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PLAN FOR GLASS WASTE FORM TESTING FOR NNWSI

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Lawrence Livermore National Laboratory

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List of Acronyms

ANL	Argonne National Laboratory
CFR	Code of Federal Regulations
CUA	Catholic University of America
DWPF	Defense Waste Processing Facility
LLNL	Lawrence Livermore National Laboratory
MCC	Materials Characterization Center, Pacific Northwest Laboratories
NNWSI	Nevada Nuclear Waste Storage Investigations
PNL	Pacific Northwest Laboratories
SCP	Site Characterization Plan
SOP	Standard Operating Procedure
SRL	Savannah River Laboratory
WCP	Waste Compliance Plan
WPAS	Work Package [Proposal and] Authorization System
WQR	Waste Qualification Report
WVDP	West Valley Demonstration Project

1.0 Purpose and Objectives

1.1 Regulatory Requirements

The purpose of glass waste form testing is to determine the rate of release of radionuclides from breached glass waste containers. This information will be used to qualify glass waste forms with respect to the release requirements of 10 CFR 60.113, and it will be the basis of the source term from glass waste for repository performance assessment modeling. This information will also serve as part of the source term in the calculation of cumulative releases after 100,000 years in the site evaluation process required by 10 CFR 960.3-1-5. It will also serve as part of the source term input for calculation of cumulative releases to the accessible environment for 10,000 years after disposal, to determine compliance with the EPA regulation (40 CFR 191.13). The glass waste form testing scientific investigation directly addresses the following information needs.

{From the 8/07/86 NNWSI Project Issues Hierarchy}

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

- 1.5.1 Waste package design features that affect the rate of radionuclide release.
- 1.5.2 Material properties of the waste forms.
- 1.5.3 Scenarios and models needed to predict the rate of radionuclide release from the waste package and engineered barrier system.

Through input to the above information needs, this investigation will also provide data used to resolve information needs 1.5.4 and 1.5.5, and issues 1.1, 1.9, 1.10, and 1.11.

The glass waste form testing scientific investigation structure closely parallels the information needs listed above. Information about the waste forms which is provided by the producer is accumulated and evaluated (1.5.1); the waste form is tested, properties are determined, and mechanisms of degradation are determined (1.5.2); and models providing long-term evaluation of release rates are designed and tested (1.5.3). As part of this investigation, there are three studies identified in the Site Characterization Plan, Chapter 8; these three studies correspond to the three information needs listed. The study under information need 1.5.2 is further subdivided into three areas of study. The titles and SCP designations of each study and their incorporated activities are given in Section 1.2.

1.2 Glass Testing Activities Grouped by SCP Studies

* Integrate Glass Waste Form Information - (SCP, information need 1.5.1, activities 1.5.1.1.2 and 1.5.1.1.3)

  - D-20-25 Integrate Glass Waste Form Information Provided by Waste Producers
  - D-20-26 Integrate Waste Package and Repository Design Information

* Characterization of the Glass Waste Form - (SCP, information need 1.5.2, study 1.5.2.2 and incorporated activities)

  Leach Testing of Glass

  - D-20-27 Conduct Unsaturated Testing of WVDP and DWPF Glass
  - D-20-28 Conduct Static Leach Testing of WVDP and DWPF Glass

  Materials Interactions Affecting Glass Leaching

  - D-20-29 Parametric Studies of WVDP and DWPF Glass Based on the Unsaturated Test
  - D-20-30 Parametric Studies of WVDP and DWPF Glass Using Static Leaching Methods
  - D-20-31 Studies of Glass Surface Layers and Precipitates
  - D-20-32 Studies of Geochemical Interactions
  - D-20-33 Studies of Scale Factor in Glass Leaching
  - D-20-34 Development of Licensing Database for Glass Waste Form Materials Interactions

  Coordinate Testing With Waste Producers

  - D-20-35 Coordinate Testing with WVDP
  - D-20-36 Coordinate Testing with DWPF/SRL

* Glass Release Modeling - (SCP, information need 1.5.? study 1.5.3.4)

  - D-20-37 Generate Models for Release from Glass
  - D-20-38 Screen Data for Incorporation in Release Model
  - D-20-39 Validate Glass Release Model

1.3 Information Flow

The goals of glass waste form testing are: to provide accurate data and models concerning glass leaching in the repository under anticipated and unanticipated conditions, and to ascertain that there is adequate information to assess the importance of all release mechanisms active under anticipated and unanticipated conditions. (There will be formal definitions of "anticipated" and "unanticipated" conditions; those definitions may change the scope of the listed activities but will not require any changes in the nature of the activities.) The activities listed will achieve these goals through:

1. Identification of important factors than can affect leaching under anticipated and unanticipated conditions at Yucca Mountain. Items may be derived from any of the activities, but activities D-20-29, D-20-30, D-20-31, D-20-32, and D-20-33 are specifically designed to address this area.

2. Determination of relevant data quantifying release rates of radionuclides from glass. Activities D-20-25 through D-20-36 generate data. The primary data comes from activities D-20-27 and D-20-28, with accessory information coming from the other activities at their conclusions. Additional data (including that determined outside NNWSI) is screened for use in activity D-20-38.

