MCC

Materials Characterization Center

**Workshop on the Leaching
Mechanisms of Nuclear Waste
Forms, October 27-28, 1981**

Summary Report

April 1982

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WORKSHOP ON THE LEACHING MECHANISMS
OF NUCLEAR WASTE FORMS, OCTOBER 27-28, 1981

SUMMARY REPORT

J. E. Mendel, Compiler

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

The leaching of nuclear waste forms is a complex phenomenon that has been studied extensively. There is a basic understanding of the various reactions involved. What remains to be done is to quantify the relationships between the different reactions so that mathematical models can be used to predict the leaching behavior of waste forms for thousands of years, several orders of magnitude beyond experimentally verifiable times. A three-year leaching mechanisms program has been set up by the high-level waste lead office to integrate the efforts of several laboratories and outside consultants to develop the requisite data base and demonstrate its application in predictive mathematical models.

The output of this program, which is being coordinated by the Materials Characterization Center (MCC), is expected to be:

- Efficient utilization of Department of Energy (DOE) waste management scientific resources through coordination by workshops and special studies that also bring in outside experts when needed.
- Documented, back-up materials data to demonstrate that DOE's predictive mathematical models for waste-form leaching are soundly based on mechanistic principles.
- A peer-reviewed, coherent, waste materials data base that relates directly to predictive mathematical models for waste form leaching and can be used to demonstrate the relationship of this leaching behavior to Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) criteria.

This document is a report of a workshop held in Seattle, October 27-28, 1981, to acquaint the participants with each other's activities and goals. It is the first in a series of leaching mechanisms workshops, planned to be held at about six-month intervals. The written proceedings of these workshops will serve as progress reports for the leaching mechanisms program.

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INTRODUCTION

The laboratories and lead investigators participating in the leaching mechanisms program are:

University of Florida (L. L. Hench)
Catholic University of America (P. B. Macedo)
Pennsylvania State University (W. B. White)
Rockwell Science Center (A. B. Harker and D. R. Clarke)
Lawrence Livermore National Laboratory (D. D. Jackson)
Pacific Northwest Laboratory (G. L. McVay)

The program is funded by DOE's high-level waste (HLW) lead office and is being coordinated by J. E. Mendel of the Materials Characterization Center. A workshop was held in Seattle, October 27-28, 1981 to initiate the program. The purpose of this informal workshop was to initiate the program and achieve the following goals:

1. Acquaint laboratory investigators (data generators) with the needs of the mathematical modelers (data users). Session I was devoted to a tutorial by D. D. Jackson, mathematical modeler for the leaching mechanisms program, on PROTOCOL, a general case waste form leaching model.
2. Define important testing parameters, based on the present state of knowledge. To achieve this, a number of important testing parameters were identified for special discussion in Session II.
3. Develop an understanding of the interrelationships between the activities of leaching mechanisms program participants, and begin definition of the specific role of each participant in the overall program.
4. Establish good communication between the leaching mechanisms program and related programs, particularly the waste form leaching program at the Savannah River Laboratory (SRL) and the various Nuclear Waste Terminal Storage (NWTs) waste package programs.

The agenda for the workshop is attached as Appendix A; a list of attendees is in Appendix B.

Because this workshop was devoted to preliminary planning for the leaching mechanisms program, the presentations and dicussions were purposely kept informal. This report represents a synopsis of the proceedings that has been prepared by the leaching mechanisms coordinator and reviewed by the workshop participants.

DESCRIPTION OF THE LEACHING MECHANISMS PROGRAM

To begin the workshop, J. E. Mendel and J. A. Stone (HLW lead office technical liaison) gave an overview of the program plan for the coordinated leaching mechanisms program. This plan is attached as Appendix C.

The program is projected to last three years. The major goal is to have at that time a defensible mathematical model(s) that can be used to predict the long-term leaching behavior of waste forms. This is related to the multi-barrier concept and the NRC's draft 10 CFR 60 fractional release requirements from a geologic repository. The model will define the fractional release behavior of the waste form as one barrier in the multibarrier system. The validation of the model(s) will be confirmed to the degree possible by laboratory testing that emphasizes solution chemistry, surface characterization and solid-state materials science.

SESSION I: MODELING

The description of PROTOCOL that was distributed to the workshop participants by Don Jackson, Lawrence Livermore National Laboratory, as background information for the three-hour session on modeling is reproduced in full below. Figure 1 is a chart of data flow in the general model.

The model is still under active development, but an example of its application was presented using Rimstidt and Barnes (1980) data on quartz dissolution as "leach rate data." These data are very suitable for verifying the PROTOCOL code, since constants are given for forward and reverse reaction rates for specific reactions. Jackson understands, however, that most waste form leach data consists only of composite rates for perhaps several competing reactions, and is prepared to use such data in PROTOCOL.

A thermodynamic data base is an integral part of PROTOCOL that will probably become increasingly important. There was a question as to whether it is even pertinent to go through the "early time rigamarole," i.e., reaction kinetics, with the model. That question appears very hard to answer until the water flow parameters expected in a repository are defined more definitely than it is apparently possible to do now. Jackson is working to expand the PROTOCOL thermodynamic data base so that the effects of temperature can be included. He also acknowledged the importance of having hydrous phases in the data base. This is a "perpetual problem" for geochemical modeling that's exacerbated for waste form leach modeling because of the many potential constituents in waste forms.

PROTOCOL: A General-Case Model for Nuclear Waste Form Leaching - Don Jackson

Context. The safe geologic disposal of nuclear wastes requires their immobilization in high-durability waste forms. One of the most critical aspects of durability is resistance to the potential leaching action of ground water. Measurements of leachabilities of advanced waste forms now under development show qualitatively that this requirement will be met. However, the complexity of leaching processes has made it difficult to translate experimental leach rates into waste element releases, and to extrapolate them to long reaction times in a repository environment.

FIGURE 1. Data Flow in the PROTOCOL General-Case Model for Nuclear Waste Form Leaching

Objectives and Approach. A general purpose model is to be constructed to serve as a framework and focus for research in the leaching mechanisms program. This is to be a device that can use experimental data to evaluate resistance to leaching, and can in the process serve as a guide to the type and formulation of information that is most readily adaptable to this purpose.

Experimental dissolution data are taken both to clarify the phenomenology of leaching and to generate rate functions. Models are then often constructed to summarize and to rationalize specific sets of observations.

It is clear that at the present state of the art, no general case model can function at the level of insight where mass transfer can be predicted without specific experimental rate data. There is, however, another level of modeling based on the premise that all leaching takes place in a system. To use data realistically, it is necessary to achieve a successful transfer from a "discovery" system to an "application" system, where these may be related in a complex way. It is these relationships, then, that must be defined in a general case model. It is further evident that it must be entirely numerical in nature, that is must be able to accommodate a variety of leaching functions, and that it must be flexible enough to function usefully with imperfect or missing data.

Consideration of the number of parameters that are likely to be significant, the amount of data that must be transferred, and the number of calculations that must be carried out, suggests strongly that the actual form of such a model must be a computer algorithm, with the required information stored in data files. In the following sections, I (Don Jackson) describe a prototype computer model that I have constructed, which attempts to meet these basic requirements.

Structure. PROTOCOL has three general attributes. It has a kinetic capability (coding + data base), an equilibrium capability (coding + data base), and a managerial function.

Simulations of reactions are carried out in a series of time increments, or steps of variable length. A sequence of both kinetic and equilibrium calculations is carried out in each time increment.

The kinetic capability makes use of specific rate data to compute mass flux from the solid. The information in the data base is organized on four levels. These pertain to the repository system, to the waste form, to the chemical phases in that form, and to the individual component elements in each phase. Its format has been designed, and a short file has been set up using the existing rate data for the phases of silica.

