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**Materials Characterization
Center Workshop on Leaching
of Radioactive Waste Forms**

Summary Report

April 1980

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

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MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON LEACHING OF RADIOACTIVE WASTE FORMS
SUMMARY REPORT

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April 1980

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CONTENTS

1.0	SUMMARY	1.1
2.0	INTRODUCTION	2.1
2.1	PURPOSE OF THE WORKSHOP	2.2
2.2	ORGANIZATION OF THE WORKSHOP	2.2
2.3	ARRANGEMENT OF THIS REPORT	2.2
3.0	WORKING GROUP REPORTS	3.1
3.1	WORKING GROUP 1--WASTE MANAGEMENT CRITERIA	3.1
3.1.1	Summary	3.1
3.1.2	Waste Management Criteria	3.2
3.1.3	Future Criteria Actions	3.5
3.1.4	General Items and Comments	3.5
3.2	WORKING GROUP 2--SCOPING TESTS	3.7
3.2.1	Summary of Group Presentations	3.7
3.2.2	Standard Scoping Static Leach Tests	3.9
3.3	WORKING GROUP 3--DATA BASE FOR MODELING	3.11
3.3.1	Discussion	3.11
3.3.2	Results of Discussions	3.12
3.4	WORKING GROUP 4--RATE CONTROLLING MECHANISMS	3.13
3.4.1	General Comments	3.13
3.4.2	Scoping Tests	3.14
3.4.3	Temperature Dependence	3.15
3.4.4	Time Dependence	3.15
3.4.5	Congruency	3.15

3.4.6	Geologic Effects	3.15
3.4.7	Surface Analysis	3.16
3.4.8	Solubility Considerations	3.16
3.5	WORKING GROUP 5--DATA RELIABILITY	3.17
3.5.1	Introduction	3.17
3.5.2	Required Accuracy and Precision of Data	3.17
3.5.3	Requirements for Procedures	3.19
3.5.4	Problems with Currently Available Data	3.20
3.5.5	Leach Units	3.20
3.5.6	Additional Comments	3.21
4.0	FOLLOW-UP ON WORKSHOP	4.1
4.1	COMPILATION OF ISSUES AND TENTATIVE RESOLUTION BY MCC	4.1
4.2	REVISION OF PROPOSED MCC LEACH TESTS	4.1
4.2.1	Revision of Overall MCC Leach Test Program	4.1
4.2.2	Revision of Detailed Scoping Static Leach Test	4.8
	PROPOSED STATIC LEACH TEST	4.9
4.3	ORGANIZATION OF A ROUND ROBIN	4.24
4.4	COORDINATION WITH MECHANISTIC RESEARCH	4.24
5.0	COMMENTS BY PARTICIPANTS	5.1
6.0	ACKNOWLEDGMENTS	6.1
	APPENDIX A--ORIGINAL MCC LEACH TEST PLANS	A.1
	APPENDIX B--WORKSHOP PARTICIPANTS	B.1
	APPENDIX C--WORKSHOP AGENDA	C.1

FIGURES

1	Development Procedure for Standard Material	3.18
2	Proposed MCC Leach Test Number 1. Static Test	4.5
3	Proposed MCC Leach Test Number 2. Autoclave Test	4.5
4	Proposed MCC Leach Test Number 3. Solubility Test	4.6
5	Proposed MCC Leach Test Number 4. Dynamic Test	4.6
6	Proposed MCC Leach Test Number 5. Soxhlet Test	4.7
7	Static Leach Test Apparatus	4.10

MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON LEACHING OF
RADIOACTIVE WASTE FORMS
SUMMARY REPORT

1.0 SUMMARY

The first Materials Characterization Center (MCC) workshop, on the leaching of radioactive waste forms, lasted two days and had 46 participants, including representatives of all of the Department of Energy (DOE) laboratories involved in high-level waste form development, most of the geologic repository development programs, several universities, industry, the National Bureau of Standards, and the Nuclear Regulatory Commission. In addition, there was a representative of the Canadian high-level waste program from the Whiteshell Nuclear Research Establishment.

There was general agreement that, after certain revisions, the proposed leach test plan set forth by the MCC^(a) can be expected to meet most of the nuclear waste community's waste form durability data requirements. The revisions give a clearer definition of the purposes of each test and the end uses of the data. As a result of the workshop, the format of the test program has been recast to clarify the purposes, limitations, and interrelationships of the individual tests.

There was also a recognition that the leach test program must be based on an understanding of the mechanistic principles of leaching, and that further study is needed to ensure that the approved data from the MCC leach tests will be compatible with mechanistic research needs. It was agreed that another meeting of the participants in Working Groups 3 and 4, and perhaps some other

(a) These proposed tests must be approved by the Materials Review Board before they will be included in the Nuclear Waste Materials Handbook. Some revisions may occur before this review process is complete.

experts, should be held as soon as possible to focus just on the definition of leach test requirements for mechanistic research. The MCC plans to hold this meeting in April 1980.

Many of the tests that will lead to increased understanding of mechanisms will of necessity be long-term tests, sometimes lasting for several years. But the MCC also faces pressing needs to produce approved data that can be used for the comparison of waste forms in the relative near-term, i.e., in the next 1 to 3 yr. Therefore, it was decided to initiate a round-robin test of the MCC short-term static leach procedure as soon as practicable. The MCC has tentative plans for organization of the round robin in May 1980.

2.0 INTRODUCTION

In early FY 1980, the DOE established the MCC, managed by the Pacific Northwest Laboratory (PNL), to provide the materials data base and supporting documentation needed to ensure safe disposal of nuclear wastes. The data base will contain information on components of the waste emplacement package, which includes either the spent fuel or processed waste form, the engineered barriers, and their interaction with the host environment. The MCC will plan materials testing, develop and document procedures, collect and analyze existing materials data, and conduct tests as necessary. After test methods and data have been approved by the Materials Review Board (MRB), managed by Argonne National Laboratory, the MCC will publish these approved methods and data in a Nuclear Waste Materials Handbook (hereafter referred to as Materials Handbook). The first edition of this handbook is scheduled to be issued in September 1981.

The MCC will hold workshops at appropriate times during the development of test methods to obtain the broadest possible consensus that a particular approach to testing will yield suitable and interpretable data. Workshop participants will be experts from universities, industry, DOE laboratories, and government agencies. The first workshop, on waste form leaching, was held in Seattle, February 12 and 13, 1980, and is the subject of this summary report. Other MCC workshops on such topics as overall data needs, canister materials, thermal effects, and radiation effects will be held as soon as appropriate.

Leaching of radioactive waste forms was selected as the topic of the first MCC workshop because chemical durability, usually expressed as a leach rate, is one of the most important properties measured on waste forms. A large body of leach rate data exists, which has been collected over the more than 20 yr during which candidate waste forms have been under development. Unfortunately, differences in experimental procedures make correlation of these data difficult. Consequently, a major function of the MCC is to provide standardized methods for assessing the chemical durability of waste forms.

2.1 PURPOSE OF THE WORKSHOP

As the first step toward a standardized methodology for these measurements, the MCC developed a set of proposed standard leach procedures. The procedures apply to high-level waste (HLW) forms, although they may also apply to transuranic (TRU) and low-level waste forms. Several different tests are believed necessary to accommodate the differing data requirements of waste form development, plant operation, repository design, and licensing. The purpose of the MCC Workshop on Leaching of Radioactive Waste Forms was to initiate a peer review of the set of proposed tests (see Appendix A) and to obtain feedback on their adequacy from users and potential users of the leach data.

2.2 ORGANIZATION OF THE WORKSHOP

Representatives from the various organizations concerned with the leaching of radioactive waste forms were invited to participate in this workshop. A list of these participants and their addresses is given in Appendix B.

The agenda of the workshop is given in Appendix C. To ensure that all issues received approximately equal attention, the participants spent about half of their time in small working groups that met in concurrent sessions. The assigned topics for the working groups were as follows:

- Working Group 1--Waste Management Criteria
- Working Group 2--Scoping Tests
- Working Group 3--Data Base for Modeling
- Working Group 4--Rate-Controlling Mechanisms
- Working Group 5--Data Reliability.

2.3 ARRANGEMENT OF THIS REPORT

The objectives of this report are to give an account of the peer review of the proposed MCC leach test development program and to document the changes in the program that are planned as a result of this review. Accounts of the discussions relating to the topics assigned the individual working groups are given in Section 3. The issues raised at the workshop are tabulated in Section 4 and their resolution by the MCC is discussed. In particular, a

tentative revision of the proposed MCC leach test procedures is presented to permit comparison with the preworkshop procedures (Appendix A). Finally, comments were solicited from the participants after the workshop. These have been collected in Section 5.

3.0 WORKING GROUP REPORTS

This section contains reports on the deliberations of the individual working groups. The reports were prepared by the discussion leaders, who incorporated comments from the working group participants.

3.1 WORKING GROUP 1--WASTE MANAGEMENT CRITERIA

The assignment for Working Group 1 was to assess if the proposed MCC leach test development plan will provide the data required to comply with the applicable criteria and to recommend any changes needed in the proposed MCC plan. The participants were as follows:

Wayne Ross, MCC, Discussion Leader

Art Bauer, Office of Nuclear Waste Isolation, Battelle-Columbus

Jeff Braithwaite, Sandia Laboratories

Albin Brandstetter, Assessment of Effectiveness of Geologic Isolation Systems, Pacific Northwest Laboratory

Malcolm Knapp, Nuclear Regulatory Commission

Larry Penberthy, Penberthy Electromelt

Hank Schilling, Human Affairs Research Center.

3.1.1 Summary

No formal criteria are currently available from which to judge the applicability of a leach test. Current draft criteria can provide some guidance. The draft NRC 10 CFR 60 criteria include the requirements for a 1,000-yr package and a release rate limited to 10^{-5} to 10^{-7} parts/yr from the repository thereafter.

One implication of the 1,000-yr package criteria is that the waste form will likely not be exposed to high-temperature leaching conditions as part of its expected performance, since the potential for high temperatures is gone after 1000 yr.

Expected repository conditions are not defined. However, it will be assumed that a repository contains water. The Office of Nuclear Waste Isolation (ONWI) has the primary responsibility to define repository conditions for DOE programs.

3.1.2 Waste Management Criteria

National Academy of Sciences^(a)

Criteria 3.4.2. "The interaction of water, repository rock, and waste material should be controlled in such a way as to minimize the rate of dissolution of the waste form."

Discussion Summary. Such criteria will be agreed to by nearly everyone, but they are not useful in designing tests or defining conditions.

Environmental Protection Agency^(b)

Draft Criteria 191.03(a). "The annual dose equivalent to any member of the public is less than 25 millirem to the whole body..." during the operational phase.

Draft Criteria 191.12. Different releases are allowable for "expected process," and "unintended events."

Draft Criteria 191.13. a) "Disposal systems... shall consist of multiple passive engineered and natural barriers."

e) "...Institutional controls shall not be relied upon for longer than 100 years after disposal."

Draft Criteria 191.14. a) "No wastes will be released to the accessible environment due to expected processes for 1,000 years after disposal.

b) Projected releases to the accessible environment are specified in curies."

(a) National Academy of Sciences, August 1978. Geological Criteria for Repositories for High-Level Radioactive Wastes.

(b) From Working Draft No. 8, 12/10/79.

Discussion Summary. Both allowable dose and specific release values require the use of mathematical models to back calculate to allowable leach rates. Model predictions may have uncertainties of 10^3 . Such a large uncertainty makes the conversion to leach rates of limited value. For comparison, projected releases were converted to release fractions. For example, ^{241}Am can be released at the rate of 10^{-12} fraction/yr; and ^{239}Pu released at 10^{-10} fraction/yr; and ^{99}Tc at 10^{-7} fraction/yr, assuming the repository contained the waste from the operating lifetimes of 100 reactors of current design.

It was commented that the Environmental Protection Agency (EPA) may be unrealistic in its expectations and that its criteria have not been given adequate peer review. The institutional control period may be important in defining scenarios for failure modes and corresponding data needs.

Nuclear Regulatory Commission--10 CFR 60.^(a)

The first part of 10 CFR 60 is the procedure rules and the second is the draft technical rules, which are our major interest.

Applicable Draft Criteria.

- 1) "Each waste package shall be designed to provide reasonable assurance of containment of radionuclides for at least the first 1,000 years... and for as long thereafter as is reasonable achievable."
- 2) "The underground facility shall be designed to provide... containment of all radionuclides for the first 1,000 years... and as long thereafter as is reasonably achievable assuming expected processes and events and that some of the waste dissolves soon after decommission."
- 3) "After the period of radionuclide containment... radionuclides present in HLW will be released from the underground facility at a rate that is as low as reasonably achievable and is in no case greater than an annual rate of one part in 100,000 of the total activity present in HLW within the underground facility 1,000 years after decommissioning..."