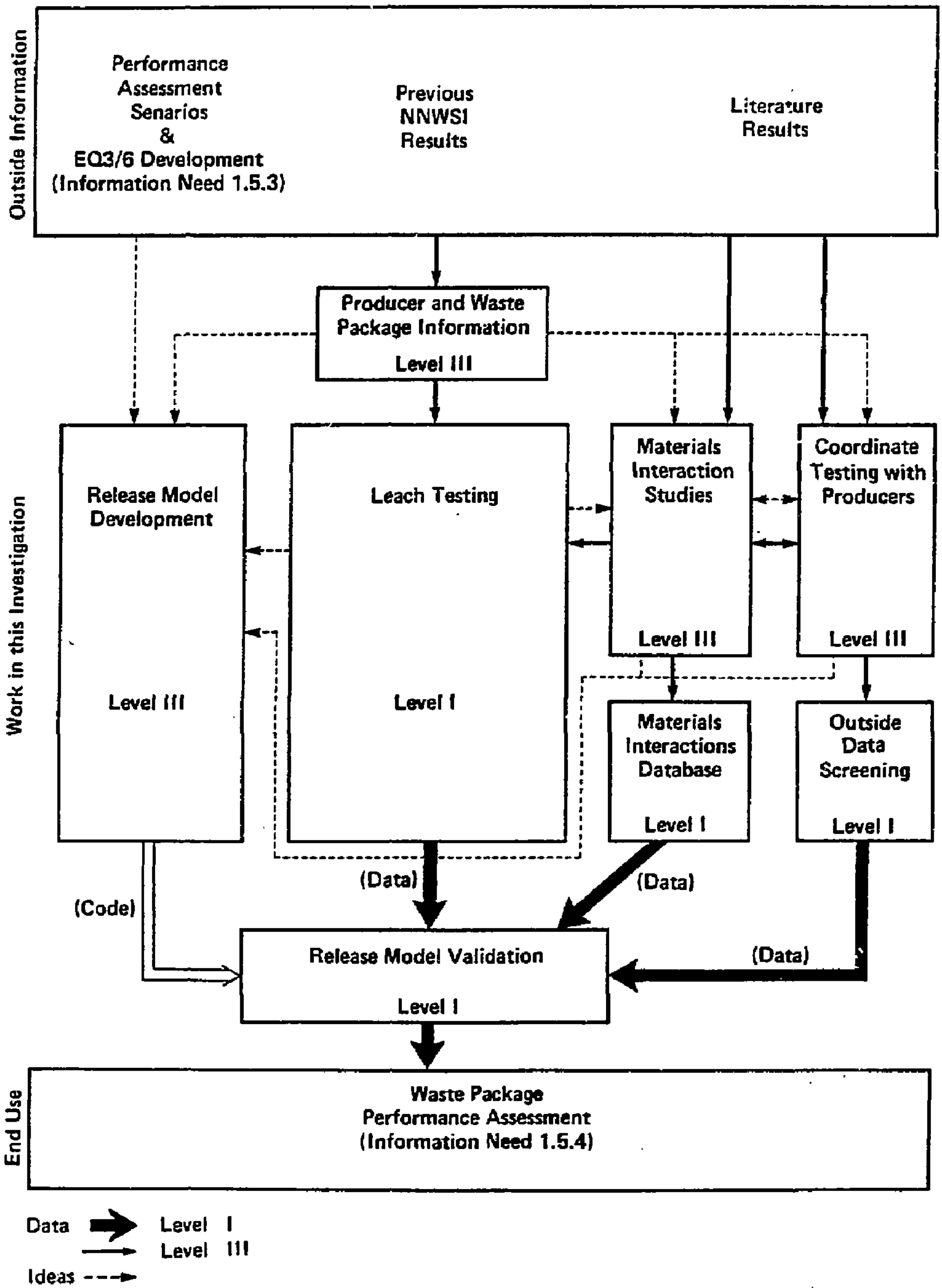
3. Development and testing of models for release under scenarios identified by performance assessment (information need 1.5.3). This work is done in activities D-20-37 and D-20-39.

Because of the large number of activities and the fact that information flows from QA Level III to QA Level I activities, a diagram of that information flow is included (Figure 1).

This investigation plan is not intended as a review of all previous NNWSI glass testing work. That review may be found in the NNWSI Site Characterization Plan, Section 7.4.3.1. Currently, only two glass waste forms have been designated for consideration by NNWSI. Those will be produced by the Defense Waste Processing Facility (DWPF) at the Savannah River Plant and Laboratory (referred to here as SRL) and by the West Valley Demonstration Project (WVDP). The DWPF product is described by Baxter (1983), and the WVDP product is described by Eisenstatt (1986). Should waste forms from the other two defense processing facilities (Hanford and Idaho) be designated for consideration, this plan will be amended to include them.

Figure 1

Glass Waste Form Testing
Information Flow



2.0 Rationale for Selected Studies and Quality Assurance Level Assignments

2.1 Introduction

The technical rationale for the listed activities will be given by type, corresponding to the three areas of study listed in Section 1.2. A rationale for the area of study, as well as for each activity, is given. Quality assurance level assignment sheets for each activity are included in Section 8.0.

The overall rationale for the work in this investigation is as follows. The extension to long times of the semi-empirical relationships discovered in laboratory testing cannot be made without understanding the mechanisms involved and assessing the effects of such factors as the slow build-up of crystalline layers on glass surfaces. Therefore, the overall goal of deriving a usable model for glass release rates can only be achieved through a coupled effort in which laboratory leaching experiments are combined with experiments designed to understand mechanisms. This experimental work is then continuously used to design geochemical models of individual interactions. At the conclusion of the process, a complete model is developed which incorporates the laboratory data and which accurately predicts the results of laboratory and natural analogue experiments. Confidence that the model is applicable to long times is achieved by basing the model on sound geochemical principles, and only using laboratory work to provide values required by the model.

2.2 Integrate Glass Waste Form Information

These activities accumulate information required by the experimental and modeling activities. The waste producer information activity entails participation in the Waste Acceptance Committee and liaison activities with WVDP and DWPF/SRL. The purpose of the activity is to ascertain that the Waste Compliance Plan and Waste Qualification Report contain the information necessary to determine the performance of the waste in a repository at Yucca Mountain. The waste package and repository information activity acquires information from other NNWSI studies. No tests or analyses are performed in either activity.

Activity No.	Name	QA Level
D-20-25	Integrate Glass Waste Form Information Supplied by Waste Producers	III
D-20-26	Integrate Waste Package and Repository Design Information	III

2.3 Characterization of the Glass Waste Form.

2.3.1 Leach Testing of Glass

These two activities are the most important data-collection activities in glass waste form testing. All work in these activities is done at QA Level I. In these two activities, leach testing is conducted under conditions identified from information need 1.5.3 as most important in calculating release rates. Any scenarios to be used in long-term modeling will be directly tested, to the extent possible on a laboratory scale, in these activities. Glasses identified in the producer's Waste Compliance Plans and the Waste Qualification Reports will be tested. Although simulated (nonradioactive) glasses representing important compositional variations will be tested, the emphasis will be on glasses containing the radionuclides expected to remain at 300 to 1000 years after emplacement. The activities have been separated based on test type because of the differing technical requirements of static and Unsaturated testing.

The key outputs from these activities are overall glass degradation rates, radionuclide release rates, and solution compositions in contact with glass.