The equilibrium capability is used primarily to monitor reactions in the aqueous phase, where reactions are sufficiently fast that local equilibrium is considered to be maintained. It redistributes dissolving components, sets solubility constraints on dissolution and identifies precipitated or converted solid phases. This equilibrium function has been provided by attachment of a geochemical code (MINEQL). Its data base, compiled from numerous literature sources, contains the thermochemical stabilities of component species of various types, both solid and aqueous.

The managerial function is to access data as they are needed, to call for calculations that are required by the stored rate functions, to interpret the results in terms of mass transfer of component species, and to write a tabular summary of the status of the system with time.

Information Requirements. The model in its present form requires, in outline form, the following information:

- SYSTEM:
 - A. Temperature
 - B. Water Parameters
 - 1. Volume flow rate
 - 2. Resident volume or film thickness
 - 3. Density
 - 4. Chemical Composition
- WASTE FORM:
 - A. Mass and Physical Dimensions
 - B. Number of Component Phases
- PHASE:
 - A. Mass and Density
 - B. Spatial Distribution
 - C. Number of Components

- COMPONENT:
- A. Mass and Density
 - B. Spatial Distribution
 - C. Molecular Weight
 - D. Leach Rate Data
 - 1. Functional form
 - 2. List of constants for forward and reverse or composite rates

Logical Operations. The parameters employed and the flow of logic are perhaps most readily conveyed by examination of the program coding: an explanatory note has been provided for most steps. The operations can be summarized in very general terms as follows.

On initialization, PROTOCOL asks the user for a waste form selection, reads the appropriate data from its kinetic file, computes waste form physical parameters, the resident water volume and flow rate, and finally enters a time loop, which is repeated to the end of the problem.

In each element of the time loop a current duration is computed, a water phase equilibration carried out, and a phase loop entered. In each element of the phase loop are performed calculations for its individual components: rate functions, mass fluxes and geometric changes. Finally, compositional changes due to water flow and mixing are determined, and entries are made in the output tables.

SESSION II: TESTING PARAMETERS

In his introductory remarks at the beginning of the workshop, John Stone listed the major factors affecting leachability. These are shown in Table 1.

TABLE 1. Factors Affecting Leachability

System Factors	Time
	Temperature
	Pressure
	Radiation ^(a)
	SA/V ^(b)
Leachant Factors	Composition ^(a)
	pH ^(a)
	Eh ^(a)
	Flow
Solid Factors	Composition
	Surface ^(a)
	Porosity

(a) Factors singled out for special discussion at this workshop.

(b) Ratio of the surface area of the test specimen to volume of leachant (units = length⁻¹).

All of these factors interact and, except for pressure which has an insignificant effect up to at least 1500 psi, play an important role in leaching mechanisms. Because of time limitations only certain of the factors were discussed at this workshop.

Radiation Effects, Discussion Leader: G. L. McVay

Although relatively small in the tests done to date, the effect of radiation is almost always to increase the leach rate of waste glasses. The effect

is greater at lower temperatures as shown in Table 2. Much of the effect is due to radiation lowering the pH of the leachant. Much of the pH lowering has been traced to dissolved nitrogen in the leachant, which is converted to nitric acid in a radiation field. The quantity of dissolved nitrogen in the ground water is expected to be very low but confirmatory analyses need to be made.

There was a consensus at the workshop that although radiolysis effects on leaching are known to be small in the short term more study is needed to be able to predict long-term behavior. These studies should include:

- Effects of Alpha and Combined Alpha-Gamma Radiolysis. Most of the careful studies of radiolysis effects on leaching have utilized ^{60}Co gamma radiation, yet in the long-term repository setting alpha radiolysis will predominate. As shown in Table 3 there are notable differences in the spectrum of radiolytic species when water is subjected to alpha rather than gamma irradiation.
- Effect on Eh. Alpha radiation, in particular, may create oxidizing conditions at the leaching surface. What effect does this have on the leaching of elements that can be solubilized in more than one valence state, such as uranium?

TABLE 2. Gamma-Irradiation Effect on Si Leach Rate from PNL 76-68 Glass^(a)

<u>Temp. °C</u>	<u>Si Release Rate (ppm/hr)</u>		
	<u>Irradiated</u> <u>1.75×10^6 R/hr</u>	<u>Unirradiated</u>	<u>Percent Increase</u>
50	2.2×10^{-2}	8.2×10^{-3}	168
70	4.0×10^{-2}	2.5×10^{-2}	60
90	6.6×10^{-2}	6.6×10^{-2}	0

(a) D.I. Water
SA/V = 20 m^{-1}

TABLE 3. Primary Radiolytic Species G Values(a) for Gamma and 5 MeV Alpha Radiation (Anbar 1968, Appleby and Schwarz 1969)

Species	H^+	e^-_{aq}	H	OH	HO ₂	H ₂	H ₂ O ₂	H ₂ O
Gamma	2.7	2.7	0.61	2.86	0.03	0.43	0.61	-4.14
5 MeV Alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	-3.3

(a) Number of molecules formed, or destroyed, as a result of the absorption of 100 eV of radiation energy.

- Effect of Radiolysis on Dissolved CO₂ and Organic Constituents of Soil Water. Dr. A. Barkatt of Catholic University presented preliminary findings from the exposure of leachates in a ¹³⁷Cs gamma irradiation facility that indicated appreciable amounts of oxalic acid may form from radiolysis of carbonate. Some repository waters may also contain organic constituents that could form oxalic and other acids upon radiation.

pH Effects, Discussion Leader: G. G. Wicks

Waste glass leaching rates exhibit a broad minimum between pH 5 and 9. This has been demonstrated for SRL defense waste glass (Figure 2) and for many other waste glass compositions. It is noteworthy that the pH of most natural ground waters also lie within the range of 5 to 9.

At the pH extremes of <5 and >9 the glass leaching is apparently controlled by a different mechanism involving more network dissolution and less ion exchange and diffusion, which predominate in the middle pH range. The question arises, why study the pH extremes if the normal waters have pHs within the range that yields minimum waste glass leach rates? The answer is that the constituents leached from the waste form itself probably control the nearfield pH, and leach tests in confined systems such as the MCC-1 Static Leach Test Method show that the pH can reach 10, or even higher, with certain waste glasses. The rationale for studying leaching mechanisms at low pH is

FIGURE 2. pH Dependence of Defense Waste Glass Leach Rate

more nebulous. As discussed earlier, radiolysis may lower the pH somewhat. The pH of aqueous systems also decreases as the temperature is raised, but in this case the increased reaction rates with the waste form due to temperature completely overwhelm the pH effect.

In summary, different leaching mechanisms predominate at different pHs, and it is important to study leaching as a function of pH, particularly between about pH 4 to 11. There is a question as to whether the MCC should define standard pH buffering techniques for use in these leaching studies. To date, individual experimentalists have been devising their own techniques.

Eh Effects, Discussion Leader: M. G. Seitz

The oxidation potential of the leachant, usually expressed in terms of Eh, must be considered as a factor potentially affecting leachability since it has been commonly accepted that the ground waters are more reducing at repository depths than are the leachants normally used in laboratory experiments. Certain radionuclides, such as technetium and uranium are less mobile in the reduced state, thus reducing conditions should inhibit the leaching of these radionuclides. Only limited testing has been done on the effect of Eh because it is a knotty problem to maintain the oxidation potential postulated for repositories (-500 mV) and to measure it experimentally.

Two approaches can be considered for achieving reducing conditions in a leach test.

1. Remove oxygen from the leachant by sparging with inert gas and hydrogen; then equilibrate with rock buffers, containing ferrous sulfide for example.
2. Force the system to be at a given Eh by adding ionic or organic redox buffers, or by use of a potentiostat.

