between finely divided colloidal material that might be generated (for example, with Fe-oxihydroxides) and those species that are truly dissolved. We suggested that solutions be passed through a 0.2 micron filter to accomplish this differentiation.

Finally, it is critical to characterize the nature of the reaction sites on these individual minerals. Recent results suggest that primary silicates do not dissolve by a general attack of the surface. Because most past work has included a generalized surface-area term in the kinetic equation, it will be critical to the accuracy of any modeling effort to understand more completely the relationship between surface reactive sites and rate; this can only be reasonably accomplished by execution of coherent dissolution experiments.

The growth of mineral phases in a repository site as a response to the chemical changes induced by fluids will have a strong impact on the possible co-precipitation of actinides as well as on the overall hydrology of the site. Therefore, it is very important to understand the precipitation kinetics (as well as the dissolution) of a number of crucial mineral phases. The ubiquitous precipitation of silica in many natural geothermal systems underscores the need to know silica precipitation kinetics. In part, these data are available for silica but they should be extended to include the kind of characterization suggested in this section.

The study of precipitation kinetics of silicates and aluminosilicates can be complicated at low temperatures (for example, 25°C) by the formation of amorphous products, which may not be fully responsible. Therefore, the most efficient way to undertake the study of precipitation reactions is to carry them out at temperatures probably above 100°C. At higher temperatures, crystalline products are more prevalent; although, for example, in the case of silica, amorphous products may still form. The precipitation reactions should follow the same procedure for characterization of solutions and solids that was outlined in the earlier section. In addition, the experiments should "seed" the growth with the desired products. Seeding avoids the problem of nucleation kinetics, which are usually minimized in nature (because of the presence of many possible nucleation sites). However, future studies may want to check the role of nucleation kinetics. The nature of the precipitation of the surface of the seed crystals should be characterized by available surface chemistry tools (for example, SEM and ESCA).

The supersaturation of the solutions should be varied over a wide range to elucidate the rate law. Furthermore, because minerals are often complex phases, the supersaturation should be varied in different ways by changing the relative concentrations of silica, aluminum, and constituent cations in solution.

An important constraint on both dissolution and growth kinetic data is the self-consistency imposed by the existence of thermodynamic equilibrium. Obviously, the rates must go to zero (from either direction), if the solids and fluids are in equilibrium. The condition of equilibrium can often be achieved in numerous ways. Therefore, the equilibrium consistency check is a powerful guide in understanding the full rate law for dissolution and precipitation.

7. SESSION IV

APPLICATIONS OF GEOCHEMICAL MODELS

Chairman: A. C. Lasaga  
Yale University

## APPLICATIONS OF GEOCHEMICAL MODELLING IN THE CANADIAN PROGRAM

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## INTRODUCTION

The Canadian Nuclear Fuel Waste Management Program is now in a generic concept assessment phase. The concept is based on immobilization of the fuel waste followed by emplacement in an underground vault 500 to 1000 m deep in a stable plutonic rock in the Canadian Shield. One of the goals of the concept assessment phase of the program is to assimilate the results of laboratory and field research to produce estimates of the potential impact of the disposal vault on man and the environment (1).

## THE CONCEPT ASSESSMENT

The assessment is being carried out with the probabilistic safety assessment code, SYVAC (2). SYVAC specifically addresses the problem of uncertainty and variability in the values of the input parameters by representing them as distributions rather than single values. Sampling a value for each parameter from its distribution characterizes a possible state of the system and defines a scenario. SYVAC contains submodels representing the vault, the geosphere (i.e., the massive rock formation surrounding the vault) and the biosphere (i.e., the environment accessible to man in everyday life). SYVAC estimates the transport of radionuclides from the vault, through the geosphere to the biosphere, and calculates the associated dose consequence. Repeated sampling of scenarios and estimation of consequence result in a histogram of frequency of occurrence versus the dose consequence estimates (3). Currently the assessment is not site specific and field data from several locations in the Canadian Shield are being used to define input parameter distributions for SYVAC.

Geochemical models provide a detailed interpretation of the laboratory and field results for the SYVAC code. They can supply input parameter distributions when such data cannot be extracted directly from experiments. They are also being used to verify whether simple approximate models used in SYVAC are adequate, by comparing detailed geochemical model calculations with simple SYVAC calculations. The following paragraphs give some examples of geochemical modelling support for the vault and the geosphere submodels.