Activity No.	Name	QA Level
D-20-27	Conduct Unsaturated Testing of WVDP and DWPF Glass	I
D-20-28	Conduct Static Leach Testing of WVDP and DWPF Glass	I

2.3.2 Materials Interactions Affecting Glass Leaching

The purpose of the activities in this area is to determine the mechanisms and nature of glass leaching in the repository environment and to ascertain that no important release mechanism has been overlooked. Extrapolation of laboratory data to the time scales required (10,000 and 100,000 years for anticipated events and processes) is not possible without a fundamental understanding of the mechanisms of glass leaching and of the nature of factors that could perturb leach rates. The data on mechanisms will drive the development of the glass leaching model in activity D-20-37. Data from these activities will be included in the glass release model, either directly or after screening for validation in activity D-20-38.

Activities D-20-29 and D-20-30 (Parametric Studies) provide a means to evaluate the many possible effects on leaching. Activities D-20-31 and D-20-32 are studies of the geochemistry of the glass system and of the layers and solid precipitates that form after extended interaction with water. These studies will provide mechanistic information and will examine the long-term effects of these processes on glass leaching rates. Activity D-20-33 investigates factors such as roughness and flow through cracks that may cause laboratory results to differ from those in actual canisters. These activities are done at QA Level III because of their experimental nature. They will determine geochemical and mechanistic data on glass behavior. Actual testing of glass waste forms, based on results of these experiments, is done in the Leach Testing activities (D-20-27 and D-20-28) at QA Level I. Data generated in these activities will be used in model development and application (D-20-37) after screening (in activity D-20-38). Data consistency will be confirmed through the use of the leaching model.

Activity D-20-34 is a QA Level I activity in which data is collected on materials interactions for the cases where experimental work has adequately defined the problem such that QA Level I tests may be conducted or data may be obtained. An example is the development of a library of infrared spectra to use in identifying surface phases. Interactions data that will be important for licensing, but which do not involve actual leach testing of glass (which would be done in activities D-20-27 and D-20-28), will be developed in this activity. In the case of interactions studied in activities D-20-29 through 33, this will involve duplicating an experimental result by using a written procedure derived from the experiment. This activity will carry through to the final input to performance assessment, though the other materials interactions activities will be phased out as the problems are experimentally defined and QA Level III work is no longer needed.

The key outputs of activities D-20-29 through D-20-33 are mechanisms and identification of important parameters affecting glass leaching. The key outputs of activity D-20-34 are values for parameters quantifying the nature of interactions affecting leaching.

Activity No.	Name	QA Level
D-20-29	Parametric Studies of WVDP and DWPF Glass Based on the Unsaturated Test	III
D-20-30	Parametric Studies of WVDP and DWPF Glass Using Static Leaching Methods	III
D-20-31	Studies of Glass Surface Layers and Precipitates	III
D-20-32	Studies of Geochemical Interactions	III
D-20-33	Studies of Scale Factor in Glass Leaching	III
D-20-34	Development of Licensing Database for Glass Waste Form Materials Interactions	I

2.3.3 Coordinate Testing With Waste Producers

Both the Savannah River Laboratory (working with the DWPF) and the West Valley Demonstration Project are conducting extensive tests of their waste glasses. The purpose of these activities is to coordinate our work with theirs and to assure that data generated by the producers would be usable to NNWSI in licensing. Actual testing will be conducted by the producers, but NNWSI will provide help with experimental design and analysis and will conduct some analyses. Work by NNWSI would be QA Level III, but much of the work by the producers is expected to be QA Level I. (NNWSI work at QA Level I in such matters would be handled under existing QA Level I activities in the appropriate area. The purpose of these activities is not to conduct a testing program but rather to cooperate with activities at DWPF/SRL.)

The key outputs of these activities are the relationships between laboratory and full-scale leaching experiments.

Activity No.	Activity	QA Level
D-20-35	Coordinate Testing with the West Valley Demonstration Project (WVDP)	III
D-20-36	Coordinate Testing with the Savannah River Laboratory and the Defense Waste Processing Facility	III

2.4 Glass Release Modeling

As input to the waste package performance assessment submodel (information need 1.5.3), the glass waste form testing investigation will generate a model for the release of radionuclides from glass under repository conditions. This model will be based upon sound geochemical principles, will use input from the activities listed above as well as from the glass testing literature, and will be validated using both laboratory experiments and natural analogue studies. The model development work is done at QA Level III, and the data and model are validated in QA Level I activities.

The key outputs for these activities are (1) models of glass leaching, (2) a database to use in those models to calculate release, and (3) the validation that the models will accurately predict glass behavior up to 10,000 years (10 CFR 60.113 and 40 CFR 191.13) and 100,000 years (10 CFR 960 3-1-5).

Activity No.	Name	QA Level
D-20-37	Generate Models for Release from Glass	III
D-20-38	Screen Data for Incorporation in Release Model	I
D-20-39	Validate Glass Release Model	I

3.0 Description of Tests and Analyses, and Previous Work

3.1 Introduction

Detailed plans for the 15 activities in Sections 2.2, 2.3, and 2.4 are given in Sections 3.2-3.4. These activities combine experimental work with analyses. Where appropriate, the relative timings of the activities are given. For activities where previous work has been done by NNWSI, a brief description of that work is given. A series of test plans (Section 6.0) will be prepared to provide further details of these activities. All expected use of computer codes is described in section 3.4.

3.2 Integrate Glass Waste Form Information

3.2.1 Integrate Glass Waste Form Information Provided by Waste Producers. D-20-25.

This activity involves participation in the Waste Acceptance Committee and liaison activities with WVDP and DWPF. Participation in the Waste Acceptance Committee assures that the information that NNWSI will need from the producers to qualify glass waste forms is in fact provided in the Waste Qualification Report. This entails review of the producer documents that describe the waste and the Waste Acceptance Plan that describes how the producer will provide the required information.

The liaison activities are to ensure that information on the glass waste forms is provided in a timely fashion, to facilitate review of formal documents and to provide sufficient time for contingency planning. An example of this type of interaction is the ongoing discussion with the waste producers concerning the expected compositions of the glasses as they evolve during the testing programs. This enables NNWSI to keep the glass testing experiments relevant to the expected actual products.

