UCID--21272

DE88 005802

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the Office of Geologic Repositories of the DOE Office of Civilian Radioactive Waste Management.

This report is based on the Waste Form-Spent Fuel Scientific Investigation Plan (SIP) for WBS element 1.2.2.3.1 for NNWSI. This SIP should be used as the reference document.

JD

PLAN FOR SPENT FUEL WASTE FORM
TESTING FOR NNWSI

Henry F. Shaw

Revision 0
Manuscript Date 10/16/87

November 1987

Table of Contents

1.0 Purposes and Objectives

1.1 Regulatory Requirements

The purpose of spent fuel waste form testing is to determine the rate of release of radionuclides from failed disposal containers holding spent fuel, under conditions appropriate to the Nevada Nuclear Waste Storage Investigations (NNWSI) Project tuff repository. The information gathered in the activities discussed in this document will be used in the following ways:

1) to assess the performance of the waste package and engineered barrier system (EBS) with respect to the containment and release rate requirements of the Nuclear Regulatory Commission (NRC) rule 10-CFR-60.113;

2) as the basis for the spent fuel waste form source term in repository-scale performance assessment modeling to calculate the cumulative releases to the accessible environment over 10,000 years to determine compliance with the Environmental Protection Agency (EPA) rule 40-CFR-191.13;

3) as the basis for the spent fuel waste form source term in repository-scale performance assessment modeling to calculate cumulative releases over 100,000 years as required by the site evaluation process specified in the DOE siting guidelines, 10-CFR-960.3-1-5.

The scientific investigations discussed herein are intended to address directly the following information needs taken from the NNWSI Project Issues Hierarchy (version dated 8/07/86):

"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, the results of the spent fuel activities will provide data to help resolve information needs 1.4.4, 1.5.4, and 1.5.5, and issues 1.1, 1.4, 1.9, 1.10, and 1.11.

The structure of this spent fuel waste form Scientific Investigation Plan (SIP) closely parallels the information needs listed above and the discussion in Chapter 8 of the NNWSI Project Site Characterization Plan (SCP) of the studies to be undertaken to resolve the information needs. In summary, information about the waste form which can be gathered from vendors, the utilities and other outside sources is accumulated and evaluated (1.5.1); the waste form is subjected to various tests to determine its properties and mechanisms of degradation and radionuclide release (1.5.2); and models to predict the long-term performance of the waste form are developed and tested (1.5.3). Chapter 8 of the SCP defines three studies that are within the domain of this SIP, one study for each of the three information needs listed above. The study for information need 1.5.2 is further subdivided into six areas of study, known as activities. The titles and SCP designations of each study and activities that compose each study are shown in section 1.2.

1.2 Spent Fuel Activities Grouped by SCP Study

Integrate Spent Fuel Information - (SCP Information need 1.5.1, activities 1.5.1.1.1 and 1.5.1.1.3)

D-20-40 Integrate spent fuel waste form information provided by vendors, utilities, and other sources

D-20-41 Integrate NNWSI Project waste package and repository design information

Characterization of the Spent Fuel Waste Form - (SCP Information need 1.5.2, activities 1.5.2.1.1 through 1.5.2.1.6)

Dissolution/leach tests of spent fuel and UO_2

D-20-42 Saturated, semi-static dissolution tests of spent fuel and UO_2

D-20-43 Unsaturated dissolution tests of spent fuel and UO_2

Oxidation tests on spent fuel and UO_2

D-20-44 Oxidation tests of spent fuel and UO_2 using a thermogravimetric apparatus

D-20-45 Oven-oxidation tests of spent fuel and UO_2

Corrosion and release tests from cladding and assembly materials

D-20-46 Corrosion/degradation/release tests on Zircaloy and stainless steel cladding

D-20-47 Corrosion/release tests on assembly hardware

D-20-48 Carbon-14 inventory and release tests

Planning and experimental design

D-20-49 Technique development for test planning and design

Generate Models for Release from Spent Fuel - (SCP Information Need 1.5.3, activity 1.5.3.3.1)

D-20-50 Generate models for release of radionuclides from the spent fuel waste form

D-20-51 Screen data for incorporation into release model

D-20-52 Finalize and validate spent fuel release model

1.3 Information Flow

The goals of the spent fuel waste form testing technical area are: to provide accurate data and models concerning the release of radionuclides from the waste form under tuff repository conditions, and to insure that there is sufficient information to assess the importance of all sources and release mechanisms active under both anticipated and unanticipated conditions. Although at this time, the formal definitions of "anticipated" and "unanticipated" conditions have not been set, any changes from the present, working definitions of these terms may change the scope of the listed activities but will not require any changes in the nature of the activities. The activities will achieve the stated goals through:

1) Identification of the range in properties and types of spent fuel currently in storage and a projection of the same for spent fuel that is yet to be generated, but which is destined for disposal in the first repository. Activity D-20-40 is designed to fulfill this goal.

2) Identification of important factors that can affect radionuclide release. These factors may be identified under any of the listed activities, but numbers D-20-42, D-20-43, D-20-44, D-20-45, D-20-46, D-20-47, and D-20-48 are specifically designed to address this area. Additional data, typically those which are generated by projects other than NNWSI, are screened for use in activity D-20-51.

3) Development and testing of models for release under the scenarios identified by performance assessment. These scenarios are gathered and integrated under activity D-20-41 and the modeling done under activities D-20-50 and D-20-52.

This Scientific Investigation Plan is not intended as a review of all previous NNWSI Project work on the spent fuel waste form. Such a review may be found in section 7.4.3.1 of the NNWSI Project SCP.

2.0 Rationale for Selected Studies and Quality Assurance Level Assignments

2.1 Introduction

In this section, the technical rationale for the listed activities are 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 of this document.

