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Nuclear Waste Form Risk Assessment for U.S. Defense Waste at Savannah River Plant Annual Report Fiscal Year 1980

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July 1981

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CONTENTS

Abstract	1
1. Introduction	1
1.1 Background	1
1.2 Technical Goals and Program	2
1.3 Summary of Progress	3
1.4 Organization of Report	5
2. Analysis of Waste Form Dissolution	5
2.1 Introduction	5
2.2 Reference Glass Dissolution	6
2.2.1 Processes and Mechanisms	6
2.2.1.1 Interdiffusion, Hydration, and Ion Exchange	7
2.2.1.2 Silica Matrix Dissolution	7
2.2.1.3 Alteration Product Formation	8
2.2.1.4 Role of Water	8
2.2.2 Models	9
2.2.3 Data, Interpretations, and Dissolution Functions	11
2.3 SYNROC Dissolution	12
2.3.1 Processes and Mechanisms	12
2.3.2 Models	12
2.3.3 Data, Interpretations, and Dissolution Functions	13
2.4 Summary and Conclusions	14
3. Waste Isolation Systems Analysis	18
3.1 Introduction	18
3.1.1 Background	20
3.1.2 Scenario Selection	20
3.2 MACRO: Deterministic Subsystem Models and Probability Methodology	24
3.3 Base Case Input Parameters	27
3.3.1 Hydrology and Transport Subsystem Parameters	27
3.3.2 Waste Form Subsystem Parameters	29
3.4 Results of Analyses	36
3.4.1 Performance Measures	36

CONTENTS (Continued.)

3.4.2	Analyses	37
3.4.2.1	Deterministic Calculations	37
3.4.2.2	Sensitivity Analyses	38
3.4.2.3	Uncertainty Analyses	50
3.4.2.4	Parametric Analyses	63
Acknowledgments		66
Appendix A	- Dissolution of Savannah River Plant Reference Lithium Borosilicate Glass	71
Appendix B	- Review and Analysis of Experiments1 SYNROC Dissolution Data	79
Appendix C	- Thermochemistry of SYNROC Phases, Associated Phases, and Aqueous Species	99
Appendix D	- Dissolution of SYNROC Phases in Water: Perovskite and Rutile	105
Appendix E	- Thermochemistry of Barium Hollandite, Zirconolite, and Related Phases	109
Appendix F	- Nuclide Activity Listing of Savannah River Plant Waste	122
References		127

NUCLEAR WASTE FORM
RISK ASSESSMENT FOR
U.S. DEFENSE WASTE AT
SAVANNAH RIVER PLANT
ANNUAL REPORT FISCAL YEAR 1980

ABSTRACT

Waste form dissolution studies and preliminary performance analyses were carried out to contribute a part of the data needed for the selection of a waste form for the disposal of Savannah River Plant defense waste in a deep geologic repository. The first portion of this work provides descriptions of the chemical interactions between the waste form and the geologic environment. We reviewed critically the dissolution/leaching data for borosilicate glass and SYNROC. Both chemical kinetic and thermodynamic models were developed to describe the dissolution process of these candidate waste forms so as to establish a fundamental basis for interpretation of experimental data and to provide directions for future experiments. The complementary second portion of this work is an assessment of the impacts of alternate waste forms upon the consequences of disposal in various proposed geological media. Employing systems analysis methodology, we began to evaluate the performance of a generic waste form for the case of a high risk scenario for a bedded salt repository. Results of sensitivity analysis, uncertainty analyses, and sensitivity to uncertainty analysis are presented.

1. INTRODUCTION

1.1 BACKGROUND

The objective of the Alternative Waste Form Program for the Defense Waste Processing Facility (DWPF) is to provide information to support the choice of a waste form by October 1983. The Lawrence Livermore National Laboratory (LLNL) projects contribute to the risk-assessment portion of the program. More specifically, we are concerned with the post-closure risks of alternate waste forms. The LLNL project will provide part of the information for key decisions. Preliminary risk assessment for candidate forms in salt, basalt,

and tuff provides information to support the preliminary selection of waste forms for tests with Savannah River Plant (SRP) waste. Subsequent updated risk assessments to reflect latest data will supply input for the final choice of waste form for the DWPF.

1.2 TECHNICAL GOALS AND PROGRAM

The general goal of our project is to provide some of the data needed for discrimination between waste forms in terms of risks associated with deep geologic disposal. We attempt to address the following questions:

- Which waste form is better?
- How good does a waste form need to be?
- What research and development will be needed to acquire the necessary data?

The project consists of two subtasks: chemistry analysis and systems analysis. The chemistry subtask is an analysis of waste-form dissolution which is approached in two complementary ways. First, we reviewed the experimental data on dissolution (leaching) of leading candidate-waste forms, borosilicate glass and SYNROC. For the former, data have been compiled by the Savannah River Laboratory (SRL). For the latter, LLNL is accumulating information from an extensive experimental program. Second, through analytical modeling we will derive procedures for data extrapolation based upon proper interpretation of experimental information. For glass, kinetics modeling was employed. For SYNROC, the thermochemical methods were adopted. Under the systems analysis subtask, we calculated the release of radioactivity to the biosphere from the waste form emplaced in a deep geologic repository. We modeled the physico-chemical processes of transport of the radioactivity from the dissolving waste form through each of a series of geologic and engineered barriers. Using a general systems code (MACRO), we performed deterministic calculations, sensitivity analyses, and uncertainty analyses. We initiated parametric analyses with the newly developed code, XCOMP.

The LLNL project is organized into three consecutive phases: preliminary risk analysis, model development and data base expansion, and final risk analyses. During the preliminary risk analysis phase, a generic region was selected to represent the siting of a repository in bedded salt within a sedimentary region. Flow through the region was modeled as a network of

one-dimensional paths. The waste form was represented as a point source. A high consequence scenario involving a flaw through the repository was chosen to enhance the impact of waste form input parameters. The time-of-peak arrival and peak curie flux were taken as performance measures for the waste form in the base case scenario. Elementary models representing waste form dissolution and radionuclide transport were assumed. During the second phase, these models will be refined as additional experimental and theoretical results become available. A more efficient code designed especially to do repository performance calculations will be developed to apply the advanced models in the final risk analyses.

1.3 SUMMARY OF PROGRESS

Under the chemistry subtask, we have studied and analyzed the existing information on the processes, mechanisms, and modeling of dissolution of borosilicate glass and SYNROC. No general method exists for predicting dissolution rate of oxides. Dissolution is a complex process involving a number of steps, any of which may determine the rate of dissolution. The main steps can be summarized as follows: interdiffusion, hydration, ion exchange, matrix corrosion, and alteration layer formation. Although these general features of dissolution have been identified, quantitative descriptions of their interactions have proved difficult. As a result, existing numerical models which attempt to interpret experimental data often take into account the effects of a limited portion of the dissolution process, and empirical constants are relied upon to compensate for inadequate description of the total dissolution process. Extrapolation of data that has been based upon such modeling is, at best, very uncertain. Both analytical and experimental investigations of chemical details are needed. Some examples of such areas which require elucidation are:

1. the interactions between solid state and interface processes and chemical reactions in solution,
2. the effects of water volume, composition, and flow rate on the rate of dissolution,
3. chemical reactions in the alteration product layer,
4. relationship between the nature of the surface and the concentrations of dissolved species, and
5. solubilities of principal matrix elements such as Litanium and silica.

We have begun to treat these and other related areas analytically through the application of thermodynamics and chemical kinetics. Some of the results obtained have pointed to new directions for experimental investigation. Ultimately, this work will enable us to predict long term dissolution of waste forms with less uncertainty.

In the systems analysis subtask, a system level model was used to evaluate the performance of alternate waste forms in terms of radiological risk to man. The system level model is an aggregation of a number of models describing physically distinct subsystems (e.g., waste form package, repository site, regional aquifer). The procedure is to calculate the sensitivity of results both to individual input parameters of the subsystem models and to the uncertainties of these parameters. The MACRO code was used to propagate the uncertainties of the input parameters through deterministic models to produce probability distributions for the output parameters which characterize performance of the overall system. As measures for the performance of a waste form, we have taken the peak release rate, Ci/yr, and the time at which this rate occurs. A dose-to-man performance measure also can be provided by the code; however, these dose results require a number of specific assumptions regarding water use systems, bio-uptake factors, population trends, and others, all of which are more difficult to justify.

In order to accentuate the impact of waste form upon risk, we chose as a base case for analysis a potentially high consequence scenario. The waste repository was located in a bedded salt layer of a generic sedimentary basin. A flaw providing a ready path for groundwater was assumed to run through the repository.

Initially, we studied the base case scenario by performing a series of deterministic calculations to provide a basis for comparison with tractable hand calculations and to scope the parametric limits. Sensitivity analyses were then carried out by holding all uncertain variables fixed at their median value and allowing each, in turn, to vary over an appropriate range. Finally, to yield probabilistic consequence, uncertainty analysis was done to calculate the range and probability of the performance measures based on all input uncertainties.

1.4 ORGANIZATION OF REPORT

Because of the distinctive technical features of the two subtasks of the project, this report is organized in a parallel fashion. Section 2 contains investigations of dissolution of borosilicate glass and SYNROC, while Section 3 is a discussion of the systems analysis effort. A series of extensive detailed appendices describe the several topics of dissolution studies.

2. ANALYSIS OF WASTE FORM DISSOLUTION

2.1 INTRODUCTION

One of the most attractive options for the disposal of radioactive wastes is their incorporation into a durable solid, followed by emplacement in a deep geologic repository. The large quantities of defense wastes generated at the Savannah River Plant (SRP) facility are to be treated in this way, and the selection of the optimum waste form for this purpose is currently being undertaken.

One task of the preliminary risk analysis being carried out by the Nuclear Waste Form Risk Assessment Project is to evaluate experimental data for candidate waste forms that have been proposed. We are presently examining two candidate waste forms for which the most data are now available: the reference waste form (i.e., lithium borosilicate glass developed by the SRL) and SYNROC compositions that are under development at LLNL. We will summarize here our interpretation of leaching data.

After closure of a repository, the release of radioactive elements from the emplaced waste packages could take place only through the leaching action of groundwater. The dissolution rates of nuclear waste forms in groundwater are therefore, important factors in their selection. The experimental data with which we are most concerned are dissolution rates in a groundwater that is characteristic of a repository site. We are concerned initially with groundwater from a salt repository; i.e., with a concentrated brine. The rate of leaching is a complex function of many parameters. There are a large number of chemical interactions in waste form/groundwater systems.

2.2 REFERENCE GLASS DISSOLUTION

2.2.1 Processes and Mechanisms

No general method exists for predicting dissolution rates of oxides, and none is likely to be developed without a more detailed understanding of the chemical mechanisms. Quantitative modeling of dissolution is in a relatively undeveloped stage at this time. Dissolution is often a composite process of several reactions, any of which may be rate-controlling. It must also be recognized that the mechanism and rate of dissolution of a solid may be very system specific. The processes described below have mostly to do with glass, but to some extent they also apply to other forms. Some of the factors that contribute to the difficulty of evaluation of the dissolution of silica and silicates are:

- Variety and variable stoichiometry of phases.
- Uncertainties in the relative roles of kinetics, equilibrium, and steady-state.
- Low dissolution rates.
- Amorphous states of solids.
- Unknown aqueous species.
- Adsorption and surface chemistry.
- Unknown and erroneous thermochemical properties.

There is agreement on the general features of dissolution processes, although their interactions have proved difficult to quantify. The main steps can be summarized as follows: interdiffusion, hydration, ion exchange, silica matrix corrosion, and alteration layer formation.

Interpretation of experimental data is made more difficult because all the required information cannot be obtained experimentally. For example, even though measurement of radionuclides released from leached solids is a very sensitive technique, the concentrations of other species released that could help to characterize the reactions taking place at low temperatures are often too low to measure. Some important phenomena that waste form dissolution models should address are interdiffusion, ion exchange, hydration, silica matrix corrosion, alteration product formation, water flow rate, and silica solubility. These are discussed in the following sections.

2.2.1.1 Interdiffusion, Hydration, and Ion Exchange

Interdiffusion during dissolution is a complex process. The most mobile species in glasses are hydrogen and alkali metal ions. These ions move into and from the near-surface regions of the glass, respectively, in response to activity gradients. The typical reactions are:

where aq and s represent species in solution and solid, respectively. These reactions have rate constants which are functions of solid and aqueous compositions and temperature. As the reactions progress, compositions change, which, in turn, affects other reactions in the system. For example, we expect that as hydration of the glass surface proceeds, diffusion coefficients for ions in it should increase. Diffusion coefficients can be measured experimentally, although one should be cautious in using them only in systems to which they are applicable. Diffusion coefficients are also composition dependent.

2.2.1.2 Silica Matrix Dissolution

The complexities of silica-water interactions are extensively documented in the chemical literature.^{1,2} However, many important problems remain incompletely resolved. Among others, these include the prediction of "corrosion" rates or rates of transfer of silica from solid phases into aqueous solutions. We should distinguish in this respect between glasses, silicate minerals, and pure silica phases. Rate functions have been determined, with some qualifications, for the dissolution of quartz, cristobalite, and amorphous silica.³

Silicate glasses and minerals show similar dissolution phenomena, except that the silica activity can be considerably different from that in pure and hydrated silica phases, due to network modification by various elements. Such bonding effects on dissolution mechanisms and rates are not yet well understood.

Chemical reactions in solution are also complex. Silica may dissolve under some circumstances as a distribution of polynuclear species, with kinetic constraints on their interconversion. Busy and Meser⁴ review studies showing that aqueous polynuclear silica species are most important at higher silica concentrations, lower temperatures and high pH. Scheffler et al.⁵ found similar phenomena in dissolving alpha-loaded glasses. Some information on polymer formation and reactions is available.^{6,7} Complexing of silica by ferric ions is well established,⁸ and probably occurs for other cations as well.

2.2.1.3 Alteration Product Formation

Many complex solids dissolve incongruently in aqueous solutions; i.e., changes in solid composition take place. We expect this will also be true for glass waste forms and much experimental evidence supports this view. Complete dissolution would, of course, result in overall congruency. Incongruency and slow kinetics of silica reactions at low temperatures permit the long term existence of metastable residual phases whose compositions and thermochemical properties vary with the conditions of their formation. These can be thought of as mixtures of hydroxides and silica that are equivalent to amorphous silicates. Leaching under some conditions, especially low pH and elevated temperatures, can remove all extraneous elements, leaving a variety of possible crystalline silica hydrates.⁹

Alteration products may also be inhomogeneous in that diffusion and preferential dissolution lead to concentration profiles for various elements in the near-surface region. In addition, species can be incorporated from the solution, either by reversible ion exchange or by irreversible sorption.

2.2.1.4 Role of Water

In the short term, the only water available for corrosion and leaching reactions in a salt repository will come from brine inclusions migrating in a thermal gradient. In an unsealed or imperfectly sealed volume, the small volume of brine from this source should evaporate completely, preventing any

dissolution. This would be a very desirable result. The dissolution performance of the waste form is thought to be of importance only if there is eventual intrusion of water from a distant aquifer.

The question also arises as to whether the kinetics of dissolution would permit continuous saturation of groundwaters under all possible flow conditions.

Experimentally, in the laboratory, changes in water composition can result from linear flow, thermal convection, stirring, and changing of water. Soxhlet extraction and one-pass leaching are worst-case experiments because the build-up of aqueous concentrations is restricted, and in general, dilute solutions tend to be aggressive leachants. Speciation is also affected by water composition, since in pure water or very dilute solutions, species are simple cations or hydroxy complexes.

Although the water flow dependence of glass leaching rates is not very well defined in experimental techniques, we can, with certain assumptions, assure that it is consistent with geologic and hydrologic parameters to be used for risk analysis. This can be done by calculating the amount of glass that could be dissolved, assuming that silica-saturation of the water is the limiting factor and estimating the amount of water that might be available in the repository for dissolving glass. A sample calculation given in Appendix A shows how solubility effects can control dissolution at some possible water flow rates. Table 1 shows our view of typical relationships between repository, experimental, and model parameters.

2.2.2 Models

As applied to glass dissolution, existing numerical models in the literature are expressions that attempt to describe a measured characteristic leach rate, usually in terms of mass flux or surface velocity. They contain parameters that are adjusted to fit experimental data, and usually account only for alkali metal ions and silica that are released into solution. They do not take into account the effects of water flow, water composition, and surface reactions on dissolution rates.

TABLE 1. Intercomparison of repository, experimental, and model parameters.

Parameter	Repository	Experimental	Model
Water flow rate	Site- and construction-specific; subject to recharge, actual hydrology, and geologic changes.	Undefined; subject to thermal convection, diffusion, and replacement at intervals.	Assumed constant
Water composition	Constant input derived from host rock but subject to continuous modification by reaction in repository.	NaCl brine modified by reaction and restored at intervals.	NaCl
Silica concentration	Site-specific, silicate saturated, modified by continuous glass leaching; possibly also by backfill and barriers.	May not always be measured or measurable.	Amorphous silica saturated
Solid surface	Mixed, amorphous hydrous oxides; element concentration profiles not known.	Mixed, amorphous hydrous oxides; concentration profiles may vary due to interactions with different solutions.	Pure amorphous silica
Solid surface/ water volume ratio	Construction-specific; and subject to void removal by collapse.	Measured by various techniques.	$2 \times 10^{-4} \text{ cm}^{-1}$
Temperature	Site-construction and waste-composition dependent.	363 K	363 K

In the case of radioactive glasses at low temperatures, activities of radionuclides can also be measured in solution, and these are used as indicators of the rate of attack on the bulk glass. Such measurements are very useful in providing a common basis for evaluation during glass compositional development. They are also evidence of the release of radioactive elements, which is, after all, one of the critical considerations in selecting a waste form. In general, however, because of incongruent dissolution, radionuclide data are less useful in modeling long term performance. Their rates are not necessarily equal to each other or linear with those of major components, such as silica. Waste form mass-loss rates are calculated on the basis of an assumed congruent dissolution of a homogeneous matrix. This practice is very useful when rough comparisons of leach rates must be made, but such rates have little physical significance unless congruent dissolution has been established.

Other factors should be kept in mind in assessing the usefulness of the models derived from measurements of concentrations of leached species. The leach rates derived always assume the availability of enough water to accomplish the projected dissolution. Also, no account is generally taken of a possible formation of an insoluble residue of alteration products or a later reprecipitation of solids from solution. In that sense, the values of leach rates derived from such data may be considered conservative.

2.2.3 Data, Interpretations, and Dissolution Functions

The basic data relative to the properties of the SRP borosilicate glass waste form are summarized in the Appendix (see Table A-1). They have been mostly extracted from Reference 10. The recommended leach rates do not include any effects of solid state diffusion and ion exchange. These are thought to be significant only at very early times (in geologic terms). It is reasonable to assume for preliminary risk analysis that such effects can be neglected, and data used from the later corrosion-dominated period of reaction.