Schedule for the Waste Acceptance Process

The schedule for this activity is tied to that of the Waste Acceptance Committee, and the activity continues to licensing. The schedule for the Waste Acceptance Committee (as presented at the Waste Acceptance Preliminary Specifications NRC briefing, July 31, 1986) is:

Waste Acceptance Preliminary Specifications completed	1/87
Waste Compliance Plans completed	3/87
Waste Qualification Reports completed	6/89
West Valley start-up	9/89
Defense Waste Processing Facility start-up	3/90

3.2.2 Integrate Waste Package and Repository Design Information. D-20-26.

This activity formally accumulates the information required to undertake the experimental and modeling activities requiring design and testing input from other NNWSI activities. No tests or analyses are performed.

3.2.3 Schedule	Start	Complete
Integrate Information Provided by Waste Producers	In Progress	6/89
Integrate Waste Package and Repository Design Information	In Progress	6/89

3.3 Characterization of the Waste Form

3.3.1 Leach Testing of Glass

This is the central area of activity in the glass testing investigation. Its objective is to generate QA Level I data on release from glass for use in performance assessment modeling and for direct use in licensing. Two activities have been defined because of the differing technical requirements of the static and Unsaturated testing. Both activities will use the same glasses and will be conducted at 90°C (principally) as well as at lower temperatures. Water representative of that expected to be found in the repository (J-13 water equilibrated with tuff rock at the test temperature) is used as well as deionized water, which is used in a small proportion of tests to provide a link to the broad body of work conducted outside NNWSI.

3.3.1.1 Conduct Unsaturated Testing of WVDP and DWPF Glass. D-20-27.

Background and Previous Work

The Unsaturated Test measures the interactions between waste glass, canister metal, and repository water that drips onto the glass/metal assembly and then runs off. This simulates the possible release scenario in which a container is perforated at more than one level, allowing water to enter the container, react with glass, and exit the container without standing for an extended length of time. In the test, a cylinder of waste glass is sandwiched between perforated pieces of canister metal, and water is dripped onto the assembly at very low rates. The Unsaturated Test and data obtained using it have been described by Bates and Gerding (1985 and 1986) and Bates et al. (1986a). The test method, along with a representative data package, is currently being prepared for submission to the Materials Review Board (Bates and Gerding, 1987).

The Unsaturated Testing conducted previously has demonstrated several interesting interactions. Because of reactions in which silica and carbonate are precipitated on the glass, it is not uncommon for the glass-metal package to gain weight during testing, which is the result of an interaction between glass and water, precipitating solid phases. Because of this type of interaction, the extent of glass reaction is best measured from the loss of highly soluble elements such as boron. Extensive interaction between the glass and canister metal is occasionally observed in the form of iron and nickel silicates precipitating on the metal and extensive discoloration of the glass where it contacts metal. This enhanced reaction may be due to chemical changes in the 304L stainless steel caused by heat treatments; the test currently uses deliberately sensitized stainless steel to examine this. This interaction will also be extensively examined in parametric studies. Even with these interactions, release rates from the short-term Unsaturated Testing conducted to date are small and are similar to those seen in saturated testing. A QA Level I Unsaturated Test of DWPF glass is currently in progress.

Planned Work

Unsaturated Testing will be conducted on both simulated and radioactive samples of waste glass from both producers. (Unsaturated Testing has already been conducted on simulated DWPF glass; WVDP glass is not yet available for testing). Testing will be done in one-year matrices until the producers publish the Waste Acceptance Plans and the samples of the projected final composition glasses (representing the range expected to be produced) are available. At this point, long-term confirmation testing may begin with open-ended matrices that will extend to licensing. These tests will use glass that is representative of that expected to be present 300 to 1000 years from closure. Unsaturated Testing will be conducted at a minimum of three sites to assure reproducibility. (Testing will be done at LLNL, ANL, and DWPF/SRL; DWPF/SRL is expected to participate in this testing under the Coordinate Testing activity, D-20-36). The details of the test matrices will follow those in the previously published reports, with possible changes derived from the results of parametric studies based on the Unsaturated Test (D-20-29).

3.3.1.2 Conduct Static Leach Testing of WVDP and DWPF Glass. D-20-28.

Background and Previous Work

Static leach testing of glass is conducted with two objectives. First, it tests the release scenario in which water accumulates inside a container and reacts continuously with the glass while overflow and refilling occur. Second, static leach testing provides the simplest and most easily interpreted method of reacting glass with water. The mechanisms and rates derived from this testing may be applied to other scenarios, and the tests are conducted by investigators from all three repository projects and by the two waste producers. This provides a large body of data for use in developing models and calculating releases.

Current static leaching is related to the MCC-1 static leach test (MCC, 1985). As written, this test is too limited to provide information on most conditions of interest to NNWSI, so separate experimental protocols have been developed. These include experiments using different ratios of glass to water and tests including repository material. In all tests, however, the test vessel is unagitated and is sampled terminally. Future static testing will also include the pulsed flow test developed at Catholic University, in which a small proportion of the test fluid is replaced at intervals, simulating an overflow/refill scenario.

NNWSI has conducted a number of static leaching experiments on DWPF glasses and PNL 76-68 glasses, which were proposed as commercial waste glasses. Work on PNL 76-68 glasses is concluded; major reports on PNL 76-68 testing are Bazan and Rego (1986a and 1986b), McVay and Robinson (1984), and Bates and Oversby (1984). Despite the fact that this glass will not be used for disposal, considerable information on mechanisms and the behavior of radionuclides in tuff-dominated systems has been obtained from this work. NNWSI testing of DWPF glasses has been reported in Bates et al. (1986b), Bates and Gerding (1985, 1986), and Bazan and Rego (1985). Collaborative work with SRL has been ongoing in this area, providing a considerable amount of mechanistic and parametric data under NNWSI conditions. No QA Level I static leach testing has been conducted to date.

Planned Work

Static leach testing will be conducted on both simulated and radioactive samples of waste glass from both producers. (Static leach testing has already been conducted on simulated DWPF glass; WVDP glass is not yet available for testing.) Testing will be done in one and two-year matrices until the producers publish their Waste Qualification Reports and the samples of the projected final composition glasses (representing the range expected to be produced) are available. At this point, long-term confirmation testing may begin. These tests will use glass with a radionuclide content that is representative of that expected to be present 300 to 1000 years from closure.