(a) Draft No. 7, August 28, 1979.

- 4) "...preserve the option to retrieve the waste during the entire operational period and for a period of 50 years after all of the waste has been emplaced if the geologic repository has not been decommissioned."

Discussion Summary. The discussion centered on defining several terms in the criteria:

- One-thousand-year protection can be provided by any barrier, even a coating on the waste form.
- The release fraction that the Nuclear Regulatory Commission (NRC) is considering is actually a range from 10^{-5} to 10^{-7} parts/yr.
- The "parts" have not been defined, but it appears that they will be defined as the then current inventory of specific nuclides.
- It is considered that water in the repository is an expected condition. NRC plans to define what conditions are to be "expected conditions." ONWI has a major responsibility in this area.
- The allowable limits will be lowered as required to compensate for uncertainty in measurements.
- NRC has chosen to apply criteria to the waste package, repository, and geology whereas EPA criteria apply to the accessible environment. NRC is trying to reduce uncertainty in performance assessments.
- The 1,000-yr protection of the waste form will allow repository temperatures to cool. Therefore, high-temperature tests only apply to "unintended conditions," and may not be needed as a major emphasis in testing.
- The retrievability requirement may also limit upper repository temperatures.

Office of Nuclear Waste Isolation

Criteria. The following comments were made about ONWI criteria:

- 1) These are to be applied to all of the Nuclear Waste Terminal Storage (NWTs) program.
- 2) The Interagency Review Group (IRG) report was cited as a reference for the need for a systems approach to multiple barriers and a defense in depth philosophy.
- 3) The ONWI criteria are subject to modifications of EPA and NRC regulations.
- 4) The waste form is to be designed to limit the release rate from the package.

Waste Isolation Pilot Plant and Seabed

Criteria. The following comments were made about Waste Isolation Pilot Plant (WIPP) and Seabed criteria:

- 1) There is no limit on leach rate for TRU wastes.
- 2) Sea sediment is given total credit in Seabed disposal. No leach requirement is currently considered.

Discussion Summary. TRU wastes have large volumes and are not well defined. The seabed program is planning to consider a tailored ceramic waste form.

3.1.3 Future Criteria Actions

NRC plans to issue an Advanced Notice of Rule Making on 10 CFR 60 about the end of April. Five to six months will probably be required after that before a proposed rule can be published.

An Interface Working Group is currently working on defining repository conditions.

3.1.4 General Items and Comments

- Concern was expressed about the ability to apply the standard leach tests to waste forms in a metal matrix.
- To apply leach data to NRC release fractions, we need to consider engineering-scale products.

- For the comprehensive tests, it will be important to determine the importance of speciation of radionuclides in the leachate.
- Waste form behavior with distilled water will not always give a good correlation with behavior in a repository. Groundwaters need to be considered in testing a waste form for a specific site.
- The effect of flow rates in dynamic tests should be understood because currently measured flow rates in geology may result in saturation of the leachate and limit releases.
- Ions which provide major dose in repository models such as ^{129}I and ^{99}Tc should be considered in leach-rate measurements.

3.2 WORKING GROUP 2--SCOPING TESTS

The assignment for Working Group 2 was to assess if the proposed MCC leach test development plan will satisfy waste form developer needs for simple, rapid screening tests. In particular, the group was to review the MCC draft standard for a scoping static leach test. The participants were as follows:

Joe Westsik, MCC, Discussion Leader
David Coles, Lawrence Livermore Laboratory
Bill Coons, Basalt Waste Isolation Program, Rockwell Hanford Operations
Kevin Flynn, Argonne National Laboratory
Alan Harker, Rockwell International Science Center
Andy Johnson, Rockwell International, Rocky Flats
Mike Kupfer, Rockwell Hanford Operations
Robert Schuman, Exxon Nuclear Idaho Co., Inc.
Richard Tallman, EG&G
John Stone, Savannah River Laboratory.

The members of Working Group 2 represented a broad spectrum of interest and experience in chemical durability measurements for such waste forms as glass, synroc, concrete, clay and alumina-based ceramics, and spent fuel. They included waste form developers, characterization experts, and those interested in the final repository.

3.2.1 Summary of Group Presentations

The working group started its activities with 10 minute presentations by each member of the group. Some of the points made during these presentations are listed below:

- 1) Multibarrier waste forms, such as metal matrices and coated ceramics, present special problems for leach testing. It may be necessary to develop special procedures to test the waste form inside the barriers. This is especially important relative to transportation.

- 2) Cold-seal vessels are not acceptable for high-temperature leaching when the solubilities of some species are exceeded.
F. W. Dickson^(a) has proposed a vessel that permits hot sampling.
- 3) It is important to consider pH, temperature, and oxygen and carbon dioxide fugacities during leach testing. Leach rate measurements should be made over several time periods so that the indicated durabilities are not influenced by changes in the waste form, e.g., a sloughed-off surface layer.
- 4) Monoliths have been observed to give higher leach rates than powdered samples of the same waste material. With powdered samples, it is important to use a screened fraction rather than a whole spectrum of particle sizes. Screening may cause some segregation of product.
- 5) The American Nuclear Society (ANS) leach test standard is inconvenient because the specified leach intervals require sampling on off-shifts and weekends. Leach tests should be convenient to the user to encourage implementation.
- 6) Weight loss measurements are not acceptable indications of durability. They do not reveal the behavior of individual ions and they are hard to obtain with sufficient accuracy, especially with high-durability waste forms.
- 7) Other conclusions were that a Soxhlet temperature of 99°C should not be required, because it exceeds the boiling temperature at higher elevations. In addition, some study of the effect of reflux rate on leach rates must be made. The drip from the condensor must not fall directly on the sample.
- 8) The surface condition of the sample can influence leach rates and subsequent surface analysis. The surface should not be touched after it has been cleaned.

(a) F. W. Dickson, January 1963. American Journal of Science. 261:61-78.

3.2.2 Standard Scoping Static Leach Tests

Discussion of the standard scoping static leach test revolved around the sample form and its preparation. Although no significant changes were recommended in the procedure, the interpretation of results must be altered. The working group did suggest a change in the temperature of the test from 40° and 99°C to 30° and 70°C.

The biggest concern in the leach test procedure was sample form and preparation. The draft procedure calls for polishing the waste form with 600-grit paper. The intent was to reduce the uncertainty in the surface condition due to cutting, interactions with molds, press linings, etc., or volatilization. The conclusion of the group, however, was that polishing created more problems than it solved. Polishing is relatively easy to do for glasses, but difficult for ceramics and concrete. With dry polishing, some waste forms may tend to chip and the chips then cut new gouges into the surface. Therefore, little is gained.

The use of powdered samples to obtain a fresh surface was discussed. Powders can give good indications of the durability of a waste form, and they release a large quantity of material to the solution, which simplifies chemical analysis. Powdered samples are harder to clean, however, due to the fines generated in the crushing operation. Crushing and sieving are not easily done in the hot cell. Results obtained at Exxon Nuclear Idaho, PNL, and Argonne National Laboratory all confirm that observed leach rates are lower for powder than for monoliths of the same waste material. Consequently, the working group preferred to use the monolithic samples or discrete samples, i.e., coated particles. The working group suggested that the MCC study the effect of surface preparation on leach rate.

Based on the considerations described above, the working group made the following recommendation: the samples are to be cleaned and leached without any additional surface preparation being required. Describe any surface treatment. After 3 days, the leachate is removed and fresh leachate is added to the bottle. The sample is then leached an additional 11 days. Both the 3- and 11-day leachates are analyzed, but the durability is based on the

11-day results. The 3-day leach serves as a preleach to reduce surface effects. However, this leachate is analyzed to detect waste forms that show unusual releases during the initial contact with water.

The use of buffers to control pH and oxygen potential was discussed. These two parameters can have a significant effect on the durability of some waste forms. For example, spent fuel will be much more soluble under oxidizing conditions than under reducing conditions. Most of the working group felt that, while there is sound scientific basis for controlling pH, and Eh in some cases, this would introduce complexities to the procedures that many people would not be willing to implement. The rejection of the International Atomic Energy Agency (IAEA) test was cited as an example of what happens when unwarranted complexities are required. However, in the long-term and autoclave tests, some type of pH and oxygen fugacity control may have to be required. It was suggested that these controls also be used when the MCC uses the scoping tests as part of tests for thermal and radiation stability. As it stands, the scoping static test is most valuable for intracomparison. The preamble to the test should be modified to emphasize this application. Since long-term detailed tests should include pH and Eh control, the scoping test may not have a direct correlation.

It was re-emphasized that weight loss should not be a primary indication of durability, though it still should be monitored. Activation analysis should be considered as an alternative method for solution analysis. Since not all wastes contain the same elements, an alkali, some of the matrix materials, and an actinide should be monitored. The elements listed in the draft procedure are not applicable to all wastes.

Keeping several particles 5 mm apart as required in the draft procedure will be difficult. The statement should be changed to indicate that the particles should not touch. Leaching individual particles in separate bottles may introduce contamination from each additional bottle.

3.3 WORKING GROUP 3--DATA BASE FOR MODELING

The assignment for Working Group 3 was to examine why almost none of the large amount of collected leach data is being used by mathematical modelers and to recommend methods to establish compatibility between the experimental leach test data base and mathematical models. The participants were as follows:

John Mendel, MCC, Discussion Leader

Ernie Bryant, Los Alamos Scientific Laboratory

Hans Claassen, United States Geological Survey

Ed Compere, Oak Ridge National Laboratory

Jeffrey Fong, National Bureau of Standards

Keith Harvey, Whiteshell Nuclear Research Establishment

Mark Harwell, Consultant

Kyo Kim, Nuclear Regulatory Commission

Stan Logan, Los Alamos Tech. Asso.

Bernie Wood, Basalt Waste Isolation Program, Rockwell Hanford Operations.

3.3.1 Discussion

Mathematical modeling, or computer modeling, is a convenient method of conducting parametric analyses of complex systems. It is being applied to risk analyses of nuclear waste disposal. These risk analyses are expected to play a major role in demonstrating the safety required by the NRC for licensing of geologic repositories.

Mathematical modeling for repository safety studies requires the combination of several subroutines, including a source term model, a migration model, a pathways model, and a dose-to-man model. The source term model defines the injection rate of radionuclides into the postulated path through the repository overburden into the biosphere. The confidence with which the source term can be defined depends on how well the leaching mechanisms for waste forms in geologic repositories are understood. At present, these mechanisms are not sufficiently understood to be incorporated into the source term models. Instead, simplifying assumptions are made; a constant leach rate is assumed,

based on examination of the data in the literature and an arbitrary selection of a "steady-state" value. The "steady-state" values has been obtained from dynamic leach test data rather than from static leach tests that probably more closely represent the real situation. It is generally agreed that the MCC leach test procedures should be designed to help rectify this situation. One way in which to help provide information on basic mechanisms is to isolate and evaluate contributory factors individually.

3.3.2 Results of Discussions

After discussion the group agreed, with various degrees of unanimity, on four resolutions:

- 1) Mechanistic research is relevant and essential in meeting regulatory requirements. There was a lack of agreement on how much emphasis should be placed on the waste form/water subsystem and how much should be placed on the overall system. The proposed NRC fractional release was discussed and it was obvious more understanding of existing data was needed.
- 2) The MCC tests should be modified to provide information on mechanistic models. Terms like "equilibrium groundwater" were not considered sufficient. Buffering of pH and Eh were given as examples. The goal is to have the tests applicable to "checkable" models.
- 3) Groups 3 and 4 should meet together in the near future to propose modifications of the MCC tests.
- 4) The MCC should recognize that requirements for data to use in models exist now and assist in supplying that data. Attention must be paid to near-term needs. Specifically, source term data are needed for initial repository site screening, site evaluation, and site selection. The more fundamental mechanistic research is also required but that will require a long time.

3.4 WORKING GROUP 4--RATE CONTROLLING MECHANISMS

The assignment of Working Group 4 was to assist the MCC in determining what information is needed to obtain leach data that fully accounts for the effects of basic leach-controlling mechanisms. The participants were as follows:

Ray Turcotte, MCC, Discussion Leader

John Bates, Argonne National Laboratory

Dave Clark, University of Florida

John Wiley, Savannah River Laboratory

Herschel Godbee, Oak Ridge National Laboratory

Howard Kingston, National Bureau of Standards

Gary McVay, Pacific Northwest Laboratory

David Silviera, Assessment of Effectiveness of Geologic Isolation Systems,
Pacific Northwest Laboratory

Joe Simmons, Catholic University

Will White, Pennsylvania State University.