We consider the recommended rates for glass as the best available estimates, with reservations on their extrapolation to very long times. These generic expressions can be used in uncertainty and sensitivity analyses, but they are not necessarily a satisfactory representation of waste form behavior in a real repository. This will be evident from the wide variations in

dissolution rates that are sometimes calculated from measurements of different dissolved elements. This variability is caused by the sensitivity of dissolving reactions to many experimental variables. Such factors include both solid and solution compositions, temperature, surface/volume ratio, as well as experimental leaching, sampling, and measurement techniques. Nevertheless, it is possible to use the estimates for leaching performance, providing that their limitations are kept in mind. A useful, if negative, result from such a procedure can be obtained if it can be shown in risk analysis that other factors are of vastly greater significance.

2.3 SYNROC DISSOLUTION

2.3.1 Processes and Mechanisms

As in the case of glass, SYNROC phases form alteration product layers in the presence of water, with hydration as an important step in the dissolving process. Oxide surfaces hydrate in a variety of ways.¹¹ Depending on the cation to which they are bound, the surface groups can respond differently to pH changes in solution. TiO_2 , in common with other oxides of type MO_2 , tends to have an isoelectric point on the acid side, depending on its origin and state of dehydration. A problem in identifying reaction mechanisms is that hydrous oxide alteration products at low temperatures are thin and amorphous; therefore, they are often difficult to characterize. These products will be mixtures of hydrates of the most stable component oxides, including those of titanium and zirconium. Such compositional changes result from incongruent dissolution or preferential leaching of one or more elements.

Among the physical factors that influence the leaching process are the water flow rate and the ratio of solid surface area to solution volume. Water flow rate and surface/volume ratio are important in that flowing water not only removes dissolved radionuclides but dilutes all leached species. This is certain to have an effect on leaching kinetics.

2.3.2 Models

Equilibrium computer models can be applied to mineral dissolution and provide valuable information to supplement experimental data. They can

identify the leaching reactions of the various phases in groundwater; therefore, they provide insight on the radionuclide species that are likely to be lost preferentially. However, they should not be expected to substitute entirely for physicochemical interpretation.

2.3.3 Data, Interpretations, and Dissolution Functions

For preliminary risk analysis, we will consider data taken to approximately the end of Fiscal Year 1980. The material was taken in part from references^{12,13} and in part from unpublished project notes of work in progress, which will not be referred to individually.¹⁴ Leaching studies are being used largely for scoping and optimization purposes. Leach rates reflect compositional changes, and must therefore be considered only indicative of the properties of materials under development. The main factors we wish to consider are the general levels of leach rates in relation to those from waste glass, time dependence, temperature dependence, nature and origin of species, and possible mechanisms. Not all of these can be determined from the available data.

Technical details and discussion of the leaching of SYNROC compositions are given in Appendix B. The data considered are for:

1. Single-pass leaching of SYNROC C,
2. Hydrothermal leaching of SYNROC C, 423 to 723 K (150 to 450°C),
3. Crushed and cored SYNROC C,
4. SYNROC D leaching, 573 K (300°C),
5. Crushed Cs-bearing Ba-hollandite.

Short term Parr bomb leaching at 423 K (150°C) has also been done for various compositions. In general, Parr leaching is suitable for its intended purpose, i.e., rapid comparative testing of the effects of fabrication and compositional variations. It does not provide information that can be readily extrapolated or compared with glass data, for several reasons: thermochemical data for 423 K are not adequate at present, complete analyses of products are not taken, and total reaction time is very short (a few days at most).

Our interpretations of the dissolution behavior of SYNROC composites were limited by the unavailability of much thermochemical stability data. Our efforts to assemble existing data for aqueous species and solid phases of titanium are described in Appendix C.

Where adequate free energy data exist, computer simulations of dissolutions can be carried out. An example of CaTiO_3 and perovskite is given in Appendix D.

Stability values for the major SYNROC phases zirconolite and Ba-hollandite were not available. In Appendix E we have attempted to estimate these values and will use them in the future to explore the dissolution processes of SYNROC.

2.4 SUMMARY AND CONCLUSIONS

As mentioned previously, we have some reservations concerning the applicability of proposed dissolution models for glass in the literature to conditions in a real repository. We do not consider them comprehensive enough to completely interpret or reliably extrapolate dissolution rates. Typically, they apply only to experimental data for one or two of the dissolution processes and do not take into account interactions with other parts of the repository system. Most corrosion rate constants, especially, are oversimplifications and cannot be considered as fundamental properties of the glass.

We cannot expect to eliminate all empirical constants, but we believe that in the future a considerable improvement can be made in relating dissolution rates to basic parameters of the system. Progress is being made in this direction; the main features of dissolution processes are understood, and we believe that an adequate numerical analysis will eventually be possible. The uncertainties that require the conservative proposed leach rates can then be reduced. To reach this goal, much more chemical detail needs to be added and the number of adjustable parameters reduced. For example, a linkage must be added between the solid state and interface processes and the chemical reactions in solution which we believe are amenable to treatment as subsystems at local equilibrium.

Measured leach rates are dependent on water change techniques and tend to be conservative. Dissolution functions will have an aqueous concentration-dependent

term, and each experimental water change can be thought of as resetting such terms to their maximum values, although the effect may not be obvious in a relatively short-term experiment. Normally, one would not expect the equivalent of a water change process in a groundwater system. A better account of the effects of flow awaits the development of models which explicitly and numerically link water volume and flow rate to chemical reaction kinetics.

Other reactions in the alteration product layer need to be treated besides the transfer of alkali, silica, water, and hydrogen ions. In fact, the alteration product layer participates chemically in the dissolution process. It can sorb material from solution and is likely to retain significant fractions of radionuclides.

There is always a question concerning the nature of the solid phase that actually controls the concentration of a dissolved species in a natural water. Our use of amorphous silica, for example, was only an expedient, although we believe it can be considered a worst case estimate. This is a place where an equilibrium code simulation could be helpful if we can identify the chemical composition of the surface material and determine or estimate its thermodynamic properties.

Eventually, modeling must explicitly take into account reactions at the interface. In concentrated brines, for example, Na^+/H^+ inter-diffusion and ion exchange should be suppressed by mass action. This would cause the pH to remain lower; therefore, the silica solubility and dissolution rate should also be lower. This seems to agree with measured data. The relations are not simple ones, of course, since they involve nonlinear diffusion rates and reactions at the interface.

Consideration of such factors will influence the way in which dissolution data are taken. For example, it may well turn out that element concentration profiles in leached glass should be determined routinely or that the effects of solution composition, volume, and flow rate should be examined in more detail.

Aside from the experimental leaching data, which show species being released at various rates from an individual waste form, there is a more fundamental property which heavily influences the relative performances of waste forms; i.e., the solubilities of the principal matrix elements. Radionuclide elements that cannot diffuse must be "excavated" by destruction

and removal of the host lattice. SYNROC has an advantage in this respect, because the solubility of titania is orders of magnitude less than that of silica. This can be seen from Fig. 1, in which the solubilities of titania and amorphous silica are plotted as a function of temperature for a solution 1 *m* in NaCl. In addition, the temperature coefficient is smaller for titania. The consequence is that, for titanate phases, alteration products should be enriched in titanium and should therefore offer more physical and chemical protection to the bulk residual waste form.

SYNROC has another advantage. It can be optimized in several ways by changes in the number, distribution, and composition of phases, oxidation potential, grain size, etc. Phases can be added and subtracted to provide more flexibility in controlling the release of certain elements than does glass. However, this property is also a built-in disadvantage. Compositions and processing conditions, such as oxidation potential and temperature, must be carefully controlled in order to prevent the formation of unwanted phases. In other words, glass may be more forgiving of fluctuations in process variables. It is not clear how well these parameters can be controlled during an actual waste form fabrication where the input stream may be of variable composition. Although these are process engineering problems that would seem to be beyond the scope of a chemical evaluation, yet they bear directly on the chemical state of the product, and hence its performance in dissolution.

In conclusion, we have probably extracted as much useful information as is justified from the available data base at this time. It is clear that SYNROC compositions are attractive as alternate waste forms with regard to leach rates and merit the continuing development effort being given them. Some problem areas in the chemistry of waste forms and their dissolution in water have been pointed out, as well as the appropriate qualifications concerning the applicability of experimental leach rates to long-term waste form performance.

We conclude that, since waste form dissolution chemistry is complex, considerable further experimental and theoretical effort will be required for a good working understanding. However, we have also shown that there is much that can be learned even with existing data.

FIG. 1. Solubilities of waste form matrix elements in 1 m NaCl.

3. WASTE ISOLATION SYSTEMS ANALYSIS

3.1 INTRODUCTION

The systems analysis subtask of the Nuclear Waste Form Risk Assessment Project is an investigation of the post-closure consequences associated with mined geologic repositories. The objective has been to assess the impact of candidate waste forms and geologic siting media on the overall performance of the waste isolation system. The many subsystems which contribute to the post-closure performance are shown in Fig. 2, and the arrows illustrate the dependencies which exist among these elements in the overall system. Individually, these subsystems can be modeled at several levels of detail (i.e., from detailed codes which reproduce experimental data to codes which model only dominant subsystem features). Each approach has its relative merits for particular applications, and each should be pursued to ensure that the resulting analyses are ultimately in agreement.

The LLNL approach has been: 1) to separate the system into physically distinct subsystems (e.g., waste form package, repository site, regional aquifer, etc.), 2) to identify and model the key features within each subsystem, and 3) to combine this understanding into an overall systems level model to evaluate the performance of alternate waste forms in terms of radiological risk to man. The focus of this task has been: 1) to calculate and assess the sensitivity of results to both individual input parameters and their uncertainties, and 2) to quantify the resulting uncertainty associated with the consequences. The MACRO computer code, designed to coordinate and execute a sequence of user-supplied models, was used to propagate uncertain inputs through the subsystem models to produce probability distributions for the outputs which measure the performance of the system. Throughout this report, the performance measure of choice has been the rate of peak activity release at the biosphere (i.e., curies released per year per canister of SRP waste). This measure was selected because it is not encumbered with the numerous assumptions implicit in a conversion to dose. The scenarios causing the hydrologic pathways were assumed to have occurred (i.e., no probabilities were associated), and the resulting consequences were computed. The base case siting scenario, described in Section 3.1.2, was selected specifically for its potentially high consequence of failure to emphasize waste form performance.

FIG. 2. Systems level models link the various elements contributing to overall performance.

3.1.1 Background

Following a recommendation by the National Academy of Sciences,¹⁵ most of the scientific investigations in the United States have centered on salt as the geologic formation suitable for the siting of a nuclear waste repository. Previous consequence analyses^{16,17} have modeled numerous post-closure failure scenarios involving the disposal of nuclear waste in a generic bedded salt medium. These scenarios were constructed to represent typical naturally occurring features such as permeable interbeds in the salt layer, extensive jointing, faults, breccia features, etc., as well as man-induced flaws such as fracture zones around engineered features, deteriorated shaft or borehole seals, etc. A variety of dissolution, transport, and exposure mechanisms have been studied, and the performance measures (e.g., curies released, dose to man, etc.) were found to be strongly dependent on the specific failure mechanism.

A comprehensive analysis must evaluate the entire system, even though the independent barrier concept requires adequate waste containment by each individual barrier. Nevertheless, analyses can be designed to emphasize the differences in waste form performance by minimizing the effects of selected barriers or by subjecting the waste form to a potentially high consequence scenario. Several flow paths resulting in high dose profiles were identified in the LLNL Bedded Salt Report¹⁸ and were considered for use as a base case in the SRL Alternate Waste Form Analysis. The selection of a particular flow path was based on several considerations:

- The credibility of the proposed geology and hydrology.
- The variety of scenarios that could be represented by the network.
- The potential for high consequence release.
- The complexity of the network describing the flow.
- A knowledge of the parameter values necessary to characterize each flow path.

3.1.2 Scenario Selection

A generic region has been selected to represent the siting of a nuclear waste repository in bedded salt within a sedimentary basin. This basin model was developed and analyzed by Naymik and Thorson,¹⁹ using the two-dimensional hydrology code, TAYLOR, and transport code, MATTRAN. A

simplified cross-section of the region is shown in Fig. 3. While not an actual site, the figure is typical of sedimentary basins containing bedded salt and should characterize any real candidate site with only minor adjustments. The essential features of the simplified five-layer geology include:

- The repository, located in a layer of bedded salt within the basin.
- Shale layers, directly above and below the salt.
- Sandstone outer layers, typical of upper and lower aquifers in the region.
- Increasing permeability in the order salt < shale < sandstone.
- Recharge, assumed to occur at the basin perimeter due to rain, snow melt, etc.
- Discharge, assumed to occur in a large flood plain associated with the river (i.e., biosphere).
- Generalized groundwater flow in the region as shown by the the arrows.

At the systems level of the detail, flow through this region is modeled as a network of one-dimensional flow paths. The results of the TAYLOR-MATTRAN detailed calculations have been used to bench-mark systems level analyses of this same region. A comparison²⁰ of the results (peak activity and mean arrival time) shows good agreement for reasonable cases, with the systems level results tending to be more conservative. The network design and input parameters which define the specific scenario considered in this analysis are presented below.

The one-dimensional series flow path shown in Fig. 4 was chosen as the base case flow network for this analysis. This five-path network represents a hydraulic connection between the lower and upper aquifers within the generic basin. The repository is assumed to be a point source containing all the waste canisters. The vertical head differences within the basin result in a net flow of water from the lower aquifer to refill the repository. This flow initiates the dissolution process and transports waste through the overlying salt and shale layers to the upper aquifer. A horizontal gradient throughout the basin carries the waste along the upper aquifer to the biosphere. Associated with each flow path are a number of hydrologic parameters (e.g., length, hydraulic conductivity, effective porosity, etc.) which are selected from the range of values appropriate to the scenario.

FIG. 3. The generic region selected for repository siting in bedded salt.

FIG. 4. The flow path network model of hydrology and transport.

3.2 MACRO: DETERMINISTIC SUBSYSTEM MODELS AND PROBABILITY METHODOLOGY

The MACRO computer code,²¹ developed at LLNL, was designed as a general tool for use by systems analysts to perform uncertainty and sensitivity analyses of systems models where the values of input or physical parameters are uncertain. The uncertainty in the value of a parameter is described by a probability distribution over the parameter values. If a model of a physical system requires an uncertain parameter as input, then the output of the model will be described by a probability distribution. MACRO is also capable of handling the case where some of the inputs to models are the outputs from one or several other models. The main function of MACRO is to propagate the input uncertainties through a sequence of deterministic calculations to produce probability distributions for the model outputs. Subsystem models do not provide for the rigorous correlations and constraints inherent in real physical systems. Input variables and elements in this analysis were treated as if they were statistically independent. This assumption of independence may, for some combinations of input data, have the effect of overstating the degree of system performance uncertainty.

The MACRO subsystem models used in these analyses explicitly consider the following system elements:

1. Time of initial release,
2. Waste form dissolution time,
3. Local hydrology and nuclide transport in the salt/shale layers,
4. Regional hydrology and nuclide transport in the aquifer layer,
5. Nuclide group retardation,
6. Activity release to the biosphere.

The first two elements, time of initial release and waste dissolution time, characterize the source term release and are described in detail in Section 3.3.2. These physical processes are currently represented in the systems model by input parameters which follow from more detailed analyses (e.g., see Section 2.0).

The hydrology and transport models assume that one-dimensional flow paths will reasonably represent the real three-dimensional hydrology and follow from studies which suggest that actual water flow will probably be through the various types of geologic flaws or along bedding planes.

Each segment of the flow path (i) is characterized by its length (L_i), hydraulic conductivity (K_i), effective porosity (ϕ_i), longitudinal dispersivity (α_i), and hydraulic gradient (G_i) or head drop (ΔH_i). The water velocity (V_i) along a given path is then computed according to D'Arcy's Law:

$$V_i = \frac{K_i}{\phi_i} G_i \quad \text{or} \quad V_i = \frac{K_i H_i}{\phi_i L_i}$$

and the corresponding transit time (T_i) is given by $T_i = L_i/V_i$. As the dissolved waste travels along each path, geologic dispersivity causes the pulse to spread out, both along the direction of flow and perpendicular to the flow. The pulse width (σ_i) along the direction of flow is given by

$$\sigma_i = \left(\frac{2\alpha_i L_i}{V_i} \right)^{1/2}$$

The one-dimensional model necessarily neglects transverse dispersivity. Transit times and pulse widths for the individual paths are summed to calculate a total transit time, $T_t = \sum_i T_i$, and a total pulse width, $\sigma_t = \left(\sum_i \sigma_i^2 \right)^{1/2}$, for the overall flow path network.

Transit times of selected nuclide groups within the waste pulse are increased due to the geochemical adsorption processes which occur during geotransport. Arrival times at the biosphere are modeled as the overall transit time multiplied by the retardation factor appropriate to the media and the nuclide group.

The activity release model represents an aggregation of several subsystem outputs. From these intermediate outputs, a Green's function can be constructed to calculate the solute flux to the biosphere. This flux, when scaled for nuclide inventory and decay, represents the nuclide activity released to the biosphere.

MACRO propagates probabilities through subsystem models by converting continuous probability density functions to finite probability distributions and applying the laws of probability to these distributions. The probability distribution of a variable, say X , is represented by doublets $(p_i, x_i)_{i=1, \dots, n}$, where p_i is the probability that X is contained in an interval whose representative value is x_i . Intervals are assigned for every uncertain variable of interest. In MACRO, several different methods for choosing the intervals are available. One choice could be to choose the

intervals on an equal ratio basis with five intervals per decade. For example, one might calculate the x_i formula:

$$x_i = 10^{i/5} ,$$

where x_i would be the representative value for the interval

$$(x_{i-1/2}, x_{i+1/2}) .$$

The calculation rules for computing the distribution for a model output variable are taken directly from probability theory. Suppose one wished to calculate the probability distribution of a model output variable, Z , where the function $f(X,Y)$ is the model,

$$Z = f(X,Y) ,$$

and the model inputs X and Y are independent and have the finite probability distributions represented by the doublets

$$(p_i, x_i)_{i=1, \dots, n} \text{ and } (q_j, y_j)_{j=1, \dots, m} .$$

Then, the probability distribution for Z , (r_k, z_k) , is formed using the rule:

$$r_k = \sum p_i q_j$$

where the sum is over all indices i and j such that $f(x_i, y_j)$ is in the interval

$$(z_{k-1/2}, z_{k+1/2}) .$$

The MACRO methodology is not limited to the assumption that X and Y are independent. Models within MACRO may have two dependent variables and generate a joint probability mass function for X and Y . The function is represented by $n \times m$ doublets

$$(p_{ij}; x_i, y_j) \text{ for } i=1, \dots, n \text{ and } j=1, \dots, m$$

where P_{ij} is the probability of X having value x_i and Y having value y_j . If X and Y are used in a subsequent model to compute Z , then

$$r_k = \sum P_{ij}$$

with the sum over all indices i and j such that $f(x_i, y_j)$ is in the k th interval for Z .