Testing will be conducted principally at 90°C, with some testing at 60°C to determine the effect of temperature on leach rate. Equilibrated J-13 water (equilibrated with tuff rock at the test temperature) will be used. Some tests will use deionized water for comparison to work done elsewhere. As identified by materials interactions testing, repository materials will be included in the testing. It is currently anticipated that tests will be done with glass alone, glass plus 304L stainless steel, and glass plus 304L plus tuff rock.

Long-term confirmation testing will begin as soon as final glass compositions are available from the producers (activity D-20-25). These tests will be conducted as described above, with matrices designed to provide the longest possible test times consistent with input to the licensing process.

3.3.1.3 Schedule

The schedule for these activities is tied to that of the Waste Acceptance Process by the availability of the final waste glass compositions for testing in the long-term confirmation phase. Long-term confirmation testing will continue to licensing to provide as long a time-span as possible of continuous testing of the final waste glasses.

	Begin	End
Unsaturated Testing of Projected WVDP and DWPF Glasses	In Progress	6/89
Static Leach Testing of Projected WVDP and DWPF Glasses	12/86	6/89
Long-Term Confirmation Testing of WVDP and DWPF Glasses Using Unsaturated Testing	6/89	1/91
Long-Term Confirmation Testing of WVDP and DWPF Glasses Using Static Leach Testing	6/89	1/91

3.3.2 Materials Interactions Affecting Glass Leaching

3.3.2.1 Introduction

These activities are intended to determine mechanisms of glass degradation and leaching and to identify important parameters controlling those mechanisms. These studies drive the creation of the glass release model (D-20-37), provide input to the design of Leach Testing (D-20-27 and D-20-28), and provide input to coordinate testing (D-20-35 and D-20-36). In the case of important parameters that are not suitable for determination by Leach Testing (D-20-27 and D-20-28) at QA Level I, this study contains a QA Level I activity for determining those parameters after they have been identified by QA Level III experimentation.

3.3.2.2 Parametric Studies of WVDP and DWPF Glass Based on the Unsaturated Test. D-20-29.

Background and Previous Work

Background and previous work for the Unsaturated Test Method are described in Section 3.3.1.1. Parametric studies based on the unsaturated test method use similar test configurations, but allow variations in test parameters to determine their relative importance. For instance, the drip rate, waste package size, or temperature of the test may be varied. These experiments examine the different scenarios under which water that is not standing may interact with glass in the repository. An important parameter identified by parametric studies, which is now being examined in QA Level I Unsaturated Testing, is the effect of heat-treated 304L stainless steel on glass degradation rates under these circumstances.

Planned Work

Experiments will be conducted to examine the effects of drip rate, sample size, glass-metal contact, metal heat treatment, glass composition, and oxidation state. Other experiments may be identified from coordinate testing (D-20-35 and D-20-36), producer information (D-20-25), or literature results.

3.3.2.3 Parametric Studies of WVDP and DWPF Glass Using Static Leaching Studies. D-20-30.

Background and Previous Work

Background and previous work in static glass testing are described in Section 3.3.1.2.

Planned Work

Because of the large amount of previous work done in this area, the majority of static leach testing will immediately be conducted in the QA Level I Leach Testing activity (D-20-28). Parametric studies will be used to develop new test methods, in particular the CUA Pulsed Flow Test, into test methods that may be used by NNWSI at QA Level I. In addition, parametric studies of glass composition will be conducted. In general, a short parametric study will be conducted prior to each QA Level I test to identify test parameters. Parametric studies for the first set of QA Level I tests in activity D-20-28 have already been completed (see Section 3.3.1.2).

3.3.2.4 Studies of Glass Surface Layers and Precipitates. D-20-31.

Background and Previous Work

Numerous investigations have shown that, under the conditions anticipated a Yucca Mt., when water contacts glass the glass will react to form surface layers composed of amorphous and crystalline precipitates. These studies have been summarized by Bates et al. (1982); the Defense Leaching Mechanisms Program (Mendel, compiler, 1984); and Aines (1986) among others. Aines (1986) discusses the reasons why these layers are expected to control glass leaching. In short, as thick layers form, leaching fluids will no longer have direct access to fresh waste glass.

These layers are critical to glass modeling for two reasons. First, the phases present in them will control the chemistry of leaching fluids. Second, elements precipitated in these phases may be permanently sequestered. For example, the cesium-rich analcime crystals reported by Bates et al. (1982) may permanently reduce the release of cesium from the waste glass; the identity, formation, and possible destruction mechanisms of these precipitates must be studied to determine this.

The principal applications of this study will be design of the glass leaching model (D-20-37) and geochemical interactions studies (D-20-32). The results will also aid in the design and interpretation of QA Level I leach testing (D-20-27 and D-20-28).

Planned Work

Surfaces of glass reacted with water in other leach testing and parametric study activities will be examined to identify the structure, nature, and composition of surface layers formed on them. Techniques used will include scanning electron microscopy, infrared and raman spectroscopy, electron microprobe analysis, X-ray diffraction analysis, ion microprobe analysis, and other techniques as required. These results will be combined with analyses done in the geochemical interactions study (D-20-32) to interpret the results of leaching tests and studies. In addition, glass surfaces will be reacted as part of this activity to generate specific surface conditions. Included in this work is the hydration of glass in a humid atmosphere to study the effect of glass hydration in the repository in the scenario in which the container is perforated but water does not immediately enter the container.

The principal outputs of this activity will be the identity of phases precipitated on nuclear waste glass, their apparent rates of formation, and their composition including sequestered radionuclides. These will be important aspects of the glass leaching model.

3.3.2.5 Studies of Geochemical Interactions. D-20-32.

Background and Previous Work

This activity examines the geochemical interactions that occur between glass, pour canister and container materials, repository materials, and surface precipitates on glass surfaces. The purpose of this activity is to perform experiments that are optimized to isolate specific interactions, and to model those interactions using EQ3/6. In many cases, previous work has been unsatisfactory in determining the nature of interactions such as that between the silica content of leaching fluids and the rate of leaching. In this study, that interaction would be isolated experimentally by altering the silica content of a leaching fluid, and the results would be modeled using EQ3/6. These experiments will drive the glass release model development.