## GEOCHEMICAL MODELLING FOR THE VAULT AND GEOSPHERE SUBMODELS

The vault submodel represents container failure, release of radionuclides from the waste forms and radionuclide transport through the buffer. The transport equation is one-dimensional and contains terms for diffusion, convection, linear sorption and radioactive decay (3).

Thermodynamic models are used to study the long-term release of radionuclides from used fuel. For example, a mathematical formula has been derived (4), using thermodynamic principles, for the calculation of  $UO_2$  solubilities as a function of temperature, pH, oxidation potential and various anion concentrations. The solubility of  $UO_2$  can, therefore, be determined from input distributions of geochemical parameters in an underground vault without the need for complex thermodynamic equilibrium programs.

Chemical kinetics models are being used to study the effects of radiolysis on the release of radionuclides from used fuel. The main problems encountered with these studies are the lack of complete kinetic data and difficulties in modelling the transport of dissolved groundwater species into cracks in the fuel.

Planned modelling work related to the vault includes evaluation of the long-term stability of the buffer and backfill components in groundwater, of the validity of leach-rate-type source models for the release of radionuclides from vitrified wastes, and of the use of elemental solubilities as one of the factors limiting radionuclide transport following release from vitrified wastes.

The geosphere submodel represents the migration of radionuclides through fractures in the rock by a one-dimensional transport equation containing terms for convection, dispersion, linear sorption and radioactive decay (3).

The sorption of radionuclides by mineral alteration products is being studied experimentally. Reaction path modelling (5) is one method of identifying which alteration products should be included in these studies. Work is in progress on deriving an internally consistent thermodynamic database for reaction path models of geochemical systems from phase equilibria experiments using linear programming (6).

Other geochemical calculations are being used to study the adequacy of linear sorption models for describing rock-radionuclide interactions (7). The effects of chemical speciation on the migration and sorption of radionuclides of special interest, e.g., technetium, will also be studied.

## CONCLUSION

Geochemical modelling is useful for many aspects of the assessment of nuclear fuel waste disposal. The tools to perform this modelling

(e.g., chemical speciation, chemical kinetics, reaction path and transport codes) are well developed. The SYVAC code uses the results of such geochemical models and experimental data to estimate the impact of a disposal vault. The difficulties encountered in some applications of the geochemical modelling tools are mostly due to lack of sufficient data. To overcome these difficulties, it is important to get reliable data. Future effort should concentrate on the most important processes that control the release and migration of radio-nuclides. These processes can be identified by performing sensitivity analyses with the SYVAC code.

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APPLICATIONS OF GEOCHEMICAL MODELING TO HIGH-LEVEL NUCLEAR WASTE  
DISPOSAL AT THE HANFORD SITE, WASHINGTON

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INTRODUCTION

The current and projected uses of geochemical models by the Basalt Waste Isolation Project (BWIP) focus on two segments of the repository system and their associated long-term goals. These segments are the waste package and far-field environments. The long-term goals relative to the waste package environment are to:

- Understand important solid/water reactions which control the waste package environment (Eh, pH, groundwater composition) during the thermal period
- Understand the controls on steady-state solution concentrations of key radionuclides to provide a source term for waste package radionuclide release modeling.

The long-term goals relative to the far-field environment are to:

- Understand important geochemical controls on dissolved constituents of the preplacement groundwater flow system
- Provide geochemical support for conceptual groundwater flow models
- Obtain bounding information relative to the geochemical fate of radionuclides along likely flow paths to the accessible environment.

## APPLICATIONS OF GEOCHEMICAL MODELING TO WASTE/BARRIER/ROCK INTERACTIONS

One of the more difficult tasks in assessing the performance of a high-level nuclear waste repository is quantifying uncertainties caused by the extrapolation of short-term (years) laboratory data to long-term ( $10^5$  years) repository time scales. Additional uncertainties arise from the inability to accurately predict temporal variations in environmental parameters such as groundwater compositions and flow rate. The problems associated with the extrapolation of short-term laboratory data can be addressed by using computer models that apply the known laws of chemistry and thermodynamics to determine reaction pathways and to predict final steady-state solution compositions and reaction products. This calculated series of reactions must be guided and bound by empirical observations from laboratory experiments and natural analog investigations to restrict the range of possible reaction pathways. Thus, at least in theory, the use of a computer program to calculate solution compositions and reaction product assemblages that are consistent with the results of waste/barrier/rock interaction experiments can assist in predicting the long-term performance of a nuclear waste repository.