An example of this procedure for independent variables appears in Figs. 5 and 6. Figure 5 shows the finite probability distributions of the variables K = permeability and dH/dx = hydraulic gradient. Figure 6 shows the resultant probability distribution of the D'Arcy velocity, Q , given by the simple product model $Q = K(dH/dx)$, which is known as D'Arcy's Law.

The current version, MACRO2, was based on the concept of a general tool, including a library of models, a user option to modify the library, and an interactive execution-time user selection of models from the library. As such, it has language features not required for specific applications to nuclear waste isolation systems. Furthermore, experience has shown that the systematic sampling of highly correlated and constrained variables (necessary to model physically real systems) may require inordinate amounts of computer time. Therefore, a Monte Carlo code, MISER, is being written to reduce computer requirements and to replace MACRO2 in our future analyses of nuclear waste isolation systems.

3.3 BASE CASE INPUT PARAMETERS

3.3.1 Hydrology and Transport Subsystem Parameters

The base case waste release scenario assumes the repository is located in impermeable salt. An underlying flaw provides a flow pathway through the lower shale and salt layers, while shaft fractures in the upper salt and shale layers complete the hydraulic connection to the upper aquifer. All flow is assumed to occur within the flow paths and in the direction of the decreasing head or gradient. This base case represents a siting scenario of potentially high consequence with performance substantially degraded below nominal expectations.

FIG. 5. Finite probability distribution of input variables K and dH/dx .

FIG. 6. Finite probability distribution of output variable Q .

Although the values assigned as input parameters to this scenario are considered to be within the realm of possibility, measured values for similar geologies range over several orders of magnitude. It must be emphasized that these inputs are neither site-specific nor average for such generic sites. Parameters which could be measured with high precision (e.g., length) are taken as certain, while those parameters subject to greater uncertainties are characterized by log normal distributions about some assumed median value. Distributions were assigned to reflect the current level of uncertainty characterizing the scenario. Similar uncertainties might be assigned to site-specific data before extensive field studies were completed. Table 2 lists the median values and, where appropriate, widths (i.e., σ = Standard Deviation of the log normal distribution) for each parameter necessary to characterize the base case hydrology and transport.

3.3.2 Waste Form Subsystem Parameters

This study considered only SRP defense waste as the source of radionuclide release from a repository in bedded salt, and input parameters describing the waste form subsystem were specifically selected to represent SRP defense waste. Other possible nuclide sources within an actual repository might include spent fuel or commercial high level waste. The methodology developed and described herein is applicable to any such source term given the appropriate input parameters. The parameters specified to characterize a waste form subsystem include:

1. Total amount of radioactive waste,
2. Nuclide specific inventory, age, and associated activities,
3. Canister breach time,
4. Waste dissolution rate.

The first two parameters depend only on the nature of the radioactive waste and are independent of the waste form matrix. An SRL memo, "Information for Waste Form Risk Assessments I - SRP Borosilicate Glass Waste Form," (5-23-80),¹⁰ provides the necessary input data. The other two parameters are functions of the entire waste form package, i.e., processing and long term performance system. These inputs characterize the source term release at the systems level and were obtained from the Waste Form Chemistry Modeling Task of this project as discussed above.

TABLE 2. Input parameters characterizing base case hydrology and transport.

Parameter, symbol (units)	Path 1		Path 2		Path 3		Path 4		Path 5	
	Shale		Salt		Salt		Shale		Aquifer	
	Median	σ	Median	σ	Median	σ	Median	σ	Median	σ
Length, L (m)	2.0×10^2	0.0	1.0×10^2	0.0	1.0×10^2	0.0	2.0×10^2	0.0	5.0×10^4	0.0
Hydraulic conductivity, K (m/yr)	3.0×10^{-1}	2.0	3.0×10^{-2}	1.5	3.0×10^{-2}	1.5	3.0×10^{-1}	2.0	1.0×10^{-2}	0.7
Effective porosity, ϕ	2.0×10^{-3}	1.0	1.0×10^{-3}	0.7	1.0×10^{-3}	0.7	2.0×10^{-3}	1.0	1.0×10^{-1}	0.7
Longitudinal disper- sivity, α_L (m)	2.0×10^1	0.3	2.0×10^1	0.3	2.0×10^1	0.3	2.0×10^1	0.3	7.0×10^1	0.5
Hydraulic head drop, ΔH (m)	Over paths 1 to 4					1.0×10^1	0.7	N/A		
Hydraulic gradient, G (m/m)	N/A		N/A		N/A		N/A		5.0×10^{-3}	0.3
Fission product retardation, RF	Retardation in Path 5 only								3.0×10^1	1.6
									1.0×10^3	2.3
Actinide retardation, RA	Retardation in Path 5 only								3.0×10^1	1.6
									1.0×10^3	2.3

N/A = parameter not applicable to this path.

The SRL defines the total inventory of SRP radioactive waste as the number of canisters (6500)²² to be produced in the DWPF multiplied by the inventory of each isotope in an average canister of SRP waste. An inventory of nuclides, with $T_{1/2} > 1$ day, contained in a reference glass-waste form is reproduced in Appendix F. The activities indicated assume repository closure in the year 2052 A.D. The radioactive contents of such a canister represent waste averaged over the 1952-2002 A.D. reactor operating period. The projected inventory calculation was performed at SRL using the ORIGEN code. From these inventories, hazard tables of activity and dose were constructed to convert geologic transport parameters into nuclear exposure levels at the biosphere. Nuclides were assigned to one of three groups (see Table 3) based on geotransport retardation properties. Activity hazard tables describe the curies per canister activity of 87 nuclides for 10^6 years after repository closure. In reporting the curies released to the biosphere at an arbitrary breakthrough time, individual nuclide activities are summed by retardation group. These activity hazard tables are plotted in Figs. 7a, 7b, and 7c for nuclide Groups I, II, and III, respectively. Dose hazard tables were constructed based on this SRP reference radionuclide inventory using the BIODOSE code.²³ In its present form, BIODOSE simulates the water-use system of a large river in the northwestern United States and calculates the environmental transport and human uptake of 53 biologically significant nuclides (representing over 99% of the total SRP waste activity). These hazard tables allow dose-to-man performance measures to be calculated from the geologic transport of each of the three nuclide groups.

The two parameters used to characterize the source term release at the systems level are: 1) T_o , waste age at the time of initial release (the sum of the waste age at emplacement and breach time) and 2) T_d , waste dissolution time. Waste age is needed to determine the level of activity initially released to the groundwater system at the source. The SRL²² defines the waste age as 0.0 years in 2052 A.D., the projected year of emplacement. The breach time, T_b , is a function of repository operation period, refill and repressurization times, and the canister corrosion time. The SRL further suggests that "credit should not be taken for leach protection by the stainless steel canister after emplacement in a repository, because there is presently no general consensus on the longevity of metal canisters;"

TABLE 3. Hazard table groupings of nuclide inventory by sorption-retardation (underlined nuclides are included only in activity tables, not dose tables).

Group I	^{14}C ,	^{99}Tc ,	^{129}I				
Fission products with no sorption.							
Group II	^{59}Ni ,	^{60}Co ,	^{79}Se ,	^{87}Rb ,	^{89}Sr ,	^{90}Sr ,	^{90}Y ,
Fission products with moderate sorption; moderate retardation.	^{91}Y ,	^{93}Zr ,	$^{93\text{m}}\text{Nb}$,	^{95}Zr ,	^{95}Nb ,	^{106}Ru ,	^{107}Pd ,
	^{110}Ag ,	^{115}In ,	$^{121\text{m}}\text{Sn}$,	^{123}Sn ,	^{125}Sb ,	$^{125\text{m}}\text{Te}$,	^{126}Sn ,
	^{126}Sb ,	$^{126\text{m}}\text{Sb}$,	^{134}Cs ,	^{135}Cs ,	^{137}Cs ,	^{142}Ce ,	^{143}Sm ,
	^{144}Ce ,	^{144}Nd ,	^{147}Pm ,	^{147}Sm ,	^{149}Sm ,	^{151}Sm ,	^{152}Eu ,
	^{154}Eu ,	^{155}Eu					
Group III	^{210}Pb ,	^{210}Bi ,	$^{210\text{m}}\text{Bi}$,	^{210}Po ,	^{222}Rn ,	^{223}Ra ,	^{224}Ra ,
Actinides and daughter products; strong retardation.	^{225}Ra ,	^{225}Ac ,	^{226}Ra ,	^{227}Ac ,	^{227}Th ,	^{228}Ra ,	^{228}Th ,
	^{229}Th ,	^{230}Th ,	^{231}Th ,	^{231}Pa ,	^{232}Th ,	^{232}U ,	^{233}Pa ,
	^{223}U ,	^{234}Th ,	^{234}U ,	^{235}U ,	^{236}U ,	^{236}Np ,	^{236}Pu ,
	^{237}Np ,	^{238}U ,	^{238}Pu ,	^{239}Np ,	^{239}Pu ,	^{240}Pu ,	^{241}Pu ,
	^{241}Am ,	^{242}Pu ,	^{242}Am ,	$^{242\text{m}}\text{Am}$,	^{242}Cm ,	^{243}Am ,	^{243}Cm ,
	^{244}Cm ,	^{245}Cm ,	^{246}Cm ,	^{247}Cm ,	^{248}Cm

FIG. 7a. Group I--Tc & I inventory activity plot for SRP waste.

FIG. 7b. Group II--Fission products inventory activity plot for SRP waste.

FIG. 7c. Group III--Actinides inventory activity plot for SRP waste.

hence, these analyses assume $T_b = 0.0$ (i.e., dissolution begins immediately upon emplacement). A parametric study, described in Section 3.4.2.4, examines this assumption in detail.

Waste form dissolution times were obtained from the leach rate studies conducted by the Chemistry Modeling Task of this project. Details of these studies for borosilicate glass and SYNROC are found in Section 2. Based on this work, the median dissolution time for borosilicate glass was taken to be 1.6×10^6 years. The distribution about the median was assumed to be lognormal with a standard deviation of 2.0. The limited data and modeling complications described earlier prohibit the selection of a single median value to characterize SYNROC dissolution; however, the 1.0×10^4 to 1.0×10^8 year range brackets the expected performance and defines the limits for the parametric waste form study described in Section 3.4.2.4.

Throughout these analyses, the following assumptions were made regarding the waste package, regardless of the matrix:

1. All waste is located at a point source defined by the location of the repository. Studies are currently underway to address the issue of a distributed waste source.²⁴
2. All groundwater flows "through the repository" and comes into contact with all the waste. The flow velocity is sufficiently fast so that the dissolution process is kinetically limited.
3. The waste matrix is a homogeneous mixture and dissolves at a uniform, constant rate.

3.4 RESULTS OF ANALYSES

3.4.1 Performance Measures

The aggregation of the various subsystems requires an integration of waste form chemistry with geo-hydrology and transport physics to calculate a performance measure which describes the effectiveness of the overall waste isolation system (see Fig. 2). Models of these physical processes and the

probabilistic methodology which links them have been outlined in Section 3.2. Each deterministic subsystem model gives rise to an intermediate performance measure (e.g., transit time) describing the behavior of that subsystem for a specific set of input parameters. A comparison of these intermediate results illustrates the relative impact of that subsystem on overall performance. The output of real interest, however, is a measure which describes the aggregated system. From these intermediate results, a Green's function can be constructed to calculate flux along a flow path. The aggregation of a series of such flow paths when scaled for nuclide inventory and decay represents the nuclide activity released to the biosphere. Throughout these analyses, overall performance measures have been keyed to this activity released. Peak curie flux (curies per canister per year) is reported to indicate individual cancer risk, and the time-of-peak arrival describes the post-closure immediacy of this risk. A dose-to-man performance measure is also possible within the methodology of these analyses. Incorporation of the BIODOSE code generated hazard tables permits calculation of maximum or average individual exposures for whole body equivalent as well as organ specific doses from the above described activity flux results. It must be emphasized, however, that these dose results require a number of additional assumptions (e.g., water use system, bio-uptake factors, population trends, etc.); hence, activity measures (curies) are the preferred performance measures.

3.4.2 Analyses

3.4.2.1 Deterministic Calculations

An initial study of the base case scenario involved a series of deterministic calculations to provide a basis for comparison with tractable hand calculations and to scope the physical limits of the overall problem. Overall performance measures, however, are not unique to a single scenario and may result from a large number of subsystem combinations. Thus, it is essential to recognize the trade-offs which influence system performance and to understand individual subsystem behavior (e.g., hydrology, transport, waste form, etc.) by exploring the impact of input parameters on intermediate performance measures.

The overall waste isolation system can be factored into geotransport and waste dissolution subsystems. To initially scope the base case siting

scenario, only geologic inputs were considered. The waste release pulse was assumed to be characterized by a delta function from a point source repository and subject only to geotransport along the local and regional flow paths (i.e., no distinction was made among radionuclide groups and all were assumed to travel unretarded).

Minimum, median, and maximum transit times and pulse widths were calculated by selecting the appropriate (median or extreme) inputs to the hydrologic transport subsystem models from the range of values appropriate to each parameter (see Table 2). The probability of such limiting cases actually occurring is exceedingly small, however, for they result only from the simultaneous selection of input extremes with individual probabilities less than 1%. The sensitivity analyses described in Section 3.4.2.2 will examine the effect on overall system performance of allowing only one input parameter at a time to range over its appropriate values. The uncertainty analyses discussed in Section 3.4.2.3 will provide the probabilities associated with these performance measures for the base case siting scenario. As a scoping study, however, these calculations served to define the limits of the problem and the deterministic results shown in Table 4 compared exactly with hand calculations. It is interesting to note that these minimum and maximum transit times are in very good agreement (about a factor of 2) with the transit time extremes reported by Cloninger²⁵ in a completely independent assessment of a similar scenario (groundwater intrusion-transport to surface water body) for waste disposal in a salt repository.

3.4.2.2 Sensitivity Analyses

Although the geotransport times reported in the previous section follow from a very simple deterministic analysis, the approach does provide an example of the range in performance measures which result from the combined variations of geologic input parameters. Additional improvements in the accuracy of calculated performance measures might be expected upon the inclusion of radionuclide retardation factors (i.e., increased transit times), waste form dissolution rates (i.e., increased pulse widths), and inventory hazard tables (i.e., activity flux measures). Because the inter-relationships among the models are complex, however, the extent of these improvements may not be immediately obvious. The sensitivity analyses, which follow, allow

TABLE 4. Deterministic analysis of base case siting scenario (hydrology and transport results).

	Minimum	Median	Maximum
Flow path 3--Transit time	1.0×10^{-1} yr	8.0×10^1 yr	8.3×10^4 yr
Pulse width	4.0×10^{-1} yr	5.1×10^1 yr	7.4×10^4 yr
Flow path 4--Transit time	2.0×10^{-1} yr	3.2×10^2 yr	6.7×10^5 yr
Pulse width	6.0×10^{-2} yr	1.4×10^2 yr	4.2×10^5 yr
Flow path 5--Transit time	2.0×10^2 yr	1.0×10^4 yr	5.0×10^5 yr
Pulse width	6.0 yr	5.3×10^2 yr	4.6×10^4 yr
Total transit time	2.0×10^2 yr	1.0×10^4 yr	1.3×10^6 yr
Overall pulse width	6.0 yr	5.5×10^2 yr	4.3×10^5 yr

examination of the effects of variations in individual input parameters on overall performance measures.

Sensitivity analyses were performed by holding all uncertain variables fixed at their median values and allowing each, in turn, to vary over an appropriate range. The more sensitive the analysis is to the variable, the larger will be the spread in the performance measure. A first analysis designed to examine the impact of each parameter in a consistent manner, allowed each parameter to range an order of magnitude about its median value (see Table 5). Later, a similar analysis used the appropriate parameter ranges defined in Table 2 to illustrate the relative impact of expected geologic variations.

The results of these analyses, however, are directly applicable only to the base case siting scenario (borosilicate glass in a flawed bedded salt repository), since each variable has domains of high and low sensitivity, depending upon the values of all the model parameters. Nevertheless, the trends observed provide an insight into other siting scenarios and this methodology can be applied to any such data set.

Results of the first sensitivity analysis are shown in Figs. 8 through 13. A performance measure is plotted along the vertical axis as each of the variables (along the horizontal axis) is allowed, in turn, to vary an order of magnitude about its median value. Table 5 identifies the variables

TABLE 5. Sensitivity analysis input parameters, normalized range, run number identification/description.

Run number	Variable name	Network path ^a	Unit	Minimum	Median	Maximum
1	Shale conductivity	1	Meter/yr	3.0×10^{-2}	3.0×10^{-1}	3.0
2	Salt conductivity	2	Meter/yr	3.0×10^{-3}	3.0×10^{-2}	3.0×10^{-1}
3	Salt conductivity	3	Meter/yr	3.0×10^{-3}	3.0×10^{-2}	3.0×10^{-1}
4	Salt porosity	3	N/A	1.0×10^{-4}	1.0×10^{-3}	1.0×10^{-2}
5	Salt dispersivity	3	Meters	2.0	2.0×10^1	2.0×10^2
6	Shale conductivity	4	Meter/yr	3.0×10^{-2}	3.0×10^{-1}	3.0
7	Shale porosity	4	N/A	2.0×10^{-4}	2.0×10^{-3}	2.0×10^{-2}
8	Shale dispersivity	4	Meters	2.0	2.0×10^1	2.0×10^2
9	Vertical head drop	1-4	Meters	1.0	1.0×10^1	1.0×10^2
10	Aquifer conductivity	5	Meter/yr	1.0×10^1	1.0×10^2	1.0×10^3
11	Horizontal conductivity	5	Meter/meter	5.0×10^{-4}	5.0×10^{-3}	5.0×10^{-2}
12	Aquifer dispersivity	5	Meters	7.0	7.0×10^1	7.0×10^2
13	Aquifer porosity	5	N/A	1.0×10^{-2}	1.0×10^{-1}	1.0
14	Group II - retardation	5	N/A	3.0	3.0×10^1	3.0×10^2
15	Group III - retardation	5	N/A	1.0×10^2	1.0×10^3	1.0×10^4
16	Waste dissolution time	N/A	Years	1.6×10^5	1.6×10^6	1.6×10^7

^aSee Fig. 4.

FIG. 8. Sensitivity of salt subsystem performance to input parameter variations.

FIG. 9. Sensitivity and shale subsystem performance to input parameter variations.

FIG. 10. Sensitivity of aquifer subsystem performance to input parameter variations.