Planned Work

This activity will provide a highly interactive environment incorporating experimental studies and glass leaching model development. If a specific interaction is identified experimentally in other activities, it will be examined in this activity to determine whether existing geochemical modeling codes are adequate to model the interaction. If more data are required about the interaction, it is obtained through experiments or from the literature if available. Conversely, this activity will also involve the experimental evaluation of interactions that are predicted to occur by the geochemical modeling codes.

Two interactions are currently planned for study. The first is the interaction between silica-containing phases, silica in solution, and the glass dissolution rate. These will be studied by adding silica in solution to leaching fluids and by adding solid phases predicted to control silica solubility. The silica content of the leaching fluids is currently thought to be the principal control on leach rates; hence, this is a critical parameter to examine fully. The second interaction that will be examined is that between heat-treated stainless steel (sensitized or pre-sensitized) and silica-rich solutions. Results from parametric unsaturated studies indicate that the formation of iron and chrome silicates may deplete the leaching fluid in silica and enhance leach rates. Since the pour canister is expected to have undergone a history resulting in heat-induced changes in the metal, this is also an important interaction.

3.3.2.6 Studies of Scale Factor in Glass Leaching. D-20-33.

Background and Previous Studies

Almost all studies of glass leaching are conducted on a laboratory scale because of the tremendous cost of full-scale testing. The one exception in work in the United States is the work of Bickford and Pellarin (1986). Full-scale testing will be conducted in cooperation with the waste producers (D-20-35 and D-20-36). To complement those studies it may also be necessary to do one or more of the following: study the same samples in the laboratory, to study the flow of water through a glass canister, or to study the disaggregation of the glass waste in the canister. The modeling of flow of water through cracks in glass in the pour canister may be critical in the determination of the relative importance of static vs. unsaturated leach testing and, accordingly the weighting of results from those types of testing, in their ultimate use in waste package performance assessment.

Planned Work

Plans will be made for this activity after the results of full-scale testing (D-20-35 and D-20-36) are known. It is anticipated that an assessment of the potential water flow paths in a glass canister will have to be made.

3.3.2.7 Development of Licensing Database for Glass Waste Form Materials Interactions. D-20-34.

Background

Activities D-20-31, D-20-32, and D-20-33 are QA Level III experimental activities designed to understand mechanisms and drive model development (D-20-37). However, it is anticipated that application of the glass release model will require that the values of the important parameters be derived from a QA Level I activity. In addition, there are aspects of materials interactions for which no QA Level III experimental work is necessary, and work can proceed directly at QA Level I. In this activity, experimental work will be used to generate test protocols such that QA Level I data may be derived for important materials interactions parameters that will be used in the glass release model. QA Level III parametric studies of leaching move to the QA Level I leach testing activities; this activity only concerns data on mechanisms and reaction rates of individual interactions that will be required by the computer model (D-20-37).

Planned Work

Most of the work in this activity will be derived from other activities as the important parameters are identified. The derivation of a library of infrared spectra of phases important to waste glass alteration will be undertaken. The samples used in this library will also be available for other characterization (such as thermodynamic constants or exchange capacity) or for QA Level I testing derived from activities D-20-31 and D-20-32.

3.3.2.8 Schedule

Each of the QA Level III activities in this study feed into a QA Level I activity, either in this activity, in leach testing (D-20-27 and D-20-28), or in model development. Each of the QA Level III activities accordingly decreases in scope as the work is fed into a QA Level I activity.

	Begin	End
Parametric Studies of WVDP and DWPF Glass Based on the Unsaturated Test	In Progress	6/88
Parametric Studies of WVDP and DWPF Glass Using Static Leaching Methods	In Progress	6/88
Studies of Glass Surface Layers and Precipitate	In Progress	8/89
Studies of Geochemical Interactions	In Progress	8/89
Studies of Scale Factor in Glass Leaching	8/88	8/89
Development of Licensing Database for Glass Waste Form Materials Interactions	6/87	8/89

3.3.3 Coordinate Testing with Waste Producers

3.3.3.1 Introduction

No testing will be conducted by NNWSI as part of this activity. NNWSI will cooperate with the waste producer's testing programs in areas of experimental and test design, in supply of repository materials such as tuff rock and J-13 water, and in post test analysis (in particular in the areas of activities D-20-31,D-20-32, and D-20-33). Both producers will be performing laboratory scale tests similar to those done by NNWSI; this activity will monitor the concurrence between those results. Both producers will also conduct full-scale tests, which NNWSI will use to validate laboratory-scale results and model calculations.

3.3.3.2 Coordinate Testing with WVDP. D-20-35.

WVDP will conduct pulsed-flow and static testing (at CUA) using J-13 water supplied by NNWSI. NNWSI will use the results of this work in designing static leach tests for WVDP glass. It is anticipated that WVDP will conduct leach tests of full-scale canisters, using J-13 water, in which the head-space in the pour canister is filled with water and maintained at 90°C. The experiment will be sampled periodically and will continue for at least two years.

3.3.3.3 Coordinate Testing with DWPF/SRL. D-20-36.

An extensive coordinate testing program with DWPF/SRL is currently underway, resulting in several publications (Bibler, 1986; Bibler et al., 1984). It is anticipated that SRL will conduct a leach test of canister sections (in 55-gallon polyethylene drums, after Bickford and Pellarin, 1986) using J-13 water and a headspace-leaching experiment as described for WVDP. In addition, SRL has conducted, and will continue to conduct, laboratory scale leach testing of fresh, fully radioactive waste glass. This testing requires remote handling for both the production and leaching phases and would be prohibitively expensive for NNWSI to undertake. The results of leaching this fully-radioactive glass will be applied to assessment of the unanticipated condition of container failure prior to the end of the 300 to 1000 year containment period. It is anticipated that SRL will conduct Unsaturated Testing according to the NNWSI Test Procedure. Finally, it is anticipated that SRL will conduct tests of water flow inside glass canisters, in conjunction with modeling and laboratory work in activity D-20-33 (studies of scale factor in glass leaching).

3.3.3.4 Schedule

The detailed schedule for these activities will be set by the producers.