The group discussion began with short presentations by each of the group members on some aspect of his philosophy concerning mechanisms of waste form leaching. We specifically discussed four areas of recurring significance in durability testing--temperature dependence, time dependence, congruency, and geologic effects. The following sections summarize the comments.

3.4.1 General Comments

The leach tests need to be directed toward evaluating mechanisms, rather than based on convenience or other reasons. Although evaluating mechanisms is an objective, the tests will also need to be conducted in hot cells as performance "proof" tests.

A significant effort on simple systems is needed, in parallel with studies of complex waste forms, and standard reference materials must be defined. The level of accuracy needed in long-duration tests is basically the best achievable, in view of the need for lengthy extrapolations. Ideally, the leach tests need to proceed sufficiently long for steady-state conditions to be defined, both with respect to solution concentration changes and

solid-state changes. Demonstration of material balance between solution and solid-state analyses is clearly desirable.

Finally, the leach problem is exceedingly complex relative to fundamental mechanisms. The test procedures will therefore need to be continuously re-evaluated (improved) as our understanding increases. One method for achieving this would be to include as a separate report within the Materials Handbook a discussion of observed problems and revised limits for the test procedure.

3.4.2 Scoping Tests

There is a better understanding of leach behavior under high-dilution conditions than in closed or limited flow tests, but the latter are more relevant to repository conditions. The static scoping test (MCC-1) should be presented in two different forms: Test A would be done by waste form developers and would include evaluation of the time dependence; e.g., 5 different time periods of up to 1 month (a different sample for each time). Test B, for process control, would be simpler; e.g., 1 or 2 time periods. The two versions are recommended because very durable materials may have a high initial leach rate; but, with time, a durable protective film, for example, may become established. Relative to quality assurance testing, the time dependence for leaching a given waste form composition (Process X) will already have been well established and only a check point will be needed.

A standard leach temperature of 99°C was viewed as too high. Exfoliation was observed in one laboratory, probably related to a boiling problem. Temperatures of 90° and 40°C were suggested as reference temperatures. It was also noted that the bottle geometry needed to be defined to avoid the possible use of a long tube as the leach container.

Surface preparation in short-duration tests was discussed. It was decided that chemical treatment (e.g., HF etching) would probably not be suitable. In addition, mechanical polishing would not be possible for porous materials. Therefore, the possibility of using diamond-sawed surfaces should be considered. A specification on the blade type and sawing conditions (coolant, etc.) is needed.

3.4.3 Temperature Dependence

There is an Arrhenius temperature dependence for both glasses and crystalline waste forms that is remarkable, since the intuitive feeling is that the mechanism is not constant even for homogeneous glasses (say from 25° to 250°C). It was also commented that there have not really been careful enough studies to see definite breaks in $1/T$ plots and that typical error bars may preclude seeing such subtleties. However, understanding the temperature dependence is less important at this time than understanding the time dependence.

3.4.4 Time Dependence

It has been generalized in the past that a square root of time dependence on the amount leached suggests diffusion control, while a linear dependence suggests a corrosion mechanism. These broad conclusions are really too simple. A better understanding of diffusivity is needed relative to chemical and physical changes occurring at the surface of the waste form.

3.4.5 Congruency

The normal mechanism of material loss from both glasses and crystalline forms is by incongruent leaching. The insoluble heavy metals tend to be left behind, except perhaps in the case of high-dilution tests. In many silicate systems, durability tests at high pH may lead to linear kinetics with respect to silica; but this does not mean that all elements accumulate in the leachate in constant proportions. The term "network dissolution" was suggested as a more appropriate term than congruent dissolution.

3.4.6 Geologic Effects

Leach testing with silicate groundwaters does not give markedly different results than distilled water and the general direction is toward suppression, likely because of back-reaction effects. Generic-simulated groundwaters containing only the major constituents would be preferable compared to use of site-specific compositions (i.e., all constituents present).

Tests with salt brine are needed since the basic leaching mechanism may be different. Brine composition needs further evaluation (for Mg especially).

A lower pH value during the tests and increased importance of ion exchange reactions are likely to be involved in salt brine reactions.

3.4.7 Surface Analysis

If any real understanding of mechanisms is to be achieved, thorough depth-profiling elemental analyses of the solid must be undertaken (e.g., ESCA, SIMS, ion microprobe, etc.).

3.4.8 Solubility Considerations

There are well known solubility/pH diagrams for simple oxides (sometimes including CO_3^{2-} or SO_4^{2-} effects) in the geologic literature which have not yet been applied to the interpretation of waste form leach kinetics. There is a very steep negative dependency of solubility with increasing pH for alkaline earths, transition elements, rare earths, etc., of approximately one order of magnitude for each unit change in pH. At the same time, it is also well known that silica shows increasing solubility with increasing pH. There is, in fact, increasing evidence of these differing chemistries (in surface profiling studies) and a corresponding need for including these dependencies in any models of the leaching process.

3.5 WORKING GROUP 5--DATA RELIABILITY

The assignment of Working Group 5 was to examine the factors involved in providing confidence in the accuracy and reproducibility of leach test data and to recommend techniques that can be used by the MCC to document leach test reliability. The participants were as follows:

Dennis Strachan, MCC, Discussion Leader
Doug Brookins, University of New Mexico
Clarence Homi, Rockwell Hanford Operations
Pete Macedo, Catholic University
Larry Machlan, National Bureau of Standards
Jim Merrill, MCC
Dan Merz, MCC
Tony Wolterman, Mound Laboratory.

3.5.1 Introduction

The group focused on the four major areas of leach rate units, required accuracy and precision, test procedure requirements, and problems with currently available data. Discussion on each of these items is summarized below. In addition, some other areas of concern are briefly summarized. The results of this working group's efforts can only hope to provide general direction, since the development of qualified test procedures by such groups as the American Society for the Testing of Materials requires many years.

3.5.2 Required Accuracy and Precision of Data

When determining the composition of the waste form, the accuracy (defined as the combination of bias and random error) of the data will more likely be dictated by analytical sample preparation rather than the analytical methods per se. The MCC should suggest analytical methods to be used in the analysis of the solids. Accuracy of the data on major components is likely to be good and will decrease for minor components as their concentration decreases. A similar statement can also be made about the analytical data for the leach solutions.

It was generally accepted that there need to be standard waste forms. Initially, these could be generic for the three major categories of high-temperature crystalline ceramics, low-temperature ceramics (i.e., cements), and vitreous forms. As time goes on, there will need to be additional standards of other types. The first standards will be made from nonradioactive materials. Prior to round robin testing of the standards and procedures, the MCC needs to perform statistical (ruggedness) tests to define components of the individual experimental tests that yield major effects on the final results. For instance, portions of the leach test procedures could lead to major changes in the measured leach rate when small changes are made inadvertently. When these are identified, the test procedure can then be written to include greater detail to ensure reliable and reproducible data from the subsequent round robin tests used to qualify standard materials. A generalized procedure for the development of a standard material is shown in Figure 1.

FIGURE 1. Development Procedure for Standard Material

3.5.3 Requirements for Procedures

As discussed above, the MCC needs to scrutinize the proposed tests for areas within the test procedure that yield major effects in the value of the desired property. (Although this workshop is concerned with the leach tests, this statement concerns all tests.) For instance, the method of preparing the surface of the sample may have a large effect on the leach rate. These effects should be clearly identified in the test procedure and the test procedure carefully worded to minimize the associated error. To best identify these effects, ruggedness or statistical testing of the procedure should be done by the MCC before the procedure is issued.

Use of a working standard by the individual laboratories was suggested as a means of routinely checking the laboratory's performance. This reduces the pressure on the limited supply of the primary standard while serving the need to ensure quality data. Although the group did not suggest a specific frequency for running primary standard checks, the frequency is likely to be low enough to make a working standard valuable. As a working standard, a commercially available borosilicate glass, which is readily available from a number of vendors in a variety of shapes, could be used. Sufficient quantities of this material would be purchased to supply the needs between periodic primary standard checks. Once "standardized" against the primary standard, this material would then serve as a working standard.

Another question discussed by the group was what to do when a laboratory is out of conformance with established data during a primary standards check. In a unanimous decision, the group indicated that the data would need to be reviewed and, if reconciliation could not be made, all data taken since the last primary standards check would be disqualified and not suitable for inclusion in the Materials Handbook. Thus, the use of a working standard was again encouraged.

Water quality may be important in the leaching of waste form samples. Therefore, the MCC should include in its ruggedness testing program the effect of water quality (i.e., dissolved gases, deionized versus distilled water,

etc.) on the leach rate of a reference material. This may lead to a specification for water treatment in the test procedure.

The required accuracy and precision of data are likely to depend upon the test (e.g., scoping versus long-term tests).

3.5.4 Problems with Currently Available Data

With few exceptions, the following problems were identified with currently available data:

- 1) lack of standards
- 2) lack of replication with an explicit statement of number of replicates and the methods of data treatment
- 3) in general, surface area measurements that are inaccurate and usually estimated
- 4) lack of sufficient characterization of the materials on which the leach tests were performed
- 5) lack of temperature control, especially in experiments run at room temperature
- 6) variability of test conditions, which make comparisons of data difficult.

3.5.5 Leach Units

Currently, leach rates are expressed in units of $\text{g}/(\text{cm}^2 \cdot \text{d})$. These are calculated using the equation

$$\text{LR} = \frac{m}{f \cdot S \cdot t}$$

where

LR = leach rate

m = total mass of element X leached from the waste form (grams)

f = mass fraction of element X in the waste form (unitless)

S = geometric surface area (cm^2)

t = time (days)

It is recommended that the MCC express leach rate in the SI units of $\text{kg}/(\text{m}^2 \cdot \text{s})$. However, in addition to the leach rate or plots of the leach rate versus time, additional data need to be presented which are of use to other scientists. Examples of the needed data are densities, solid composition (actual or calculated from the batch), and leachate composition versus time.

Generally it was determined that the unit of normalized moles/ cm^2 as given by the expression

$$\text{normalized mol}/\text{cm}^2 = \frac{\text{mass of element X leached}}{\left[\begin{array}{l} \text{at. frac. of} \\ \text{element X in} \\ \text{waste form} \end{array} \right] \cdot \left[\begin{array}{l} \text{at. wt. of} \\ \text{element X} \end{array} \right] \cdot \left[\begin{array}{l} \text{surface} \\ \text{area} \end{array} \right]}$$

would not yield any additional information to the presentation of the data.

3.5.6 Additional Comments

A few additional comments from this working group are as follows:

- Ruggedness tests should be done using materials with both high and low leach rates.
- Ruggedness tests must include the randomization usually found in such tests.
- Meetings of this working group may be necessary when round robin tests begin.

4.0 FOLLOW-UP ON WORKSHOP

The MCC has taken several steps as a result of the workshop. These are described in the following subsections.

4.1 COMPILATION OF ISSUES AND TENTATIVE RESOLUTION BY MCC

A summary of the many issues that were discussed at the workshop is given in Table 1. Although an effort has been made to group related issues together, it is believed that completeness is more important than precise categorization at this time. In addition, there has been little attempt to represent priorities by the relative placement of the issues in Table 1. The proposed resolution of each of the issues is indicated in the table and, in most cases, is discussed further in the following subsections.

4.2 REVISION OF PROPOSED MCC LEACH TESTS

Peer review of an outline of the total set of leach tests proposed by the MCC (Appendix A) and a detailed Scoping Static Leach Test was initiated at the workshop. Modifications have been made in both as a result of contributions from the workshop.