The objectives of using geochemical modeling techniques are to: (1) determine the stability of reaction products, (2) determine the yield of reaction products after the system has attained a steady-state condition, (3) determine the final solution composition, Eh, and pH, and (4) estimate radionuclide solubilities.

There is a possibility that the reaction products, which form during waste/barrier/rock interaction experiments, are metastable and may later transform to a more stable phase assemblage. This is a key concern because it is these reaction products that determine the solubilities of radionuclides. The question of stable versus metastable assemblages can be addressed by a comparison of the observed experimental reaction products and those predicted by an equilibrium geochemical model.

Most experiments performed in the laboratory at temperatures below  $200^{\circ}\text{C}$  are not driven to completion over the time period of the experiment. That is, a certain amount of primary reactant still remains at the termination of the experiment. Even though many aqueous components reach steady-state concentrations during experiments, a geochemical model can, in a sense, "complete" the experiment by incrementally dissolving all of the primary reactant and then calculate the total yield of reaction products formed. A geochemical model can be used to predict the final solution composition, Eh, and pH that will exist after the primary reactant is consumed.

It is also possible, in theory, that a geochemical model can predict the solubilities of radionuclides. Such a model would need to have a data base that includes the actual radionuclide-bearing reaction products that will form in the repository environment. At this time, such a data base does not exist. However, the fully radioactive waste/barrier/rock interaction testing program, which is currently in progress at the BWIP, will identify and characterize the radionuclide-bearing products that form under repository-relevant conditions. This information can then be placed in the data base of a geochemical model to increase the accuracy of the model predictions.

The BWIP is currently evaluating the PHREEQE and EQ3/EQ6 geochemical codes (1,2) for modeling the waste/barrier/rock interactions which will occur during the lifetime of the proposed high-level nuclear waste repository located at a depth of one kilometer. Initially, only the basalt/groundwater system will be considered. Predicted fluid composition and reaction products will be compared with results from experiments in this system (3). If the PHREEQE and EQ3/EQ6 codes are able to reproduce the experimental results, then additional materials such as low carbon steel (container material) and sodium bentonite (packing material) will be added to the system. If the code is again able to reproduce the experimental results in these more complex systems, then waste forms will be added to the system.

#### APPLICATIONS OF GEOCHEMICAL MODELING TO THE FAR-FIELD

During the past year, the BWIP has initiated a geochemical modeling program using the MINTEQ code developed by Pacific Northwest Laboratory (PNL) to evaluate water samples representing all components of the hydrologic system at the Hanford Site. This program is aimed at establishing the activities of chemical species in solution and determining the saturation state of solid phases appropriate to the basalt system under ambient conditions. The present BWIP data base incorporates aqueous geochemical information from precipitation-monitoring stations, stream and spring sampling sites, an extensive network of boreholes from which the unconfined aquifer is sampled, and nearly 300 samples from more than 40 boreholes representing the major, confined water-bearing units in the three principal basalt formations underlying the Hanford Site (Saddle Mountains, Wanapum, and Grande Ronde).

While this investigation is the most recent and ambitious modeling project undertaken to date, results from several other studies have been reported. For example, Deutsch et al. (4, 5, 6) modeled a limited number of groundwaters from all stratigraphic levels within the mid-Columbia Plateau region. Relatively few of these samples were obtained on the Hanford Site and many came from boreholes open to more than one water-producing zone. Therefore, incomplete knowledge of the depth of the samples exists. In addition, the BWIP reported modeling results for a small number of groundwaters from basalts at the Hanford Site in

DOE/RL 82-3 (7). Significant limitations exist for both of these studies. First, groundwater samples were modeled at collection rather than in situ temperatures. Secondly, corrections to saturation indices due to hydrostatic pressure were not included for sensitive phases (e.g., calcite, fluorite).