	Begin	End
Coordinate Testing with WVDP	6/87	6/89
Coordinate Testing with SRL/DWPF	In Progress	6/89

3.4 Glass Release Modeling

3.4.1 Introduction

The release of radionuclides from glass waste forms may occur if water contacts a container that has breached. As input to the waste package performance assessment submodel, the glass waste form testing investigation will generate, validate, and apply a model for the release of radionuclides from waste glass under repository conditions. The output from this model will be fed in either tabular or simple functional form to the performance assessment submodel. The model will be based upon sound geochemical principles and will not be a simple fit to laboratory data; on the contrary, the laboratory data will provide the values of important parameters in the model, and laboratory and natural analogue studies will be used as part of the validation of the model.

3.4.2 Generate Models for Release from Glass. D-20-37.

Background and Previous Work

The objective of this activity is to design models for glass release based on the scenarios identified in information need 1.5.3. The geochemical modeling code package EQ3/6 will be an important part of these models. The extension to long times of the semi-empirical relationships discovered by laboratory testing cannot be made without understanding the mechanisms involved and assessing the effects of factors such as the slow build-up of crystalline layers. The model to be developed will account for glass degradation and radionuclide release using EQ3/6 in a combination of equilibrium and kinetic calculations. The EQ3/6 codes have been described by Wolery (1979, 1983, and 1986) and their proposed application to glass modeling was described by Aines (1986).

Description

Glass performance modeling will depend upon two basic concepts. First, the rate of release from the thermodynamically unstable waste glass is a kinetically controlled process. No formal equilibrium can exist. Second, once components are released from glass, the formation of solids and composition of fluids may be modeled by equilibrium processes. The final outcome of these equilibrium processes will be modeled, providing important limits on the behavior of radionuclides. In addition, the kinetics of these processes may be modeled to provide more accurate estimates of radionuclide concentrations in waste package fluids as a function of time throughout the life of the repository.

The model for glass degradation will incorporate the following items, presented here in the order in which they will be developed:

1. Calculation of the composition of the solutions that are in true equilibrium with the solid phases that precipitate on the surface of nuclear waste glasses.

2. Calculation of the rate of degradation of glass using kinetic rate laws based on transition state theory, deriving rate constants from experimental and natural-analogue studies.

3. Calculation of the rate of formation of solid precipitates, and the concomitant rate at which radionuclides are permanently sequestered in those stable phases.

4. Calculation of the effects of repository materials on the above items, including heat-affected stainless steel from the pour canister.

5. Calculation of the composition of fluids leaving a glass waste package by combining the above items.

In each case the appropriate analytical expressions will be identified from experimental work, from review of the glass degradation literature, and from geochemical modeling concepts incorporated in EQ3/6. Calculations will be performed using EQ3/6 and, if necessary, additional codes serving as pre- and post processors to EQ3/6; the extent to which these are necessary will be determined by future EQ3/6 development and the nature of the performance assessment scenarios identified for the glass release model. Current plans for EQ3/6 code development (EQ3/6, 1986) include one major item required for glass modeling, that being development of a flow-through model where a stationary reacting assemblage (the waste package) reacts with successive packets of water.

3.4.3 Screen Data for Use in Release Model. D-20-38.

Background and Previous Work

An extensive literature on the mechanisms and rates of glass dissolution may be addressed in designing and executing the glass release model. All data generated outside NNWSI will be screened in this activity, including that generated by waste producers. The objectives will be to establish the accuracy and precision of individual parameters and to ascertain that the glass release model uses only accurate and verifiable data. It is anticipated that the principal values and equations in the model will be derived by NNWSI under QA Level I conditions. This activity allows the large body of outside data to be used to corroborate and support the NNWSI data, and it allows important data and ideas generated outside NNWSI to be used in the model.

Description of Planned Work

Data generated outside NNWSI will be collected and examined to determine whether it is consistent with NNWSI data. If it is not, an examination of both data sets will be made to determine the origin of the discrepancy. When outside data is determined to be critical to the operation of the glass model (for example, data from full-scale testing by the producers), the NNWSI SOP-03-03 for using non-NNWSI data will be implemented. It is anticipated that critical producer data will be obtained under QA Level I.

An important aspect of this activity is the comparison of NNWSI data to that collected outside the project. This comparison will ensure that NNWSI is able to confirm that the glass release model is consistent with applicable data that may arise in licensing. When the data are inconsistent, an assessment of the cause of the discrepancy will be prepared. In the instance of the NNWSI data being incorrectly collected or applied, this activity allows the problems to be resolved and new data obtained under one of the data collection activities (D-20-27 through D-20-36). A formal mechanism for this screening process will be established.

3.4.4 Validate Glass Release Model. D-20-39.

Description of Planned Work

Validation of the glass model will be done in two stages. First, the model will be developed in concert with experimental work and will be tested for its ability to describe accurately the experimental work. An important aspect of this is the use of modeling to aid in understanding the physical processes that are important in glass degradation in activity D-20-32 (studies of geochemical interactions). Second, the results of long-term modeling will be compared with extrapolations of laboratory data and with natural analogues. This second effort will both test the validity of the model and, more importantly, determine whether the experimental work has examined all the important geochemical interactions that are predicted to occur over long periods of time.

Because EQ3/6 will be a fundamental part of the glass release model, validation activities for that family of codes will be established in conjunction with the other users of the code. The validation areas are:

1. Database. Critical database items will be reviewed under the data screening activity.
2. Code Operation. A series of benchmark validation code runs will be established for EQ3/6 to test major operations common to all applications.
3. Laboratory Experiment Matching. The glass release model must accurately predict the result of laboratory and full-scale leach testing.
4. Natural Analogues. To determine whether the glass release model accurately predicts solution compositions after long-term contact with glass, it will be used to model natural groundwaters in contact with glass.

All four of these validation areas are required to confirm that the model accurately predicts the behavior of glass/water systems for thousands of years.

3.4.5 Schedule

The schedule for model development is tied to the schedules of performance assessment and EQ3/6 code development.

	Begin	End
Generate Models for Release from Glass	In Progress	3/89
Screen Data for Incorporation in Release Model	6/87	6/89
Validate Glass Release Model	10/87	8/89

4.0 Application of Results

The information provided by this investigation will provide the source term for radionuclide release from waste packages. The information directly addresses the following information needs.

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

1.5.1 Waste package design features that affect the rate of radionuclide release.

1.5.2 Material properties of the waste forms.

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

Through input to the above information needs, this investigation will also provide data used to resolve information needs 1.5.4 and 1.5.5, and issues 1.1, 1.9, 1.10, and 1.11.