FIG. 11. Sensitivity of combined geologic subsystem performance to input parameter variations

FIG. 12. Sensitivity of time-of-peak flux to input parameter variations (overall performance measures by Group).

FIG. 13. Sensitivity of peak activity flux to input parameter variations (overall performance measures by Group).

of interest and their associated range and median values. The subsystem performance measures examined include transit times and pulse widths along each flow path as well as the total transit time and pulse width. The peak curie flux at the biosphere and the time of peak flux represent overall system performance. Note that these results include retardation and waste release effects as well as geologic contributions to the isolation system previously considered.

Figures 8, 9, and 10 illustrate the impact of uncertainties associated with the salt, shale, and aquifer related parameters on their respective subsystem performance measures. The combined geologic performance (see Fig. 11), however, is most sensitive to variations in aquifer related parameters, while other subsystem effects are masked by the magnitude of the aquifer's contribution in the chosen scenario. Overall performance measures, time of peak curie flux (see Fig. 12), and peak curie flux (see Fig. 13) are similarly sensitive to uncertainties in the aquifer related parameters as well as the uncertainties in the waste dissolution times and nuclide retardation factors. Particular caution must be exercised in interpreting performance measures for Group III nuclides because the 10^3 year retardation factor delayed the entire range of Group III peak flux arrival times beyond 10^6 years. Although Group III activity could be approximated at these arrival times by extrapolation from the ORIGEN hazard plots calculated through 10^6 years, such results are highly suspect and do not warrant inclusion. An example of parameter impact ranking by sensitivity analyses is shown in Fig. 14a. Here the performance measure is the peak activity flux (curies per canister per year) for the Group II nuclides. The relative sensitivity of the subsystems:

salt/shale < aquifer < waste form,

is consistent with the trends established in Figs. 11 to 13. Sensitivity analyses, using the appropriate variable ranges defined in Table 2, duplicated the above trends, but (as shown in Fig. 14b) the impact upon performance was weighted by the actual range of geologic variability associated with each parameter.

- Note:
- Performance measure: peak activity, fission products (Ci/canister/yr)
 - Order of magnitude variation about median input values
 - Head drop across the salt/shale layers, ΔH (m)
 - Gradient along the upper aquifer, G (m/m)
 - Waste dissolution time, WDT (yr)
 - Resulting relative sensitivity: salt/shale < aquifer < waste form

FIG. 14a. Parameter impact ranking by sensitivity analysis (order of magnitude variation about input parameters).

- Note:
- Performance measure: peak activity, fission products (Ci/canister/yr)
 - One sigma variation about median input values
 - Head drop across the salt/shale layers, ΔH (m)
 - Gradient along the upper aquifer, G (m/m)
 - Waste dissolution time, WDT (yr)
 - Resulting relative sensitivity: salt/shale < aquifer < waste form

FIG. 14b. Parameter impact ranking by sensitivity analysis (one Sigma variation about input parameters).

3.4.2.3 Uncertainty Analyses

To provide a probabilistic consequence analysis of the waste isolation system, uncertainty analyses were performed to calculate the range and probability of performance measures, based on all input uncertainties. The base case siting scenario (see Section 3.1.2) was taken to represent such a system for the purposes of this analysis. The geotransport and waste form subsystem input parameters were assumed to be characterized by the lognormal distributions described in Sections 3.3.1 and 3.3.2, respectively. Given such a scenario, this analysis calculates the probability distributions of peak activity release rates and the time of peak release rate for each nuclide group. These results, however, characterize only this particular system's performance. The probability of encountering such a scenario in the spectrum of geologic siting conditions has not been explicitly considered.

The effect of each parameter's uncertainty was studied by:

- 1) associating probability distributions with all model input parameters,
- 2) computing probability distributions of the performance measures, using the system model, and 3) observing the effects on performance distributions caused by narrowing individual parameter distributions. The MACRO code (see Section 3.2) managed the probability distributions as illustrated in Fig. 15.

Sensitivity of uncertainty analyses examined how the distributions of the performance measures for this base case siting scenario are affected by narrowing input parameter distributions one at a time. Peak activity flux and time of peak flux were calculated by holding one uncertain input parameter at its median value, while all others assumed their assigned distributions. The more significant the parameter, the narrower will be the resulting performance distribution. This portion of the analysis was carried out in two phases.

In the first phase, uncertain variables were allowed to range plus and minus one order of magnitude about their median values. This approach revealed the model dependent sensitivities to parameter uncertainties. Typical distributions of the arrival time of peak curie flux are shown for each nuclide group in Fig. 16a as a function of subsystem input parameters. The minimum and maximum arrival times were taken at the 10th and 90th percentile values of the computed probability distributions. Median values are indicated by the solid circles. Eliminating the uncertainty associated with individual salt/shale subsystem input variables did little to sharpen the

FIG. 15. Uncertainty analysis methodology.

FIG. 16a. Uncertainty limits for time-of-peak activity flux (one order of magnitude uncertainty on input parameters).

FIG. 16b. Uncertainty limits for time-of-peak activity flux (one standard deviation uncertainty on input parameters).

time of peak activity flux performance distribution. Setting individual aquifer related parameters as certain resulted in some narrowing of this performance distribution. Similarly, eliminating retardation factor uncertainty had a modest influence on the appropriate group arrival time. Fixing the waste dissolution times did not affect the time of peak activity flux performance distributions in this scenario. A similar plot of the distribution of peak activity fluxes for Groups I and II is shown in Fig. 17a. Although the time of peak distribution is narrowed by fixing aquifer-related parameters, the peak activity flux distribution shows little change due to the "flatness" of the activity vs time plots (see Figs. 7a and 7b) over the transit times appropriate to the scenario. Fixing the waste dissolution time was observed to narrow the overall peak activity flux performance distribution. The activity plots for Group III nuclides were not included because all Group III arrival times were beyond 10^6 years and required extrapolations from the ORIGEN data.

Figures 16b and 17b illustrate the distribution of the time of peak activity release and peak activity flux performance measures, respectively, resulting from the second phase of this analysis; i.e., allowing plus and minus one standard deviation variation about the median input parameters to reflect the impact of predicted geologic uncertainties (see Table 2). The technique of fixing one input at a time and calculating the corresponding range in performance measures was identical to that described above in phase one.

Performance measure distributions were also calculated allowing all the uncertain model parameters which characterize the base case siting scenario to be simultaneously uncertain. Input parameters were characterized by lognormal distributions of one standard deviation about the median value, as defined in Section 3.3. As previously described, the MACRO code was used to propagate these input distributions through a series of deterministic subsystem models and to calculate the performance measure distributions summarized in Table 6. Individual plots of probability distributions for time of peak flux and peak activity flux for each of the three nuclide groups are presented in Figs. 18a, 18b, 19a, 19b, 20a, and 20b, respectively. Again, the activity results for Group III must be interpreted with caution; Fig. 20b is based on an extrapolation beyond the 10^6 year ORIGEN inventory data.

FIG. 17a. Uncertainty limits for peak activity flux (one order of magnitude uncertainty on input parameters).

FIG. 17b. Uncertainty limits for peak activity flux (one standard deviation uncertainty on input parameters).

TABLE 6. Results of uncertainty analysis (all parameters simultaneously uncertain by one standard deviation).

		10th percentile	Median	90th percentile
GROUP I (I, Tc)				
	Time-of-peak arrival (yr)	1.7×10^3	1.4×10^4	1.5×10^5
	Peak curies released (Ci/can/yr)	6.1×10^{-6}	1.1×10^{-6}	1.8×10^{-7}
95	GROUP II (Fission Products)			
	Time-of-peak arrival (yr)	1.5×10^4	2.5×10^5	5.1×10^6
	Peak Curies Released (Ci/can/yr)	3.8×10^{-6}	4.7×10^{-7}	5.1×10^{-9}
GROUP III (Actinides)				
	Time-of-peak arrival (yr)	3.6×10^5	8.0×10^6	1.9×10^8
	Peak curies released (Ci/can/yr)	3.2×10^{-7}	2.8×10^{-11}	2.1×10^{-17}

FIG. 18a. Uncertainty analysis--Group I results.

FIG. 18b. Uncertainty analysis--Group I results.

FIG. 19a. Uncertainty analysis--Group II results.

FIG. 19b. Uncertainty analysis--Group II results.

FIG. 20a. Uncertainty analysis--Group III results.

FIG. 20b. Uncertainty analysis--Group III results.

3.4.2.4 Parametric Analyses

Results of the scenario specific analyses raised several questions of a general nature. During the coming fiscal year, a series of parametric analyses will be performed to study the impact on overall performance of waste form properties under a range of geologic conditions. The goal of this approach is to span the range of input parameters without being scenario specific to: 1) quantify expected and abnormal performance, 2) determine siting conditions which yield a high consequence of failure, and 3) identify the parameter ranges over which systems models are nonconservative and/or invalid. The parametric analyses described below illustrate this approach. The performance contours were based on the group activity hazard plots (Figs. 7a, 7b, and 7c) for SRP waste and, where necessary, extrapolations from this data.

The first parametric study examined the impact of the previous assumption that no credit be taken for leach protection by the waste canister after emplacement. Peak curie flux was calculated as a function of transit time (over the range 10^1 to 10^7 years) for each of the three nuclide groups in the SRP waste. The calculation was repeated for several waste form breach times, T_b . The results shown in Figs. 21a, 21b, and 21c are representative of the dependence upon breach time. The peak curie flux of the Group I (Tc and I) nuclides is essentially independent of breach time for any transit time. A similar independence is observed for the Group II (Fission Product) and Group III (Actinide) hazards at transit times greater than about 10^3 to 10^4 years; however, for shorter transit times, the longer breach times can significantly reduce the hazard. For all groups, breach times serve to delay the time of peak arrival. However, the effect is only significant for transit times less than or equal to the breach time itself.

A second parametric study was conducted to assess the impacts of Waste Dissolution Time, T_d , Transit Time, T_t , Dispersive Spread, S , and Nuclide Group (I, II, and III) on the performance measures. Performance contour plots of peak activity rates (curies per year per canister of SRP waste) were calculated as a function of T_d and T_t . Both T_d and T_t were independently allowed to vary over the 10^2 to 10^6 year range and S was bracketed by considering physically reasonable cases where $1.0 \leq T_t/S \leq 10.0$.

FIG. 21a. Parametric breach time analysis--Group I.

FIG. 21b. Parametric breach time analysis--Group II.

FIG. 21c. Parametric breach time analysis--Group III.

No credit was taken for breach time, T_b . The performance measure contours for each of the three nuclide groups are shown in Figs. 22 through 24. For comparison, the limiting cases of $T_t/S = 1.0$ and 10.0 are presented for Group II in Figs. 23a and 23b, respectively.

Because almost all the activity in Group I is due to ^{99}Tc and because the ^{99}Tc half-life ($T_{1/2} = 2.1 \times 10^5$ yr) is longer than most transit times considered, the Group I peak activity contours with decay (see Fig. 22) are essentially identical to peak normalized (i.e., no decay) flux contours. The results of this model suggest the value of peak normalized flux to be relatively independent of T_d for $T_d < T_t$ and similarly independent of T_t for $T_t < T_d$. The peak activity rate is dependent on T_t (even when $T_t \ll T_d$) when T_t is greater than or equal to half-life ($T_{1/2}$) of a dominant contributor to the group activity. This decay effect is responsible for the slanted vertical segment of the peak activity rate contours of Groups II and III (see Figs. 23 and 24). The effect of changing from low geologic dispersivity ($T_t/S = 10.0$) to high geologic dispersivity ($T_t/S = 1.0$) (see Figs. 23a and 23b) produces only small shifts in the T_t axis intercept of the contours. The T_d intercepts appear to be independent of the T_t/S ratio.

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FIG. 22. Parametric analysis--peak activity rates--Group I, $T_t/S = 1.0$.

FIG. 23a. Parametric analysis--peak activity rates--Group II, $T_t/S = 1.0$.

FIG. 23b. Parametric analysis--peak activity rates--Group II, $T_L/S = 10.0$.

FIG. 24. Parametric analysis--peak activity rates--Group III, $T_t/S = 1.0$.

Appendix A

DISSOLUTION OF SAVANNAH RIVER PLANT REFERENCE LITHIUM BOROSILICATE GLASS

A. SOLUBILITY RESTRICTIONS ON DISSOLUTION RATES

The present state of development of numerical modeling of glass dissolution does not provide a very firm mechanistic basis for evaluating long-term release of waste radionuclides. In order to better relate leaching to measurable physical quantities, we can use the water solubility of silica as the basic parameter. This is a somewhat more conservative approach, in that kinetic restrictions are not included. However, it does consider water volume and flow rates, which will be significant factors.

Assume as a worst case that because of enhanced permeability around a canister all the groundwater flowing upward is channeled past the waste form surface and is available for dissolution. The repository cross-sectional area, A , affecting each canister is:

$$A = S^2 \text{ (cm}^2\text{/canister)} \quad (1)$$

where S is the canister spacing in cm. The water volume flow rate R_v past each canister is then

$$R_v = S^2 R_1 P \text{ (cm}^3\text{/yr)} \quad (2)$$

where R_1 is the linear flow rate of water in cm/yr and P is the fractional effective porosity of the medium. The maximum rate of dissolution of silica is

$$R_s = S^2 R_1 P C_s \rho \text{ (g SiO}_2\text{/yr)} \quad (3)$$

where ρ is the solution density in g/cm³ and C_s is the silica saturation concentration in g SiO₂ per g total solution. The rate of dissolution of glass, R_g , is

$$R_g = S^2 R_1 P C_s / F \quad (4)$$

where F is the mass fraction of silica in the glass. The density of saturated brine from 298 to 373 K is approximately 1.2 g/cm^3 (its temperature dependence could be expressed more accurately in analytical form if necessary).^{26,27}

The following composite temperature function was derived for the solubility of amorphous silica in saline solutions:²⁸

$$C_s = 10^{-(1.673+626.2/T)} \text{ g SiO}_2/\text{g H}_2\text{O} \quad (5)$$

where C_s is the dissolved silica concentration and T is the temperature in degrees Kelvin. At 363 K (90°C), for example, this concentration would be approximately 400 ppm. To check the reasonableness of such a value, we examined the literature for compositions of hot volcanic brines. It appears that 400 ppm is well within the range of measured values.²⁹ Relationships similar to Eq. (5) can be derived for silica solubility as a more precise function of salt concentration and pH, if these should appear warranted.

Substituting Eq. (5) and appropriate values for ρ , S , P , and F into Eq. (4), the initial glass dissolving rate R_g can be computed as a function of the linear flow rate of water, R_l , as shown in Fig. A-1. The non-flow-dependent value; i.e., reaction-controlled constant dissolution rate of $1.2 \times 10^{-7} \text{ g/cm}^2/\text{d}$ in brine is also shown.

The result is that, within the limits of error of our assumptions, the dissolution rate in brine is reaction-controlled above a water linear flow rate of about .5 cm/yr, and water flow-rate-controlled below this value. This, then, is a transition point in the dissolution function, below which we should not use the experimental value but the saturation-control value.

It might appear that calculations based on an elevated temperature solubility are not appropriate in a system where flowing groundwater must cool after it leaves the immediate vicinity of the repository. However, for some soluble elements such as cesium, it is conceivable that dissolving and

FIG. A-1. Glass dissolving rate as a function of water linear flow rate, for 363 K (90°C) brine (1% porosity, 609.6 m (20 ft) canister spacing).

re-precipitating the host matrix in a thermal gradient would be sufficient for release. Temperature will also appear again below as a parameter in experimental release rate functions.

B. GEOMETRY AND CORROSION RATE

A suitable algorithm for cylinders of different ratios of length/radius appears in the corrosion part of a model by Ewest.³⁰

$$F = \frac{M}{M_0} = 2 \left[\left(\frac{1}{p} + 1 \right) \tau - \left(\frac{2}{p} + \frac{1}{2} \right) \tau^2 + \left(\frac{1}{p} \right) \tau^3 \right] \quad (6)$$

with M = released mass (g),

F = released mass fraction,

M_0 = total mass of sample (g),

$p = L/r$ = cylinder length/cylinder radius,

where

$p = 2$ is valid for spheres,

$\tau = \frac{R(t-t_0)}{gr}$ = dimensionless time parameter,

with R = leaching rate ($\text{g}/\text{cm}^2\text{d}$ or $\text{g}/\text{cm}^2 \text{ yr}$),

t = time (d or yr),

t_0 = start of leaching process (d or yr),

g = glass density (g/cm^3),

r = cylinder radius (cm).

The assumption is that the cylinder shrinks uniformly; the leaching rate is constant. Using this expression and the parameters specified in Table A-1, we carried out a series of corrosion calculations. The results are shown in Figs. A-2 and A-3. Figure A-2 shows total dissolution time as a function of L/r . Figure A-3 shows the cumulative mass fraction removed for the recommended leach rates in water and brine, where the L/r ratio is constant at 7.8. This corresponds to the nominal value for SRP glass cylinders. We did not consider any increment in area due to cracking, which would have reduced total dissolution time somewhat.

TABLE A-1. Summary of assumed repository and glass waste form parameters.

Canister spacing	6.096×10^2 cm	(20 ft)
Canister length	2.311×10^2 cm	(7 ft 7 in.)
Radius	2.953×10^1 m	(11.625 in.)
L/r	7.826	
Initial surface area	4.8×10^4 cm ²	
Mass	1.480×10^6 g	(3263 lb)
Density	2.5 g/cm ³	
Loading	35%	(dry, uncalcined waste)
Silica content	42.2%	
Leach rate at 363 K	1.2×10^{-7} g cm ⁻² d ⁻¹	(in brine)
Leach rate at 298 K	9.6×10^{-8} g cm ² d ⁻¹	
Repository cross-sectional area per cylinder	3.72×10^5 cm ²	(400 ft ²)
Salt effect porosity	1%

FIG. A-2. Computed dissolution times for waste form cylinders, as a function of leach rate and length/radius ratio.

FIG. A-3. Computed cumulative fraction of waste from cylinder dissolved as a function of leach rate and time (length/radius = 7.8).

C. TEMPERATURE AND CORROSION RATE

In the regime of reaction-controlled dissolution, we make use of the suggested rate change from 298 to 363 K in Table A-1. In terms of the form of the rate equation recommended by SRL, the mass dissolving rate is

$$R_g = 6.67 \times 10^{-4} \times 10^{(-990/T)} \text{ g/cm/yr} . \quad (7)$$

The activation energy corresponding to this relationship is about 8.4 kJ/mole (2 kcal/mole), a remarkably low value which implies a transport-controlled process.

For the purpose of estimating release rates for risk analysis, the start time and reaction temperature will be input from other models. Note that the dissolution rate is a function of temperature, which, because of radioactive decay, will not be constant throughout the life of the repository. It will also be determined by loading, age and type of waste. Note also that the above functions in the water-flow-rate-limited dissolution regime are dependent on a specific canister spacing, and are therefore not valid for other spacing options.