The overall justification for the work in this investigation is as follows. The extension to long times of the empirical relationships determined by laboratory testing cannot be made without an understanding of the physical and chemical mechanisms involved in a given process. Therefore, the overall goal of producing a usable model for the release of radionuclides from the spent fuel waste form can only be achieved by coupling the laboratory experiments to an effort to identify and model the process at some more fundamental level. This effort is by its nature, interactive: results of the experimental work drive model development which in turn, suggests new experiments aimed at corroborating and refining the model. At the conclusion of this process, one hopes that a model will result that incorporates the laboratory data and which accurately predicts the results of experiments that were not used in constraining the model. Confidence that the model is applicable to long times will be achieved by basing the model on sound physio-chemical principles and laws.

2.2 Integrate Spent Fuel Information

These activities accumulate information required by the experimental and modeling activities.

Activity D-20-40 entails participation in the Spent Fuel Working Group and liaison activities with the Office of Storage and Transportation Safety (OSTS), the Materials Characterization Center (MCC), and any other groups that may provide data on spent fuel. The purposes of the activity are to accumulate data on the population statistics of spent fuel, insure that representative samples of spent fuel are available for testing, and identify the as-fabricated and as-irradiated characteristics of spent fuel that could affect the inventory and release of radionuclides.

Under activity D-20-41, waste package and repository information that is generated from other NNWSI studies is accumulated. This information is required so that the experimental work can be done under conditions relevant to the repository.

Both of these activities are conducted at QA Level III. Data accumulated under activity D-20-40 that will be used in the release model presented for licensing will be screened before inclusion under the QA Level I activity D-20-51. It is anticipated that all data accumulated under activity D-20-41 that will be used in the spent fuel release model for license application will already be at QA Level I. One function of D-20-41 will be to separate NNWSI Project-generated information that was acquired under QA Level I conditions from that acquired under QA Level III conditions so that only Level I data are used in the model.

Other technical areas within the NNWSI Project Waste Package Task or the Project in general may have need for some of the information assembled by these activities. The validation of data pertaining the spent fuel waste form that is not used in the spent fuel release model, but is used by other areas is the responsibility of the user.

No tests or analyses are performed in either activity.

Activity No.	Name	QA Level
D-20-40	Integrate spent fuel waste form information provided by vendors, utilities, and other sources	III
D-20-41	Integrate NNWSI Project waste package and design information	III

2.3 Characterization of the Spent Fuel Waste Form

2.3.1 Dissolution/leach tests of spent fuel and UO_2

These two activities are the most important data-collection activities in spent fuel waste form testing. All work in these activities is done at QA Level I. The testing is done under conditions identified by activity D-20-41 and D-20-50 (Information Need 1.5.3) as most important in calculating release rates. Any scenarios to be used as the basis for long-term modeling will be tested to the extent possible on a laboratory scale. Spent fuel with characteristics spanning the range identified in activity D-20-40 will be tested. In addition, oxidized fuel produced under activity D-20-45 will be tested. The two dissolution activities have been separated based on the different technical requirements of the semi-static and unsaturated tests.

The key outputs from these activities are the dissolution rate of irradiated fuel, the release rates of radionuclides from spent fuel, and the solution chemistry of water in contact with spent fuel.

Activity No.	Name	QA Level
D-20-42	Saturated, semi-static dissolution tests of spent fuel and UO_2	I
D-20-43	Unsaturated dissolution tests of spent fuel and UO_2	I

2.3.2 Oxidation tests of spent fuel and UO_2

The purposes of the activities in this area are to determine the rates and mechanisms of oxidation of irradiated UO_2 fuel and to assess the possibility of oxidation of the fuel in the repository. The oxidation of UO_2 to higher O/U ratios may affect the rate of release of radionuclides from the fuel and, due to the volume changes associated with oxidation, may cause enlargement of pre-existing cladding failures. All work in this area is to be done at QA Level I. Some of the oxidized fuel specimens produced under activity D-20-45 will be used in activity D-20-42 and/or D-20-43. The two oxidation activities have been separated based on the different techniques involved in conducting the tests.

The key outputs of activities D-20-44 and D-20-45 are experimental data on the rate of oxidation of irradiated UO_2 as determined from weight-gain curves. These data will be used to drive the generation of a mechanistic model for the oxidation of UO_2 in activity D-20-50.

Activity No.	Name	QA Level
D-20-44	Oxidation tests of spent fuel and UO_2 using a thermogravimetric apparatus	I
D-20-45	Oven-oxidation tests of spent fuel and UO_2	I

2.3.3 Corrosion and release tests of cladding and assembly materials

The testing done in this area is designed to:

1) evaluate the corrosion and failure rate of cladding;

2) determine the rate of release of radionuclides from cladding;

3) determine the rate of release of radionuclides from assembly hardware parts.

The rate at which cladding fails in the repository will, in part, determine the release rate of radionuclides from the enclosed fuel. In addition, both the cladding and other assembly parts contain radionuclides and thus must be characterized with respect to their corrosion and release characteristics. All of the tests conducted in these activities will be done at QA Level I. Because of the different materials involved, work on cladding and hardware have been separated into two different activities. Work on the release of carbon-14 has been put into a third, separate activity because, unlike other radionuclides of concern, it can be released in gaseous form as CO_2. Because of this, the types of tests required to characterize the inventory and release of carbon-14 are quite different than those used for the other radionuclides.

The key outputs of activity D-20-46 are the rates of various failure modes of cladding, and the rate of release of radionuclides from cladding. Activity D-20-47 will provide data on the inventory and release of radionuclides from assembly components. Activity D-20-48 will determine the inventory, distribution, and release characteristics of carbon-14 as gaseous $^{14}CO_2$ from the waste form. The data generated by activities D-20-46 through D-20-48 will be used in the radionuclide release model developed under activity D-20-50.