4.2.1 Revision of Overall MCC Leach Test Program

A major criticism was that the purposes of the different proposed MCC leach tests were not sufficiently defined. The major end uses of the leach test data can be described as follows:

- 1) developing an understanding and obtaining a consensus on the mechanisms that control leaching from various solidified waste forms
- 2) defining "quantitative" values for the agreed-upon mechanistic parameters so that mathematical models can be used to predict long-term leaching behavior
- 3) comparing the chemical durability (resistance to leaching) of different types of waste forms, i.e., intercomparison of waste forms

TABLE 1. Compilation and Proposed Resolution of Issues Discussed at Workshop

Issues	Proposed Resolution
1. The NRC is proposing a fractional release/yr specification for geological repositories. It is not clear how the MCC leach tests relate to this proposed specification.	It is an MCC responsibility to develop this relationship; however, this cannot be done until the NRC specification is defined more fully.
2. Purposes of different leach tests in MCC test development plan were not well defined.	Definition will be expanded. See the section on revision of proposed leach tests.
3. The MCC tests should be modified to provide information on mechanistic models.	Another meeting will be held to focus on this issue. See section on coordination with mechanistic research.
4. The presence of rocks makes the results of leach test difficult to interpret.	Rocks have been deleted from MCC leach tests. They will be included in "systems" tests. See section on revision of proposed leach tests.
5. Interfaces of MCC leach test development program with other organizations and programs, such as WRIT, mechanistic research, and NBS, are not well defined.	MCC is a new program; interfaces will evolve with time if good communication is maintained. The MCC will take the initiative in this area.
6. Methods to be used in reporting MCC leach test results need to be clarified.	Resolution is not required at this time. The raw data can always be consulted.
7. Methods have not been established for determining the statistical testing requirements for leach procedures.	This is an MCC responsibility. See section on organization of a round robin.
8. Although there was agreement on the desirability of conducting a round robin with an MCC leach procedure, details remained undefined.	Another meeting may be held to focus on this issue. See section on organization of a round robin.
9. There was agreement on the need for standard materials and standard solutions that can be used for checking procedures in individual laboratories, but no mechanism exists for defining what kind and how many standards are needed.	This is an MCC responsibility. The MCC will obtain a consensus on the needs and implement procurement in cooperation with NBS.
10. There were questions concerning whether the MCC should concern itself with scoping (screening) tests, or whether it should concentrate on more rigorous long-term tests.	The MCC tests will be designed to rigorously define behavior over long periods; however, they can be adapted for screening purposes simply by running for only a short time. See section on revision of proposed leach tests.
11. The surface condition of samples is a key element in leach testing. Agreement must be obtained on how to standardize this key element.	Some consensus toward standardization on a diamond-sawed surface was obtained. This will be evaluated in the MCC leach test development plan.
12. Multibarrier and matrix waste forms pose problems in sample preparation, particularly concerning how the samples should be prepared when the results will be used to compare these composite waste forms with noncomposite forms.	Standardization in this area appears undesirable. It will probably be necessary to test the components of composite waste forms separately <u>and</u> to test the composite as a whole.
13. The proposed NRC requirements of a waste package that retains its integrity for 1,000 yr essentially precludes contact of water with the waste form at temperatures above 100°C, yet the MCC leach test program includes temperatures to 250°C.	The high-temperature tests are not emphasized in the MCC program; but they are included as a convenient way of accelerating reactions to steady-state.
14. There are a large number of variables that can potentially affect leach rate and the relative impact of the variables is waste form dependent. The standard tests should have the flexibility to permit measurement of these effects.	The MCC tests will have the required flexibility. There will be certain recommended conditions but other conditions are permitted, <u>provided they are defined with sufficient analytical precision and accuracy by the test operator.</u> See section on revision of proposed leach tests. This will permit the use of site-specific geological fluids, for example.

- 4) comparing the leach rate of different batches of the same type of waste form (to optimize compositions in a research and development program or as a quality control measurement in an operating plant), i.e., intracomparison of waste forms.

This list probably represents the basic priorities of the MCC in descending order. The MCC will be the authoritative source of fundamental nuclear waste form leaching data. Therefore, its first priority must be to ensure that MCC leach data can be interpreted as well as possible in terms of mechanistic principles and statistical reliability, which in turn can be the bases of mathematical models for extrapolating expected behavior far into the future.

It is also recognized that an immediate need exists in many laboratories for standardization of tests for inter- and intra-comparison of waste forms. This type of data will be too voluminous to expect more than a small fraction of it to ever be included in the Materials Handbook; yet ideally it should all be "traceable" to the authoritative data in the Materials Handbook. The proposed MCC tests permit this "traceability" because the tests all include time as a variable. For much of the routine testing that is done for inter- or intra-comparison, the tests can be terminated after short times; to produce authoritative data for the Materials Handbook, the tests would be continued to full term.

The MCC leach tests fall into two basic categories--static and dynamic. The tests thus evaluate behavior at the two limiting boundary conditions with respect to flow rate of the leachant. The static tests apply to the "saturated" boundary condition, where concentrations of leached ions can build up on the surface and slow the reaction rate. It is probable that most of the leaching that occurs in the repository will occur at conditions that approximate the "saturated" boundary case.

The other limiting boundary case is that of infinite dilution at the surface of the waste form. This is a hypothetical case, which can only be approximated in nature, but which is convenient to treat mathematically, and

may represent the maximum possible release rate situation. It can be considered to be representative of a waste form exposed to a high flow rate of water.

The proposed MCC leach tests as revised to reflect the results of the workshop are shown in outline form in Figures 2 through 6. They may be compared with the original tests (Appendix A) by consulting Table 2.

The physical setup of the MCC leach tests has been kept simple to facilitate use with radioactive samples in hoods, gloveboxes, or hot cells. Slight modifications could be required in some radioactive tests, for instance, in a gamma pit with limited dimensions; but even in these cases, it should be possible to retain the basic test parameters.

The major change in the revised leach tests is the elimination of rocks as a test parameter. This was done as the result of comments received at the workshop. It will simplify interpretation of the waste form leach data. There is no intent to denigrate the importance of the effects of rocks in actual repository situations. Their presence can significantly alter steady-state conditions by "buffering" Eh and the concentration of important anionic and cationic species. Data on these important effects will be obtained for insertion in the Materials Handbook by conducting systems tests in which the type and amount of rock are major test parameters. The systems tests are in effect proof tests of a very complex aggregation of interactions. The

TABLE 2. Equivalence of MCC Proposed Leach Tests

Leach Test Identification Number	
<u>New</u>	<u>Old</u>
1	1 and 3
2	5A and 5B
3	5C
4	4
5	2

PURPOSE: OBTAIN DATA ON REACTION KINETICS (SHORT TIME VERSIONS OF TEST CAN BE USED TO OBTAIN RAPID INFORMATION FOR R & D PROGRAMS AND FOR QUALITY CONTROL IN OPERATING PLANTS)

PARAMETERS

STD TIME: 3, 7, 14*, 28, 42, 91, 182, 364 d

STD TEMPERATURES: 40°, 70°, 90°C*

SOLUTIONS: DI H₂O*, REFERENCE REPOSITORY SOLUTIONS, OTHERS

SAMPLE SURFACE AREA/VOLUME OF SOLUTION: 1/100 mm
(4 x 10² mm²/4 x 10⁴ mm³ RECOMMENDED)

ANALYSES

SOLUTION ANALYSES REQUIRED
(+ ACID RINSE ANALYSES)

WEIGHT LOSS RECOMMENDED

DEPTH PROFILING RECOMMENDED FOR THIN REACTION FILMS
(e.g., ESCA, SIMS)

SEM PROBE REQUIRED FOR THICK REACTION DEPTHS
(e.g., ≥ 5 μm)

PNL/MCC
0107

* REFERENCE TEST CONDITIONS

FIGURE 2. Proposed MCC Leach Test Number 1. Static Test

PURPOSE: OBTAIN DATA ON HIGH-TEMPERATURE KINETICS

PARAMETERS

STD TIMES: 3, 7, 14, 28, 42 d

STD TEMPERATURES: 150°, 200°, 250°C

SOLUTIONS: DI H₂O, REFERENCE REPOSITORY SOLUTIONS, OTHERS

SAMPLE SURFACE AREA/VOLUME OF SOLUTION: 1/100 mm
(4 x 10² mm²/4 x 10⁴ mm³ RECOMMENDED)

ANALYSES

SOLUTION ANALYSES REQUIRED

SEM PROBE REQUIRED

HOT SOLUTIONS ARE
QUENCHED WITH DILUTION

PNL/MCC
0108

FIGURE 3. Proposed MCC Leach Test Number 2. Autoclave Test

PURPOSE: OBTAIN DATA ON STEADY STATE "SOLUBILITY"

PARAMETERS

STD TIMES: 3, 7, 14, 28, 42 d (AND LONGER IF REQUIRED)

STD TEMPERATURES: 40°, 70°, 90°, 150°, 200°, 250°C

SOLUTIONS: DI H₂O, REFERENCE REPOSITORY SOLUTIONS, OTHERS

SAMPLE SURFACE AREA: POWDERED, MESH SIZE TO BE DETERMINED

ANALYSES

SOLUTION ANALYSES REQUIRED

SOLUTIONS ARE QUENCHED WITH DILUTION

PNL/MCC
0109

FIGURE 4. Proposed MCC Leach Test Number 3. Solubility Test

PURPOSE: OBTAIN DATA ON REACTION KINETICS UNDER FLOW CONDITIONS

PARAMETERS

STD TIMES: 3, 7, 14, 28, 42, 91, 182, 364 d

STD TEMPERATURES: 40°, 70°, 90°C

SOLUTIONS: DI H₂O, REFERENCE REPOSITORY SOLUTIONS, OTHERS

FLOWRATES: TO BE DETERMINED

ANALYSES

SOLUTION ANALYSES REQUIRED
(+ ACID RINSE ANALYSES)

DEPTH PROFILING RECOMMENDED AT SHORT TIMES

SEM PROBE REQUIRED AT LONG TIMES

PNL/MCC
0110

FIGURE 5. Proposed MCC Leach Test Number 4. Dynamic Test

PURPOSE: OBTAIN DATA ON REACTION KINETICS

PARAMETERS

STD TIMES: 3, 14* d

STD TEMPERATURES: 40°, 70°, 90°C*

ANALYSES

**SOLUTION ANALYSES REQUIRED
(+ ACID RINSE ANALYSES)**

SEM PROBE REQUIRED

WEIGHT LOSS RECOMMENDED

*** REFERENCE TEST CONDITIONS**

PNL/MCC
0111

FIGURE 6. Proposed MCC Leach Test Number 5. Soxhlet Test

individual interactions, such as leach rate of the waste form, should be understood as well as possible independently in order to evaluate their contribution to the overall result of the proof tests.

The tests shown in Figures 2 through 6 should be considered as a set, each test being of approximately equally importance; i.e., none of the tests can be considered a priori to outweigh the others in significance. It is expected, however, that Test 1 will become the "workhorse" and be used more than the others. The tests are designed to yield data on the kinetics of the approach to "saturation" (Tests 1 and 2) and on the limiting "saturation" conditions (Test 3). Test 4, in which flow rate is a test parameter, enables investigation between the two limiting boundary conditions, and Test 5 approximates the infinite dilution boundary case as closely as possible.

For each standard leach test procedure, it will be important to know the magnitude of both the random and systematic errors that are to be expected when the procedure is used at a particular laboratory on a given waste form. In addition to knowing the expected magnitudes of these errors, it is also

important to understand which of the potential sources of error are actually the major contributors so that their contribution can be carefully controlled. An efficient approach to obtaining such information is through the use of statistical experimental designs along with an examination of the experimental data using analysis of variance. Factorial designs and nested designs have proven to be valuable in such studies. An analysis of variance of data from an appropriately designed experiment will permit the partitioning of the total variation into contributing sources such as 1) differences among test specimens, 2) differences among samples from the leachant, and 3) differences due to the analytical measurements. If standard waste forms having assigned leach rates are incorporated in the experimental design, then the expected systematic errors (biases) also can be investigated.

4.2.2 Revision of Detailed Scoping Static Leach Test

As shown in Table 2, the Scoping Static Leach Test is now incorporated in revised Test Number 1. As a result of comments made at the workshop, some minor revisions have been made in the details of the Static Leach Test. The revised Static Leach Test is presented below.

DRAFT

PROPOSED STATIC LEACH TEST (MCC-1)^(a)

Materials Characterization Center
Pacific Northwest Laboratory
Richland, Washington
March 20, 1980

I. SCOPE

The static leach test provides a set of reference conditions for both routine and long-duration evaluation of nuclear waste solids. Short experiments may be used to develop waste forms through studies of compositional effects, heat treatment, radiation effects, etc. A single reference condition is suggested (14 days, deionized H₂O, 90°C) for use as a screening or quality assurance test.

When the procedure is followed to long times, it provides a kinetic evaluation of the limited-water-volume boundary condition. Other tests define kinetics at the high-dilution boundary and as a function of flow rate within these two limits. The static test provides data needed to estimate the time required to reach maximum "steady-state" solution concentrations as a function of temperature and groundwater chemistry. In essence, the test is one of the simplest conceivable, requiring only that a solidified, monolithic material of known surface area isothermally contact water of a fixed volume. The reference condition specifies that the geometric sample area/water volume = $4 \times 10^2 \text{ mm}^2 / 4 \times 10^4 \text{ mm}^3$. There are standard conditions of temperature, time, and water composition. Each data point for a given time, temperature and solution requires a separate sample and leach container. A schematic of the leach apparatus is presented in Figure 7.