In the most recent study conducted for the BWIP by PNL, several dozen spring samples and more than 100 groundwater analyses from all major water-bearing units on the Hanford Site were chosen for modeling. Speciation for the samples was first computed at the temperature and pH values measured at the time of sampling and at atmospheric pressure. The total mass of hydrogen was determined and used as a mass balance constraint, and the pH value of the sample was calculated at the correct in situ pressure and temperature. Pressure corrections to the thermodynamic data for aqueous species were included. Finally, the corrected pH value was used to determine the speciation and solubility equilibria for the sample using pressure corrections to the thermodynamic data.

The results of this preliminary study suggest that amorphous silica and allophane are at or near saturation for spring waters and nearly all groundwaters from the shallow confined aquifers (Saddle Mountain Formation). Most groundwater from deeper aquifers (Wanapum and Grande Ronde Formations) tend to be undersaturated with respect to these phases. Conversely, calcite and fluorite generally are undersaturated in the shallowest groundwaters but tend to reach saturation with increasing depth. Nearly all of the clays and zeolites in the MINTEQ data base are oversaturated in groundwaters from all stratigraphic zones. While this observation does not preclude their formation, it does suggest that they do not control the groundwater composition.

Of the principal phases that compute to be in permissible equilibrium with groundwaters at the Hanford Site, only silica and calcite have been positively identified. This observation suggests that future solids characterization work might focus on the search for the other phases. The documented occurrence of a variety of secondary clays (smectite) and zeolites (e.g., clinoptilolite, mordenite) in basalts at the Hanford Site (8, 9) and their apparent oversaturation in the associated groundwaters suggests that incorporation of a reaction kinetic capability into geochemical models might be fruitful.

Linking the results of speciation calculations with conceptual groundwater flow models by use of mass balance or reaction path models such as BALANCE (10) and EQ6 (2), respectively, is a potentially useful avenue for future research. These codes offer the possibility of making reasonable assumptions as to the identity of solid/water reactions from which the progressive evolution of groundwater composition can be predicted (11). The value of merging the results of hydrologic and geochemical studies is that reaction path modeling may be able to provide geochemical support for conceptual flow models that are derived from physical hydrologic measurements.

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## MATRIX DIFFUSION COEFFICIENTS FOR THE NNWSI WASTE PACKAGE ENVIRONMENT

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The Nevada Nuclear Waste Storage Investigations (NNWSI) project is evaluating the tuffaceous rock units at Yucca Mountain, located on the western boundary of the Nevada Test Site, as a potential location for a high level radioactive waste repository. Within the NNWSI project, Lawrence Livermore National Laboratory (LLNL) has been assigned responsibility for the design and qualification of the waste package. This task includes the determination of the waste package environment, the characterization of waste package--repository material interactions and the analysis and testing of the waste package performance in the repository environment.

Details of the package environment and material interaction tests have been reported elsewhere (1). Geochemical modeling of these experiments provides a basis for extending the results of these short-term canister corrosion and waste form release tests to the calculation of the waste package source term at the long times of interest needed for performance assessment. Calculation of this source term also requires an understanding of the flow and transport mechanisms operating within the waste package. This paper describes an ongoing analysis of experimental work to determine the matrix diffusion coefficient for the NNWSI waste package environment.

Diffusion coefficients are required for the flow and transport modeling effort of waste package performance analysis. Mechanisms modeled for a given waste package component depend on the conceptualization of flow within that component. Porous media or fractured media flow and transport will be assumed as dominant mechanisms within the waste forms and in the near-field host rock and possible packing materials. A falling fluid mechanism will be investigated to represent flow along

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\*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

impermeable package components (e.g., overpack, canister and fuel rod cladding). The diffusion coefficients being discussed herein will be of use in the porous or fractured media modeling used in packing material or surrounding host rock.

Contaminant transport modeling using convection-dispersion theory requires a coefficient of molecular diffusion for the transported species in the particular porous media. The coefficient is specific, not only to individual contaminants, but to the particular porous matrix as well. In this case, the matrix is a welded, devitrified ash flow tuff. Hydrologically, the rock is unsaturated, and characterized by significant fracturing and a low matrix permeability to liquid water (2). However, due to the low permeability and low recharge flux, very little liquid water is assumed to move through the fractures. Therefore, molecular diffusion in the tuff matrix is foreseen as an important transport process.