Activity No.	Name	QA Level
D-20-46	Corrosion/degradation/release tests on Zircaloy and stainless steel cladding	I
D-20-47	Corrosion/release tests on assembly hardware	I
D-20-48	Carbon-14 inventory and release tests	I

2.3.4 Planning and Experimental Design

Many of the tests performed under activities D-20-42 through D-20-48 require a certain amount of initial experimentation to determine the best way to conduct the test. In addition, there are many experimental protocols and examination techniques that, though potentially applicable to the problems being investigated, have never been tried under the conditions relevant to the NNWSI Project spent fuel testing program. This activity is intended to provide a mechanism whereby new experimental techniques can be evaluated with respect to their applicability to a particular test and their ability to provide useful information. This activity is to be conducted at QA Level III in order to allow the maximum flexibility in adapting procedures to the NNWSI testing program while maintaining the cost-effectiveness of the program. If a technique examined under this activity is judged useful or valuable for the spent fuel testing program, then procedures will be written to allow its use in QA Level I activities. It is likely that some of the techniques tried will not work and will never be used in other activities.

The key outputs of this activity are experimental techniques and testing or examination methods that can be used in testing activities conducted at QA Level I.

Activity No.	Name	QA Level
D-20-49	Technique development for advanced test planning and design	III

2.4 Generate Models for Release from Spent Fuel

As input to the waste package performance assessment model (Information Need 1.5.3), the spent fuel waste form testing program will produce a model for the release of radionuclides from the spent fuel waste form under tuff repository conditions. This model will be based on sound physio-chemical principles and will use data from the above experimental activities, as well as the literature as input data. The model will be validated using laboratory experiments, and, if suitable examples can be identified, studies of natural analogues. The model will consist of several sub-models: a sub-model for the release of radionuclides from spent fuel, cladding, and assembly hardware; a sub-model for the failure rate of cladding; and a sub-model for the oxidation of UO_2. The chemical and kinetic aspects of the models will make extensive use of the geochemical modeling code EQ3/6 (Wolery, 1979; 1983; 1987). Initial model development work will be done at QA Level III; however, the model is finalized and the data and model are validated under QA Level I activities (Activities D-20-51 and D-20-52).

The key outputs for these activities are:

1) a model or models for the release of radionuclides from the spent fuel waste form, consisting of several sub-models;

2) a database to use in these models and sub-models;

3) the validation that the model(s) and sub-models can realistically predict the behavior of the waste form for 10,000 years (10-CFR-60.113 and 40-CFR-191.13) and 100,000 years (10-CFR-960.3-1-5) to the degree necessary to supply source term information to the Performance Assessment areas.

Activity No.	Name	QA Level
D-20-50	Generate models for the release of radionuclides from the spent fuel waste form	III
D-20-51	Screen data for incorporation into the release model	I
D-20-52	Finalize and validate the spent fuel release model	I

3.0 Description of Tests and Analyses, and Previous Work

3.1 Introduction

Detailed plans for the 13 activities covered by this Scientific Investigation Plan are given in Sections 3.2 through 3.4. Where appropriate, the relative timings of the activities are given. When previous work has been done by the NNWSI Project in an activity, a summary of that work is given. For each activity, a series of test plans (Section 6.0) will be prepared to provide further details of the tests in an activity. For many of the activities, several test plans have already been issued. All expected use of computer codes is described in Section 3.4.

The current schedule calls for the start of long-term confirmation tests in mid-1990 to mid-1991. At the present time, it is impossible to predict what these will involve; their content will depend upon the results of the tests conducted over the next four years. If the current schedule holds, an addendum to this Scientific Investigation Plan will be issued that will cover the activities involved in long-term confirmation testing.

3.2 Integrate Spent Fuel Information

3.2.1 Integrate spent fuel waste form information provided by vendors, utilities, and other sources. D-20-40

This activity involves participation in the Spent Fuel Working Group (SFWG) and liaison activities with OSTS, the MCC, and other groups that may provide information on the characteristics of spent fuel. Participation in the SFWG and interaction with the MCC insures that samples of fuel are available for testing that are representative of the population of fuel in storage. This participation consists of attendance at SFWG meetings, and timely review of documents that are generated as a result of SFWG undertakings.

Several efforts are underway by DOE projects to assemble information on both the as-fabricated and the as-irradiated characteristics of fuel. The sources of this information are largely fuel vendors and the utilities. The liaison activities provide a means of providing input to these efforts so that the information required by the spent fuel activities of the NNWSI Project is included in the list of information to be gathered.

No tests or analyses are performed in this activity.

3.2.2 Integrate NNWSI Project waste package and repository design information. D-20-41

This activity provides a mechanism to formally accumulate the information required for the experimental and modeling activities requiring design or testing input from other NNWSI Project activities. No tests or analyses are performed.

3.3 Characterization of the Spent Fuel Waste Form

3.3.1 Dissolution/leach tests of spent fuel and UO_2

This is the primary area of activity in the spent fuel testing program. Its objective is to generate QA Level I data on the release of radionuclides from spent fuel 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 saturated and unsaturated tests. Both types of test will use a variety of irradiated fuels that are representative of the population of fuel expected to be emplaced into the first repository. Testing will be done at temperatures below 90°C. Water representative of that expected to be found in the repository (J-13 well water) will be used in most of the tests (Oversby, 1984; Glassley, 1986). A small amount of testing has been done using deionized water to provide a link with similar tests done by others and to assess the effect of water chemistry on release rates. Additional parametric tests of the effect of water chemistry on dissolution rates and equilibrium elemental concentrations are planned.

3.3.1.1 Saturated, semi-static dissolution tests of spent fuel and UO_2. D-20-42

Background and previous work

Saturated dissolution testing of spent fuel is done for two reasons. First, it simulates the scenario in which water accumulates within a failed container and continuously reacts with fuel in rods with failed cladding. Second, it is the simplest and most easily interpreted method of reacting water and fuel. The release mechanisms and rates derived from these tests can be compared with similar tests done by others, and can be modeled relatively simply.