It is expected that many laboratories involved in waste form development or characterization will use this test method, at least in short duration studies. The conditions defined in the following text are reference

(a) This proposed test must be approved by the Materials Review Board before it will be included in the Nuclear Waste Materials Handbook. Some revision may occur before this review process is complete.

FIGURE 7. Static Leach Test Apparatus

conditions chosen through experience. Their general use will allow unambiguous comparison of results between laboratories.

II. LIMITATIONS

There are no fundamental limitations concerning the composition or type of waste form, although inorganic systems are assumed in the cleaning procedure. The material must be in a consolidated form with surfaces ordinarily prepared by cutting with a diamond saw. Because the static test defines a closed system without other contributing solids, the waste form becomes the major factor in controlling pH and the leachate composition. It becomes more dominant in either distilled water or silicate groundwaters the longer the test proceeds. In the case of concentrated salt brines or highly buffered solutions, the waste form may never dominate the leachate chemistry. While this is a limitation in a sense, the test is meant to provide a framework by which these effects can be systematically studied. Although reference conditions of surface area of sample and volume of leachate, and leachate compositions (distilled water and NaCl brine) are defined, the procedure can also be

used to evaluate these parameters over broad ranges and under site-specific conditions. When short-duration tests are used, the primary importance of the sample surface should be recognized. Comparison of results of solution analyses and elemental depth profiling of the leached solid may be needed to establish that behavior representative of the bulk material is being observed.

The Static Leach Test has obvious technical limitations, by design, in order to evaluate one major part of the problem. Other tests will be used to evaluate other aspects, as briefly described in the following section.

III. BACKGROUND AND RELATED TEST PROCEDURES

Well-defined test conditions are needed to systematically evaluate the durability of waste materials. Obviously, the tests should have relevance with respect to the conditions of final application, which in the current waste management philosophy involves disposal in deep geologic formations. The proposed static test can simulate this environment by use of specific groundwaters, but deionized water is the reference leachant. In this mode, the test isolates the waste form from geologic interactions, which are secondary compared to the interaction of water itself.

There have been a variety of tests used in evaluating waste solids, including several proposed by national and international groups. None of these closely matches the underlying philosophy of the test proposed here, because this test is designed to be compatible with several other methods being developed by the MCC, which will be used to fully evaluate all relevant parameters. At this time, the conceptual test areas which will be established within the MCC include:

- MCC-1--Static Test
- MCC-2--Autoclave Test
- MCC-3--Solubility Test
- MCC-4--Dynamic Test
- MCC-5--High-Flow-Rate Test.

Table 3 defines immediate and potential uses of the five different leach tests. There are no doubt additional categories that could be added to such a

TABLE 3. Potential Uses of Leach Tests(a)

Variable Studied	Leach Test				
	1 (static)	2 (autoclave)	3 (solubility)	4 (dynamic)	5 (high flow)
Temperature	●	●	●	●	●
Flow Rate		0		●	●
pH	●	0	●	●	
Eh	0	0	0	0	
Radiolysis	●	0	0	0	
Water Composition	●	●	●	●	0
<u>End Use (user)</u>					
Kinetics	●	●	●	●	●
Solubility	●	●	●		
Waste Form Development	●				●
Product QA	●				●

(a) Solid dots ● indicate planned.
 Open circles 0 indicate possible future studies.
 Blank indicates no probable application.

table. The end product is a description of leaching kinetics under all reasonable conditions. In addition, several of the tests provide important limiting data, especially with respect to maximum solution concentrations (Tests 1, 2, and 3) and, at the other extreme, high dilution leach rates (Test 5). The static leach test, defined by this procedure, is expected to be the most highly used test method.

As a matter of reference, other leach tests that have been formally proposed by various national and international groups include the following:

- IAEA--periodic water placement
- ISO--Soxhlet periodic water replacement
- ASTM--closed bottle, with shaking
- ANS--periodic water replacement

- TRU—periodic water replacement
- DIN—static/grains/acid titration

All of the previously proposed tests can give meaningful comparative data but give limited understanding of the leaching process. The static test proposed here is somewhat simpler than all of these. It gives a kinetic description of behavior in limited water volumes, which has been poorly defined until now. Moreover, the test is part of a broad approach evaluating all major leaching parameters.

IV. SPECIFICATIONS (SUMMARY)^(a)

The following specifications are recommended for comparative evaluation. Obviously, other time, temperature, and water chemistries can and should be used to thoroughly evaluate material properties. Underlined specifications define the primary reference conditions in the following summary:

A. Specimen

- monolithic
- geometric surface area = $4 \times 10^2 \text{ mm}^2$
- surface finish^(b)—diamond-sawed surface using commercial equipment (~5 in. wheel) or equivalent. Isopropyl alcohol should be used as the cutting fluid.
- cleaning procedure—acetone/ethanol

B. Leachant

- volume = $4 \times 10^4 \text{ mm}^3$ ($\text{SA/V} = \underline{1/(100 \text{ mm})} \pm 2\%$)
- deionized water
- brine, 80 saturated NaCl (269 g/l)
- others as desired

(a) Standard International (SI) units are used throughout this report.

(b) A study of surface finish effects on short-time leach behavior showed differences of 5% to 40%, depending on treatment. A diamond-sawed surface with no further mechanical or heat treatment steps gives a conservative (high) leach rate.

C. Apparatus

- nonreactive sealed container (e.g., Teflon® or polyethylene)
- sample near centroid of leach volume (see Figure 7)
- leach container maintained at constant temperature ($\pm 1^{\circ}\text{C}$) in bath or oven.

D. Standard Conditions

- temperatures-- 40° , 70° , $90^{\circ}\text{C} \pm 1^{\circ}\text{C}$
- times--3, 7, 14, 28, 42, 91, 182, 364, and longer times (days $\pm 2\%$).

V. PROCEDUREA. SpecimenWaste Form Preparation

The nominal composition, as well as chemical and microstructural analyses of the material, must be reported. The method of preparation, heat treatment, visual appearance, and any other pertinent descriptions(s) of the material should also be reported. Samples to be tested will normally be cut (e.g., diamond core-drilled or sawed) from a larger piece to avoid effects caused by interaction with the preparation container or by loss of volatiles during preparation. The geometry is not fixed, but monolithic shapes such as right cylinders or thick plates are assumed. A knotted fiber, a solid form with narrow saw cuts into the body (to adjust surface area), and powdered material are examples of unacceptable geometries, because of unknown effects due to surfaces in near contact. Although a monolithic specimen is recommended, several (≤ 4) smaller samples may be used, provided only point contact occurs.

The surface is very important, especially in short-duration tests. Experience so far suggests the cleaning procedure (removal of fines) may be more important than the surface finish. The following steps provide a standard treatment.

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1. All surfaces will normally be obtained using diamond-impregnated core drills and saws, which produce relatively smooth surfaces with some saw marks visible. A low-speed saw is recommended. The appropriate cutting speed will vary depending on the material. Isopropol alcohol should be used as the cutting fluid. Further surface treatment by machine or hand polishing may be needed for some materials. Experience with glass and crystalline ceramics suggests a diamond-sawed surface is the best compromise.
2. The specimen will be rinsed first in acetone, then in ethanol at room temperature for 10 min each, using 20-ml volumes of fresh solvent for each sample. Ultrasonic agitation is recommended.

B. Leachant

The reference leachant will be deionized or distilled water. The pH will be in the range 5 to 7 and there will be no cation impurities above 0.5 ppm. Typical analysis for the leachant, especially in those cases where pure water is not used, will be reported, including anion (especially carbonate) and total organics analyses. Reagent grade NaCl should be used to prepare the brine leachant.

C. Apparatus

Nonreactive leach containers must be used. These will ordinarily be made of Teflon® or other durable organic such as polyethylene or polycarbonate. At 90°C, leakage through the walls of polyethylene bottles has been observed in as little as 21 days. Containers should be checked for impurity content by direct analysis of the container or by analysis of a 1.0 molar HNO₃ acid leach (e.g., fill the bottle and maintain at 90°C for 3 days) before routine use. The leach bottle should be rinsed immediately before use with boiling distilled water. Figure 7 shows the recommended bottle and sample configuration. The specimen is held near the center of the bottle by a thin, coarse-woven screen (also made of Teflon® or plastic). Other methods may also be used, e.g., suspension from above by a fiber; but contact of a significant portion of the sample area with the container bottom or walls must be avoided.

The leach container must be sealed or otherwise contained in such a way that there is no appreciable loss of fluid (i.e., loss <5%).

The leach bottle should be placed into a preheated bath or oven with temperature control $\pm 1^\circ\text{C}$ throughout the working volume. In the case of the relatively small water volumes recommended in this test ($4 \times 10^4 \text{ mm}^3$), zero time may be taken as the moment of insertion into the heated chamber.

D. Standard Conditions and Analyses

Recommended temperatures and times are as follows:

- temperature— 40° , 70° , $90^\circ\text{C} \pm 1^\circ\text{C}$
- time—3, 7, 14, 28, 42, 91, 182, 364, and longer times (days $\pm 2\%$).

The reference temperature and time is 90°C , 14 days, using deionized water and leachant and with $SA/V = 1/100 \text{ mm} = 4 \times 10^2 \text{ mm}^2 / 4 \times 10^4 \text{ mm}^3$.

At the conclusion of the leach test, the bottle should be removed from the heated chamber and the sample(s) removed as soon as the bottle nears room temperature. The leachate pH should be measured as soon as room temperature is achieved with a calibrated meter to ± 0.05 units and recorded. At this point the leachate volume should be measured and divided into two ($2 \times 10^4 \text{ mm}^3$) portions. One portion should be stored in a sealed container without acidification as an archive sample for possible analytical needs. The second portion should be returned to the original leach bottle along with $2 \times 10^3 \text{ mm}^3$ of ultrahigh purity HNO_3 and $1.8 \times 10^4 \text{ mm}^3$ deionized water. The acidified leachate should be left in contact with the leach bottle for 12 hr before withdrawing all of the solution, or an aliquot, for chemical analysis. Note that a concentration correction of X2 will be required in evaluating results. Although the leachate should be stabilized by the acid addition, chemical analysis is recommended without delay. If analyses are made later than 1 week after removal of the sample from the leach container, the delay in analysis should be noted in reporting the results. In the event that acidification causes precipitation or the analytical method intended requires nonacid solutions, the archive portion of the original leachate can be analyzed.

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The solid sample(s) should have been removed with a minimum of handling, rinsed for two seconds in deionized water, then heated to 110°C in a conventional drying oven for 1 hr. The sample may then be cooled and weighed. In a 3-day experiment, a sample with $SA = 4 \times 10^2 \text{ mm}^2$ may lose 0.1 mg for a gravimetric leach rate of $1 \times 10^{-9} \text{ kg}/(\text{m}^2 \cdot \text{s})$. Since a realistic limit of weighing accuracy for a material with a corrosion film is likely not better than $\pm 0.1 \text{ mg}$, weight loss measurements will probably only be useful in long duration tests, or for low durability waste forms. Other surface/profile analyses of the solid may be undertaken at this point.

Because weight loss is an inadequate measure of durability for complex waste forms and relatively insensitive for monolithic samples, it should not be used as the primary measurement. Multi-element chemical analysis of the leachate is required. Analysis for Na, Cs, Sr, rare earth elements (when present) and two or more matrix elements (e.g., Si and B in glasses or Ti and Zr in "tailored" ceramics) will ordinarily be the minimum reported for inclusion of data in the Materials Handbook. There may be instances in which the concentrations of Cs, Sr, or the rare earths (considered here as stand-in elements for the actinides) are too low in the solid waste for detection in the leachate. In these cases, analyses for Na should be used as a limiting case in evaluating the material. Analytical guidelines for both solution and solid state analyses, as used in the MCC, will be defined later. The Support Methods (SM) which will be described include:

- MCC-SM-1 Bulk elemental analysis by X-ray fluorescence
- MCC-SM-2 Bulk elemental analysis by fusion/solution analysis
- MCC-SM-3 ICP solution analyses
- MCC-SM-4 Cs solution analyses
- MCC-SM-5 X-ray diffraction analysis
- MCC-SM-6 Scanning electron microscope evaluation
- MCC-SM-7 Optical microscopy evaluation

E. Error Evaluation

It is important to include some replication in all experimental work using this test method. Because the depth of study will vary in different laboratories, it is difficult to specify precisely what level of replication

should be used. To be included in the Materials Handbook, mathematical evaluation of errors must be presented. In time-dependent studies planned within the MCC, triplicate data will be obtained for about one of every three times in a series.

Between-laboratory variations can be established by conducting experiments on reference glass (MCC-76-68). Limited quantities of this glass are available from the MCC, as are directions for preparation of larger quantities.