A cooperative test effort between the Waste Package Task at LLNL and the Savannah River Laboratory (SRL) is underway to investigate the behavior under various conditions of waste forms that may be produced by the Defense Waste Processing Facility at Savannah River. In the first phase of this work, these tests consisted of immersion of glass waste forms containing radioactive and nonradioactive waste constituents in groundwater taken from a well (J-13) in the host rock. The waste form, was contained in a reaction vessel made of the tuff, immersed in groundwater, and then placed in a closed Teflon container. The entire assembly was then heated to 90°C, and concentrations of waste leachates were sampled at 1, 3, and 6 months.

The experiment was not designed specifically for measuring the coefficient of molecular diffusion through the tuff matrix; however, it was carried out in such a manner as to avoid convective flux through the matrix. Therefore, ions that behave like tracers can be modeled as migrating by simple diffusion processes. Ions that react with the tuff matrix are modeled as diffusion with retardation. Both methods allow estimation of diffusion coefficients. Results presented herein are preliminary. Further analysis is underway to determine the effect of a highly soluble caliche material in the tuff samples. As will be described, measures were taken to minimize the impact of caliche dissolution. Subsequent phases of these tests will take additional steps to remove caliche prior to the experiment, and will attempt to reflect unsaturated conditions.

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APPLICATIONS OF GEOCHEMICAL MODELING TO  
SITE CHARACTERIZATION AND RADIONUCLIDE  
TRANSPORT IN THE NNWSI PROJECT

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INTRODUCTION

The Nevada Nuclear Waste Storage Investigations project (NNWSI) is studying a site at Yucca Mountain, in southern Nevada, as a possible nuclear waste repository. Los Alamos National Laboratory is responsible for the geochemical aspects of site characterization at Yucca Mountain. Geochemical models are being used in site characterization to help understand (a) local water chemistry, (b) local mineralogy, (c) the relation between water chemistry and mineralogy, and (d) the effects of water chemistry and mineralogy on waste-element solubility and transport.

GEOCHEMICAL MODELS

A number of geochemical models are being used by the NNWSI project. Chemical-equilibrium and reaction-path modeling are being done with EQ3/6 (1). A significant part of the work involves extension of the EQ3/6 database to include thermodynamic data for important waste elements (2). A version of MINEQL with an electrical double-layer sorption model was recently obtained (3); this code will be used to model the effects of solution chemistry on sorption for actinides and other waste elements with complex solution chemistry. A transport code with chemistry and sorption models, CHEMTRN, has also been obtained recently (4). CHEMTRN will be used in a preliminary study of the effects of solution chemistry on waste-element transport. The transport code TRACR3D is being used to study waste-element transport, including colloids, in porous and fractured media (5). This code employs equilibrium and kinetic sorption models, but only simple chemistry models. Results of studies with EQ3/6, MINEQL, and CHEMTRN will be used to assess the need for adding more complex chemistry models to TRACR3D.

## APPLICATIONS

EQ3/6 has been used for calculating (a) speciation, redox state, and saturation state of water, (b) pH buffer capacity of water and water plus minerals, (c) stability of local zeolites and clays, and (d) solubility of waste elements in water from Yucca Mountain (6, 7). The reaction-path calculations of water chemistry and mineral formation at Rainier Mesa, a location that is nearby and similar to Yucca Mountain, are an example of this work (7). These calculations model the dissolution of volcanic glass in water that is initially saturated with CO<sub>2</sub>. Thermodynamic data for three zeolites were estimated for use in the calculations. When solid silica phases more stable than cristobalite were not allowed to precipitate, aqueous silica activity was maintained at high levels and cristobalite, smectite clays, clinoptilolite, and mordenite were predicted to precipitate. Calculated water compositions were in general agreement with observations. When aqueous silica activity was controlled at lower levels (in equilibrium with quartz), zeolites were no longer stable.