At the present time, two series of saturated dissolution tests have been completed and a third is in progress. Descriptions of the three tests are given in test plans (Wilson 1983, 1984, 1986) and final reports are available for the first and second test series. (Wilson, 1985, 1987). Work thus far has focused on using Zircaloy clad, pressurized water reactor (PWR) fuel of average burnup and fission gas release (Turkey Point fuel and H. B. Robinson fuel - ATM-101 (Barner, 1985)). Series 1 tests used deionized water while Series 2 used water from well J-13. Both Series were conducted at ambient hot-cell temperature in silica reaction vessels with loose-fitting lids. Series 3 tests are being conducted in sealed, 304L stainless steel vessels (the NNWSI Project reference container material) at ~85°C with J-13 well water as the leachant. One specimen is being run at ~25°C in the same vessel type for comparison with the Series 2 results. An interim report describing the early results of this test has been published (Wilson and Shaw, 1986). All the test Series thus far have included specimens of bare fuel, clad segments of fuel with induced cladding defects, and undefected rod segments.

Each Series produces extensive data on the chemistry of the solution in contact with the fuel sample as a function of time. Both the concentration of radioactive species and non-radioactive species are monitored. In addition, the fuel specimens are examined before and after the test by a variety of methods to determine if any physical changes in the fuel have occurred.

The Series 1 tests were conducted prior to the institution of QA Levels, however testing was done in such a way as to be compatible with the current QA requirements for a Level I activity. If data from this test are needed to support the license application, it will be qualified as Level I using NNWSI SOP-03-03 or NNWSI SOP-15-01. Both Series 2 and Series 3 tests have been conducted under QA Level I. All work to date has been performed by the Westinghouse Hanford Co. at the laboratories of the Hanford Engineering Development Lab., (HEDL-WHC).

Planned work

Saturated dissolution testing will continue using a wider variety of fuel types, including, but not limited to: high-burnup fuel, high-gas-release fuel, boiling water reactor (BWR) fuel, oxidized fuel of known O/U ratio produced under activity D-20-45, and stainless-steel-clad fuel. It is anticipated that fuels that will be used in future tests will be ATM materials provided by the MCC. Tests will also be conducted in an effort to separate the effects of the experimental variables from other, more significant causes. Tests that fall into this category include, but are not limited to, varying the fuel-to-water ratio used in the tests, conducting tests in stainless steel vessels, but with loose-fitting lids to allow free access of oxygen to the tests, and examining the effect of the presence of Zircaloy cladding in the test vessel. Parametric tests will be conducted on both unirradiated UO_2 and spent fuel to determine the effect of other parameters, such as water chemistry and temperature. At least one duplicate test Series will be conducted by a second investigator at an independent laboratory facility in order to check the reproducibility of the results obtained from the primary investigator and laboratory.

3.3.1.2 Unsaturated dissolution tests of spent fuel and UO_2. D-20-43

Background and planned work

The unsaturated test is designed to measure the interactions between the spent fuel waste form, the canister material and the repository water that drips onto a failed fuel assembly and then runs off. This simulates the scenario in which a container has multiple perforations which allow water to enter the container, contact the fuel, and exit the container without maintaining contact for an extended period of time. The unsaturated test for spent fuel will be adapted from the procedure used for unsaturated testing of the glass waste form (Bates and Gerding, 1985, 1987; Bates et al., 1986). No QA Level I unsaturated dissolution tests on spent fuel have yet been performed. These tests are currently in the planning stages.

Unsaturated testing will be conducted on a variety of fuel types; however, it is unlikely that unsaturated testing will include as many different fuels as is planned for the saturated dissolution tests. Two test series are currently planned, with each Series involving many different fuel specimens. Due to the nature of these tests, each Series will run for at least one year and probably more. As in the saturated tests, it is expected that the data obtained from these tests will include detailed information on the chemistry of the solutions contacting the fuel as a function of time. Pre- and post-test characterization of the solids will be conducted to determine if any physical changes in the fuel or other components of the test have occurred.

3.3.2 Oxidation tests on spent fuel and UO_2

These activities are intended to determine the oxidation rate and mechanism of spent UO_2 fuel as a function of time and various environmental parameters. The data from the tests conducted in these activities will be used in activity D-20-50 to construct a model to predict the oxidation state of the uranium in the oxide fuel matrix as a function of time in the repository. A discussion of the potential for spent fuel oxidation in a tuff repository can be found in the report by Einziger and Woodley (1985). Oxidation of the fuel may affect the dissolution rate of the fuel and thus the rate of release of radionuclides from the fuel. In addition,there is a large positive volume change associated with the production of U_3O_8; the oxidation of fuel to this phase would put a large strain on the cladding leading to the possibility of enlargement of pre-existing cladding failures.

There are two oxidation activities, corresponding to the two different techniques used in testing: a thermogravimetric apparatus (TGA), and an oven-oxidation apparatus. Both tests use the weight gain of the sample to monitor the progress of the oxidation, but the two methods provide complimentary information. A TGA test yields a continuous record of the weight gain of a relatively small sample. The oven-oxidation tests do not provide a continuous record of the weight, but can be run for longer periods of time at lower temperatures and can utilize larger samples. This latter point is important because it will be necessary to produce well-characterized samples of oxidized fuel for dissolution tests conducted under activity D-20-42. A discussion of the experimental approach and justification for the chosen test parameters is given by Einziger (1985).

Both techniques maintain the spent fuel specimen in a constant-temperature, constant-humidity environment. The effect of humidity on oxidation rate is being investigated as is the effect of different fuel types. Testing to date has used moderate-burnup, low gas release PWR fuel (Turkey Point fuel). Future work will involve a wider variety of fuel types using ATMs provided by the MCC. The oven-oxidation tests are more suited to testing a wider variety of fuel types than is the TGA because of the capability to run many specimens simultaneously.