This information will also serve as part of the source term in the calculation of cumulative releases after 100,000 years in the site evaluation process required by 10 CFR 960.3-1-5. It will also serve as part of the source term input for calculation of cumulative releases to the accessible environment for 10,000 years after disposal, to determine compliance with the EPA regulation (40 CFR 191.13).

The interrelationships among the activities in this investigation have been discussed in each section. In general, the goal of the investigation is to provide input to the waste package performance assessment submodel in the form of output from the glass release model. Important parameters in this model are quantified in the Leach Testing activities (D-20-27 and D-20-28), the materials database activity (D-20-34), and the data screening and validation activities (D-20-38 and D-20-39). The principles, mechanisms, and ideas for the release model are developed in experimental activities and data collection activities (D-20-25, D-20-26, D-20-29 through D-20-33, D-20-35, and D-20-36). In each case, ideas are developed in QA Level III activities, and data for use in the model is derived in QA Level I activities arising from the QA Level III activities.

5.0 Schedule and Milestones

5.1 Discussion and Assumptions

The schedule for individual activities has been discussed in Section 3.0. The overall schedule for the waste package performance assessment investigation is tied to two other schedules: (1) the information required to construct and use the waste package performance assessment code, currently planned for 8/89; and (2) the schedule for the Waste Acceptance Process controls when the final qualification reports are available, currently planned for 6/89. Long-term confirmation testing, using the final waste glass compositions, will continue beyond that date to verify the shorter-term results that will have been input earlier into the performance assessment models. Because of the late date for the final qualification reports, the long-term confirmation testing must be conducted after the initial input to the performance assessment model is made.

This schedule was prepared according to the funding levels in the FY 1988 WPAS. Reductions in funding levels would result in concomitant slippage of the schedule and milestones. Several activities outside this investigation can possibly affect this schedule. (1) The waste producers must meet the June 1989 deadline for production of the WQR. The waste described in the WQR must be reasonably similar to that currently planned; if it is not, new parametric and experimental studies would have to be undertaken in addition to QA Level I testing. Schedule slippage would depend on the degree to which the actual waste glass differs from that described by the current producer documents (Baxter, 1983 and Eisenstatt, 1986). (2) The container material must be selected according to the current scheduled milestone in September 1987. If a container material other than austenitic stainless steel is chosen, some slippage could occur while preliminary tests of that material are conducted in D-20-30 and D-20-32. (3) If the results of exploratory shaft testing, other materials testing, and waste package environment testing do not confirm the current estimates of the package environment, as described in the SCP, schedule slippage concomitant with the degree of discrepancy will occur.

5.2 Schedule

	Start	Complete
<u>Integrate Glass Waste Form Information</u>	In Progress	6/89
Integrate Glass Waste Form Information Provided by Waste Producers. D-20-25.	In Progress	6/89
Integrate Waste Package and Repository Design Information. D-20-26.	In Progress	6/89
<u>Leach Testing of Glass</u>	In Progress	6/89
Conduct Unsaturated Testing of Projected WVDP and DWPF Glasses. D-20-27.	In Progress	6/89

Conduct Static Leach Testing of Projected WVDP and DWPF Glasses. D-20-28.	12/86	6/89
(Long-term confirmation testing will be conducted as a continuation of activities D-20-27 and D-20-28)		
Long-Term Confirmation Testing of WVDP and DWPF Glasses Using Unsaturated Testing. D-20-27.	6/89	1/91
Long-Term Confirmation Testing of WVDP and DWPF Glasses Using Static Leach Testing. D-20-28.	6/89	1/91
Materials Interactions Affecting Glass Leaching	In Progress	1/89
Parametric Studies of WVDP and DWPF Glass Based on the Unsaturated Test. D-20-29.	In Progress	6/88
Parametric Studies of WVDP and DWPF Glass Using Static Leaching Methods. D-20-30.	In Progress	6/88
Studies of Glass Surface Layers and Precipitates. D-20-31.	In Progress	8/89
Studies of Geochemical Interactions. D-20-32.	In Progress	8/89
Studies of Scale Factor in Glass Leaching. D-20-33.	8/88	8/89
Development of Licensing Database for Glass Waste Form Materials Interactions. D-20-34.	6/87	8/89
Coordinate Testing with Waste Producers	In Progress	6/89
Coordinate Testing with WVDP. D-20-35.	6/87	6/89
Coordinate Testing with SRL/DWPF. D-20-36.	In Progress	6/89
Glass Release Modeling	10/86	8/89
Generate Models for Release from Glass. D-20-37.	In Progress	3/89

Screen Data for Incorporation in Release Model. D-20-38.	6/87	6/89
Validate Glass Release Model. D-20-39.	10/87	8/89

5.3 Milestones

Number	Title	Date
	Report on Unsaturated Testing of DWPF glass.	9/87
C397	Report on Glass Release Model	9/87
M009	Initiate long-term testing of WVDP and DWPF HLW.	10/87
	Determine release from DWPF glass at 60°C relative to that at 90°C.	11/87
	Report on alteration of glass surfaces and geochemical interactions.	11/87
W208	Complete parametric testing of glass.	6/88
M269 & P112	Complete testing for design purposes.	9/88
	Report on database for glass modeling and required model validation exercises.	3/89
	Initiate long-term confirmation testing of WVDP and DWPF glass.	6/89
	Complete study of alteration of glass surfaces.	8/89
M012	Model long-term expected performance of waste forms under repository conditions.	8/89
	Report on leaching of waste glass for license application.	10/89
	Complete long-term confirmatory testing of waste glass.	6/91

6.0 List of Test Plans to Support this Plan

The following test plans will describe in detail the activities described in this investigation plan.

Test Plan	Scheduled Completion Date
NNWSI Plan for Leach Testing of Glass Waste Forms	11/86
Plan for NNWSI Testing of Materials Interactions Affecting Leaching of Glass Waste Forms	3/87
Plan for Coordinate Testing Between NNWSI and Glass Waste Form Producers (DWPF/SRL and WVDP)	5/87
NNWSI Plan for Generation, Testing, and Validation of a Model of Release of Radionuclides from Glass Waste Forms	1/87

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