Preliminary calculations with CHEMTRN have been used to assess the effect of aqueous complex formation on sorption of strontium. In water from Yucca Mountain and vicinity, aqueous complexes with sulfate account for 0-15% of the strontium. One-dimensional, porous-flow transport calculations with CHEMTRN indicate that nonsorbing-complex concentrations of 0-25% have only a minor effect on the extent of strontium transport. These conclusions should also apply to other elements with similar chemistry such as cesium and radium.

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CHEMICAL MODELING OF NUCLEAR WASTE REPOSITORIES  
IN THE SALT REPOSITORY PROJECT

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Salt deposits contain small amounts of water as brine in fluid inclusions in halite and in hydrous minerals, e.g., clays, kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) and carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ). For the candidate salt deposits, the total amounts of water as volume percent brine are: Palo Duro Basin, Texas, approximately 1.8; Paradox Basin, Utah, approximately 5.0 for the "carnallite-marker" zone, and less than approximately 0.5 below this zone; Gulf Coast salt domes, less than 0.15. For the Palo Duro and Paradox salt, the brines are Mg-rich (approximately 20,000 mg/L to approximately 100,000 mg/L) and sometimes Ca-rich (up to about 20,000 mg/L) NaCl brines. Brine migration calculations have been made using calculations of the time-variant thermal gradient around the waste packages and conservatively high brine volumes in the salt (5.0 volume percent for the Texas and Utah sites and 0.5 volume percent for the Gulf Coast) as input data. The maximum amounts of brine that eventually migrate to each waste package are about  $1.0\text{m}^3$  (for 5.0 volume percent brine) and  $0.2\text{m}^3$  (for 0.5 volume percent brine). With current conceptual designs for waste package overpacks (10 to 15 cm thick low-carbon steel), the waste package is not breached by uniform corrosion within 10,000 years. In brines this material thus far shows only uniform corrosion. For the expected conditions, where the brine is provided solely by brine migration, the brine is consumed by reaction with the iron of the overpack nearly as fast as it migrates to the waste package. Therefore, for the expected conditions, data about corrosion rates, radiolysis, etc., are not important. However, it is essential that accurate volumes of in-migrating brine can be calculated.

Disruptions of the expected conditions may occur and lead to a significantly different chemical environment. Human intrusion scenarios commonly lead to external ground waters entering the repository and becoming brines by dissolution of the salt. These brines are saturated in halite ( $\text{NaCl}$ ) and  $\text{CaSO}_4$  and have low Mg concentrations ( $<500$  mg/L). The amount of these brines may be effectively unlimited. Data on the

corrosion mechanism and rates of the overpack material are now of major importance in calculating waste package lifetimes. The calculated lifetimes are greater than 1,000 years for all salt sites, assuming uniform or near uniform corrosion.

Disruptive scenarios can only lead to radionuclide release from the repository if there is a path for contaminated water to leave the repository and if some waste packages have been breached. Only in such scenarios is it expected that accurate calculations of activity coefficients in brines will be important.

Disruptive scenarios causing radionuclide release from the repository lead to the possible application of chemical calculations in assessing the behavior of radionuclides in the far-field. However, when ground water travel times to the accessible biosphere are very long, e.g., much more than 10,000 years, these chemical calculations are of little value. These long travel times are currently expected for all sites.

In summary, the role of chemical modeling and the type of model needed varies significantly with the situation, i.e., expected conditions versus disrupted conditions. At this point in the Salt Repository Project, we are establishing the modeling capability for both expected and disrupted conditions.

## ION-INTERACTION MODELING OF DEEP BRINES, PALO DURO BASIN

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Nine sites are currently being considered for the first U.S. high-level nuclear waste repository. Seven salt sites are included. Brines exist in deep aquifers at each salt site and in fluid inclusions in each salt deposit. The chemical and thermodynamic properties of brines present special problems because of the very high concentration (>20wt percent) of material dissolved in them. As a consequence, the ion-interaction approach (1) has been used to accurately model the activities of both major and minor ions in deep brine systems at elevated temperatures.

Ion-interaction calculations have been used to examine brine geochemistry in deep aquifers in the Palo Duro Basin, Texas (2). Solubility relationships were examined for anhydrite ( $\text{CaSO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), celestite ( $\text{SrSO}_4$ ), barite ( $\text{BaSO}_4$ ), and radium sulfate ( $\text{RaSO}_4$ ) in brines of the Wolfcamp and granite wash aquifers. Sodium chloride brines with molal ionic strengths ranging from 2.89 to 4.76 and temperatures up to  $41^\circ\text{C}$  were collected and analyzed for a number of constituents from three wells in the Palo Duro Basin.