3.3.2.1 Oxidation tests of spent fuel and UO_2 using a thermogravimetric apparatus. D-20-44.

Background and previous work

The TGA provides detailed information on the rate of weight gain of a fuel sample. This information will be very important in the effort to document the mechanism of oxidation of spent fuel. In these tests, a fuel sample weighing approximately 200mg is suspended from a balance into a constant temperature oven. The weight is continuously monitored on a recorder. At intervals, samples of the cover gas are taken and analyzed for released fission gasses. The lowest temperature at which it is practical to obtain data using this technique is ~140 - 150°C. At lower temperatures, the rate of weight gain is too slow for a measurable gain to occur within a reasonable time.

A series of TGA tests have been already been conducted for the NNWSI Project and the tests are continuing. The test matrix and experimental procedures are documented in the test plan by Einziger (1986a). The interim results of these tests have been documented in unpublished letter reports. A final report on the current TGA test series is due in the summer of 1987. In general, the oxidation rate obtained from these tests has been in good agreement with rates determined by extrapolating the results of oxidation experiments conducted at higher temperatures.

At the conclusion of a TGA run, the fuel sample is examined using a variety of techniques (X-ray diffraction, ceramography, etc.) to document the types of phases present and to look for physical changes in the fuel. Pre-test characterization of the samples is done to establish a baseline for comparison. There are two QA Level III experiments being conducted under activity D-20-49 that involve the development of new techniques for examining fuel using the ion-microprobe and transmission electron microscope (TEM). When appropriate techniques have been established, this work will be upgraded to QA Level I and become a part of this activity and activity D-20-45.

All TGA tests have been conducted at QA Level I or its equivalent. Results of tests conducted before the institution of the current QA plan will be upgraded to QA Level I through the use of NNWSI SOP-03-03 or NNWSI SOP-15-01.

Planned work

Additional TGA tests are planned using BWR fuel and fuel with higher burnup and gas release. The effect of grain size will also be investigated. The effect of humidity on oxidation rate will continue to be evaluated.

3.3.2.2 Oven-oxidation tests of spent fuel and UO_2. D-20-45.

Background and previous work

The oven oxidation tests are intended to extend the results of the TGA tests to lower temperatures and longer times. In addition, by the nature of the experimental apparatus, many samples of fuel can be oxidized at one time with little additional cost, thus greatly increasing the amount of data that can be acquired for use in licensing. A test was begun in December of 1986 and is scheduled to run for at least 2 years. As additional fuel samples become available, they will be added to the test.

The tests are actually conducted in dry baths rather than conventional ovens. A description of the apparatus is given in the test plan for these tests (Einziger, 1986b). The baths are being run at three different temperatures: 110°C, 130°C, and 175°C. The last temperature overlaps the range of temperatures at which TGA testing has been done and provides a means of checking on the reproducibility of oxidation rates obtained using the two techniques. As in the TGA tests, runs are being conducted at the same temperature but different dew points to assess the effect of humidity on oxidation rate.

All oven-oxidation work to date has been conducted at QA Level I. Testing has been conducted at HEDL-WHC.

Planned work

As noted above, it is planned to add samples of different fuel types to the apparatus as the fuel becomes available. At the least, fuel from BWR reactors, higher burnup and gas release fuels, fuels with different grain size, and Gd-doped BWR fuels will be tested.

At intervals, specimens of the oxidized fuel will be removed and examined by appropriate techniques (X-ray diffraction, ceramography, etc.). The results of these examinations will be compared to pre-test characterization results. It is also planned to examine the oxidized fuel using ion-probe and TEM techniques currently being developed at QA Level III under activity D-20-49. When appropriate techniques are established for these methods, they will be upgraded to QA Level I and performed as a part of this activity.

3.3.3 Corrosion and release tests on cladding and assembly materials

The testing done in this area has several purposes:

1) evaluate the corrosion and failure rate of cladding;

2) determine the rate of release of radionuclides from cladding;

3) determine the rate of release of radionuclides from assembly hardware parts.

The rate at which cladding fails in the repository will, in part, determine the release rate of radionuclides from the enclosed fuel. In addition, both the cladding and other assembly parts contain radionuclides and thus must be characterized with respect to their corrosion and release characteristics. Because of the different materials involved, work on cladding and hardware have been separated into two different activities. Work on the release of carbon-14 has been put into a third, separate activity because, unlike other radionuclides of concern, it can be released in gaseous form as CO_2. Because of this, the types of tests required to characterize the inventory and release of carbon-14 are quite different than those used for the other radionuclides.

3.3.3.1 Corrosion/degradation/release tests on Zircaloy and stainless steel cladding. D-20-46.

Background and previous work

Work in this activity has two related purposes: to determine the rate at which cladding failure can be expected under repository conditions; and to measure the groundwater-mediated release of radionuclides from cladding. The work to date in this area has been limited to scoping experiments conducted at QA Level III (activity D-20-49) that were designed to develop test methods and test parameters that will be used in QA Level I tests. This was done to maximize the amount of useful data for licensing that could be obtained for a given funding level.

An overview of the matrix of experiments to determine Zircaloy cladding degradation rate is given in Smith (1985). The choice of specimen types to be evaluated is discussed in Smith (1984a). Several failure modes are being considered: stress corrosion cracking (SCC); generalized corrosion; hydride embrittlement; and hydride reorientation. The rationale for the selection of these mechanisms for study is given in the report on potential cladding failure mechanisms by Rothman (1984). No work on cladding materials other than Zircaloy has been performed at the time of this writing. Neither have detailed studies been performed on the release of radionuclides from various cladding materials.

Planned work

Beginning in FY 1987, work on the failure of Zircaloy cladding by generalized corrosion, SCC, and stress rupture will be upgraded to QA Level I. The results of these tests will be used to model the failure rate of cladding in the repository. The generalized corrosion test will also provide information of the release of radionuclides from cladding. Work on the effect of hydrides on cladding strength is in the planning stages.