Dr. Seitz described studies of neptunium migration through rocks that he has done using the first approach. In experiments in which the neptunium should have been reduced it migrated at about the same rate as under oxidizing conditions.

More investigations of the effect of Eh on leaching are needed. However, in the meantime it should be noted that the routine leaching being done with leachants in equilibrium with atmospheric oxygen are yielding conservative results. No mechanisms by which reducing conditions can increase leach rates have been identified. It should also be noted that as more testing is done it is being found that reducing conditions at repository depths are not as ubiquitous as once thought, thus the Eh may vary considerably at different candidate repository sites. The basalt site at Hanford is definitely reducing; the tuff site in Nevada may have about the same Eh as surface waters.

Surface Condition, Initial and Final, Discussion Leader: D. E. Clark

The application of various surface analysis techniques to leached surfaces has enabled large advances to be made in the understanding of leaching mechanisms in the past few years. However, Dr. Clark emphasized the importance of coupling surface analysis and solution analysis. Neither can tell the whole mechanistic story alone.

The MCC leach tests specify cutting the leach specimens with a 200-grit diamond saw or core-drill. This is followed by ultrasonic cleaning but there is no polishing of the surfaces before leaching. It is noteworthy that many investigators, while following other aspects of the MCC leach tests, are deviating from the MCC specification in this regard and are polishing their leach specimens, usually to a 600-grit finish. This is absolutely necessary if surface analysis techniques such as infra-red reflectance spectroscopy (IRRS) are to be used, and is probably desirable when any kind of surface analysis is to be done.

Specific Ion Effects, Solubility Limits, Discussion Leaders: D. Rai, B. Grambow, and C. Q. Buckwalter

Experiments have been conducted by D. Rai at PNL for 4 to 5 years to predict the maximum concentration of Np and Pu that can occur in leachates. It has been found that the maximum concentrations are controlled by the solubility of NpO_2 and PuO_2 .

Quinhydrone was used as a redox buffer ($pe + pH = 12$) over a pH range of 3 to 8. In tests lasting more than 4 years the same Np concentration was found where the solution was in contact with Np-doped simulated waste glass or NpO_2 or Np-doped simulated waste glass plus NpO_2 . Similarly, when PuO_2 was added to a test with Pu-doped simulated waste glass the Pu concentration in the solution was not changed. In all of these experiments the solutions are passed through 18 Å filters before analysis. It is interesting that the Np and Pu concentrations in the solutions were considerably below the mpc for drinking water.

These experiments seem to indicate that Np, Pu and perhaps Am (much less data is available) concentrations in the leachate will be controlled thermodynamically at very low concentrations, independent of the waste form. More investigations are required to:

- Develop a good thermodynamic data base that includes all of the potential actinide compounds and solution complexes.
- Determine to what extent colloidal suspensions may abrogate simple solubility control in an actual waste package-repository setting.

Other work at PNL has shown the importance of doing tests with all of the system components present. C. Buckwalter has found, for instance, that if metallic lead is present it will act somewhat like a sacrificial anode. The lead is corroded more rapidly while the leach rate of the waste glass is greatly suppressed. Simple addition of lead ions to the solution does not produce the same inhibiting effects. More work is being done to develop an understanding of the lead effect. When the phenomenon is better understood it may be possible to utilize it in improved waste package designs. But from the standpoint of leaching mechanisms, it clearly demonstrates that leaching cannot be considered as an isolated water-waste form reaction, independent of the surroundings.

SESSION III: PROGRAM PLANNING

Each laboratory participating in the leaching mechanisms program will coordinate its special area of expertise with the other participants of the program so that the overall goals of the program can be achieved most effectively. Brief summaries of the major areas to be covered by each participating laboratory, as discussed at the workshop, are given below. It should be emphasized that these represent a very early view of the leaching mechanisms program. The program is flexible and will be modified as necessary to follow promising technical leads and to accommodate changes in policy. Examples of areas where changes may occur include the following:

- As originally set up, emphasis in the program was evenly divided between glass and crystalline waste forms. It is likely that, at least initially, there will be more overall emphasis on glass.
- Although it was always recognized that waste form leaching is very dependent on the other components of the waste package and on the repository site, it is expected that there will be even more of an effort to make the leaching mechanisms studies repository relevant.

Pennsylvania State University

Area of Special Expertise: Geochemistry, reaction kinetics.

The program at Pennsylvania State University will be divided into three parts.

A. Dissolution Kinetics of Single-Phase Ceramic Components

The initial candidate phases are zirconolite, magnetoplumbite, spinel, and perovskite. The dissolution kinetics of these phases will be investigated individually as follows:

1. Determine chemical reactions when crystals are placed in contact with aqueous solutions. Identify solid reaction products to some extent, and speciation of dissolved species in solution.
2. Calculate, where available thermochemical data permit, the solubility product constants and saturation limits for reactions.

3. Determine reaction kinetics as function of time, temperature and activity of pertinent species in solution. If possible, reactions are to be run to saturation for determination of back-reaction rates.
4. Compile all of the above into empirical rate equations that provide explicit statements of the time dependence of reactions, the power function dependence of (H^+) and other reacting species, an Arrhenius term of temperature, and a surface/volume term. With numerical values for the rate constants, such empirical rate equations should be usable directly in computer models for the waste form dissolution behavior.

B. Surfaces and Interactive Effects

1. Conduct detailed characterization of reacted surfaces on single crystal specimens and the build up of corrosion layers by Auger and ion scattering spectroscopy. Conduct depth profiling of hydrated layers by sputter-induced photon spectroscopy.
2. Use ellipsometry to design an in situ measurement of surface reaction.
3. Prepare mixed-phase ceramics from pure phases and determine reaction kinetics of the mixed-phase material to ascertain interactive effects.
4. Evaluate role of Eh as a system variable: prepare critical evaluation of redox potential as it influences the dissolution rates of ceramics and glasses. Assess the importance of this variable and review of methods for its control and experimental determination.

C. Natural Analogs for Crystalline Waste Forms

1. Carry out a literature review to extract data from mainly the geochemical literature that would have a bearing on the

dissolution rates of ceramic waste forms. Recast these data in a form that will allow evaluation or prediction of the long-term behavior of the synthetic materials.

Catholic University of America

Area of Special Expertise: Slow-flow rate experiments, solution chemistry.

The studies conducted at Catholic University will consist of the following:

1. Flow tests will be conducted in water at very low flow rates on three materials, two simulated waste glasses and a simulated waste ceramic. There are seven flow rates proposed which include 1 daily, 3 weekly, 2 monthly and 1 quarterly exchanges, as shown in Table 4.

At these extremely low flow rates, diffusion plays a major role. The effect of diffusion versus flow rate will be considered in developing the model. The flow rates listed in the table assume a rock porosity of 16 percent. If other porosities are used, the linear flow rates will be proportional to the reciprocal of the porosity.

TABLE 4. Catholic University Flow Test Conditions

<u>Linear Flow Rates for 16% Rock Porosity</u>	<u>Darcy Flow Rates</u>	<u>SA/V</u>	<u>Time Between Leachant Exchanges (a)</u>
0.57 m/yr	0.09 m/yr	8	7 days
0.57 m/yr	0.09 m/yr	56	1 day
0.1 m/yr	0.016 m/yr	56	7 days
0.02 m/yr	0.003 m/yr	56	28 days
0.02 m/yr	0.003 m/yr	224	7 days
0.005 m/yr	0.0008 m/yr	224	28 days
0.0015 m/yr	0.00024 m/yr	224	84 days

(a) Only 25 percent of the leachant is exchanged each time.