Solubility products as a function of temperature were obtained for comparison with modeled ion-activity products. Solubility data as a function of temperature and pressure for gypsum, celestite, and barite were obtained, chemically modeled, and solubility product equations were fit to the results. The solubility product equations for anhydrite and radium sulfate were obtained using the "principle of equally balanced like charges" (3). Modeling results indicate that brines from the Palo Duro Basin are saturated with anhydrite, celestite, and barite (Table 1). Radium concentrations throughout the basin are not controlled by  $\text{RaSO}_4$ , but perhaps by solid solutions with other sulfate minerals.

Table 1. Mineral Saturation Indices\*

Mineral	Sawyer Well Wolfcamp	Sawyer Well Granite Wash	Mansfield Well Zone 1 Wolfcamp	Mansfield Well Zone 2 Wolfcamp	Zeeck Well Zone 3 Wolfcamp
Anhydrite ( $\pm 0.2$ )	-0.12	-0.06	-0.12	-0.07	-0.20
Gypsum ( $\pm 0.2$ )	+0.07	0.00	-0.08	-0.02	-0.11
Celestite ( $\pm 0.3$ )	+0.05	+0.22	-0.19	-0.16	-0.09
Barite ( $\pm 0.5$ )	-0.17	+0.34	-0.65	-0.20	-1.44
RaSO <sub>4</sub> ( $\pm 0.5$ )	-5.1	-6.3	-6.1	-6.1	-5.8

\* Mineral saturation indices,  $\log \left( \frac{\text{ion activity product}}{\text{solubility product}} \right)$ , are given for five brines. The  $\pm$  values shown in parentheses after the mineral names are the permissible range of values, above and below zero within which the brines are considered saturated with respect to that mineral.

The application of ion-interaction calculations to other species in these brines has been limited by a lack of suitably well defined coefficients, e.g., for carbonates.

In summary, the ion-interaction approach to geochemical modeling is the preferred method for obtaining accurate activity coefficients for alkaline-earth sulfates in sodium chloride brines. These sulfates are expected to be important in assessing the outcome of various human intrusion and other breaching scenarios that produce conditions significantly different from those expected for an undisrupted repository.

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B0287		11a. TYPE OF REPORT				
10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)		Conference Proceedings				
Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Washington, DC 20555		b. PERIOD COVERED (Inclusive dates)				
12. SUPPLEMENTARY NOTES						
WM-10, 11, 16						
13. ABSTRACT (200 words or less)						
<p>A conference on the application of geochemical models in the assessment of high-level nuclear waste repositories was held to discuss the current status of geochemical code development, thermodynamic data bases, reaction kinetics, and coupled-process models as applied to site characterization and performance assessment activities. These proceedings include extended abstracts of the technical presentations given at the conference, a discussion of the role of geochemical modeling in predicting the performance of repositories, and a set of recommendations that identify the key developments needed in order for geochemical models to become more applicable for quantitative evaluations of repositories. Detailed recommendations relevant to the following subjects are discussed: (1) improved simulation of repository performance through inclusion of additional important geochemical processes and parameters into current geochemical models, (2) more careful attention to uncertainties associated with geochemical model calculations, (3) assigning priorities to (through sensitivity studies and critical evaluations) and then improving and/or obtaining important thermodynamic data, and (4) addressing the importance of kinetics in simulating repository behavior.</p>						
14. DOCUMENT ANALYSIS - a. KEYWORDS/DESCRIPTORS		15. AVAILABILITY STATEMENT				
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b. IDENTIFIERS/OPEN-ENDED TERMS		16. SECURITY CLASSIFICATION				
		<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center;">(This page)</td> </tr> <tr> <td style="text-align: center;">Unclassified</td> </tr> <tr> <td style="text-align: center;">(This report)</td> </tr> <tr> <td style="text-align: center;">Unclassified</td> </tr> </table>	(This page)	Unclassified	(This report)	Unclassified
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Unclassified						
		17. NUMBER OF PAGES				
		18. PRICE				