3.3.3.2 Corrosion/release tests on assembly hardware. D-20-47.

Background and planned work

As noted above, the non-fuel assembly hardware such as springs, spacers, etc. are a significant reservoir of certain radionuclides, especially nickel isotopes and carbon-14. Since these radionuclides have the potential for release by means of dissolution and/or corrosion of the hardware, it will be necessary to conduct tests to determine the release rate of radionuclides from this portion of the waste form. At the time of this writing, work in this area has not yet begun.

As a part of this Investigation, a series of tests to determine the release rate of radionuclides from assembly hardware will be conducted. The test procedures and environmental conditions have not been established yet; however, the tests will likely resemble the saturated and unsaturated test methods used in the dissolution/leach tests of spent fuel (activities D-20-42 and D-20-43). Corrosion work carried out as part of the container material selection process may be applicable to some of the materials used as assembly hardware. This may aid in reducing the amount of new experimental work necessary to characterize the release from this source. Initial experiments to optimize procedures will be carried out at QA Level III under activity D-20-49. That activity will feed into this one.

3.3.3.3 Carbon-14 inventory and release tests. D-20-48.

Background and planned work

Unlike other radionuclides present in the spent fuel waste form during the controlled release period, which require the presence of liquid water for transport, carbon-14 can be released as gaseous CO_2. It appears that approximately half of the carbon-14 inventory of the waste form is associated with the cladding and of that, some fraction is available for relatively rapid release as CO_2 by oxidation in air (Van Koynenburg et al., 1984; 1986). The only available data on the release of $^{14}CO_2$ in air is from a single cask test conducted for the Dry Storage Program. More data are clearly needed to define the inventory, distribution, and release characteristics of carbon-14 in the spent fuel waste form.

No work has been conducted in this activity to date. Development of an experimental setup to etch sequential layers from the outer surface of cladding segments and measure the carbon-14 released is currently underway as part of activity D-20-49. That work will be transferred to this activity at a later time and testing at QA Level I under this activity will then begin.

The test mentioned above, using an etchant to remove sequential layers of cladding material, will provide information on the radial distribution of carbon-14 in the cladding. A second test will involve the exposure of cladding segments to air at elevated temperature. The quantity of carbon-14 that is evolved as CO_2 will be measured. By conducting tests at different temperatures, the temperature coefficient of release can be determined.

Both tests will utilize cladding material that spans the range of known variability in reactor type, burnup, amount of crud deposits, and other variables that may influence the inventory or release of carbon-14.

3.3.4 Planning and experimental design

Many of the tests performed under activities D-20-42 through D-20-48 require a certain amount of initial experimentation to determine the best way to conduct the test. In addition, there are many experimental protocols and examination techniques that, though potentially applicable to the problems being investigated, have never been tried under the conditions relevant to the NNWSI Project spent fuel testing program. This activity is intended to provide a mechanism whereby new experimental techniques can be evaluated with respect to their applicability to a particular test and their ability to provide useful information. This activity provides a mechanism for maintaining maximum flexibility in adapting procedures to the NNWSI testing program while maintaining the cost-effectiveness of the program. Those techniques that are examined under this activity and are judged useful or valuable will then be upgraded to QA Level I and used in the other experimental activities. It is likely that some of the techniques tried will not work and will never be used in other activities.

3.3.4.1 Technique development for advanced test planning and design. D-20-49.

Background and previous work

Several activities include tests and/or techniques that have already been "cycled through" this activity. These include the several tests in Zircaloy corrosion activity (D-20-46). Each of the Zircaloy experiments is documented in a test plan (Smith, 1984b; 1986a,b) and each will be or has been documented in a final report (e.g. Smith, 1987). Current experiments being conducted under this activity are:

Evaluation of ion probe techniques for determining the location and amount of oxygen uptake during spent fuel oxidation experiments (for activities D-20-44 and D-20-45).

Development of TEM and STEM techniques for examining fuel structure and phase relations on very fine scale (for activities D-20-42, D-20-43, D-20-44, and D-20-45).

Development of techniques to determine the spatial distribution of carbon-14 in the spent fuel waste form (especially the cladding), and its release characteristics (for activity D-20-48).

Development of an unsaturated test method for dissolution testing of spent fuel (for activity D-20-43).

Development of techniques for saturated dissolution testing of oxidized spent fuel (for activity D-20-42).

All of these experiments are likely to be yield test methods that will be incorporated into the appropriate QA Level I activities given in parentheses above. At that time, the QA Level III experiments will be documented in written reports and the work conducted under this activity will cease.

Planned work

New experiments will be initiated under this activity as potentially useful techniques are discovered. It is anticipated that this activity will continue throughout the life of the entire spent fuel testing program; however, as the program matures, the number of experiments that will be performed under this activity will decline greatly. All work in this activity will be conducted at QA Level III.

3.4 Generate Models for Release from Spent Fuel

3.4.1 Introduction

The primary means of release of radionuclides from the spent fuel waste form is by means of liquid water contacting the fuel in a breached container. There is the possibility of the release of some fraction of the carbon-14 in the waste form as gaseous CO_2, a process that does not require the mediation of liquid water. As input to the waste package performance assessment model, the spent fuel waste form testing Investigation will, in collaboration with the performance assessment task, generate and validate a model for the release of radionuclides from the spent fuel waste form under repository conditions. The output of the modeling activities is expected to be a combination of functional relationships and look-up tables that can be incorporated into the performance assessment model.

3.4.2 Generate models for release of radionuclides from the spent fuel waste form. D-20-50.

Background and planned work

The purpose of this activity is to design and use models for the release of radionuclides from the spent fuel waste form based on the scenarios identified in Information Need 1.5.3. The model will consist of several sub-models: a sub-model for the release of radionuclides from spent fuel, cladding, and assembly hardware; a sub-model for cladding performance; and a sub-model for the oxidation of UO_2.