2. The mechanisms which control leaching at these conditions will be determined by analyzing the following:
 - a) dissolved components in leachate
 - b) solution pH
 - c) cation/anion balance
 - d) saturation of components, including silica-based complexes
 - e) precipitation and crystal growth of saturated components
 - f) Al_2O_3 concentrations and their effect on the formation and durability of the protective layers
 - g) accelerated dissolution of ceramics by intergranular leaching
 - h) effects of temperature and pressure
 - i) $\text{Fe}_2\text{O}_3/\text{FeO}$ concentrations and their effect on formation and durability (both chemical and mechanical) of the protective layers.
3. Evaluation and predictive tests will be developed for very low flow rate conditions.

University of Florida

Area of Special Expertise: Effect of glass composition and system components on leaching.

Several studies will be conducted in parallel that are a continuation or an outgrowth of the program that has been conducted at the University of Florida for several years. The major components of the program will be:

1. Low Flow Tests. These will be single-pass MCC-4 tests. Some of them will utilize the same test materials, leachants and SA/V ratios as are being used in the Catholic University tests. These tests are considered very important and having them conducted independently at two different laboratories will increase confidence in the data. Some of the low flow rate tests will be multi-year tests to document whether or not steady state is actually achieved at different flow rates.

2. Systems Tests. The University of Florida has been active in the investigation of the effects of backfill in the leaching of waste glasses. The new studies will build upon the expertise that has already been developed in that area. The studies will be systematically expanded to include different candidate materials from the waste disposal system, including repository rocks, to determine what effect they have on waste form leaching.
3. Fundamental Studies. Studies will be conducted on the effects of surface finish of leach specimens, on solution saturation, and on wet-dry cycling. Many of these studies will be done on simple glasses so that it will be easier to interpret the results and gain an understanding of the fundamental mechanisms. When the mechanisms are understood for simple systems, that understanding can be extended to the more complex waste-glass systems.

Rockwell Science Center

Area of Special Expertise: Surface science.

The Rockwell Science Center contribution will be to study three main areas of waste form dissolution, including grain boundary dissolution in multi-phase ceramic waste forms, individual phase dissolution, and surface layer formation on glass and ceramic waste forms. The specific tasks to be performed in these areas are:

1. Grain Boundary Dissolution and Surface Product Formation
 - a) The volume fraction of non-crystalline grain boundary material and its elemental content will be determined by analytical scanning transmission electron microscopy (STEM) characterization of ion-thinned foils of the selected ceramic material.
 - b) Thin foils prepared for (a) above will be leached under selected repository conditions for time periods of 10 minutes to 24 hours and re-examined by analytical STEM to establish semiquantitative dissolution rates for the intergranular material and to observe recrystallization/precipitation products.

- c) If the selected ceramic form is found to contain a significant volume fraction of non-crystalline material, the technique of examining intergranular fracture surfaces by x-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and scanning Auger spectroscopy (SAM) will be used. Fracture surfaces, characterized as intergranular by SEM and XPS will have the thickness of the amorphous layer determined by calibrated ion beam depth profiling, and their elemental content determined by XPS. The surfaces will then be subjected to short-term leaching as in (b) above with surface elemental depletion determined as a function of time of exposure. Chemical state changes and surface layer formation as well as the role of surface features will be observed by XPS, SAM and SEM in the combined analysis technique spectrometer.
- d) Data from the above tasks will be integrated to provide a mechanistic and semiquantitative description of amorphous grain boundary dissolution and subsequent surface layer formation in the selected ceramic form. Direct comparison against available solution analysis leach data from monoliths for elements preferentially concentrated in the grain boundaries will be used to validate the description.

2. Individual Phase Dissolution

- a) The microscopic dissolution tests conducted in 1(a) and 1(b) will also provide direct data on the dissolution mechanism dominating in individual grains of the separate mineral phases. The individual grains will be studied by x-ray analysis to determine if individual cations are being preferentially released or ion-exchanged, while grain morphology will be examined to determine if congruent dissolution or recrystallization is occurring. Again, surface products associated with individual grains will be analyzed for elemental content.
- b) The results of Task 2(a) will be compared against known pure-phase dissolution mechanisms to assess the extent of interactional

effects between unlike grains in the polyphase ceramic. Samples of pure phase and combined two or more phase ceramics will also be examined by x-ray diffraction (XRD), XPS, SAM and SEM to assess the role of phase interactions in individual elemental leaching and surface-layer formation.

3. Surface-Layer Formation

Tasks 1 and 2 will provide direct observation of the phase or phases whose dissolution lead to surface-layer formation. The kinetics of surface-layer formation and the extent to which such layers passivate the ceramic to further leaching will be examined.

- a) The formation of surface layers will be examined as a function of time and solution flow rate to determine the extent of surface passivation and the role of localized saturation and precipitation using monolithic samples. Surface layers will be crystallochemically characterized by XRD and Raman microprobe. Elemental depth profiles and layer thicknesses will be determined by XPS, secondary ion mass spectroscopy (SIMS), and SAM ion-beam elemental depth profiling. The extent to which the layers produce passivation will be determined by studying the increase of elemental depth depletion as a function of time under conditions where solution saturation does not occur.

Pacific Northwest Laboratory

Area of Special Expertise: Radiation chemistry, surface analysis.

The PNL investigations will emphasize the following areas:

A. Radiolysis Effects

These tests will begin by utilizing a single alpha emitter, ^{238}Pu , and a single gamma source, ^{60}Co . Later the testing will be extended to evaluate the possibility of synergistic effects when alpha and gamma radiation are combined. The radiolysis effects study will include the following components:

1. Determine leach rate as a function of dose rate.
2. Determine pH change as a function of dose rate and leachant composition. Can changes in leach rate be ascribed wholly to pH change?

3. Determine Eh change as a function of dose rate and leachant composition. The method to be used for performing this task has not yet been worked out but it is expected that the waste forms utilized will contain uranium, an element whose leaching behavior is affected by redox potential. Close cooperation will be maintained with Pennsylvania State University.

B. Actinide Leaching Behavior

After 1000 years in a repository the leaching behavior of the actinides is of most interest. The results of the actinide-doped glass leaching experiments done in the NWTs program will be corroborated and the tests expanded to include other waste forms. Later the testing may be expanded to include ^{99}Tc , and perhaps 1 or 2 other long-lived fission products that are present in the waste in minor amounts.

C. Systems Tests

These interactive tests will be done in cooperation with the University of Florida. The same materials will be used and in some cases the experiments will be duplicated, so that by having been obtained in two separate laboratories, the validity of the data will be reinforced. However, most of the tests done at PNL will be done in autoclaves in order to extend the interactive test data to higher temperatures.

D. Fundamental Studies

Surface-charge effects may be a fundamental factor responsible for some observed leaching behavior. Zeta potential measurements and other techniques will be used to study surface-charge effects. It has been postulated that as the surface film matures it may slough off hydrous particles, some of colloidal dimensions. The subsequent migration of these colloidal particles, if they are actually formed, will be dependent on surface change. Experiments directed at determining the presence of colloidal particles and their surface charge will be part of this study. Further investigations of SA/V effects will also be conducted in conjunction with Catholic University and the other leaching mechanism program participants.

RELATED PROGRAMS

An important goal of the workshop was to promote interactions between the leaching mechanisms program and other related DOE programs. To this end investigators of the defense waste glass leaching program at SRL and the Office of Nuclear Waste Isolation (ONWI)-sponsored waste package modeling programs were invited to the workshop. At the end of the workshop, presentations were made by representatives of both these related programs.

SRL Defense Waste Glass Leaching Program

George Wicks is directing a comprehensive investigation of the leaching of SRL defense waste glasses. Among the many topics discussed by Wicks were the following:

Devitrification. The time-temperature dependence of the ingrowth of crystalline phases in three different candidate glass compositions has been studied. Devitrification occurred mainly in the 550° to 900°C temperature range. It was concluded that extensive devitrification is unlikely to occur during storage or disposal of waste glass, but could occur during the manufacturing processing, depending on how the canisters are cooled.