VI. REPORTS

A standard format for reporting the results is provided for data to be included in the Materials Handbook. The report includes the following subsections:

1. Test conditions, sample preparation, and description
2. Leachant analysis
3. Leachate analyses
4. Post-leach sample analyses
5. Leach rates
6. Discussion of results (observations, problems, comments)
7. Error analysis

A description (or outline) of the various reports is given in this section.

1.0 TEST CONDITIONS, SAMPLE PREPARATION AND DESCRIPTION

1.1 TEST CONDITIONS

Material, temperature(s), time(s), container, SA/V ratios, etc. should be defined.

1.2 COMPOSITION OF TEST MATERIAL

Nominal and analyzed compositions should be reported in tabular form.

1.3 MATERIAL PREPARATION AND DESCRIPTION

The method of fabrication, cleaning procedure, microstructural and phase analysis or other descriptive information should be briefly presented.

2.0 LEACHANT ANALYSES

Analysis of the starting leach solution will include:

- pH
- elemental analysis - cation
 - anion
 - total organics.

3.0 LEACHATE ANALYSES

The post-leach solution analytical data should be presented in tabular form, giving for each data point the pH and elemental concentrations in mg/ . In all cases, detection limits and/or error limits should be indicated.

4.0 POST-LEACH SAMPLE ANALYSES

This section provides a means for reporting solid-state analyses, including weight loss, microstructural photographs, microprobe analyses, depth profile elemental analyses, X-ray diffraction data, or other supportive solid-state data. No formal method of presentation is defined, since these analyses are optional and highly variable with respect to extent and type of information collected.

5.0 LEACH RATES

5.1 METHODS

Several graphical methods of reporting the data are defined in the following sections. The methods chosen are the same as, or are variants of methods used in a number of laboratories. In a sense, the choice of reporting

units is somewhat arbitrary but each of the plots suggested in the following subsections allows evaluation of specific technical questions. Very simply, the figures include presentation of:

1. Losses as mass of element per unit area versus time
 - to present basic data, without assumptions
2. Leachate composition versus time
 - to assess solution chemical effects (e.g. solubility limits)
3. Normalized mass of element per unit area versus time
 - to assess cumulative elemental losses and the extent of congruency
4. Normalized-instantaneous elemental leach rates
 - to evaluate instantaneous behavior

5.1.1 Cumulative Elemental Losses

The elemental leach data given in Section 3.0 should be converted to losses per unit area and plotted as

$$\log \left(\frac{m_i}{A} \right) \text{ versus } \log (\text{seconds});$$

where m_i is the mass of element "i" formed in the leachate at the end of each leach period in kg and A is the surface area of the sample in m^2 .

The pH of the leachant should also be plotted versus time.

5.1.2 Leachate Composition

The concentration of each element analyzed in the leachate should be plotted as

$$\log (\text{molarity})_i \text{ versus } \log (\text{seconds})$$

5.1.3 Normalized Cumulative Elemental Losses

The leach data should be normalized by the solid sample elemental concentration according to the following equation:

$$NL_i = \frac{m_i}{f_i \cdot A}$$

where

NL_i = the normalized mass lost per unit surface area (kg/m^2), normalized to the behavior of element "i".

f_i = the mass fraction of element "i" (mass of element "i" in initial sample in kg /total mass of initial sample in kg)

These data are then plotted against time in seconds as NL_i versus time. If the duration of the experiment approaches one year or the normalized mass losses range over several orders of magnitude it may be necessary to display the data as $\log NL_i$ versus $\log t$. However, when using the log-log plot caution must be used when calculating leach rates. Preferably, enough data have been taken that the data can be fit to a polynomial equation which should then be reported and used in Section 5.1.4.

Also it should be noted that by dividing the normalized elemental mass losses per unit area by the density of the sample, an "effective leachant penetration" depth is obtained for each element. Since only a constant is involved, the penetration depth may be shown in the same plot as NL_i by including a right-hand ordinate, appropriately scaled. Penetration depth is given in millimeters by the following equation

$$P_i = \frac{NL_i}{\rho} \times 10$$

where NL_i is in kg_i/m^2 and the density (ρ) is in kg/m^3 .

5.1.4 Normalized Instantaneous Leach Rates

In the past, leach rates have been calculated by dividing the mass of element "i" in solution at time "t" by the fraction of element "i" in the sample, the surface area and the time "t". This, however, gives a cumulative leach rate which is at times misleading. By differentiating the curves obtained in Section 5.1.3 the instantaneous normalized leach rate at any time

"t" may be derived. A plot of the log of this leach rate versus log time gives a more sensitive description of the variation of leach rate with time. To obtain the instantaneous normalized leach rate (R_i) of element "i" the slope of the curve of NL_i versus t is found at any time "t". This may be done mathematically, if the equation of the curve is known, or estimated graphically.

The leach rates should be plotted as $\log R_i$ versus $\log t$ (seconds), where R_i is in units of $[\text{kg}/\text{m}^2 \cdot \text{s}]$.

6.0 DISCUSSION

6.1 DISCUSSION OF RESULTS

A brief discussion (abstract) of the significance of results presented should be given. Reference should be made here to reports or open literature presentations containing further discussion of the data presented, correlation to other work, etc.

6.2 TEST PROCEDURE

Observations/problems or other comments concerning the test procedure should be presented.

6.3 SOURCE OF DATA

A listing of responsible personnel and the laboratory reporting the data should be given.

7.0 ERROR ANALYSES

This section will ordinarily discuss error estimates for the particular data being reported. No format is specified.

At this time, replicate data from short duration studies using the static test method are available for glass, supercalcine and concretes. A statistical evaluation of these results may be summarized as follows. For glass 76-68, repeatability, expressed as the relative standard deviation

(S_x/X), is better than $\pm 5\%$ for all elements. For super calcine and concretes, the relative deviation is in the range $\pm 5\%$ to 80% , depending on element.

Because of the expected importance of this test method, additional data are required to determine short-term and long-term repeatability, bias errors and intra-laboratory reproducibility. We believe these needs are best met by detailed study of individual waste forms since errors are not likely to be waste form independent. A multilaboratory "round robin" evaluation of this test method is being planned.

4.3 ORGANIZATION OF A ROUND ROBIN

There was a consensus in both Working Groups 4 and 5 that a round robin should be organized by the MCC as soon as practicable based on the Scoping Static Leach Test procedure (now revised Test 1). The MCC plans to do this. A number of unresolved issues remain, some of which may impact the time when the round robin can be initiated.

Examples of the issues that need resolution are

- identification of the type and number of test specimens
- degree of "informality." A desire for "informality" was expressed at the workshop. This would probably achieve faster feedback than could be obtained if a more formal round robin is organized. The results of the informal round robin could probably not be submitted to the MRB, however, and this could be counterproductive for the MCC.
- number and identification of participants
- cost.

It may be possible to organize the round robin without a meeting of the participants. If not, a meeting will probably be held in May.

4.4 COORDINATION WITH MECHANISTIC RESEARCH

Study Group 3, Data Base for Modeling, concluded that "mechanistic research is relevant and essential in meeting regulatory requirements" and that "the MCC tests should be modified to provide information on mechanistic models." The MCC believes the tests as now defined are flexible enough to provide all of the mechanistic data needed. For instance, they permit use of ^2H or ^{18}O tracers in the leachant and any kind of surface profiling analyses desired. The problem is not so much modification of the tests, as it is definition of which parameters should be established at what level within the framework of the existing test matrix to obtain the desired mechanistic data. It was emphasized that the MCC is not a research and development organization. But it does establish a means of recording authoritative data that can be used for interpretation of leaching in terms of mechanistic mathematical models.

A follow-on meeting that will focus on "Data Base for Leach Modeling" will be held in Denver, April 22 and 23. Attendees will be Working Groups 3 and 4 from this workshop, plus additional experts. Subjects to be discussed include the following:

- Improved understanding of the state-of-the-art is needed. Considerable progress has already been made in modeling the leaching of glass and cement waste forms at ORNL, SRL, and elsewhere, and in the modeling of rock weathering at the USGS and in universities. The meeting will serve as a forum for discussion of this work.
- The data needs of those who are modeling repository behavior have not been communicated to the laboratory experimentalists in a clear-cut fashion. The meeting will serve as a first step in formalizing this communication.
- There seems to be general agreement that mathematical modeling of the long-term release of radionuclides from the waste form will be required in licensing, e.g., this would be part of NRC's proposed 10^{-5} to 10^{-7} fractional release per year equation. But it is not clear that existing models suffice for this purpose. Models and data needs will be discussed in this context at the meeting.

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5.0 COMMENTS BY PARTICIPANTS

This section contains comments received from participants following completion of the workshop. Each participant commented on the rough draft of this report. At that time they were also encouraged to submit formal comments for inclusion in this report, if they wished to do so.

JOHN STONE, (a) WORKING GROUP 2

The Materials Characterization Center is to be congratulated for its positive response to the many diverse viewpoints expressed at the workshop. MCC appears to be moving quickly to implement a leach test development plan that has been greatly revised from the earlier version.

In a new program at SRL, we will perform comparative tests on alternative waste forms for the Savannah River high-level defense waste. The results of these tests will play a major role in the final selection of the waste form to be manufactured in a proposed Defense Waste Processing Facility. The waste-form decision will be made at the end of FY-1983. To meet this schedule, we must start our leach test program in the last quarter of FY-1980, and preparations for the program are underway now.

We believe that the draft MCC Static Leach Test, as outlined in this Summary Report, will meet our needs at SRL for a reliable long-term test to intercompare waste forms. A fully approved MCC test may not be available in time to be incorporated into the initial phases of the SRL program. Nevertheless, we feel that close liaison with MCC in choosing an interim test will be essential to ensure acceptability of the test data. Therefore, we would like to see the draft Static Leach Test approved with a minimum of changes.

Developers of individual waste forms have the responsibility for research programs to determine leaching mechanisms and repository-specific leaching behavior of their own forms. The entire set of MCC leach tests will be

(a) Savannah River Laboratory (SRL).

required for these studies. However, developers associated with forms for Savannah River waste also must start with interim, non-approved leach tests, in order to meet the rather tight schedule.

It is interesting to note that the proposed MCC static test has no provision for periodic leachant replacement to determine time dependence with a single sample. Rather, the time-integrated leaching of multiple samples leached for different periods is measured. The workload for sample procurement and preparation is increased manyfold over that of a classical long-term test. Users of the test should be prepared for the logistical problems that could arise.

RICHARD TALLMAN,^(a) WORKING GROUP 2

P. 3.8, 3.2.1 "Weight Loss Measurements..." (See comments on p. 4.14 for more detail.)

Weight losses smaller than 100 μg would be difficult and expensive to measure. Furthermore, surface hydration and other effects on weight loss must be determined in order to interpret weight loss measurements.

P. 3.9, 3.2.2 Standard Scoping Static Leach Tests

Predictions of long-term leaching may be weakened more by the irreproducibility of leaching data than by the lack of ideality of leaching behavior represented. For some waste forms, abrasion and polishing can provide more reproducible leaching behavior from a more defined surface. Using wheels with running water should remove the chips which could gouge the surface. This preleaching and subsequent preleaching by water in an ultrasonic cleaner could serve to provide a more reproducible leach rate by reducing effects of the surface condition on the initial leaching.

The advantages of such a procedure should be available to those who can use it. The limitations of hot cell and glove box operations, or of particular waste forms, should not be imposed on all leaching studies.

(a) Principal Contractor to DOE at the Idaho National Engineering Laboratory (INEL).

P. 4.7, Figure 6

I would like to be able to use our glass soxhlet apparatus at the local boiling point of about 96°C.

I believe that the syphoning action of the common soxhlet apparatus may provide reproducibility which the flow-through system pictured may lack because of flow pattern variation effects on the extremely accelerated leach rates.

The value and purpose of tests so expensive and so accelerated need to be established.

P.4.11, Draft Static Test (MCC-1), II. Limitations (See also comments for P. 3.9)

Diamond sawing cannot be relied upon to produce uniform shapes. Final shaping by abrasion may be desirable.

Sharp edges should be rounded or beveled slightly to eliminate mechanical losses in handling or by leachant action.

P. 4.15, V. Procedure, A. Specimen, Waste Form Preparation

Ultrasonic cleaning for only two minutes may be inadequate to remove from pores debris from cutting and/or abrasion. Also, any mechanically weak surface particles should be removed because they can increase the variance of the leaching measurements. Two hours of ultrasonic cleaning would be more effective in some cases.

P. 4.16, V. Procedure, C. Apparatus

The meaning of the sentence beginning "Containers should be checked for impurity content . . ." is not clear. Surely such procedures could result in long lists of contaminant levels measured by sensitive techniques. Such measurements could not be subtracted as blanks, nor could they serve to reject bottles.