In order to extrapolate the results of laboratory time scale tests to times relevant to the repository, it will be necessary to develop an understanding of the physical and chemical mechanisms involved in all significant processes affecting the waste form. It is recognized that it may not be possible to identify unique mechanisms for all the operant processes. In these cases, an analysis will be performed to determine the sensitivity of the model to the assumption of the different mechanisms. For licensing, the most pessimistic, and hence most conservative, relevant assumptions will be used.

By far the most important sub-model that will be developed is the one that predicts the rate of radionuclide release from the spent fuel, cladding, and assembly hardware. This model will include at least six components:

1. Elements whose release is controlled by the matrix dissolution rate.

2. Elements present in part in the pellet-cladding gap and which are available for rapid release.

3. Elements present in part on grain boundaries and which may show an enhanced release rate.

4. Elements contained in the fuel cladding.

5. Elements contained in stainless steel or other materials used in assembly components.

6. Elements present in any part of the waste form that can be released in a gaseous form (such as carbon-14) and which do not require the mediation of liquid water for their release.

Items 1 through 3 above may be a function of the fuel oxidation state; hence, the necessity for the development of a sub-model for predicting how the fuel will oxidize as a function of time. Since the presence of intact cladding will prevent the release of radionuclides from items 1 through 3 above, a sub-model for the failure rate of the cladding as a function of time will also be necessary for the proper description of the performance of the waste form.

The output of this activity will be the composition of fluids (including gasses) that issue from a failed waste package as a function of time. The geochemical modeling code EQ3/6 (Wolery, 1979; 1983; 1987) will be used extensively as the basis for calculating the composition of the radionuclide-bearing liquid water that exits a failed container. These analyses will involve a combination of equilibrium and kinetic calculations. It is likely that additional computer codes will need to be developed to serve 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 in the resolution of Information Need 1.5.3. Current plans for EQ3/6 code development (EQ3/6, 1986) include a major item that is required for the realistic modeling of spent fuel in a failed container: the development of a flow-through model in which a stationary reacting assemblage (the waste form and container) reacts with successive packets of water.

3.4.3 Screen data for incorporation into release model. D-20-51.

Background and planned work

There is extensive literature on the mechanisms of the dissolution and oxidation of UO_2, both irradiated and unirradiated. These data may be of use in the development of the release model for the spent fuel waste form. All data generated outside of the NNWSI Project will be screened in this activity, as well as the data that are gathered under the QA Level III activities, D-20-40 and D-20-41. The objective will be to establish the accuracy and precision of this data and to insure that the spent fuel release model uses only accurate and verifiable data. It is anticipated that the release model will be based predominantly on data generated within the NNWSI Project under QA Level I activities. This activity allows the large body of outside data to be used to corroborate and support the NNWSI Project data. In addition, this activity allows important data and idea generated outside of the NNWSI Project to be used in the model.

Data generated outside of the NNWSI Project will be collected and analyzed to determine if it is consistent with comparable NNWSI Project data. If it is not, an examination of all applicable data sets will be made to determine the origin of the discrepancy. Though it is not currently anticipated that outside data will be a critical part of the spent fuel waste form release model, if such data are found to be critical to the model, the NNWSI SOP-03-03 (DOE, 1986) for using non-NNWSI Project data will be implemented.

It is likely that some of the data used in the release model will require a peer review to establish their validity. Similarly, peer review is likely to be the only way to validate some of the concepts and interpretations made use of in the model. The procedures for conducting such a review are given in 033-NMWP-P-2.2 of the Quality Assurance Program Plan for the NNWSI Project (Lawrence Livermore National Lab., 1987).

The most important aspect of this activity is the comparison of NNWSI Project data to that collected outside of the Project. This comparison is designed to ensure that the Project will be able to affirm during the licensing process that the spent fuel release model is consistent with all applicable data. When there are inconsistencies in the data, as is probably inevitable, an assessment of the possible causes of the discrepancy will be prepared. In the case of the NNWSI Project data being improperly collected, interpreted, or applied, this activity allows the problems to be resolved and new data obtained under one of the data collection activities. A formal mechanism for this screening process will be established in conjunction with the Glass Waste Form Task.

3.4.4 Finalize and validate spent fuel release model. D-20-52.

Background and planned work

Validation of the spent fuel waste form model will be done in two stages. First, the model will be developed in parallel with the experimental work and will be tested for its ability to describe accurately the experimental results. Some additional tests on simpler systems than that represented by the waste form itself may be necessary to validate the model properly. Second, the results of long-term modeling will be compared with extrapolations and with natural analogues if appropriate analogues can be identified. Even if exact analogues cannot be found in nature, it is likely that even dissimilar natural systems will provide a means of at least testing the validity of the principles used in the fuel model. The second part of the validation effort will test both the validity of the model and determine whether the experimental work has examined all the important chemical processes and interactions that may occur over long periods of time. Thus, the final model development will actually be conducted under this activity. This will most likely involve simply a "fine tuning" of the model developed under Activity D-20-50.

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

1. Database. Critical database items will be reviewed under the data screening activity (D-20-51).

2. Code Operation. A series of benchmark code runs will be established for EQ3/6 to test major operations common to all applications.

3. **Experiment Matching.** The spent fuel model must accurately predict the results of laboratory testing.

4. **Natural Analogues.** To determine if the EQ3/6 code accurately predicts the behavior of actinide-bearing systems, it will be used to model natural uranium-rich deposits in contact with groundwater.

4.0 Application of Results

The information provided by this Investigation will provide the source term for radionuclide release from waste packages containing the spent fuel waste form. This information will be used by the waste package performance assessment task to model the performance of the waste packages under repository conditions. The information obtained by this Investigation 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 that is required to resolve Information Needs 1.4.4, 1.5.4, and 1.5.5, and Issues 1.1, 1.4, 1.9, 1.10, and 1.11.