Pressure. "There is no significant effect of pressure up to 1500 psi at 90°C on leachability of simulated SRP waste glass, studied in deionized water."

Backfill Effects. Preliminary results indicate that significant differences in waste glass leaching can occur when candidate backfill materials, such as bentonite, are added to the system. Depending on the type of bentonite, the leach rate can be enhanced or suppressed.

Surface Layers. Study of the surface layers formed on waste glass is a large component of the SRL leaching program. "The leached SRL glasses have surface layers rich in Fe, Mn and Mg. These layers are thought to form primarily as a result of the insolubility of these constituents in the leachate. The presence of these layers indicates a) minor constituents of waste glass are important during leaching, b) surface-layer formation should be expected during long-term storage, and c) layers would be expected to have a beneficial effect on retarding subsequent glass corrosion by inhibiting dissolution processes."

OWNI Waste Package Modeling

Presentations were made by Bill Kuhn, PNL, and Aviva Brecher and Dave Leland of A. D. Little. The waste package subsystem model is being developed as a submodel in the SCEPTER (Systematic Comprehensive Evaluation of Performance and Total Effectiveness of Repositories) program. Other subsystem models required in the program are a repository model, a geotransport model and a biosphere pathways and dose-to-man model.

The components of the waste package subsystem include the waste form, the canister, one or more additional metal barriers (overpacks), backfill, and the near-field repository rock. Bill Kuhn discussed modeling the subsystem from the standpoint of mass balances across a series of mass transfer inhibitors in pseudo steady-state.

Brecher and Leland discussed the A. D. Little waste package subsystem model that has been under development for over a year. Of special interest to the leaching mechanisms investigators was the list of inputs required for the model (Table 5). The model is scheduled to be published in mid-1982.

Table 5

Arthur D. Little, Inc. Leach Process Model Input Requirements

WASTE PACKAGE SUBSYSTEM: LEACH PROCESS MODEL

INPUT: CONSTANTS

<u>Quantity</u>	<u>Description</u>	<u>Units</u>
ISNANN	Number of radii	ND
SHTWP	Height of waste package	m
ISNUC	Number of radionuclides being tracked	ND
SQREP	Volumetric flux of fluid through the waste package	m ³ /sec
WCSAT (ISNUC)	Saturation concentrations of nuclides	g/m ³
WCSATM	Saturation concentration of matrix component	g/m ³
WDIFFK (ISNUC)	Leach rate coefficients for diffusion for each nuclide	g/m ² -sec ^{+1/2}
WDISSK (ISNUC)	Leach rate coefficients for dissolution for each nuclide	g/m ² -sec
WLRHLF	Leach rate coefficient for diffusion for matrix component (exp = 1/2)	g/m ² -sec ^{+1/2}
WLRONE	Leach rate coefficient for dissolution for matrix component (exp = 1)	g/m ² -sec
WEACT	Activation energy	kcal/g-mole
WGASCN	Universal gas constant	kcal/g-mole°K
WRHOWF	Bulk density of wasteform	g/m ³
WDBULK (ISNUC)	Diffusion coefficients in bulk water for nuclides	m ² /sec
WDBULM	Diffusion coefficient in bulk water for matrix component	m ² /sec
WDBFL (ISNUC)	Diffusion coefficients in backfill for	m ² /sec

<u>Quantity</u>	<u>Description</u>	<u>Unit</u>
	nuclides	
WDBFLM	Diffusion coefficient in backfill for matrix component	m^2/sec
WKDBF (ISNUC)	Sorption coefficients for nuclides	ml/g
WKDBFM	Sorption coefficient for matrix component	ml/g
WETABF	Porosity of backfill	ND
WRHOBf	Bulk density of backfill	g/m^3
SRADII (ISNANN)	Barrier radii	m
SLEFA	Leach enhancement factor due to α -damage	ND
SLEFR	Leach enhancement factor due to radiolysis	ND
SDENSF	Density degradation factor for wasteform	ND
SRADTX (ISNUC)	Mass inventory of user-selected radionuclides being tracked	g
STEMP (1)	Temperature of wasteform	K
SADFA (ISNANN)	Areal degradation factors	ND
SAREWF	Fracture surface area of wasteform	m^2

REFERENCES

- Anbar, M. 1968. Fundamental Processes in Radiation Chemistry. P. Ausloos, editor. Interscience. New York. p. 651.
- Appleby, A. and H. A. Schwarz. 1969. "Radical and Molecular Yields in Wastes Irradiated by Gamma Rays at Heavy Ions." J. of Phys. Chem. 73:1937-1941.
- Rimstidt, J. D. and H. L. Barnes. 1980. The Kinetics of Silica-Water Reactions," Geochim. et Cosmochim. Acta. 44:1982-1699.

APPENDIX A

AGENDA

FIRST WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS

APPENDIX A

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FIRST WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS

Battelle Seattle Research Center
October 27-28, 1981

MONDAY, OCTOBER 26

8:00 p.m. Social Hour Suite C-5

TUESDAY, OCTOBER 17 - Lecture Hall

8:30 a.m. Introduction J. E. Mendel and
P. H. Permar

8:35 The Leaching Mechanisms Program J. E. Mendel and
J. A. Stone

SESSION I: MODELING

9:00 Tutorial on the General Case D. D. Jackson
Waste Form Leaching Model

10:00 - 10:15 Break

12:00 Lunch

SESSION II: TESTING PARAMETERS

1:00 p.m. Radiation Effects
(Discussion Leader: G. L. McVay)

1:40 pH Effects
(Discussion Leader: G. G. Wicks)

2:20 Eh Effects
(Discussion Leader: M. G. Seitz)

3:00 Break

3:15 Surface Condition, Initial and Final
(Discussion Leader: D. E. Clark)

4:00 Specific Ion Effects, Solubility Limits
(Discussion Leaders: D. Rai, B. Gambow,
and C. Q. Buckwalter)

5:30 Social Hour Suite C-5

6:30 Dinner BSSP Dining Room

WEDNESDAY, OCTOBER 28 - Lecture Hall

8:15 a.m. Recap of Previous Day J. E. Mendel

SESSION III: PROGRAM PLANNING

8:30 Pennsylvania State University
(Principal Investigator: W. B. White)

9:30 Coffee Break

10:00 Catholic University of America
(Principal Investigator: P. B. Macedo)

11:00 University of Florida
(Principal Investigators: L. L. Hench
and D. E. Clark)

12:00 Lunch BSSP Dining Room

1:00 p.m. Rockwell Science Center
(Co-principal Investigators:
A. B. Harker and D. R. Clarke)

2:00 Pacific Northwest Laboratory
(Principal Investigator:
G. L. McVay)

3:00 Break

3:15 Related Savannah River Laboratory
Programs G. G. Wicks

3:45 Related NWTs Programs Aviva Brecher and
W. L. Kuhn

4:15 Wrap up J. E. Mendel

APPENDIX B

MATERIALS CHARACTERIZATION CENTER
LEACHING MECHANISMS WORKSHOP PARTICIPANTS
BATTELLE SEATTLE RESEARCH CENTER
SEATTLE, WASHINGTON
OCTOBER 27-28, 1981

APPENDIX B

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APPENDIX C

PROGRAM PLAN FOR
COORDINATED LEACHING MECHANISMS PROGRAM

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PREFACE

The high-level waste lead office is funding a three-year leaching mechanisms program, coordinated by the Materials Characterization Center (MCC). This program plan describes the elements of the coordinated program, the interrelationships, and the anticipated final results of the program. The plan will be updated and revised as required in August 1982 and August 1983.