Appendix B

REVIEW AND ANALYSIS OF EXPERIMENTAL SYNROC DISSOLUTION DATA

SYNROC C

The first experimental data sets for SYNROC C were for powdered samples of composition S05HP4A.¹² These were single-pass leaches in which cesium, strontium, calcium, barium, and zirconium were measured as a function of temperature in water and in .03 normal bicarbonate solution.

No significant influence of ligand concentration is evident in the experimental data, although our calculations indicate that the principal calcium, strontium, and barium species in alkaline carbonate solutions are carbonate complexes (see Fig. B-1), while in pure water they are the simple divalent cations. Therefore, we infer that although the dissolutions appear to be limited by some transport process, carbonate and bicarbonate ions are not directly involved. Minor rate differences in carbonate solution may result from pH effects.

The experimental temperatures were 298 and 348 K (25 and 75°C). We must assume that experiments run at different temperatures are indeed duplicates in every other respect, so that temperature coefficients are significant. We have elected to plot rates (Figs. B-2 to B-10) as a function of reciprocal temperature, so that progressive sampling times appear as families of curves. We wished to obtain as much effective activation energy information as possible, in the hope of better understanding the mechanisms involved, although two data per curve is very scanty for this purpose.

A temperature coefficient for the measured rates is also necessary if we are to compare SYNROC and glass data at similar temperatures. Experimental determinations of the dissolution of minerals are usually carried out in acid solutions, where rates are relatively high. They are usually found to be controlled by chemical reactions in the solid phase at or near the surface rather than by the transport of some species in solution. Such reactions usually have activation energies^{31,32} in the range of 50 to 67 kJ/mole (12 to 16 kcal/mole). Sangwal,³³ for example, found 57.8 kJ/mole (13.8 kcal/mole) for the dissolution of MgO. Although there are reports of energies even higher than 67 kJ/mole (16 kcal/mole),³⁴ a more conservative value might be 50 kJ/mole (12 kcal/mole). In principle, dissolution reactions that involve

FIG. B-1. Calculated degree of complexation of aqueous barium and strontium by HCO_3^- and CO_3^{2-} in 0.3 N NaHCO_3 .

FIG. B-2. Comparison of effective activation energies for dissolution reactions and temperature effects on rates.

FIG. B-3. Release rates of cesium from SYNROC C, single-pass leaching by water.

FIG. B-4. Release rates of cesium from SRP glass 21-35-15.

FIG. B-5. Release rates from SYNROC C, single-pass leaching by .03 N NaHCO_3 solution.

FIG. B-6. Release rates of strontium from SYNROC C, single-pass leaching by water.

FIG. B-7. Release rates of strontium from SYNROC C, single-pass leaching by 0.3 N NaHCO_3 solution.

FIG. B-8. Release rates of strontium from SYNROC C, single-pass and hydrothermal leaching by water.

FIG. B-9. Release rates of strontium from SRP glass 21-35-15.

FIG. B-10. Release rates of barium from SYNROC C, single-pass leaching by water.

H⁺ could become transport-limited in groundwaters, which are normally alkaline. In order to better visualize effective activation-energy relationships, several slopes are plotted in Fig. B-11 on the same scale as the experimental data.

Cesium, strontium, and barium each show a different pattern of temperature coefficient vs time function, indicating that they experience complex and essentially unrelated leaching processes (Figs. B-3 to B-11). Cesium has a pronounced temperature coefficient, however, which becomes smaller with time and suggests a surface depletion and shift to a solid state diffusion limited reaction. Insofar as we can generalize, the release rates of the various elements from SYNROC phases seem to approach experimental activation energies of about 15 kJ/mole (3.6 kcal/mole) at longer times.

The few data available at higher temperatures than 348 K are consistent with the two single-pass series. There are reported ten day hydrothermal rates for strontium, 423 to 723 K (150 to 450°C), which are close to the extrapolated 298 to 348 K data (see Fig. B-8). For comparison, we have included a plot (see Fig. B-4) of release of cesium at 30 days in distilled water at 298 and 348 K (SRP glass 21-35-15).³⁵ The water release data are not very different from those for SYNROC C (see Fig. B-3).

We have also plotted strontium release from this glass (see Fig. B-9) on the same scale as strontium from SYNROC C (298 K, 1 and 78 d). In this case, the strontium release from SYNROC C is seen to be lower by factor of 3 to 10.

The two values for zirconium in this series are the only available data for the dissolution of zirconolite. Presumably, the calcium also released from this phase is masked by calcium released from perovskite. It would be of considerable interest to compute a total release of zirconium and compare it to the solubility of the most probable product phase Zr(OH)₄. However, the data and lack of thermodynamic information for required species at 348 K do not allow this.

The second set of experimental data for SYNROC is a study of leach rates of crushed vs cored material.¹² This series was intended primarily to examine the effects of surface area on leaching rates; i.e., to verify the

FIG. B-11. Release rates of barium from SYNROC C, single-pass leaching by .03 N NaHCO₃ solution.

validity of extrapolating powder leach data to monoliths. It was found that cesium release from powders was anomalously high. It was also concluded that cesium and barium were released from hollandite, while calcium and strontium come from perovskite.

These conclusions are probably correct. We also calculated the ratios of release rates (see Figs. B-12 to B-15). If powdered and massive samples are chemically equivalent (i.e., if their distribution of elements and phases are the same) the two sets of plots should be very similar, no matter what the various absolute rates may be or whether surface areas exposed to the solution are precisely known.

Strontium and calcium dissolved for six weeks at a constant ratio of about 2, with no significant depletion. They appear to come from a single phase, probably perovskite (see Figs. B-14 and B-15). Strontium is leached preferentially; the release ratio Sr/Ca is about 200 times the mole ratio in the solid. We cannot identify any calcium as coming from zirconolite.

Barium rates decrease more rapidly than those of strontium or calcium, implying that hollandite will be a more durable host phase than perovskite. Strontium/barium/calcium ratios are reasonably consistent between powders and cores (see Figs. B-14 and B-15).

In the case of cesium, leach behavior is seen to be different at early times. Not only is it released much more rapidly from powdered material than from massive pieces, but the cesium/barium ratio changes in the opposite direction for the two materials. A comparison of the trends in ratios in Figs. B-12 and B-13 indicates that at longer times they are approaching the same values for crushed and massive forms. In other words, the initial pulse of cesium seems to be a transient effect. We interpret this to mean that cesium is present in more than one phase. As Coles¹² suggests for the dissolution of cesium-bearing hollandite, it is possible that part of the cesium is in intergranular material that has been exposed preferentially by crushing, and which has a relatively high dissolution rate. We have no way of knowing what the chemical effects of core preparation might have been.

The implication is that the dissolution of powders should not be used to predict long term performance unless it can be shown that no chemical artifacts have been introduced by crushing, or that they have dissipated. However, this possibility is simple to check by a release ratio analysis. In the present example, a fairly long term leaching experiment was necessary.

FIG. B-12. Release ratios from powdered SYNROC C.

FIG. B-13. Release ratios from massive SYNROC C.

FIG. B-14. Release ratios from powdered SYNROC C.

FIG. B-15. Release ratios from massive SYNROC C.

We suggest that it would be possible with more detailed analytical data and multivariate analysis, to extract considerable information on compositions and mechanisms with a very reasonable effort.

Cs/Ba-HOLLANDITE

A release rate ratio plot was made of data taken at 298 K for Cs/Ba-hollandite (see Fig. B-16). A comparison with Fig. B-13 shows a similar time dependence for Cs/Ba, although not so great in magnitude. It is not at all similar to powdered SYNROC C, Fig. B-12. This probably indicates better loading of cesium into the hollandite phase. Perhaps the Cs/Ba release rate ratio could be used as a diagnostic, in that gross differences in leaching behavior are observable in the first few days.

SYNROC D

The first item of information on leaching characteristics of SYNROC D compositions was a set of preliminary data at 573 K. The material examined was a composite of perovskite, zirconolite, spinel, and nepheline. The releases of cesium, sodium, and silicon are consistent with leaching of the nepheline as the main reaction. We should not really place any emphasis on this very preliminary determination, but it is of interest in the number of concentrations of dissolved elements measured. We have arbitrarily applied the temperature coefficient from Fig. B-17 (plotted on the same scale) to each value to see what rates would result at 298 K. The effect is the same as for SYNROC C materials: all elements except the alkali metals leach at very low rates, below $10^{-7} \text{ g cm}^{-2} \text{ d}^{-1}$. It appears that composition optimization with respect to the release of cesium is the main problem.

FIG. B-16. Release ratios for Cs-bearing hollandite, 298 K.

FIG. B-17. Estimated temperature effects, dissolution of SYNROC D.

Appendix C

THERMOCHEMISTRY OF SYNROC PHASES, ASSOCIATED PHASES, AND AQUEOUS SPECIES

Computer simulations using thermodynamic stability data are of value in interpreting leaching rates of nuclear waste forms. For this purpose, a data file has been assembled for aqueous species and for titanate and associated oxide phases that are characteristic of SYNROC compositions. Authoritative tabulations and critically reviewed values have been used wherever possible. The stabilities of some titanium species are controversial; quite different values can be obtained from various sources. In addition, the actual state of TiO_2 in aqueous systems is in some question. It hydrates and forms amorphous hydroxides of variable composition and poorly known thermodynamic properties.

The aqueous species and solid phases of titanium are listed with references in Tables C-1 and C-2, respectively. Several non-titanium-bearing phases associated with SYNROC compositions are given in Table C-3. We have elected to describe the hydrated phases of titanium as $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$ instead of $\text{TiO}(\text{OH})_2$ and $\text{Ti}(\text{OH})_4$, respectively, to emphasize their relationship to the anhydrous oxide TiO_2 . Similarly, other phases are so written as to show the stoichiometry in terms of their component oxides. These are usually the end-members of extensive and complex solid solutions, for which little data exists.

It will be noted that many entropy values for aqueous species are missing. This is unfortunate, because they are required for the estimation of free energies at higher temperatures. Unavailable values can be estimated, of course, but we would prefer to avoid this source of uncertainty. In addition to the values at 298 K, there exists a considerable amount of elevated temperature stability data which we may use to construct data files. Calculations involving reactions with groundwaters should not require stabilities at temperatures much greater than 373 K. However, information on phase relationships during high temperature fabrication and changes during cooling are likely to help clarify the chemical durability of a composite material.

TABLE C-1. Aqueous titanium species.

Species	ΔG_F^0 (kJ/mole)	S_{298}^0 J/mole-K	See Reference No.
Ti^{4+}	-354.18	---	36
$TiOCl^+$	-764.46	---	37
$TiOCl_2^0$	-893.45	---	37
$TiOCl^{3-}$	-1018.85	---	37
$TiOCl_4^{2-}$	-1137.59	---	37
TiF_6^{2-}	-2118.36	83.68	38
$TiOF^+$	-950.73	---	37
$TiOF_2^0$	-1257.42	---	37
$TiOF_2^-$	-1561.59	---	37
$TiOF_4^{2-}$	-1864.77	---	37
$Ti(OH)_3^+$	-1092.53	---	36
$Ti(OH)_4^0$	-1318.38	---	36
$HTiO_3^-$	-956.04	---	39
$TiOH^{3+}$	-614.00	---	36
$Ti(OH)_2^{2+}$	-869.56	---	36
$TiOH^{2+}$	-574.42	---	40
$(TiOH)_2^{4+}$	-1153.36	---	40
$TiOHSO_4^+$	-1042.52	---	41
$TiOSO_4$	-1390.55	---	37

TABLE C-2. Solid titanium phases.

Phase	Mineral name	ΔG_F^0 (kJ/mole)	S_{298}^0 (J/mole-K)	See Reference No.
TiBr ₄		-590.27	243.63	38
TiCl ₄		-735.66	208.91	38
TiF ₄ (am)		-1559.38	133.97	42
TiI ₄		-371.54	249.37	42
TiO ₂ ·2H ₂ O		-1281.77	--	36
TiO ₂ ·H ₂ O		-1112.94	--	38
TiO ₂	Anatase	-884.50	49.92	42
TiO ₂	Rutile	-889.52	50.33	42
CaO·TiO ₂ ·SiO ₂	Sphene	-2461.22	129.20	43
CaO·TiO ₂	Perovskite	-1575.35	93.72	43
FeO·TiO ₂	Ilmenite	-1159.24	105.86	43
MgO·TiO ₂	Geikielite	-1484.44	74.56	43
ZnO·TiO ₂		--	94.98	38
2ZnO·TiO ₂		-1534.27	143.01	42
3CaO·2TiO ₂		-3750.54	234.72	38
2MgO·TiO ₂	Orthotitanate	-2048.49	115.10	44
MgO·2TiO ₂	Karrooite	-2370.03	138.91	44
Na ₂ O·TiO ₂		-1456.87	121.75	45
Na ₂ O·2TiO ₂		--	173.64	46
Na ₂ O·3TiO ₂		-3279.42	233.89	45
NiO·TiO ₂		-1115.87	83.26	47
CdO·TiO ₂		-1146.88	105.02	48
K ₂ O·TiO ₂		-1532.60	237.23	38
ZrO ₂ ·TiO ₂		-1939.70	92.88	49
2NiO·TiO ₂		-1318.80	--	44
SrO·TiO ₂		-1588.41	108.78	50
2SrO·TiO ₂		-2178.61	158.99	50
BaO·TiO ₂		-1572.35	107.95	50

TABLE C-2. (Continued.)

Phase	Mineral name	ΔG_f^J (kJ/mole)	S_{298}^0 (J/mole-K)	See Reference No.
$2\text{BaO} \cdot \text{TiO}_2$		-2133.00	196.65	50
$\text{BaO} \cdot \text{SrO} \cdot \text{TiO}_2$		-2167.73	191.63	50
$(\text{BaO})_{0.453} (\text{SrO})_{0.457} \cdot \text{TiO}_2$		-1574.86	114.64	46
$\text{Li}_2\text{O} \cdot \text{TiO}$		-1580.84	91.63	51
$4\text{CaO} \cdot 3\text{TiO}_2$		-5382.88	328.44	51
$2\text{FeO} \cdot \text{TiO}_2$	Ulvospinel	-1424.69	169.03	46,51
$\text{CoO} \cdot \text{TiO}_2$		-1127.63	96.86	51
$4\text{SrO} \cdot 3\text{TiO}_2$		-5417.90	376.56	51
$\text{MnO} \cdot \text{TiO}_2$	Pyrophanite	-1287.42	105.85	51
$2\text{MnO} \cdot \text{TiO}_2$		-1655.02	169.45	51
$2\text{CoO} \cdot \text{TiO}_2$		-1344.32	153.97	51
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	Tialite	-2482.65	109.62	51
TiF_2		-784.41	75.31	52
TiI_2		-270.13	147.69	38
TiO		-494.97	34.77	42
$\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{TiO}_2$	Ba-hollandite	(-6736.00)	--	est.
$\text{Ba/FeO} \cdot 7\text{TiO}_2$	Ba-hollandite, Fe end-member	--	--	--
$\text{CaO} \cdot \text{ZrO}_2 \cdot 2\text{TiO}_2$	Zirconolite	(-3556.00)	--	est.
$\text{CaO} \cdot \text{ZrO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$	Pseudobrookite	--	156.48	43
$\text{CaO} \cdot \text{ZrO}_2 \cdot \text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{TiO}_2$	Pseudobrookite, solid solution	--	--	--
$\text{K}_2\text{O} \cdot \text{TiO}_2$		--	237.23	38
$\text{PbO} \cdot \text{TiO}_2$		-1093.24	111.92	51
Ti_3O_5		-2316.68	129.29	38
TiS_2		-421.75	78.37	53

TABLE C-2. (Continued.)

Phase	Mineral name	ΔG_f^0 (kJ/mole)	S_{298}^0 (J/mole-K)	See Reference No.
TiBr ₃		-523.84	176.56	42
TiCl ₃		-653.54	139.75	42
TiF ₃		-1342.87	102.51	38
TiI ₃		-336.87	192.46	38
Ti(OH) ₃		-1049.77	--	39
Ti ₂ O ₃		-1434.28	78.78	42
NiO·2TiO ₂		-1873.60	--	47
TiBr ₂		-375.05	130.12	38
TiCl ₂		-464.42	87.45	42

TABLE C-3. Non-titanium bearing phases.

Phase	Mineral name	ΔG_f^0 (kJ/mole)	S_{298}^0 (J/mole-K)	See Reference No.
NaAlSiO ₄	Nepheline	-1960.71	124.26	46
Na _{0.78} K _{0.22} ·AlSiO ₄	Nepheline	-1982.38	126.36	46
FeO·Al ₂ O ₃	Hercynite	-1859.54	106.27	46

In addition to the tabulated references for species and phases, we have included five review papers⁵⁴⁻⁵⁸ we consider useful in providing access to much of the literature on experimental studies of these materials. Thermochemical properties of phases with the pseudobrookite structure are discussed by Navrotsky,⁵⁴ who tabulates stability data at high temperatures. She concludes that some of the titania-rich phases (see Table C-4) are only marginally stable with respect to their component oxides. However, note the inconsistency with Table C-2 in the case of $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$. Navrotsky also discusses^{55,56} the thermodynamics of formation and cation distribution in various spinels at high temperatures, including a number of titanates and their solid solutions. This information could be useful in designing compositions to accommodate various waste elements. Kubaschewski⁵⁷ tabulates data for double oxides, including many titanates. Resnitskii⁵⁸ gives a recent and very extensive review (289 references) of titanate thermochemistry, which includes high temperature data.

TABLE C-4. Conditionally stable titanate phases.

Stable only at high temperatures	Stable in solid solutions but not as end members at any temperature
$\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$	
$\text{Ga}_2\text{O}_3 \cdot \text{TiO}_2$	
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	$\text{NiO} \cdot 2\text{TiO}_2$
$\text{CoO} \cdot 2\text{TiO}_2$	$\text{MnO} \cdot 2\text{TiO}_2$
$\text{FeO} \cdot 2\text{TiO}_2$	
$\text{MgO} \cdot 2\text{TiO}_2$	

Appendix D

DISSOLUTION OF SYNROC PHASES IN WATER: PEROVSKITE AND RUTILE

The CaTiO_3 (perovskite) phase of a SYNROC-D composite accommodates most strontium, trivalent rare earth and actinide elements in defense waste sludges. Its resistance to water leaching is therefore of considerable importance in assessing the performance of this waste form.