The test description should specify or recommend: 1) cleaning procedures for plastic bottles, including cleaning for re-use, 2) preparation of blanks, 3) use of blank analytical data, and 4) acceptable limits for blank analytical data.

P. 4.17, D. Standard Conditions and Analyses

Individual weighings need not be accurate. Only the accuracy of the weight change is of importance. Therefore, the individual weighings need to be accurate relative to unchanging tare weights (which are generally inaccurate). Buoyancy correction is unnecessary because only the change in the buoyancy correction affects the weight change. However, the buoyancy change for leaching specimens is unlikely to be greater than 5 μg , so that correction for buoyancy change is not generally needed.

Proving that tare weights remain unchanged is difficult. My work with a Mettler ME 22 microbalance shows changes in enclosed stainless steel tare weights greater than 0.01 mg (10 μg). Although it seems reasonable to assume that such tare weights remain unchanged, my measurements show unquestionable unexplained changes the limitations of which remain to be determined. The accuracy of weight loss measurements made with my balance can be poorer than ± 0.01 mg (± 10 μg), and is, in general, not yet well known.

The effects of hydration, possible carbonate formation, and possible oxidation on specimen weight appear to exceed 0.01 mg for some specimens. Drying to constant weight to ± 0.01 mg before and after leaching may not be possible. For example, heating to 190°C in air for 20 h and 64 h resulted in successive increases in weight of 440 and 630 μg , respectively, for an air-dried leached specimen with a geometric area of 5.6 cm^2 . Weight loss measurements are unlikely to be routine and are likely to require development. Satisfactory measurements of weight losses of the order of 0.1 mg and smaller are likely to be difficult in most cases and unachievable in many cases.

On the other hand, in some cases weight loss studies may add to understanding. Corroboration of leachant analyses by correlation with weight losses could add validity to both.

MARK HARWELL, (a) WORKING GROUP 3

The MCC Working Group 3 was established to examine the proposed leaching tests in the context of data needs for modeling. However, there is a diverse set of modeling activities for the analysis of the effectiveness of nuclear waste isolation. This merely reflects the complexity of the systems involved in geologic isolation. The result is that data appropriate for some modeling activities may not be useful elsewhere.

The background and emphasis of most of the members of Working Group 3 relate to the specifics of leaching mechanisms. Modeling of mechanisms must be directed towards the testing of alternate hypotheses of how leaching occurs under various specific conditions. Thus, tests initiated to supply data for mechanistic modeling must be highly specified and controlled, and the number of parameters which affect leaching should be minimized within any set of such tests.

There is no question about the need for such data, models, and hypothesis testing. The nature of the licensing process currently anticipated involves the probability of adversarial proceedings, with a concomitant need for a state-of-the-art defensibility which those tests will address. However, it seems very unlikely now that those types of tests will be sufficient to meet the broader needs of repository safety analyses.

The particular inadequacy of mechanism tests lies with the complexities of the repository environment which may be experienced by various waste forms. The actual environment will be highly heterogeneous both spatially and temporally, and it will be affected by a large, diverse set of factors, many of which will be scenario specific. Leaching rates are highly dependent on a number of these interacting parameters. In such a situation, the uncertainty of long-term predictions based solely on reductionistic models will be unacceptably high, and safety assessments will have to rely on empirical data from simulation experiments. Scientific defensibility then will be dependent on mechanistic explanations for the results of complex systems simulation

(a) Consultant.

experiments rather than on assembling a predictive capability to describe those complex systems. In that circumstance, the important task is to relate the simulation experiments to actual repository conditions at the time of a breach.

The other imperative for systems simulation experiments is to have data available in the period of time before mechanistic models could be developed. The empirical simulation data are essential to provide source terms for the necessary geotransport modeling. Site evaluation, selection, and licensing processes are ongoing and safety assessments are required now. These analyses simply cannot wait for completion of mechanistic studies. Further, there is a danger that mechanistic hypothesis testing could continue indefinitely or along pathways which will have no importance in the context of the total isolation system's response.

Thus, systems tests are needed for modeling the long-term safety of repositories. The MCC tests do not provide for this need. Indeed, such tests may be outside the scope of MCC and more properly addressed by the WRIT or other programs. Nevertheless, MCC should recognize the necessity for differing types of tests, especially if it is to fulfill its charter to provide the materials data base needed to ensure the safe disposal of nuclear wastes.

HANS CLAASSEN,^(a) WORKING GROUP 3

I wish to emphasize that the logical sequence for design of testing procedures should be as follows:

1. Determine what your needs are--what do you want to find out?
2. Design procedures which will give you everything you want.
3. Use or modify existing procedures whenever possible but...
4. use completely new procedures if none of the old ones will work.

In other words, do not let pre-existing procedures dictate what you need to know!

(a) United States Geological Survey.

It was my impression that those involved in glass-dissolution work had indicated the existence of models for such dissolution processes. Although there may be some question regarding whether the mechanisms are operative under all possible repository conditions, they still provide a sound basis for experimental design. The impression that I get from the draft report is that the MCC will have to "reinvent the wheel" to rectify the lack of understanding. It would be more appropriate to indicate that existing models will be incorporated into leach-test design.

The use of geometric surface area will probably introduce large errors and large discrepancies in any comparative study. The observed variability in leach rate of the same material prepared in different ways (e.g., powdered versus monolithic sawed) is, I believe, due for the most part to inappropriate surface areas. I would suggest that a BET surface be used; although some problems exist with this method, it is a large improvement over geometric methods. Cost can probably be reduced to about \$25 per sample, or less, using commercial instruments costing less than \$3000.

Unless a case can be made for repository leach conditions approaching those of distilled water, I can see no scientific or engineering use for the data. Distilled water presents a totally unbuffered system, whereas, in any real system, some buffering capacity exists. If the leaching mechanism is pH-dependent (which it most probably is), short-term results will be highly dependent on the leaching fluid used. At the very least, I would suggest a standard leaching solution having a composition representing a "nominal" groundwater, although a "variable-state" experiment would be better. Since the data will be used for engineering purposes only, the composition would not be critical, but at least would be realistic. Distilled water is not realistic and does not offer the advantages of a good "engineering leachate." I believe use of distilled water violates all the objectives stated in para. 4.2.1. It may be that distilled water was chosen because it represented a simple system but the nature of aqueous interaction with the solid results in DW being a rather complex reagent. A pH-stated experiment (as opposed to buffered) would be an alternative which is scientifically valid but more expensive to run than the "nominal" or mean groundwater. The mean groundwater may be a more practical alternative.

The following points are aimed at associated long-term studies, and data requirements and mechanisms for long-term models.

1. Long-term mechanisms are expected to be expressed in terms of kinetic and mass transport mechanisms as generally used in physical chemistry and chemical engineering. Dissolution rate constants, diffusion coefficients, adsorption constants, equilibrium constants (including solubility product values, etc.) are the common language of such approaches. The presentation and examination of leach data should be related wherever possible to the controlling mechanisms and parameters.
2. Leach rate should always be stated in association with other factors important if the process could be other than steady congruent corrosion; the total duration of exposure is particularly important if diffusion could be involved.
3. The leach rate is an incremental flux normalized for original concentration, $[(\text{amount area}^{-1}\text{time}^{-1})]/[\text{amount (mass or volume)}^{-1}]$ and can vary with time and other factors. The use of mass concentration in the expression (e.g., $\text{g cm}^{-2} \text{d}^{-1}$) has no redeeming values for modeling application, whether in SI units or not. A leach rate unit of possible value, $(\text{amount m}^{-2} \text{y}^{-1})/(\text{amt cm}^{-3})$ equivalent to millimeters/millennium or micrometers/year direct corrosion, in addition to having a straightforward relation to mass transport parameters, should be intelligible to the general public in describing long-term isolated waste leaching behavior. This unit, already used by astute investigators at BNWL and Catholic U., among others, may not require the use of negative powers of ten.
4. Fractional release used without an associated statement of specimen volume/surface area, or (preferably) shape and dimension, is an

(a) Oak Ridge National Laboratory.

attribute of the individual specimen, not the material. Consequently, fractional release should be used only if accompanied by these specimen characteristics.

5. The phenomena or factors defining the transition from diffusional to corrosion control must be known for useful modeling, but are seldom established. These could be related to internal diffusion profiles, dissolution of outer layers, erosion, sloughing, or other mechanisms.
6. The factors establishing the active surface area of the waste form over an extended time are poorly defined. Cracking, devitrification, and radiation damage must be evaluated. A statement of area subject to leaching will be an early and continuing requirement in almost any model.
7. The effects of leachant composition, including stagnation, are only vaguely defined but observation indicates that the effects are important. Though experiments should embrace the range of anticipated field variables, a major effort should be to establish mechanisms involving leachate transport, kinetic and equilibrium effects, rather than to simulate field situations. Factors affecting mass transport through the liquid film, and hydrous film, must be studied carefully, and articulated in models.
8. Diffusion of atoms in the glass below a hydrous layer could be an important factor in leach rates of individual species and in lack of congruency. Solubility limits for some species should affect release, but mechanisms of release are not well defined and leach data has not been interpreted from this viewpoint to any extent.
9. It is important to establish the presence or absence of coupling between the long-term leach rate behavior of the various mobile species. Is the diffusion coefficient of various species in the hydrous layer the same? Is the rate of release at the interface between solid and hydrous layer the same?

STAN LOGAN,^(a) WORKING GROUP 3

Long-term risk analysis modeling has been underway for a number of years and is continuing at this time. An objective of the MCC is to provide a documented data base for components of the waste emplacement package. While the first edition of the Nuclear Waste Materials Handbook is scheduled to be issued in September 1981, it should be recognized that there are interim needs by persons doing risk assessment work who have earlier milestones to meet. Interim peer review of currently available data to provide guideline leach rates for a few representative waste forms, for several categories of radionuclides, the effects of parameters such as pH and temperature, and the expected changes in leach rates over long time periods would be helpful. As the MCC work proceeds, new information on the basic mechanisms and the effects of individual parameters can then be incorporated as refinements in the risk models.

WILL WHITE,^(b) WORKING GROUP 4

It is important to take into account the varying types of alternate waste forms in designing the standard leaching tests. We could consider four broad categories of generic waste forms: i) glass which has been most intensively discussed by the workshop; ii) tailored ceramics of which there have been three or four specific ones proposed; iii) what we might call encapsulant waste forms--these are waste forms in which the radionuclides are held in the interstices or pore volume of another material, the main constituents of which do not themselves contain radionuclides. Some of the special cements are examples as are certain of the ceramic waste forms; iv) finally, there is spent fuel which under certain repository conditions is an encapsulant waste form since uraninite is a pretty insoluble material. Cesium, strontium and other elements are in spent fuel in a water-soluble form but in fact the leach rates for these elements from spent fuel pellets are quite small. A possible

(a) Los Alamos Technical Associates, Inc.

(b) Pennsylvania State University.

explanation is that the soluble phases are encapsulated in closed pore volumes. Although these encapsulant materials may have a high porosity they have a low permeability.

We see three or four different dissolution mechanisms that may be in operation depending on the waste form. Leaching, in the sense of transport of one element by diffusion and by ion exchange through a matrix of other elements occurs in glass and probably in some of the silicate crystalline phases in ceramics. There is equilibrium dissolution of phases which may have an intrinsically low solubility but a rapid dissolution kinetics. Several of the molybdate and phosphate crystalline phases may dissolve in this way. In addition, the tailored ceramics will have several mechanisms operating. One is the dissolution of the crystalline phases and the second is an extraction of more soluble material trapped on grain boundaries or in pore volume. An ideal ceramic would have a zero release from the second source but in the development phase one is likely to find grain boundary phases and it is in the development phase that the standard leach tests will be most useful. The extraction of soluble material from encapsulant-type waste forms will depend in part on the permeability of the material and the rate at which the leach fluid can migrate through. We are trying to propose tests which can cover all of these mechanisms. Applying the tests to metal matrix or coated waste forms may be even more difficult.

The tests and discussion of the tests have skirted the issues of pH and Eh control but the dissolution of many waste forms, spent fuel being an outstanding example, is going to be very sensitively a function of pH and of oxidation potential. It is not clear that the scoping leach test, which simply tries to avoid these issues, will give useful values. In the way it is arranged the test is conducted in an oxidizing environment and this may give an inappropriate comparison between waste forms, especially if the repository design provides for a reducing environment (which could be done by using oxygen buffers in the overpack or using a rock type such as basalt which itself provides a reducing environment. The comparison in the lab may not be the comparison one would find in the repository.