1.0 INTRODUCTION

The leaching of nuclear waste forms is a complex phenomenon that has been studied extensively. There is a basic understanding of the various reactions involved. What remains to be done is to quantify the relationships between the different reactions so that mathematical models can be used to predict the leaching behavior of waste forms for thousands of years, several orders of magnitude beyond experimentally verifiable times. A three-year leaching mechanisms program has been set up by the high-level lead office to integrate the efforts of several laboratories and outside consultants to develop the requisite data base and demonstrate its application in predictive mathematical models.

The output of this program, which is being coordinated by the Materials Characterization Center (MCC), is expected to be:

- Efficient utilization of DOE waste management scientific resources through coordination by workshops and special studies that also bring in outside experts when needed.
- Documented, back-up materials data to demonstrate that DOE's predictive mathematical models for waste-form leaching are soundly based on mechanistic principles.
- A peer-reviewed, coherent, waste materials data base that relates directly to predictive mathematical models for waste form leaching and can be used to demonstrate the relationship of this leaching behavior to EPA and NRC criteria.

2.0 ORGANIZATION OF THE TECHNICAL PROGRAM

The technical program is organized as a three dimensional matrix, shown in Figure 1. There are two major Study Areas. These are described in more detail in Section 4.0. The first study area, "Fundamental Data and Mechanistic Research" is divided into three subareas that emphasize the major materials aspects of leaching, i.e., solid state phenomena, surface phenomena and solution phenomena. The other major study area, "Model Development and

FIGURE 1. Technical Elements of the Leaching Mechanisms Program

Verification" is divided into two subareas in recognition that model development is an evolutionary process. Initially, there must be considerable reliance on empirical relationships; later, as knowledge concerning the basic mechanisms increases, the models can become more self-sustained and independent of empiricism.

The second dimension of the matrix in Figure 1 is Testing Methods. These are fully discussed in Section 5.0. The emphasis in Testing Methods will be on assuring that all experimental techniques are carefully controlled and well documented. MCC leach test methods will be utilized as much as possible.

The third dimension of the leaching mechanism program matrix shown in Figure 1 is Test Materials. An important aspect of the coordination of the program will be furnishing uniform test materials to the participating laboratories. The goal will be to obtain a large amount of statistically-valid data on a few well-characterized waste forms. After the interrelationships between the reactions controlling the leaching of these reference waste forms are well defined, tests will be made to determine the effect of changes in waste form composition. The test materials, which are described in more detail in Section 6.0, will be evenly divided between glass and crystalline waste forms.

Individual elements of the three dimensions of the technical program are identified by Roman numerals, capital letters, and arabic numerals as shown in Figure 1. These will be used as a convenient key to each program activity, for example, III.D.3 identifies surface studies of the reference defense waste ceramic after leaching at temperatures of 110°C, or higher, by the MCC-2 Static High-Temperature Leach Test Method. Integration of the technical program will be facilitated by applying identification keys to the activities of the participants.

3.0 RELATIONSHIP WITH OTHER PROGRAMS

The leaching mechanisms program will cooperate closely with waste form development programs, repository development programs and the regulatory agencies. The cooperation will be maintained by exchange of technical reports and

frequent personal contact. Semiannual workshops, sponsored by the leaching mechanisms program and with representation from the other programs, are planned to have a major role in fostering the desired cooperation.

Waste form development for high-level wastes is directed by the Savannah River Laboratory. This development program includes extensive leaching studies being done at SRL, Lawrence Livermore National Laboratory, and the Rockwell Science Center. Frequent information exchanges will be maintained that will benefit both the waste form development program and the leaching mechanisms program.

An especially close interface will be maintained with the repository development programs and, in particular, with the waste package development program directed by the Office of Nuclear Waste Isolation (ONWI), since the waste form is an integral part of the waste package and waste form leaching must be understood to evaluate the overall performance of the package. The repository development programs are performing generic waste-form leaching studies to provide radionuclide source terms to the mathematical models describing waste package performance. Liaison will be maintained to prevent overlap and foster synergism between these closely related programs. Although the programs are closely related the scope of the leaching mechanisms program is much more limited. This limited scope is shown pictorially in Figure 2. The emphasis is on the reactions of the waste form with fluids that may intrude through the remnants of a corroded canister, and how these reactions are influenced by the composition and condition of the waste form. Part of the liaison with the repository development programs will be consultation on how the various repository and waste package designs may affect the composition of the intruding fluids.

The ultimate goal of the program is to relate the leaching behavior of waste forms to criteria prescribed by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC). Present proposed criteria relate only to the overall repository system, but suggest that the system consist of a series of barriers, each of which is optimized to provide as much

FIGURE 2. Pictorial Description of the Scope of the Leaching Mechanisms Program.

protection as is practical by itself. Thus, the purpose of the leaching mechanisms program is to define how much protection the waste form provides by itself. There will be frequent interchanges between the program and the regulatory agencies to maintain current knowledge of regulatory policies, and to provide technical information that may assist in formulating these policies.

4.0 STUDY AREAS

The two major study areas, "Fundamental Data and Mechanistic Research" and "Model Development and Verification," have an iterative parallel relationship. Leaching models will be developed based on mechanistic postulates. The data collected in the experimental studies will be directed toward refining the understanding of mechanisms and testing the models, which may have to be modified as new data become available.

A brief description of the five study areas identified in Figure 1 follows. The approach adopted in the leaching mechanisms program will be to review the existing knowledge in these areas and to do active investigations only where more information is needed.

4.1 Solid-State Phenomena

Solid state, in this context, refers not only to the three-dimensional microstructure of the material and how diffusional processes are affected by the microstructure, but also to grosser phenomena such as brittle fracture.

The effects of radiation and temperature on waste forms may be thought of as "aging" effects, since they occur gradually over long periods. The aging effects on waste glass, such as radiation-induced density change and transmutation and thermally-induced devitrification have been studied extensively. Less study of aging effects has been done on crystalline waste forms, since they have only been under development for a few years.

Solid-state diffusion would appear to be an important factor in leaching, since it is the more readily diffusible monovalent and divalent cations that are found to leach most readily from both glass and crystalline waste forms. The cation diffusion is apparently affected by the inward diffusion of hydrogen or hydronium ions since solid-state diffusion coefficients for sodium in glass, for instance, are many orders of magnitude different than those that are calculated based on the leaching behavior of sodium. More information on the diffusional process in waste forms is needed, with particular attention to the inward diffusion of water or water components through the bulk material and along grain boundaries and microcracks. Attention to natural phenomena such as the formation of hydration rinds in obsidian, and the weathering processes leading to "rotten" rock, should be helpful in this regard.

It appears that some cracking of glass waste forms will be unavoidable although techniques are being developed to minimize the amount of cracking. Studies have been made that indicate the additional surface area produced by the cracking does not lead to a proportional increase in leaching. This is probably due to a combination of saturation effects in the confined crack space and liquid diffusion control. More definitive information concerning the effects of cracking in the waste form is needed.

4.2 Surface Phenomena

Surface analysis is a powerful tool for elucidating leaching mechanisms. Incongruent leaching of waste glasses produces surface layers that are depleted in some constituents, as would be expected, but when the surface layers are analyzed it is usually found that they are also enriched in some constituents and may even have a laminar structure because of variable enrichments with depth. The incongruent leaching that occurs with crystalline waste forms does not usually form the same type of surface layers that are formed on glasses; instead the incongruity is apparently due to preferential attack of single phases or at grain boundaries.