A literature search disclosed no solubility data for CaTiO_3 in aqueous solutions. As an alternative, we have attempted an equilibrium calculation for 298 K, where existing thermochemical data appear adequate. The basis was the free energy data listed in Appendix C. Fortunately, the dissolution reactions of the calcium end-member are uncomplicated by questions of oxidation potential of the system. Note that for all calculations in this report, we have used pure 1 m NaCl solution to survey salinity effects. All activity coefficients for aqueous species have been set to unity. Although compositions of actual brines are available,⁵⁹ we have elected not to introduce at this time complexing ligands other than chloride, or to attempt to estimate activity coefficients for species in concentrated electrolytes. The calculation was run as a simulated precipitation with total titanium content of 10^{-7} m and excess calcium as CaCl_2 . At these concentrations, there was always a titanium-bearing solid oxide phase formed. It was found that the equilibrium solid phase up to a pH of 10.2 was TiO_2 (rutile), even at very high calcium/titanium ratios.

At pH = 10.2 and higher, TiO_2 was also the solid phase at Ca^{++} molalities less than 9.57×10^{-3} m. CaTiO_3 was formed between .0095 and .1040 m Ca^{++} . The pH and Ca^{++} effects can be understood qualitatively by considering their mass action in Eq. (8).

At Ca^{++} molalities greater than .105, the phase $4\text{CaO} \cdot \text{TiO}_2$ was formed, by the reaction in Eq. (9), which has a large negative free energy.

These relationships are shown schematically in Fig. D-1. Species distributions and solubilities were computed for the TiO_2 and CaTiO_3 phases between $3.0 < \text{pH} < 11.4$ and are shown in Fig. D-2. It is evident that the titanium-chloride complexes are weak, and would not contribute significantly at 298 K for any pH above 3. In very acid solutions, the lower hydroxy complexes $\text{Ti}(\text{OH})^{3+}$ and $\text{Ti}(\text{OH})_2^{2+}$ would also contribute to a solubility increase. At pH values above 3, the predominant species is $\text{Ti}(\text{OH})_4$ (neutral), and the solubility of TiO_2 is constant at about 10^{-8} m . This value is based on the free energy data of Vasilev,³⁶ who in turn derives it from the experimental data of Schulling.⁶⁰ Schulling measured TiO_2 solubilities in 1 M NaCl of 2.78×10^{-3} and $3.28 \times 10^{-3} \text{ m}$ at 473 and 573 K, respectively. The extrapolation shown in Fig. D-3 also leads directly to the solubility at 298 K, as it should if there is only one significant reaction.

In the restricted stability field of CaTiO_3 , total solubility would decrease considerably with increasing pH. However, the pH and Ca^{++} concentration requirements for the existence of this phase are unlikely to be met in a real groundwater, as shown very approximately in Fig. D-1.⁶¹ Therefore, if perovskite is exposed to a natural water, the pH and Ca^{++} concentration should rise, and the removal of calcium (and a much smaller amount of titanium) would create a two-solid phase system of $\text{CaTiO}_3 + \text{TiO}_2$. If the water is flowing, calcium will continue to leach until only TiO_2 is left. In other words, we believe that CaTiO_3 does not have a true solubility under normal conditions but dissolves incongruently at a rate controlled by some unknown intermediate reaction. Of course, this rate can be very low. It should also be pointed out that such rates decrease with time in static or nearly static systems because of concentration effects.

This system that we considered is much simpler than SYNROC + groundwater. Other species, both aqueous and solid, may participate in the dissolution process. If the perovskite phase is a solid solution containing elements of variable oxidation state, such as $\text{Fe}^{++}/\text{Fe}^{+++}$, the dissolution rate is expected to be some function of the oxidation potential of the system, as is the case with ilmenite.^{62,63} Zirconolite is another phase which is a potential source of calcium and titanium.

FIG. D-1. Stability fields of rutile and calcium titanates in simple aqueous solutions.

FIG. D-2. Speciation in $\text{TiO}_2/\text{CaTiO}_3$ dissolution, $1 \mu \text{ NaCl}$.

FIG. D-3. Solubility of TiO_2 in 1 m NaCl .

Appendix E

THERMOCHEMISTRY OF BARIUM HOLLANDITE, ZIRCONOLITE, AND RELATED PHASES

A. INTRODUCTION

Barium hollandite and its solid solutions are also major components of SYNROC compositions. Their chemistry, including leaching behavior, is presently being studied experimentally in the mineral waste form development program at LLNL. Useful insight into the leaching processes of stable crystalline phases often can be gained through equilibrium thermochemical analysis. Mechanisms which limit solubilities and response to variations in water composition and volume often can be established.

The hollandites and zirconolites are relatively little-known phases, and there does not appear to be any published thermodynamic data for them at any temperature. We have, therefore, summarized existing chemical evidence relating to their stabilities and attempted to estimate them. Their application to the evaluation of leaching processes will be briefly discussed.

B. STABILITIES OF BARIUM HOLLANDITE AND ZIRCONOLITE

The unknown free energy of formation of a solid phase can be estimated from several types of information. Entropy and enthalpy of formation themselves sometimes can be estimated. Alternatively, a correlation analysis of free energy data for chemically related phases can be carried out. Thermochemical cycles of reactions can be used to establish limits for the required value. In the case of Ba-hollandite, the higher temperature part of the stability range has been explored to a limited extent in the course of preparation of SYNROC compositions. Synthesis has shown that it is stable with respect both to its component oxides and to complex oxides above about 1173 K (900°C), and that its actual composition is $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{TiO}_2$.

Although we require low temperature stabilities for dissolution analysis, the following calculations will also make use of data from high temperature reactions. There is a reasonable amount of thermodynamic information for simple titanates, aluminates, and zirconates.

A review by Kubaschewski⁵⁷ provides a convenient source of analytical functions for the free energies of formation vs T for double oxides. We have used these to compute the discrete values of Table E-1. Two additional phases have been included: $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ and $\text{BaO} \cdot \text{Al}_2\text{O}_3$. The function for $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ was generated from two values: ΔH_f^0 and S_{298}^0 from Kubaschewski,⁵¹ and the observation of decomposition to the component oxides at and below 1273 K.⁶⁴ Data for $\text{BaO} \cdot \text{Al}_2\text{O}_3$ were estimated from ΔH_f^0 and S_{298}^0 by assuming the same rate of change of ΔG_f^0 with temperature as $\text{CaO} \cdot \text{Al}_2\text{O}_3$; i.e., 261.5 J/degree/mole. Data for TiO_2 (rutile) and alpha Al_2O_3 are from JANAF.⁶⁵

The tabulated free energies of the titanates were converted to a common basis of kJ/mole of oxygen consumed in the formation reaction and used to construct an Ellingham chart, Fig. E-1.^{66,67} This chart is a convenient device for comparing stabilities in families of chemically related phases. Table E-1 and Fig. E-1 show a fairly consistent value of $d(\Delta G)/dT = 176 \pm 25$ J/degree/mole of oxygen, indicative of a nearly constant entropy of formation for these materials per mole of oxygen.

The relationships among titanates of different elements coincide qualitatively with what we know of their chemistry. For example, the curves for calcium, strontium, and barium are very similar both in magnitude and slope, reflecting the ease with which they substitute for each other in titanate phases at all temperatures. Titanates of lithium, aluminum, and magnesium are slightly less stable, and those of iron, cobalt, and nickel have a much decreased stability (more positive free energy). From such considerations, we would expect that alkaline earth titanate solid solutions containing these latter elements would be thermodynamically less stable than the end members.

With this information, we might establish a reasonable approximation to the thermodynamic properties of Ba-hollandite from a single unambiguous point, such as might be obtained from the free energy or equilibrium constant for some reaction. We note that such free energy values for several other titanates at one temperature (298 K) do exist, so that their properties at elevated temperatures could also be estimated, if necessary. In the case of Ba-hollandite, no such value has been found.

TABLE E-1. Free energies of formation of double oxides.

DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****	DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****
Li2O.TiO2	298.	-1582314.	MgO.2TiO2	298.	-2376720.
	400.	-1550848.		400.	-2328432.
	500.	-1519714.		500.	-2281583.
	600.	-1488356.		600.	-2235043.
	700.	-1456811.		700.	-2188786.
	800.	-1425106.		800.	-2142771.
	900.	-1393260.		900.	-2096967.
	1000.	-1362044.		1000.	-2050807.
	1100.	-1330783.		1100.	-2004372.
	1200.	-1299872.		1200.	-1958045.
				1270.	-1925676.
2MgO.TiO	298.	-2055891.	3CaO.2TiO2	298.	-3800029.
	400.	-2015552.		400.	-3733460.
	500.	-1976426.		500.	-3668491.
	600.	-1937631.		600.	-3603754.
	700.	-1899113.		700.	-3539209.
	800.	-1860831.		800.	-3474830.
	900.	-1822755.		900.	-3410595.
	1000.	-1783775.		1000.	-3346488.
	1100.	-1744069.		1100.	-3282496.
	1200.	-1704424.		1200.	-3216714.
	1270.	-1676706.		1270.	-3170311.
MgO.TiO2	1280.	-1672748.	6 4CaO.3TiO2	1280.	-3163686.
	1300.	-1664835.		1300.	-3150438.
	1400.	-1620314.		1400.	-3084251.
	1500.	-1561481.		1500.	-3018146.
				298.	-5380533.
	298.	-1485436.		400.	-5285761.
	400.	-1455648.		500.	-5193288.
	500.	-1426728.		600.	-5101163.
	600.	-1398032.		700.	-5009327.
	700.	-1369523.		800.	-4917739.
	800.	-1341172.		900.	-4826367.
	900.	-1312962.		1000.	-4735138.
	1000.	-1284331.		1100.	-4644132.
	1100.	-1255366.		1200.	-4550806.
	1200.	-1226457.		1270.	-4484979.
	1270.	-1206253.		1280.	-4475580.
	1280.	-1203368.		1300.	-4456787.
	1300.	-1197601.		1400.	-4362902.
	1400.	-1166301.		1500.	-4269140.
	1500.	-1127866.			

TABLE E-1. (Continued.)

DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****	DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****
CAO.TIO2	298.	-1573836.	SRO.TIO2	298.	-1588291.
	400.	-1545355.		400.	-1559338.
	500.	-1517579.		500.	-1531186.
	600.	-1489920.		600.	-1503217.
	700.	-1462357.		700.	-1475400.
	800.	-1434876.		800.	-1447714.
	900.	-1407468.		900.	-1420142.
	1000.	-1380123.		1000.	-1392374.
	1100.	-1352837.		1100.	-1364404.
	1200.	-1324971.		1200.	-1336378.
	1270.	-1305356.	2BAO.TIO2	298.	-2163854.
	1280.	-1302555.		400.	-2125839.
	1300.	-1296955.		500.	-2098716.
	1400.	-1266986.		600.	-2051710.
	1500.	-1241057.		700.	-2014799.
2SRO.TIO2	298.	-2175917.		800.	-1977972.
	400.	-2135990.		900.	-1941216.
	500.	-2097164.		1000.	-1902851.
	600.	-2058589.		1100.	-1863372.
	700.	-2020222.		1200.	-1823946.
	800.	-1982033.		1270.	-1796376.
	900.	-1944001.		1280.	-1792440.
	1000.	-1905512.		1300.	-1784568.
	1100.	-1866562.		1400.	-1745234.
	1200.	-1827448.		1500.	-1705941.
	1270.	-1799979.	BAO.TIO2	298.	-1580347.
	1280.	-1796049.		400.	-1550121.
	1300.	-1788185.		500.	-1520634.
	1400.	-1748783.		600.	-1491263.
	1500.	-1709252.		700.	-1461988.
4SRO.3TIO2	298.	-5368817.		800.	-1432797.
	400.	-5270985.		900.	-1403677.
	500.	-5175854.		1000.	-1373784.
	600.	-5081340.		1100.	-1343364.
	700.	-4987340.		1200.	-1312996.
	800.	-4893779.		1270.	-1291767.
	900.	-4800602.		1280.	-1288736.
	1000.	-4706578.		1300.	-1282676.
	1100.	-4611688.			
	1200.	-4516523.			
	1270.	-4449756.			
	1280.	-4440209.			
	1300.	-4421106.			
	1400.	-4325457.			
	1500.	-4229592.			

TABLE E-1. (Continued.)

DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOL F. *****	DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****
FeO.TiO2	298.	-1164550.	NiO.TiO2	800.	-975795.
	400.	-1137921.		900.	-948592.
	500.	-1111962.		1000.	-921452.
	600.	-1086118.		1100.	-894371.
	700.	-1060370.		1200.	-867341.
	800.	-1034706.		1270.	-848450.
	900.	-1009113.		1280.	-845753.
	1000.	-983585.		1300.	-840360.
	1100.	-958114.		1400.	-813423.
	1200.	-932695.		1500.	-786528.
	1270.	-914931.	2ZnO.TiO2	500.	-1454664.
	1280.	-912396.		600.	-1418399.
	1300.	-907325.		700.	
	1400.	-881399.		800.	
	1500.	-856714.		900.	
				1000.	
2FeO.TiO2	298.	-1412252.	AL2O3.TiO2	1100.	
	400.	-1379597.		1200.	-1194358.
	500.	-1347730.		1270.	-1155447.
	600.	-1315978.		1280.	-1149902.
	700.	-1284323.		1300.	-1138823.
	800.	-1252751.		1400.	-1083621.
	900.	-1221250.		1500.	-1028730.
	1000.	-1189814.		298.	-2482391.
	1100.	-1158435.		400.	-2431003.
	1200.	-1127109.		500.	-2380438.
	1270.	-1105210.		600.	-2329725.
	1280.	-1102083.		700.	-2278898.
COO.TiO2	1300.	-1095831.		800.	-2227965.
	1400.	-1064597.		900.	-2176941.
	800.	-995318.		1000.	-2125838.
	900.	-969775.		1100.	-2074662.
	1000.	-944297.		1200.	-2023420.
	1100.	-918876.		1270.	-1987516.
	1200.	-893508.		1280.	-1982384.
	1270.	-875779.		1300.	-1972119.
	1280.	-873248.		1400.	-1920762.
	1300.	-868188.		1500.	-1869354.
	1400.	-842912.			
	1500.				

TABLE E-1. (Continued.)

DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****	DOUBLE OXIDE *****	KELVIN TEMPERATURE *****	DELTA G DOUBLE OXIDE, J/MOLE *****
3CAO.AL2O3	800.	-3118453.	BAO.AL2O3	298.	-2226770.
	900.	-3059173.		400.	-2201045.
	1000.	-2999748.		500.	-2175453.
	1100.	-2940194.		600.	-2149681.
	1200.	-2878626.		700.	-2123651.
	1270.	-2835051.		800.	-2097436.
	1280.	-2828822.		900.	-2071059.
	1300.	-2816360.		1000.	-2043700.
	1400.	-2753995.		1100.	-2015626.
	1500.	-2691537.		1200.	-1987434.
				1270.	-1967635.
CAO.AL2O3	298.	-2209367.	BA-HOLLANDITE	1280.	-1964802.
	400.	-2169678.		1300.	-1959134.
	500.	-2130436.		1400.	-1930734.
	600.	-2090933.		1500.	-1902242.
	700.	-2051214.		298.	-6736240.
	800.	-2011308.		400.	-6611103.
	900.	-1971241.		500.	-6488824.
	1000.	-1931029.		600.	-6366864.
	1100.	-1890688.		700.	-6245169.
	1200.	-1849596.		800.	-6123702.
	1270.	-1820630.		900.	-6002432.
CAO.2AL2O3	1280.	-1816488.		1000.	-5880503.
	1300.	-1808200.		1100.	-5758146.
	1400.	-1766705.		1200.	-5635933.
	1500.	-1725117.		1270.	-5550464.
	800.	-3439714.		1280.	-5538259.
	900.	-3368265.		1300.	-5513853.
	1000.	-3296528.		1400.	-5391894.
	1100.	-3224531.		1500.	-5270049.
	1200.	-3151666.			
	1270.	-3100394.			
	1280.	-3093061.			
	1300.	-3078389.			
	1400.	-3004912.			
	1500.	-2931250.

FIG. E-1. Free energies of formation of double oxides, from the elements.

There is other useful evidence, however. We can write a set of decomposition reactions (8) to (11) that experimental preparations imply do not take place and can, therefore, compute from them several maximum values of free energy of formation:

Since excess TiO_2 is formed in these reactions, decompositions to form BaO or CaO or to phases lower than 1:1 in TiO_2 were not considered. The first reaction that might be expected is to form the next most titanium-rich phase in the Ba-Al-Ti-O system. Higher aluminum titanates are not known, and among the alkaline earth titanates, only magnesium is known to form a $\text{MeO} \cdot 2\text{TiO}_2$ phase. Therefore, we consider only the monotitanates of calcium, barium, and aluminum. Reaction (11) evidently does not proceed as written, since Ba-hollandite and perovskite can coexist.⁶⁸ We have assumed that changes in free energy due to the formation of solid solutions can be neglected. In Fig. E-2, we have plotted the minimum stabilities for Ba-hollandite, computed by assuming that the free energies of decomposition reactions (8) to (11) are zero.

These reactions agree fairly well on a lower bound for the stability of Ba-hollandite (maximum free energy). Reaction (8) requires it to be not higher than -6719 kJ/mole at 298 K. Although we do not know how much lower the free energy of formation might be, there is some additional evidence from the fact that two-phase Ba-hollandite + zirconolite can be prepared. Therefore, we consider zirconolite in the following paragraph.

It is true that we also do not know the thermodynamic properties of zirconolite at any temperature, but we know the stabilities of several of its possible decomposition products, and can write the following reactions:

FIG. E-2. Free energy maxima for Ba-hollandite.

It is known that reactions (12), (14), and (15) proceed as written in the temperature range 1473 to 1573 K (1200 to 1300°C) and reaction (12) at 1273 K (1000°C).⁶⁹ The lowest temperature for which there is actual evidence of zirconolite stability is 1073 K (800°C), where it can be prepared by annealing the metamict phase.⁷³ Assuming that the free energies of reactions (12) to (15) are zero or negative at 298 K, it sets the maximum free energy of zirconolite at -3443, -3460, and -3515 kJ/mole, respectively. This trend of free energy changes as the component oxides undergo increasing degrees of bonding indicate a free energy of formation near -3556 kJ/mole (-850 kcal/mole).

The analogues of zirconolite in which strontium^{70,71} or barium⁷² replace calcium have not been observed, although extensive solid solutions are formed at high temperatures.

With a value for zirconolite, it is possible to evaluate the stability of Ba-hollandite by computing limiting free energies for its decomposition reactions (16) to (21).

The additional data required for use in reactions (16) to (21) are listed in Table E-2. We found no evidence for the existence of phases that might result in alternatives to reactions (16) to (21).⁷²⁻⁷⁴ Other possible alkaline earth zirconates are either unknown or unstable at lower temperatures. Aluminum zirconate is not known.⁷⁴ Ternary titanates formed with alumina + calcia or alumina + zirconia were not found.