It would seem prudent to maintain a certain degree of flexibility in these leach tests so that it would be possible to incorporate research findings to a new generation of leach tests.

JOHN BATES,^(a) WORKING GROUP 4 AND KEVIN FLYNN, WORKING GROUP 2

1. The importance of sample preparation and surface characterization in a short-term test cannot be overemphasized. These effects, which likely will be most important for the shortest term, lowest temperature test, can be minimized by producing either a well characterized surface or a consistent surface. The latter possibility seems most consistent for a scoping test but evidence is needed to show this goal can be achieved.
2. The use of geometric surface area (GSA) while acceptable for a scoping test seems too simplistic for a long-term test used to produce extrapolatable data. The actual surface area of a cut sample is likely to be greater than GSA and it could change significantly during the leaching process, especially under hydrothermal conditions.
3. The information included in reporting data should be sufficient to allow a complete understanding of the experiment, thus facilitating comparison with other results.

Our thoughts on the round robin are that it should be done as quickly as possible yet still yield results that can be presented to the MRB. We see no reason for a planning meeting.

TONY WOLTERMAN,^(b) WORKING GROUP 5

The accuracy of the leach rate is governed by the combination of the individual errors of measurements and conditions involved.

(a) Argonne National Laboratory.
(b) Mound Laboratory.

$$\sigma_{LR}^2 = \sigma_m^2 + \sigma_f^2 + \sigma_F^2 + \sigma_t^2 + \sigma_T^2$$

where σ_{LR} = error of the leach rate

σ_m = error of the analysis of the leachant

σ_f = error of the analysis of the waste form

σ_F = error of the determination of geometric surface area

σ_t = error in measuring time

σ_T = error caused by the leach test variability (e.g., pH, temperature, oxygen fugacity of leachant, sloughing of surfaces).

The above is a root sum square model and assumes the independence of error terms. By trying mathematical examples one can see that the largest error terms(s) strictly dominate the σ_{LR} because of the squared relationship of the terms. The round robin exchange should help identify the dominant term for corrective action. It is thought that for most experiments σ_T will dominate. If this is true, in order to gain significant improvement in the accuracy of the leach rate, the MCC must put its effort into reducing the leach test variables (σ_T). The ruggedness test to identify the dominant variables will be most important.

With respect to the error involved in predicting the leach rate of 1000 year repositories, the error in modeling will far outweigh errors involved in leach rate determinations. This is especially true for radioactive waste forms where heat and radiation damage will probably continually change the rate if not the mechanism of leaching. The MCC must put a strong emphasis on mechanistic studies especially those involving radioactive materials.

I. Units

- A. Leach rates in $\text{kg/m}^2\text{d}$ or m/d would be acceptable for scientific community.
- B. Reporting data for management (and for public) may be easier in $\text{kg/m}^2\text{d}$.
- C. Equivalent "risk" units (Σmrem are over specified Δt or mrem/d) should be prepared for management and public.

II. Accuracy and Precision

- A. Both should be as good as possible.
- B. Leach rate versus t curves usually exhibit sharp breaks at some point after initial leaching.

Recommendation:

- 1. Run initial experiments in replicate to:
 - See if break point (t_B) can be predicted.
 - Stop experiment after the break point and inspect surface of sample/standard by microprobe analysis, TEM, etc. This may allow reduction in degree of randomness of " Δt " to t_B , and this is needed to isolate errors on $t(x)$ axis.
 - Diffusion versus dissolution must be demonstrated, especially if crystallites form (i.e., natural glasses).
- 2. Long-term experiments must receive same (or more) attention than scoping experiments.
- C. Errors on leach rate can probably be reduced if experimentalists follow carefully outlined procedures.
- D. The number of standards to be run needs to be resolved (i.e., to assist experiments).

III. Procedure Requirements

- A. "Ruggedness" needs clarification. Tests should be designed to allow proper statistical treatment.

(a) University of New Mexico.

B. Pyrex as a standard is satisfactory if T_M , etc., is reasonable for comparison with waste-bearing glass.

1. Parallel experiments with Pyrex and waste glasses should be run early to examine crystal growth, "spalling" off of rind, devitrification, etc.

C. One to two metric tons Pyrex is suitable for glass.

IV. Presently Available Data

A. Standards are needed for solids and solutions.

B. Routine testing must include

- replicate analyses
- SA determination
- characterization of starting material (chemical, WRC, SC, domains, etc.); also FT, TEM (to slabbing for cross checks)
- Constant T, P condition (i.e., should pressure effects be included as well?).

C. Secondary standards are essential.

D. More work is needed on naturally occurring glasses.

V. Presentation of Final Data

A. This must include relevant data (R, SA, composition, , etc.) for inspection by scientific community and for lay inspection.

B. Satisfactory input to MRB can only be assured if principal investigators follow experimental procedures carefully.

Comment: The possibility of data being taken without running standards can be avoided. The experimental conditions for initial round robin testing should be as rigorous as guidelines for lunar principal investigators (by NASA) some 11 yr ago.

Comment: Randomness in experimental design can be minimized if not avoided. MCC and MRB guidelines should be very clear here.

Comment: Ways to address Items II to V for materials other than glass must be undertaken. R versus t for any material with discrete phases will probably pose many more problems than glass (i.e., one faces not

only t_B problems, but growth of new phases, loss of elements from numerous sites--each with different E_a if diffusion is a rate-controlling mechanism). If leaching is incongruent for glass, then it is certainly "more" incongruent for crystalline material. More detailed preliminary TEM-EDS, MRA should be planned for scoping and long-term experiments.

ACKNOWLEDGMENTS

The success of the workshop was due to the enthusiasm of the participants and their willingness to share expertise and valuable time. This is gratefully acknowledged.

The workshop also owes much to the arrangements chairman, Orv Hill, and to DeeAnn Olson of the Battelle Seattle Conference Center. Special thanks go to Billie Neth, who was invaluable from start to finish, and to Judy Hooper, editor, for straightening out our prose all along the way.

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APPENDIX A

ORIGINAL MCC LEACH TEST PLANS

STATIC SCOPING TEST (1) -- EXPERIMENTAL

SOLID WASTE + SOLUTION

SA/V = 1/10 (4 cm²/40 cm³ RECOMMENDED)

STD TIMES: 3*, 14d

STD °C: 99*, 40

SOLUTIONS: DI H₂O*, YOUR CHOICE

SOLUTION ANALYSIS REQUIRED

(+ ACID RINSE ANALYSIS)

SURFACE ANALYSIS RECOMMENDED

WT. LOSS RECOMMENDED

*** PRIMARY CONDITIONS**

**PNL/MCC
0020**

STATIC SCOPING TEST (1) -- TYPICAL RESULTS

PNL/MCC
0021

DYNAMIC SCOPING TEST (2) -- EXPERIMENTAL

SOLID WASTE + DISTILLED WATER
SOXHLET - RELATED APPARATUS
FIXED FLOW RATE AND SA

STD TIMES: 3, 14d
STD °C: 99, 40
DISTILLED H₂O
SOLUTION ANALYSIS
REQUIRED
(+ACID RINSE ANALYSIS)
METALLOG/SEM
WT. LOSS RECOMMENDED

DYNAMIC SCOPING TEST (2) -- TYPICAL RESULTS

PNL/MCC
0023

STATIC LONG-TERM TEST (3) -- EXPERIMENTAL

SOLID WASTE + EQUILIBRATED GROUNDWATER + ROCK

$$SA_{\text{SAMPLE}} / SA_{\text{ROCK}} / V_{\text{SOL}} = 4 \text{ cm}^2 / X \text{ cm}^2 / 40 \text{ cm}^3$$

STD TIMES: 3, 14, 42, 90, 180, 360d

STD °C: 99, 40

SOLUTIONS:

- GENERALLY
EQUIL. GROUNDWATER
- SOLUTION ANALYSIS
REQUIRED
- SURFACE/PROFILING
RECOMMENDED AT
SHORT TIMES
- SEM/PROBE REQUIRED
AT LONG TIME

TEST 3A = NO ROCKS, DI H₂O

PNL/MCC
0024

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STATIC LONG-TERM TEST (3) -- TYPICAL RESULTS

PNL/MCC
0025

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DYNAMIC LONG-TERM TEST WITH GEOLOGY (4) -- EXPERIMENTAL

SOLID WASTE + EQUILIBRATED GROUNDWATER + ROCK

$$SA_{\text{SAMPLE}} / SA_{\text{ROCK}} / \text{FLOWRATE} = 4 \text{ cm}^2/\text{x/y}$$

- STD TIMES: 3, 14, 42, 90, 180, 360D
- STD °C: 99, 40
- SOLUTIONS:
 - GENERALLY EQUIL. GROUNDWATER
 - SOLUTION ANALYSIS REQUIRED.
- SURFACE ANALYSIS RECOMMENDED AT SHORT TIMES
- SEM/PROBE REQUIRED AT LONG TIMES
- TEST 4A = NO ROCKS/DI H₂O

A.7

DYNAMIC LONG-TERM TEST WITH GEOLOGY (4) -- TYPICAL RESULTS

PNL/MCC
0027

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AUTOCLAVE TEST - REACTION KINETICS (5A, 5B) -- EXPERIMENTAL

(5A) SOLID WASTE + GROUNDWATER + ROCK

TIMES: 3, 14, 42 DAYS

SOLUTIONS: • GENERALLY EQUIL. GROUNDWATER
• HOT SOLUTIONS ARE QUENCHED, WITH DILUTION

SOLUTION ANALYSIS REQUIRED
METALLOGRAPHY/SEM REQUIRED

(5B) SAME AS (5A), EXCEPT NO ROCK, DI H₂O

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0028

AUTOCLAVE TEST - REACTION KINETICS (5A, 5B) -- TYPICAL RESULTS

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0029

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AUTOCLAVE TEST - SOLUBILITY LIMITS (5C) -- EXPERIMENTAL

- **SAME APPARATUS AS 5A**
- **POWDERED WASTE (MESH X)**
- **TEMP. 40°, 99°, 150°, 200°, 250°C**
- **TIMES TO BE ESTABLISHED: 3, 14, 42 d**

**① WASTE + GROUNDWATER + ROCK
(RATIO TO BE DETERMINED)**

OR

**② WASTE + DI WATER
(RATIO TO BE DETERMINED)**

A.11

**PNL/MCC
0030**

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AUTOCLAVE TEST - SOLUBILITY LIMITS (5c) -- TYPICAL RESULTS

PNL/MCC
0031

APPENDIX B

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APPENCIX C

WORKSHOP AGENDA

MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON LEACHING OF WASTE FORMS

Battelle Seattle Research Center
Seattle, Washington
February 12-13, 1980

O. F. (Orv) Hill, Arrangements Chairman
J. E. (John) Mendel, Technical Chairman

AGENDA

February 11	8:00 p.m.	Informal get-together in Research Center Lounge	
February 12	8:15 a.m.	Welcome	Orv Hill
	8:25	Materials Characterization Organization	Phil Permar
	8:40	Introduction to MCC	Ron Nelson
	8:50	Review of Existing leach test methods	John Mendel
	10:00	Coffee break	
	10:15	Proposed MCC Leach Test Development Program	Ray Turcotte
	11:00	Study group topic introduction	John Mendel
		- Waste management criteria	Wayne Ross
		- Scoping tests	Joe Westsik, Jr.
		- Data base for modeling	John Mendel
		- Rate-controlling mechanisms	Ray Turcotte
		- Data reliability	Denis Strachan
	12:00	Lunch	
	1:00 p.m.	Separate meetings of study groups	
	2:30	Coffee break	
	2:45	Continuation of study group discussions	

	4:30	Meeting of whole workshop for progress reports from study groups discussion leaders	Orv Hill, Moderator
	5:00	Cocktail hour	
	6:00	Dinner, with study groups dining together	
	Evening	Open. Those who wish to continue discussions may do so. Group discussion leaders prepare reports for typing.	
February 13	8:00 a.m.	Entire workshop meeting for arrangements update	Orv Hill
	8:15	Separate study group meetings to comment on and revise discussion leader reports.	
	10:00	Coffee break	
	10:15	Report to whole workshop by discussion leaders on conclusions of their study groups (open comment encouraged)	Orv Hill, Moderator
	10:20	Waste management criteria	Wayne Ross
	11:00	Scoping tests (includes obtaining comments on draft of 1st MCC leach test procedure)	Joe Westsik, Jr.
	12:00	Lunch	
	1:00 p.m.	Data base for modeling	John Mendel
	1:45	Rate-controlling mechanisms	Ray Turcotte
	2:30	Coffee break	
	2:45	Data reliability	Denis Strachan
	3:30	Wrap-up	John Mendel and Ron Nelson

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