The new surface analysis techniques that have been developed in the last one to two decades will be used to study the surfaces of waste forms before and after leaching to gain insights into the mechanisms that control leach rates. It is known that the surface alterations that occur in leach-resistant waste forms are different from those that occur in more leachable waste forms. The surface studies will be directed toward defining more quantitatively what these differences are. The techniques used will include many of those listed in Table 1, and perhaps others. As shown in the Table, some of the techniques are capable of examining surface depths of only a few angstroms; others can examine cross sections of the surface and study alterations that extend deep into the solid.

Emphasis will be not only on the kinetics of surface alteration but also on defining the fully developed alteration that might be expected on waste forms after long contact with geologic fluids. The latter will require an understanding of the mechanisms involved. Temperature will be used as an accelerating mechanism, but there will be careful evaluation to determine if different mechanisms control the alteration at different temperatures.

Most of the surface analytical methods shown in Table 1 require that the specimen be in an evacuated chamber. The drying that occurs alters hydrous surface layers that form on waste glasses and may cause them to crack and curve. One task in the surface work area will be to try to develop in situ surface analytical techniques so that surface films can be studied while their full hydrous character is retained.

TABLE 1. Instrumental Techniques for Analyzing Waste Form Surfaces

<u>Method</u>	<u>Depth of Analysis</u>
Electron Spectroscopy for Chemical Analysis	5-20 Å
Auger Electron Spectroscopy	5-20 Å
Ion-Scattering Spectroscopy	5-20 Å
Secondary Ion Mass Spectroscopy	5-20 Å
Ion-Beam Induced Radiation	5-20 Å
Ar Ion Beam Milling with the Above Techniques	5-2000 Å
Ellipsometry	<10->1000 Å
Infrared Reflection Spectroscopy	0.2-0.5 μm (2000-5000 Å)
Electron Beam Microprobe	1.5 μm
Scanning Electron Microscopy (SEM - with Energy-Dispersive Analysis by X-ray (EDAX))	1.5 μ
Surface Dielectric Analysis	~1-10 μm
X-ray Fluorescence Spectroscopy	10 μm

4.3 Solution Phenomena

The characteristics of the solution contacting the waste form strongly affect the leach rate. Among the most important solution parameters are pH, approach to saturation, complexant content, Eh, and radiolysis. The effect of pH on the leaching of waste glasses is well known; the effect is less well documented on crystalline waste forms. Leaching is usually lowest at pH ~7. Leaching increases at low pH's, but it is improbable that the waste form will ever be subjected to low pH solutions. Leaching also increases at high pH, and high pH's (pH>9) will probably occur in the vicinity of the waste forms

because of the incongruent leaching of alkali ions. The leaching mechanism of high-silica content wasteforms will change at high pHs because silica dissolution becomes enhanced. More studies will be conducted to quantify the leaching reactions occurring at high pH. It may be necessary to exclude atmospheric CO_2 from the experiments to avoid pH buffering.

The leach rate decreases as the contacting solution approaches saturation. Since the intruding geologic fluids may already be nearly saturated in some waste form constituents, such as silica, it is important to know the compositions of the geologic fluids representative of repository situations and to use them in the studies. The flow rate of the fluids past the waste form also exerts a large influence on the approach to saturation. Close liaison will be maintained with the repository development programs to assure that realistic values for those important parameters are used in the leaching mechanisms program.

Other important parameters that will also require close liaison with the repository developers in order for them to be properly evaluated are the concentration of organic complexants and the Eh of the repository fluids. Organic complexants could potentially increase the leaching rate. Since the Eh at repository depths is probably reducing, and the reduced form of multivalent radionuclides, such as technetium and most of the actinides, are less mobile, the leaching rate will probably be decreased by this factor.

Another important factor that is unique to waste form leaching is radiolysis of the leachants. Radiolysis produces species such as H_2O_2 that may change the Eh. Some studies of leaching have been done in radiation fields, but more are needed.

Finally, but probably most fundamental of all, is an experimental factor involving the solution, namely, the analytical detection limits and precision capabilities for the constituents of interest. It is this analytical data that will be used to verify the models and which will be used in the predictions of long-term behavior. The verifications and predictions can only be as good as the experimental data allows. Often the guiding parameter will be only a slight change in concentration, or lack of any change in concentration with

time, of a given constituent in the leachate. Careful measurements will be a feature of this program, with frequent cross checks between laboratories.

4.4 Empirical Modeling

Although the modeling effort will be a coherent entity within the program, it is divided into two parts, reflecting different emphases. Empirical modeling, in the context of this program, refers to the modeling that depends wholly on leach test data for definition of the factors in its terms. The terms usually include time to the $1/2$ and $1st$ power, with perhaps another term having a negative coefficient to account for "back reactions." These are practical, if inelegant models, that have a composite mechanistic basis, that is, the $t^{1/2}$ term is attributed to an "apparent" diffusion rate, the t is attributed to "uniform corrosion" of the matrix, and the back reaction term includes such mechanisms as saturation or common ion effects in the hydrous surface layer of glasses and reprecipitation of elements as constituents of new compounds.

These empirical models appear to adequately account for observed leaching behavior of waste glasses, at least for periods up to a few months, and it is anticipated they will also serve for crystalline waste forms but this remains to be shown. There is not adequate long-term leaching data, extending for several years, for either class of waste form. Obtaining such data is one of the goals of this program.

The long-term data will also be used to fix the effect of temperature more firmly. There are many examples in the literature showing the Arrhenius relationship for short-term leach rates, but there is also evidence that the apparent activation energy changes as leaching is continued.

A further simplification of empirical models can be made if only "steady-state" data are utilized. This type of modeling has been done at Catholic University and will be continued under the leaching mechanisms program. It has been found that steady-state conditions can be achieved in low-flow laboratory tests in just a few weeks, and by making certain assumptions concerning the ratio of the waste-form surface area to the volume of repository fluid, the useful bottom-line relationship shown in Figure 3 can be defined.

FIGURE 3. A "Bottom Line" Output from Empirical Modeling of Waste Form Leaching

The disadvantage of empirical models is that they cannot predict behavior for systems for which leaching data are not available. The ultimate goal of the leaching mechanisms program is to be able to predict waste form leaching behavior under any postulated or imaginary set of conditions. This capability requires models that are based on more fundamental principles, as described in the following section.

4.5 Mechanistic Modeling

Mechanistic modeling of complex systems has become potentially practicable with the advent of the computer age. Computers are required to handle the computations because mechanistic modeling utilizes basic thermodynamic and kinetic data for all of the competing reactions that can feasibly occur between the constituents in a given starting system and, through a series of iterative calculations, predicts the species present and their concentrations in the final system. In this plan, time-independent models based on thermodynamics will be utilized because a larger thermodynamic data base is available, while

very little basic kinetic data exists for the systems of interest, and because over the time frame of interest, thousands of years, at least pseudoequilibrium conditions will exist and kinetics will be of second-order importance.

The approach to mechanistic modeling adopted in the program will be as follows:

1. Utilize existing geochemical soil water models to develop a "straw man" waste form-water interactions model.
2. Identify gaps in the data base, e.g., actinide and fission product speciation.
3. Work with other modelers, especially the waste package and repository modelers, and with the experimentalists, to fill in the data gaps.
4. Test the "straw man" model, using "best guesses" for still-missing gaps in the data base, against solution and solid-state analyses from leach tests.
5. Continue to refine the model based on the results of tests against experimentally derived results until a defensible model for predicting long-term waste-form leaching behavior is achieved.

Mechanistic models based on thermodynamics are most applicable to crystalline waste forms. Since glass is by definition a metastable material, waste glasses are not directly amenable to thermodynamic modeling, however such modeling can be applied to the crystalline products of waste glass-water interactions. It is probable that the major effort in modeling waste glass leaching will utilize empirical models, as described in Section 4.4.