If the decomposition product phases of reactions (16) to (21) are not observed experimentally on annealing two-phase zirconolite + hollandite preparations, the free energies of reaction must be zero or positive. This requires maximum free energies of formation for Ba-hollandite of -6636, -6615, -6573, -6669, -6632, and -6611 kJ/mole, respectively, for reactions (16) to (21). It is interesting and encouraging to note that these do not differ greatly from the maxima determined by reactions (8) to (11).

We believe that from reaction (8), the most reasonable value that can be derived at this time for Ba-hollandite is $\Delta G_{f,298}^0 = -6736$ kJ/mole (-1610 kcal/mole). Values much more negative than this do not seem reasonable, from the fact that the analogues in which beryllium or magnesium substitute for barium do not appear in the high temperature ternary systems.^{68,69} Therefore, we have interpolated between this value and the maximum at 1500 K as determined from reaction (10) to obtain the estimated stability values for Ba-hollandite given in Table E-1. Better values could no doubt be obtained by experimental studies of high temperature equilibria designed specifically for this purpose.

C. LEACHING BEHAVIOR

We believe that the resistance of oxide compositions to water leaching depends largely on the solubilities of major phases that can be formed as hydrolysis/alteration products. For elements that do not diffuse rapidly in the solid state at low temperatures, little leaching will take place unless these protective outer layers are removed. End-member Ba-hollandite is particularly favorable in that oxides and hydroxides of aluminum and titanium are not very soluble in groundwaters.

TABLE E-2. Stabilities of phases containing zirconium.

Phase	ΔG_{298}^0 (kJ/mole)	See
		Reference No.
ZrO ₂	-1039.72	65
CaO•ZrO ₂	-1680.71	58
SrO•ZrO ₂	-1694.52	58
BaO•ZrO ₂	-1694.52	58
ZrO ₂ •TiO ₂	-1941.38	49

Consider the various reactions by which barium can be released into solution. Reaction (9) at 298 K need not be considered. ΔG_{298}^0 for reactions (8), (10), and (11) are +56.1, +83.7, and +104.6 kJ/mole, respectively. Each might take place as written, however, if coupled with an energetically favorable reaction producing aqueous species. Reactions (8) and (10) then become (22), while reaction (11) becomes (23):

The Cl^- and OH^- ligands do not strongly complex barium, so that its principal aqueous species in a simple NaCl solution would be Ba^{++} . The ΔG_{298}^0 for reactions (22) and (23) are -58.6 and 0 kJ/mole, respectively. Then, the evidence is that Ba-hollandite should dissolve incongruently, releasing barium to the solution and leaving a more or less hydrated residue of TiO_2 and Al_2O_3 . However, such simplified calculations do not give completely unambiguous results, since the system can be modified by other reactions such as complexation in solution or the formation of alternate solid phases. For example, as previously noted in Appendix D, $\text{CaO} \cdot \text{TiO}_2$ in reaction (23) will release Ca^{++} , and Al_2O_3 will release a variety of species. From mass

action considerations, an alkaline groundwater or high concentrations of complexing ligands for aluminum would tend to promote leaching reactions (22) and (23). In general, computer simulation will be necessary to evaluate the extent of the possible alternative reactions, and we will examine these in the future.

D. SUMMARY AND CONCLUSIONS

Zirconolite and Ba-hollandite, proposed as matrices for the fixation of nuclear waste elements, have poorly understood chemical properties. The fact that their stabilities as a function of composition are not well known does not, of course, affect their practical usefulness, but much more detail on their properties will eventually be required to predict their reactions in a wide variety of disposal scenarios. Although it has been possible to extract considerable information from the literature, it is clear that the data for major SYNROC phases remain somewhat uncertain. This examination of decomposition phases that could be expected and the assembly of data for them may prove useful in interpreting experimentally observed reactions and in designing compositions for the accommodation of waste elements.

A considerable amount of investigation of SYNROC phases remains to be done. The spinels have not yet been specifically addressed. In addition, it will be necessary to determine the thermodynamics of the very extensive solid solutions that are formed, as a function both of composition and temperature. The propensity to form such solutions is, of course, the basis of their usefulness.

Appendix F
NUCLIDE ACTIVITY LISTING OF SAVANNAH RIVER PLANT WASTE

TABLE F-1. Nuclide activity listing of Savannah River Plant waste radionuclides with $T_{1/2} > 1$ d ci/canister.¹⁰

Time-->	0.0 Yr	1.0 Yr	3.0 Yr	10.0 Yr	30.0 Yr	100.0 Yr	300.0 Yr	1,000.0 Yr	3,000.0 Yr	10,000.0 Yr	30,000.0 Yr	100,000.0 Yr	300,000.0 Yr	1,000,000.0 Yr
Co 60	5.01804E-02	4.39310E-02	3.37852E-02	1.34227E-02	9.60404E-04	9.41033E-08	3.30931E-19	2.69895E-59	0.0	0.0	0.0	0.0	0.0	0.0
Se 79	1.40595E-01	1.40594E-01	1.40591E-01	1.40580E-01	1.40550E-01	1.40445E-01	1.40146E-01	1.39103E-01	1.36165E-01	1.26365E-01	1.02079E-01	4.83639E-02	5.72297E-03	3.26195E-06
Rb 87	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06	9.33697E-06
Sr 90	5.61305E-03	5.47629E-03	5.21268E-03	4.38603E-03	2.67803E-03	4.76344E-02	3.43052E-00	1.08742E-07	4.08135E-29	0.0	0.0	0.0	0.0	0.0
Y 90	5.61452E-03	5.47772E-03	5.21404E-03	4.38717E-03	2.67873E-03	4.76468E-02	3.43141E-00	1.08770E-07	4.08241E-29	0.0	0.0	0.0	0.0	0.0
Zr 93	1.87861E-00	1.87861E-00	1.87860E-00	1.87860E-00	1.87857E-00	1.87847E-00	1.87820E-00	1.87774E-00	1.87450E-00	1.86494E-00	1.83791E-00	1.74633E-00	1.50907E-00	9.05198E-01
Tc 99	2.54545E-00	2.54544E-00	2.54542E-00	2.54536E-00	2.54520E-00	2.54462E-00	2.54296E-00	2.53718E-00	2.52071E-00	2.46394E-00	2.30869E-00	1.83838E-00	9.58911E-01	9.82829E-02
Nu 106	2.00956E-13	1.01188E-13	2.56560E-14	2.10568E-16	2.31196E-22	3.20673E-43	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pd 107	9.45340E-03	9.45339E-03	9.45339E-03	9.45339E-03	9.45337E-03	9.45329E-03	9.45310E-03	9.45239E-03	9.45037E-03	9.44331E-03	9.42318E-03	9.35305E-03	9.15555E-03	8.4456E-03
Ag 110	2.01651E-22	7.38397E-23	9.90077E-24	8.73969E-27	1.64168E-35	4.71633E-66	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
In 115	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26	2.31811E-26
Sn 121m	1.26282E-02	1.24542E-02	1.21134E-02	1.09924E-02	8.32912E-03	3.15405E-03	1.96755E-04	1.19294E-08	1.06459E-20	7.14702E-63	0.0	0.0	0.0	0.0
Sn 123	6.66445E-45	9.36398E-46	1.84864E-47	1.99859E-53	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sn 126	1.56082E-02	1.56082E-02	1.56082E-02	1.56081E-02	1.56079E-02	1.56071E-02	1.56050E-02	1.55974E-02	1.56758E-02	1.55003E-02	1.52868E-02	1.45623E-02	1.26760E-02	7.80040E-03
Sb 125	3.72910E-04	2.89292E-04	1.74101E-04	2.94394E-05	1.83477E-07	3.50650E-15	3.10022E-37	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sb 126	2.18515E-03	2.18515E-03	2.18514E-03	2.18513E-03	2.18510E-03	2.18500E-03	2.18469E-03	2.18363E-03	2.18061E-03	2.17004E-03	2.14015E-03	2.03872E-03	1.77464E-03	1.09206E-03
Sb 126m	1.56082E-02	1.56082E-02	1.56082E-02	1.56081E-02	1.56079E-02	1.56071E-02	1.56050E-02	1.54138E-02	1.33952E-02	1.33303E-02	1.31466E-02	1.25236E-02	1.09014E-02	6.70834E-03
Te 125m	9.10664E-05	7.06465E-05	4.25163E-05	7.18925E-06	4.48059E-08	8.56302E-16	7.57087E-38	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I 129	2.05051E-21	2.05051E-21	2.05051E-21	2.05051E-21	2.05050E-21	2.05050E-21	2.05048E-21	2.05042E-21	2.05024E-21	2.04961E-21	2.04782E-21	2.04158E-21	2.02345E-21	1.96298E-21
Ce 134	2.17321E-05	1.35229E-05	7.91972E-06	7.51265E-07	8.97789E-10	5.29691E-20	3.14656E-49	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ce 135	6.18755E-02	6.18755E-02	6.18754E-02	6.18753E-02	6.18749E-02	6.18736E-02	6.18699E-02	6.18568E-02	6.18195E-02	6.16892E-02	6.13182E-02	6.00374E-02	5.65232E-02	4.57664E-02
Ce 137	6.57230E-03	6.42269E-03	6.13359E-03	5.22045E-03	3.29373E-03	6.57082E-02	6.56783E-00	6.55734E-07	6.52770E-27	0.0	0.0	0.0	0.0	0.0
Ce 142	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85808E-06	9.85807E-06	9.85806E-06	9.85802E-06

TABLE F-1. (Continued.)

Time-->	0.0 Yr	1.0 Yr	3.0 Yr	10.0 Yr	30.0 Yr	100.0 Yr	300.0 Yr	1,000.0 Yr	3,000.0 Yr	10,000.0 Yr	30,000.0 Yr	100,000.0 Yr	300,000.0 Yr	1,000,000.0 Yr
Ce 144	4.81904E-17	1.97858E-17	3.33533E-18	6.55978E-21	1.21549E-28	1.05268E-55	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hd 144	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10	5.00690E-10
Pm 147	6.22246E-03	4.77745E-03	2.81621E-03	4.42901E-04	2.24387E-06	2.07694E-14	2.31382E-37	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sm 147	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06	2.58607E-06
Sm 143	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12	5.81073E-12
Sm 149	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12	1.80116E-12
Sm 151	1.42678E-02	1.41617E-02	1.39521E-02	1.32424E-02	1.14073E-02	6.76787E-01	1.52281E-01	8.22842E-02	2.73681E-08	5.80775E-31	0.0	0.0	0.0	0.0
Eu 152	1.08394E-01	1.02762E-01	9.29415E-02	6.35751E-02	2.38700E-02	5.22178E-04	1.21187E-08	7.29638E-25	0.0	0.0	0.0	0.0	0.0	0.0
Eu 154	3.38684E-00	3.12440E-00	2.65896E-00	1.51189E-00	3.01281E-01	1.06428E-03	1.05094E-10	3.17973E-35	0.0	0.0	0.0	0.0	0.0	0.0
Eu 155	7.22417E-02	6.25216E-02	4.68288E-02	1.70295E-02	9.46299E-04	3.82761E-08	1.07447E-20	1.25920E-64	0.0	0.0	0.0	0.0	0.0	0.0
Pb 210	1.42114E-07	1.50686E-07	1.68808E-07	2.43323E-07	5.63728E-07	3.32825E-06	3.13316E-05	4.07261E-04	3.19168E-03	1.86550E-02	6.03080E-02	1.44475E-01	1.55641E-01	2.59462E-02
Bi 210	1.40529E-07	1.49008E-07	1.66936E-07	2.40656E-07	5.57692E-07	3.29380E-06	3.10140E-05	4.03173E-04	3.15973E-03	1.84604E-02	5.97049E-02	1.43030E-01	1.54085E-01	2.56868E-02
Bi 210m	4.02012E-15	4.35293E-15	5.07756E-15	8.33244E-15	2.58192E-14	2.68249E-13	5.34355E-12	1.91419E-10	5.07010E-09	1.00149E-07	1.09228E-06	8.85378E-06	3.97543E-05	7.02056E-05
Po 210	1.34194E-07	1.44063E-07	1.61929E-07	2.33592E-07	5.28521E-07	2.57472E-06	1.91527E-05	1.91645E-04	1.54537E-03	6.84911E-03	2.04376E-02	5.56032E-02	2.60982E-02	3.64231E-02
Rn 222	4.12426E-07	4.31504E-07	4.71192E-07	6.26717E-07	1.22393E-06	5.43247E-06	4.02290E-05	4.42063E-04	3.25101E-03	1.87364E-02	6.03908E-02	1.44554E-01	1.55694E-01	2.59540E-02
Ra 223	3.27017E-08	3.37530E-08	3.58603E-08	4.35614E-08	6.70191E-08	1.56603E-07	4.22749E-07	1.37606E-06	4.30701E-06	1.61858E-05	6.08332E-05	1.99847E-04	3.30518E-04	3.45399E-04
Ra 224	4.10541E-03	4.06591E-03	3.98806E-03	3.72711E-03	3.07186E-03	1.56136E-03	2.25837E-04	2.61808E-07	1.84209E-09	2.83599E-09	5.95094E-09	1.82607E-08	5.39402E-08	1.78466E-07
Ra 225	4.75482E-09	4.94579E-09	5.33521E-09	6.84494E-09	1.21994E-08	4.32086E-08	2.39447E-07	2.23700E-06	1.90555E-05	1.76338E-04	9.73636E-04	3.74780E-03	8.01475E-03	9.11236E-03
Ra 226	4.12710E-07	4.31796E-07	4.71499E-07	6.27081E-07	1.22447E-06	5.43378E-06	4.02330E-05	4.42076E-04	3.25104E-03	1.87366E-02	6.03919E-02	1.44567E-01	1.55766E-01	2.61935E-02
Ra 228	4.91329E-12	5.03099E-12	5.26652E-12	6.09177E-12	8.45316E-12	1.67437E-11	4.06124E-11	1.26173E-10	3.86289E-10	1.42879E-09	4.87738E-09	1.75487E-08	5.36793E-08	1.78462E-07
Ac 225	4.74729E-09	4.93824E-09	5.32751E-09	6.83588E-09	1.21873E-08	4.31024E-08	2.37700E-07	2.19335E-06	1.88381E-05	1.76199E-04	9.73634E-04	3.74780E-03	8.01474E-03	9.11236E-03
Ac 227	5.28170E-05	3.58692E-08	3.59983E-08	4.36848E-08	6.71584E-08	1.56919E-07	4.25112E-07	1.40952E-06	4.58361E-06	1.91967E-05	7.72151E-05	2.53506E-04	3.43840E-04	3.45443E-04
Th 227	2.87561E-08	2.96797E-08	3.15488E-08	3.82968E-08	5.89082E-08	1.37741E-07	3.73300E-07	1.23793E-06	4.02581E-06	1.68609E-05	6.78200E-05	2.22662E-04	3.02005E-04	3.03413E-04

TABLE F-1. (Continued.)

Time-->	0.0 Yr	1.0 Yrs	3.0 Yrs	10.0 Yrs	30.0 Yrs	100.0 Yrs	300.0 Yrs	1,000.0 Yrs	3,000.0 Yrs	10,000.0 Yrs	30,000.0 Yrs	100,000.0 Yrs	300,000.0 Yrs	1,000,000.0 Yrs
Th 228	4.10483E-03	4.06534E-03	3.98750E-03	3.72659E-03	3.07143E-03	1.56114E-03	2.25805E-04	2.61573E-07	1.95328E-09	2.93095E-09	6.20884E-09	1.84216E-08	5.39405E-08	1.78466E-07
Th 229	4.76598E-09	4.95697E-09	5.34662E-09	6.85835E-09	1.22173E-08	4.32437E-08	2.39530E-07	2.23726E-06	1.90562E-05	1.76340E-04	9.73638E-04	3.74780E-03	8.01475E-03	9.11236E-03
Th 230	4.38755E-05	4.50687E-05	4.74873E-05	5.62809E-05	8.40179E-05	2.04932E-04	6.53515E-04	2.41760E-03	7.42560E-03	2.40658E-02	6.46498E-02	1.46159E-01	1.55198E-01	2.60252E-02
Th 231	5.49971E-05	5.50043E-05	5.50187E-05	5.50691E-05	5.52129E-05	5.57157E-05	5.71468E-05	6.20910E-05	7.56802E-05	1.17525E-04	1.99550E-04	2.90805E-04	3.04722E-04	3.04556E-04
Th 232	2.94324E-12	3.00211E-12	3.11984E-12	3.53189E-12	4.70919E-12	8.82972E-12	2.06026E-11	6.18072E-11	1.79530E-10	5.91505E-10	1.76810E-09	5.88070E-09	1.75841E-08	5.80036E-08
Th 234	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00961E-04	3.00967E-04	3.00985E-04	3.01041E-04	3.01166E-04
Pa 231	5.79563E-08	5.91187E-08	6.14437E-08	6.95864E-08	9.28851E-08	1.74835E-07	4.12395E-07	1.28304E-06	4.08875E-06	1.69921E-05	6.81662E-05	2.23556E-04	3.03158E-04	3.04570E-04
Pa 233	9.38726E-03	9.39081E-03	9.39794E-03	9.42317E-03	9.49633E-03	9.74328E-03	1.03180E-02	1.13419E-02	1.18092E-02	1.18025E-02	1.17262E-02	1.14634E-02	1.07443E-02	8.56462E-03
U 232	3.99531E-03	3.95688E-03	3.88111E-03	3.62715E-03	2.98947E-03	1.51949E-03	2.19780E-04	2.54514E-07	1.56734E-09	1.50258E-09	1.33194E-09	8.73461E-10	2.61637E-10	3.84860E-12
U 233	2.02711E-06	2.06799E-06	2.14979E-06	2.43657E-06	3.26019E-06	6.19165E-06	1.49317E-05	4.81353E-05	1.49046E-04	4.99256E-04	1.43880E-03	4.10536E-03	8.14232E-03	9.08846E-03
U 234	1.37144E-01	1.38390E-01	1.40853E-01	1.49173E-01	1.70557E-01	2.23611E-01	2.80558E-01	2.94734E-01	2.93130E-01	2.87384E-01	2.71582E-01	2.22824E-01	1.26680E-01	1.79458E-02
U 235	5.46370E-03	5.46370E-03	5.46370E-03	5.46370E-03	5.46370E-03	5.46370E-03	5.46370E-03	5.46370E-03	5.46369E-03	5.46365E-03	5.46355E-03	5.46317E-03	5.46209E-03	5.45831E-03
U 236	1.19494E-03	1.19507E-03	1.19535E-03	1.19630E-03	1.19901E-03	1.20846E-03	1.23507E-03	1.32389E-03	1.54423E-03	2.03317E-03	2.42393E-03	2.47248E-03	2.45792E-03	2.40751E-03
U 238	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00959E-04	3.00958E-04	3.00957E-04	3.00954E-04	3.00944E-04	3.00912E-04
Np 236	1.79202E-08	1.79201E-08	1.79199E-08	1.79191E-08	1.79170E-08	1.79094E-08	1.78878E-08	1.78125E-08	1.75991E-08	1.68720E-08	1.49559E-08	9.80780E-09	2.93784E-09	4.32146E-11
Np 237	9.38728E-03	9.39083E-03	9.39796E-03	9.42320E-03	9.49635E-03	9.74329E-03	1.03180E-02	1.13419E-02	1.18092E-02	1.18025E-02	1.17262E-02	1.14634E-02	1.07443E-02	8.56462E-03
Pu 236	4.99665E-08	3.95265E-08	2.49199E-08	5.84781E-09	1.62753E-09	1.59398E-09	1.59206E-09	1.58535E-09	1.56636E-09	1.50164E-09	1.33111E-09	8.72916E-10	2.61474E-10	3.84620E-12
Pu 238	4.41611E-02	4.38136E-02	4.31269E-02	4.08070E-02	3.48436E-02	2.00441E-02	4.12944E-01	1.64053E-01	4.64706E-08	3.26814E-22	8.02210E-62	0.0	0.0	0.0
Pu 239	7.30713E-00	7.30692E-00	7.30650E-00	7.30502E-00	7.30082E-00	7.28611E-00	7.24426E-00	7.09966E-00	6.70222E-00	5.47841E-00	3.07942E-00	4.10036E-01	1.29113E-03	2.76201E-12
Pu 240	4.59196E-00	4.59148E-00	4.59050E-00	4.58711E-00	4.57741E-00	4.54363E-00	4.44847E-00	4.13085E-00	3.34788E-00	1.59370E-00	1.91965E-01	1.64325E-04	7.48523E-14	5.04335E-46
Pu 241	3.54969E-01	3.38620E-01	3.08145E-01	2.21516E-01	8.62650E-01	3.17936E-01	2.55056E-01	1.17941E-19	1.30210E-60	0.0	0.0	0.0	0.0	0.0
Pu 242	6.16502E-03	6.16502E-03	6.16501E-03	6.16495E-03	6.16479E-03	6.16418E-03	6.16225E-03	6.15471E-03	6.13271E-03	6.05629E-03	5.84318E-03	5.15464E-03	3.60266E-03	1.02828E-03
Am 241	3.59835E-01	3.59814E-01	3.59696E-01	3.58609E-01	3.51803E-01	3.17039E-01	2.30107E-01	7.48601E-00	3.02609E-01	4.01873E-06	4.68187E-20	7.98934E-69	0.0	0.0

TABLE F-1. (Continued.)