5.0 TESTING METHODS

The HLW lead office has requested that the MCC coordinate its leaching mechanisms program to assure that the program yields statistically valid data. This will require the use of standardized procedures as much as is possible without inhibiting research creativity. The MCC leach test methods have been defined to have a large amount of flexibility in selection of test parameters and it is expected that it will be possible to utilize these methods for much

of the testing. The goal is to be able to put a major portion of the test data into the Nuclear Waste Materials Handbook to provide a readily available, authoritative and permanent record. Some of the testing judged most crucial for achieving program goals will be carried out in parallel at different laboratories to reinforce the validity of the results.

The MCC leach test methods are being approved by the Materials Review Board (MRB) on a provisional basis. The methods will be given full approval when certain technical concerns are allayed and after it is shown that a consensus exists on the usefulness of the methods. Utilization of the MCC methods in the leaching mechanisms program will help demonstrate their usefulness and can also assist in alleviating some of the technical concerns such as the effect of Eh and CO₂ from the atmosphere on test results.

A major feature of the MCC leach test methods is the emphasis upon detailed characterization, both of the bulk material and the leached surfaces. This emphasis will be even increased in the leaching mechanisms program.

It is expected that MCC-1 through 4 leach test methods will all be used in the program, but that MCC-3 and 4 will be used most. MCC-3 is an agitated powder leach test method that covers the temperature range 40° to 190°C and determines the final time-independent concentrations in a closed system. MCC-4 is a slow-flow-leach test method that covers the temperature range 40°-90°C. Leachant compositions can be varied in both tests. Both tests utilize one standard specimen surface area to leachant volume (SA/V) ratio. This limitation probably cannot be countenanced in the leaching mechanisms program since it has been shown that SA/V ratio affects steady-state leachate concentrations of at least some waste constituents. A more thorough examination of the effect of SA/V ratio will be included in the leaching mechanisms program.

The presently defined MCC test methods are not sufficient for some other needs of the leaching mechanisms program also. The MCC has not yet defined systems tests or fully radioactive leach test methods. Both will be utilized, but only to the minimum extent necessary, in the leaching mechanisms programs. Systems tests include other components in addition to the waste form, fluid and degraded canister shown in Figure 2, such as backfill material and repository

rocks. Systems tests are utilized most extensively in the waste package development programs where the emphasis is on assessing the interactions of all of the systems components to determine if the desired overall behavior is being achieved. Close liaison will be maintained with the waste package program systems tests. In particular, a waste form tie-in will be established if possible, so that both programs are using some of the same reference waste forms. But, because the leaching mechanisms program will be addressing a broader spectrum of potential waste forms, it will be necessary for the leaching mechanisms program to do limited systems testing of a scouting nature to ascertain that other parts of the system do not have an unexpected impact on the waste form fluid reactions that are the primary concern of the leaching mechanisms program.

Similarly, it must be ascertained that the presence of radioactivity does not produce effects that abrogate conclusions reached on the basis of non-radioactive data, which will form the preponderant portion of the data base available to the leaching mechanisms program. Some leaching will be performed in a ^{60}Co gamma facility as part of the leaching mechanisms program, but to be most cost-effective the leaching mechanisms program will interact as closely as possible with personnel conducting fully radioactive leach testing at SRL, and perhaps elsewhere. The need for additional fully radioactive testing will be assessed periodically as the leaching mechanisms data base is developed. The need for tests in which only selected radionuclides of special interest, such as ^{99}Tc , ^{237}Np and ^{226}Ra , are studied will also be assessed.

6.0 MATERIALS

One of the first goals in the leaching mechanisms program will be to define the formulations of the four reference materials shown in Figure 1 and arrange for the manufacture of large quantities of each that can be distributed as quickly as possible to the participants in the program. These reference materials will be representative of each of the components of the basic high-level waste form matrix, i.e., two wastes, either defense or commercial, and two matrix materials, either glass or crystalline ceramic. They will be

used to develop a detailed baseline of mechanistic data. In the case of the two reference crystalline ceramics, parallel routes to the baseline data will be pursued. One route will study the crystalline components individually; the other will study the total assemblage so that grain boundary and phase interactions effects are included.

As the program continues the data base obtained from the four reference materials will be expanded to include the effects of compositional variations. These compositional variations will be of two types. One will be the inclusion of radionuclides in the reference formulations. For the initial basic mechanisms studies, the formulations will have been completely nonradioactive, or only contain uranium. The other type of compositional variation to be incorporated later will be an evaluation of the effects of changes in the bulk composition of the waste forms.

Finally, it is anticipated that limited testing will be done on another class of materials entirely. These are archeological or natural materials, sometimes called natural analogs. If the mechanisms by which these materials leach can be elucidated, and if the mechanisms are similar to those that control waste-form leaching, then they can provide valuable truly long-term data points, not obtainable in other ways, to relate to short-term data obtained in laboratory leach tests.

7.0 SCHEDULE

The schedule for the major activities in the three-year program is shown in Figure 4. The major output of the program will be a final report at the end of FY-1984 that describes an "official DOE" mathematical model for the leaching of waste forms that can be used for the prediction of long-term behavior and that has been tested and validated to the extent possible in laboratory experiments. If it proves necessary to use different models for glass and crystalline waste forms then there may be two "official DOE" mathematical models. The heavy lines in Figure 4 show the major activities that will lead to this final output of the leaching mechanisms program. The important peripheral activities, as shown in Figure 4, include semiannual workshops, interfacing with other programs and progress reports. The workshops, held on

FIGURE 4. Schedule of Major Activities in Leaching Mechanisms Program

an approximately 6-month schedule, will be the focal point of these activities. It is anticipated that each workshop will be of at least two days duration, and that the different participants on the program will host the workshops on a rotating basis. The program participants will report their progress at the workshops and future work plans will be discussed. Programs doing related work will be invited to have representatives at the workshops and to interact freely. In addition, contracts will be set up with consultants and they will be present at the workshops, either to provide expertise on special topics or to peer review the overall program.

The proceedings of each workshop will be published as an MCC blue-cover document in less than 3 months after the date of the workshop. The only other formal reporting will be brief letter reports to describe progress made each month. These will be due from the program participants to the MCC on the 25th of each month. The MCC will compile these reports and submit a summary to SRL by the 10th of the following month. In addition the program participants will be encouraged to publish their work in the open literature and topical reports and to present papers at technical society meetings. Drafts of all such publications and papers must be given to the MCC for review 3 weeks before they are issued or presented. The fine structure for the schedule of the major activities, shown as heavy lines in Figure 4, has not been developed completely and won't be. These are research-type activities and are not amenable to rigid scheduling. The directions of this research can be delineated, and a schedule for the assessment of progress can be established (biannually) but the timing and description of the final products has to remain somewhat flexible. Therefore, except for the overall generalized schedule shown in Figure 4, this program plan will be limited to FY 1982. The FY 1982 milestones that will be used to assess performance of the leaching mechanisms program are shown in Table 2. The program plan and the milestones will be updated annually to reflect research progress, and changes of direction dictated by new research findings.

TABLE 2. Fiscal Year 1982 Milestones

<u>Milestone</u>	<u>Completion Date</u>
First Leaching Mechanisms Workshop	October 1981
Final Agreement on Work Statements for All Participants	November 1981
Issue Program Plan	November 1981
PNL Contracts with All Participants	January 1982
Agreement on "Mark 1" Leaching Model(s)	January 1982
First Workshop Report	January 1982
Decision on CO ₂ Control in Leaching Tests	February 1982
Reference Materials to Participants	March 1982
Begin Multiyear Tests (2 Labs)	April 1982
Begin Eh Testing	May 1982
Second Leaching Mechanisms Workshop	June 1982
Update Program Plan	August 1982
Second Workshop Report	September 1982

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