Time-->	0.0 Yr	1.0 Yr	3.0 Yr	10.0 Yr	30.0 Yr	100.0 Yr	300.0 Yr	1,000.0 Yr	3,000.0 Yr	10,000.0 Yr	30,000.0 Yr	100,000.0 Yr	300,000.0 Yr	1,000,000 Yr
Am 242	1.06312E-02	1.05829E-02	1.04868E-02	1.01573E-02	9.27189E-03	6.73803E-03	2.70665E-03	1.11194E-04	1.21640E-08	1.66551E-22	4.08823E-62	0.0	0.0	0.0
Am 242m	5.08583E-05	5.06269E-05	5.01673E-05	4.85911E-05	4.43554E-05	3.22338E-05	1.29483E-05	5.31935E-07	5.81907E-11	7.96757E-25	1.95575E-64	0.0	0.0	0.0
Am 243	5.92283E-03	5.92227E-03	5.92116E-03	5.91726E-03	5.90614E-03	5.86738E-03	5.75804E-03	5.39117E-03	4.46674E-03	2.31243E-03	3.52490E-04	4.87439E-07	3.30132E-15	8.44149E-44
Cm 242	8.81790E-03	8.77778E-03	8.69809E-03	8.42481E-03	7.69042E-03	5.58875E-03	2.24499E-03	9.22278E-05	1.00892E-08	1.38143E-22	3.39092E-62	0.0	0.0	0.0
Cm 243	1.04614E-03	1.02101E-03	9.72530E-04	8.20284E-04	5.04325E-04	9.19017E-05	7.09229E-07	2.86355E-14	2.14559E-35	0.0	0.0	0.0	0.0	0.0
Cm 244	1.21620E-02	1.17053E-02	1.08427E-02	8.79425E-03	3.85766E-03	2.64691E-04	1.25374E-07	2.89966E-19	1.64837E-52	0.0	0.0	0.0	0.0	0.0
Cm 245	6.83139E-06	6.83084E-06	6.82972E-06	6.82581E-06	6.81465E-06	6.77575E-06	6.66581E-06	6.29490E-06	5.34500E-06	3.01512E-06	5.87348E-07	1.91628E-09	1.50782E-16	2.06062E-41
Cm 246	5.42741E-07	5.42662E-07	5.42503E-07	5.41946E-07	5.40360E-07	5.34845E-07	5.19397E-07	4.68758E-07	3.49671E-07	1.25358E-07	6.68758E-09	2.34519E-13	4.37850E-26	1.23144E-70
Cm 247	6.74318E-13	6.74318E-13	6.74318E-13	6.74318E-13	6.74317E-13	6.74315E-13	6.74310E-13	6.74288E-13	6.74229E-13	6.74019E-13	6.73420E-13	6.71329E-13	6.65389E-13	6.45012E-13
Cm 248	7.04085E-13	7.04083E-13	7.04080E-13	7.04070E-13	7.04041E-13	7.03941E-13	7.03654E-13	7.02649E-13	6.99788E-13	6.89863E-13	6.62277E-13	5.74125E-13	3.81742E-13	9.15045E-14
All	2.46935E 04	2.41223E 04	2.30199E 04	1.95491E 04	1.22898E 04	2.54841E 03	1.15861E 02	2.59591E 01	1.53491E 01	1.21369E 01	8.50545E 00	5.76964E 00	4.22051E 00	1.42961E 00

REFERENCES

1. W. Eitel, Silicate Science (Academic Press, New York, NY, 1964-1976) 8 vols.
2. R. K. Iler, The Chemistry of Silica (John Wiley & Sons, New York, NY, 1979).
3. J. D. Rimstidt and H. L. Barnes, "The Kinetics of Silica-Water Reactions," Geochimica et Cosmochimica Acta **44**, 1683-1699 (1980).
4. R. H. Busey and R. E. Mesmer, "Ionization Equilibria of Silicic Acid and Polysilicate Formation in Aqueous Sodium Chloride Solutions to 300°C," Inorganic Chemistry **16**, 2444-2450 (1977).
5. K. Scheffler, V. Riege, K. Louwrier, H. J. Matzke, I. Ray, and H. Thiele, Long Term Leaching of Silicate Systems: Testing Procedure, Actinides Behaviour and Mechanism, Gesellschaft für Kernforschung, m.b.h., Karlsruhe, West Germany, KFK 2456 (1977).
6. A. D. Bishop and J. L. Bear, "The Thermodynamics and Kinetics of the Polymerization of Silicic Acid in Dilute Aqueous Solution," Thermochim. Acta **3**, 399-409 (1972).
7. B. H. W. S. de Jong and G. E. Brown, Jr., "Polymerization of Silicate and Aluminate Tetrahedra in Glasses, Melts and Aqueous Solutions - II. The Network Modifying Effects of Mg^{2+} , K^+ , Na^+ , Li^+ , H^+ , OH^- , F^- , Cl^- , H_2O , CO_2 and H_3O^+ on Silicate Polymers," Geochimica et Cosmochimica Acta **44**, 1627-1642 (1980).
8. E. J. Reardon, "Complexing of Silica by Iron (III) in Natural Waters," Chemical Geology **25**, 339-345 (1979).
9. C. Frondel, "Crystalline Silica Hydrates from Leached Silicates," American Mineralogist **64**, 799-804 (1979).
10. T. H. Gould to F. R. Kovar, Information for Waste Form Risk Assessments I: SRP Borosilicate Glass Waste Form, Savannah River Laboratory Memorandum (23 May 1980).
11. G. A. Parks, "The Isoelectric-Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," Chem. Rev. **65**, 177-198 (1965).
12. D. G. Coles and F. Bazan, Continuous-flow Leaching Studies of Crushed and Cored SYNROC, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-84679 (1980).

13. D. G. Coles, A Continuous-flow Leach Testing Method for Various Nuclear Waste Forms, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-85006 (1980).
14. Mineral Waste Form Development Project Status Reports, Lawrence Livermore National Laboratory, Livermore, CA, (1980).
15. The Disposal of Radioactive Waste on Land, National Academy of Sciences, National Research Council, Publication 519 (1957).
16. W. J. O'Connell, Mock Site A Assessment, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-52718 (1980).
17. M. S. Giuffre et al., Bedded Salt Repository Analysis: Final Report - TR-1797-8, prepared by The Analytical Sciences Corporation for Lawrence Livermore National Laboratory, Livermore, CA, UCRL-12536 (1980).
18. F. R. Kovar and T. L. Steinborn, The Bedded Salt Report, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-52737 (1980).
19. T. G. Naymik and L. D. Thorson, Numerical Simulation of Transport in a Regional Groundwater Flow System, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-52556 (1978).
20. G. D. Pollak, Adaptation and Validation Results for Effective Transverse Dispersion Model and Numerical Requirements of Finite Element Transport Code, Lawrence Livermore National Laboratory, Livermore, CA, WM-80-459-D (1980).
21. L. L. Edwards, MACROL: A Code to Test a Methodology for Analyzing Nuclear-Waste Management Systems, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-52736 (December 14, 1979).
22. T. H. Gould, Savannah River Laboratory, revising SRL Memorandum (23 May 1980),¹⁰ private communication, June 1980.
23. J. J. Duffy and G.P. Bogar, User's Manual for Biosphere and Dose Simulation Program (BIODOSE), TR-1797-3, prepared by The Analytic Sciences Corporation for Lawrence Livermore National Laboratory, Livermore, CA, UCRL-15188 (1980).
24. L. L. Edwards and T. F. Harvey, The Point Source Repository Assumption and Predicted Individual Doses, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-85349 (January 1981).

25. M. O. Cloninger, C. R. Cole, and J. F. Washburn, Systems Study on Engineered Barriers, Pacific Northwest Laboratory, Richland, WA, PNL-3356 (1980).
26. Chemical Engineers Handbook, R. H. Perry and C. H. Chilton, Eds. (McGraw-Hill Book Company, New York, NY, 1973) 5th ed.
27. W. F. Linke, Solubilities of Inorganic and Metal-Organic Compounds, (American Chemical Society, Washington, D.C., 1965) 4th ed.
28. R. K. Iler, The Chemistry of Silica (John Wiley & Sons, New York, NY, 1979).
29. D. E. White, "Magmatic, Connate, and Metamorphic Waters," Geol. Soc. America Bull. 68, 1658-1662 (1957).
30. E. Ewest, "Calculations of Radioactivity Release Due to Leaching of Vitrified High Level Waste," G. J. McCarthy, Ed., Scientific Basis for Nuclear Waste Management - Proc. Symposium on Science Underlying Radioactive Waste Management, Boston, Massachusetts, 1978 (Plenum Press, New York, NY, 1979).
31. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes (McGraw-Hill, New York, NY, 1941).
32. M. B. Abramson and C. V. King, "The Rate of Dissolution of Iron in Acids," J. Am. Chem. Soc. 61, 2290-2295 (1939).
33. K. Sangwal, T. C. Patel, and M. D. Kotak, "On the Kinetics and Mechanism of Dissolution of MgO Crystals," J. Materials Sci. 14, 1869-1876 (1979).
34. A. F. M. Barton and S. R. McConnell, "Rotating Disc Dissolution Rates of Ionic Solids Part 3 - Natural and Synthetic Ilmenite," J. Chem. Soc. (London), Faraday Transactions I, Physical Chemistry 75(4), 971-983 (1979).
35. M. J. Plodinec and J. R. Wiley, Evaluation of Glass as a Matrix for Solidifying Savannah River Plant Waste: Properties of Glasses Containing Li₂O, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC, DP-1498 (1979).
36. V. P. Vasilev, P. M. Vorobev, and I. L. Khodovskii, "Standard Free Energies of Formation of Titanium Hydroxo-complexes and of the Ti +4 Ion in Aqueous Solution," Russ. J. Inorg. Chem. 19(10), 1481 (1974).
37. L. G. Sillen and A. E. Martell, Stability Constants, The Chemical Society, London, U.K., Special Publication No. 17 (1964).

38. M. Kh. Karapet'Yants and M. L. Karapet'Yants, Thermodynamic Constants of Inorganic and Organic Compounds (Ann Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, 1970).
39. R. M. Garrels and C. Christ, Solutions, Minerals, and Equilibria (Freeman, Cooper and Company, San Francisco, CA, 1965).
40. C. F. Baes and R. E. Mesmer, The Hydrolysis of Cations (John Wiley and Sons, New York, NY, 1976).
41. R. M. Smith and A. E. Martell, Critical Stability Constants: Inorganic Complexes, (Plenum Press, New York, NY, 1976) vol. 4.
42. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. H. Schumm, and K. L. Churney, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Technical Note 270-5 (1971).
43. R. A. Robie and D. R. Waldbaum, Thermodynamic Properties of Minerals and Related Substances at 298.15 K (15.0°C) and One Atmosphere, (1.013 Bars) Pressure and at Higher Temperatures, U.S. Geological Survey Bulletin 1259 (1968).
44. K. K. Kelley and A. D. Mah, Metallurgical Thermochemistry of Titanium, U.S. Bureau of Mines Report of Investigations 5490 (1959).
45. K. O. Bennington and R. R. Brown, Thermodynamic Properties of Three Sodium Titanates, U.S. Bureau of Mines Report of Investigations 7778 (1973).
46. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodarovsky, Handbook of Thermodynamic Data, I. Barnes and V. Speltz, Eds., G.J. Soleimani, Transl., U.S. Geological Survey, USGS-WRD-74-001 (1974).
47. A. D. Mah and L. B. Pankratz, Contributions to the Data on Theoretical Metallurgy XVI. Thermodynamic Properties of Nickel and Its Inorganic Compounds, U. S. Bureau of Mines Bulletin 668 (1976).
48. I. Barin, O. Knacke, and O. Kubaschewski, Thermochemical Properties of Inorganic Substances (Springer-Verlag, New York, NY, 1973, Supplement, 1977).
49. A. S. Berezhnoi, "Thermodynamic Properties of Some Calcium and Zirconium Titanates and of Calcium Zirconate," Dopovidi Akad., Nauk, Ukr., RSR, pp. 387-390 (1962).
50. V. B. Parker, D. D. Wagman, and W. H. Evans, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Tech. Note 270-6 (1971).

51. O. Kubaschewski and C. B. Alcock, Metallurgical Thermochemistry, (Pergamon Press, New York, NY, 1979) 5th ed.
52. C. E. Wicks and F. E. Block, Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides, U.S. Bureau of Mines Bulletin 605 (1963).
53. W. J. Cooper and D. A. Scarpiello, Thermodynamic Properties of the Metal Bromides, Iodides, Sulfides, Sulfates, Chromates, Metaphosphates, Ortho-Phosphates, Molybdates, Tungstates, Borates, and Hydroxides, Sandia Corporation, Albuquerque, NM, SC-RR-64-67 (1964).
54. A. Navrotsky, "Thermodynamics of Formation of Some Compounds with the Pseudobrookite Structure of the FeTi_2O_5 - Ti_3O_5 Solid Solution Series," American Mineralogist **60**, 249-256 (1975).
55. A. Navrotsky and O. J. Kleppa, "The Thermodynamics of Cation Distributions in Simple Spinel," J. Inorg. Nucl. Chem. **29**, 2701-2714 (1967).
56. A. Navrotsky and O. J. Kleppa, "Thermodynamics of Formation of Simple Spinel," J. Inorg. Nucl. Chem. **30**, 479-498 (1968).
57. O. Kubaschewski, "The Thermodynamic Properties of Double Oxides, (A Review)," High Temperatures - High Pressures **4**, 1-12 (1972).
58. L. A. Reznitskii and A. S. Guzei, "Thermodynamic Properties of Alkaline Earth Titanates, Zirconates and Hafnates," Russian Chemical Reviews **47**(2), 99-119 (1978).
59. H. C. Claiborne, L. D. Rickersten, and R. F. Graham, Expected Environments in High-Level Nuclear Waste and Spent Fuel Repositories in Salt, Oak Ridge National Laboratory, Oak Ridge, TN, ORNL-TM-7201 (1980).
60. R. D. Schuiling and B. W. Vink, "Stability Relations of Some Titanium-Minerals (Sphene, Perovskite, Rutile, Anatase)," Geochimica et Cosmochimica Acta **31**, 2399-2411 (1967).
61. V. Stumm and J. J. Morgan, Aquatic Chemistry (John Wiley & Sons, New York, NY, 1970).
62. A. F. M. Barton and S. R. McConnell, "Rotating Disc Dissolution Rates of Ionic Solids. Part 3 - Natural and Synthetic Ilmenite," J. Chem. Soc. (London), Faraday Transactions, I. Physical Chemistry **75**(4), 971-983 (1979).

63. G. Teufer and A. K. Temple, "Pseudorutile - A New Mineral Intermediate Between Ilmenite and Rutile in the Alteration of Ilmenite," Nature 211, 179-181 (1966).
64. G. Bayer, "Thermal Expansion Characteristics and Stability of Pseudobrookite-type Compounds, Me_3O_5 ," J. Less-Common Metals 24, 129-138 (1971).
65. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan.
66. H. J. T. Ellingham, J. Soc. Chem. Ind. 63, 125 (1944).
67. C. W. Danat and H. J. T. Ellingham, Discussions Faraday Society 4, 126 (1948).
68. A. E. Ringwood, Safe Disposal of High Level Nuclear Reactor Waste (Australian National University Press, Canberra, Australia 1978).
69. Yu A. Pyatenko, "Behavior of Metamict Minerals on Heating and the General Problem of Metamictization," Geochemistry International 9, 1077-1083 (1970).
70. Kh. Sh. Iskhakov and E. K. Keler, "Solid-Phase Reactions in the $\text{SrO-TiO}_2\text{-ZrO}_2$ System," Russ. J. Inorg. Chem. 7(8), 1005-1010 (1962).
71. Kh. Sh. Iskhakov and E. K. Keler, "Conditions of Formation and Electrical Properties of $\text{SrTiO}_3\text{-SrZrO}_3$ Solid Solutions," Russ. J. Inorg. Chem. 7(8), 1010-1013 (1962).
72. E. M. Levin, C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists (American Ceramic Society, Columbus, OH, 1964).
73. E. M. Levin, C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists, 1969 Supplement (American Ceramic Society, Columbus, OH, 1969).
74. E. M. Levin and H. F. McMurdie, Phase Diagrams for Ceramists, 1975 Supplement (American Ceramic Society, Columbus, OH, 1975).