The spent fuel information will also be used to develop the source term in the calculation of cumulative releases of radionuclides to the accessible environment for 10,000 years as required in order to comply with EPA regulation 40-CFR-191.13. It will also be used as part of the source term for cumulative release calculations for 100,000 years after disposal in the site evaluation process required by 10-CFR-960.3-1-5.

5.0 List of Test Plans to Support this Study Plan

5.1 Previously Issued Test Plans	Issue date
Test plan for spent fuel cladding containment credit tests., C. N. Wilson (HEDL TC-2353-2).	11/83
Test plan for Series 2 spent fuel cladding containment credit tests., C. N. Wilson (HEDL TC-2353-3).	10/84
Zircaloy spent fuel cladding electrochemical scoping experiment., H. D. Smith (HEDL TC-2562).	12/84
Technical test description of activities to determine the potential for spent fuel oxidation in a tuff repository., R. E. Einziger (HEDL-7540).	6/85
Zircaloy cladding corrosion degradation in a tuff repository: initial experimental plan., H. D. Smith (HEDL-7455, Rev. 1).	7/85
Test plan for Series 2 thermogravimetric analyses of spent fuel oxidation., R. E. Einziger and R. E. Woodley (HEDL-7556).	2/86
"C-ring" stress corrosion cracking scoping experiment for Zircaloy spent fuel cladding., H. D. Smith (HEDL-7546).	3/86
Zircaloy spent fuel cladding electrochemical corrosion experiment at 170°C and 120PSIA H_2O., H. D. Smith (HEDL-7545).	4/86
Test plan for Series 3 NNWSI spent fuel leaching/dissolution tests., C. N. Wilson (HEDL-7577).	4/86
Test plan for long-term, low-temperature oxidation of spent fuel, Series 1., R. E. Einziger (HEDL-7560).	6/86

5.2 Additional Test Plans

Test plan for parametric dissolution tests of spent fuel.

Addendum and amendments to TGA oxidation test plan.

Test plan for NNWSI Zircaloy corrosion tests.

Test plan for dissolution tests of partially oxidized fuel (NNWSI Series 4).

Test plan for carbon-14 inventory and release tests.

Test plan for release tests on assembly hardware.

Plan for data screening, and model generation, testing and validation for spent fuel release.

Additional test plans or addenda and amendments to the above test plans will be issued should the need arise.

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

6.0 References

Barner, J. O. (1985) Characterization of LWR Spent Fuel MCC-Approved Testing Material -- ATM-101. PNL-5109 Rev. 1, Pacific Northwest Lab., Richland, WA.

Bates, J. K. and Gerding, T. J. (1985) NNWSI Phase II Interaction Test and Preliminary Results. ANL-84-81, Argonne National Lab., Argonne, IL.

Bates, J. K. and Gerding, T. J. (1987) The NNWSI Unsaturated Test Method. Lawrence Livermore National Lab. Contractor Report, (in prep.).

Bates, J. K., Gerding, T. J., Abrajano, T. A., and Ebert, W. (1986) NNWSI Waste Form Testing at Argonne National Laboratory: Semi Annual Report. July-December, 1985. UCRL-15801, Lawrence Livermore National Lab., Livermore, CA.

DOE, U. S. Department of Energy (1986) Acceptance of Data or Data Interpretation Not Developed Under the NNWSI QA Plan. NNWSI-SOP-03-03, Rev. 0.

Einziger, R. E. (1985) Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository. HEDL-7540, Westinghouse Hanford Co., Richland, WA.

Einziger, R. E. (1986a) Test Plan for Series 2 Thermogravimetric Analyses of Spent Fuel Oxidation. HEDL-7556, Westinghouse Hanford Co., Richland WA.

Einziger, R. E. (1986b) Test Plan for Long-Term, Low-Temperature Oxidation of Spent Fuel, Series 1. HEDL-7560, Westinghouse Hanford Co., Richland, WA.

Einziger, R. E. and Woodley, R. E. (1985) Evaluation for the Potential for Spent Fuel Oxidation Under Tuff Repository Conditions. HEDL-7452, Westinghouse Hanford Co., Richland, WA.

EQ3/6 (1986) Geochemical Modeling Plan. Office of Civilian Radioactive Waste Management Program, Scientific Investigation Plan for NNWSI, UCID-20864, Lawrence Livermore National Lab., Livermore, CA.

Glassley, W. E. (1986) Reference Waste Package Environment Report. UCRL-53726, Lawrence Livermore National Lab., Livermore, CA.

Lawrence Livermore National Laboratory (1987) Quality Assurance Program Plan. Nevada Nuclear Waste Storage Investigations. Lawrence Livermore National Lab., Livermore, CA.

Oversby V. M. (1984) Reaction of the Topopah Spring Tuff with J-13 Well Water at 90°C and 150°C. UCRL-53552, Lawrence Livermore National Lab., Livermore, CA,

Rothman, A. J. (1984) Potential Corrosion and Degradation Mechanisms of Zircaloy Cladding on Spent Nuclear Fuel in a Tuff Repository. UCID-20172, Lawrence Livermore National Lab., Livermore, CA.

Smith, H. D. (1984a) Spent Fuel Cladding Characteristics and Choice of Experimental Specimens for Cladding-Corrosion Evaluation Under Tuff Repository Conditions. HEDL-TC-2530, Westinghouse Hanford Co., Richland, WA.

Smith, H. D. (1984b) Zircaloy Spent Fuel Cladding Electrochemical Corrosion-Scoping Experiment. HEDL-TC-2562, Westinghouse Hanford Co., Richland, WA.

Smith, H. D. (1985) Zircaloy Cladding Corrosion Degradation in a Tuff Repository. HEDL-7455, Rev. 1, Westinghouse Hanford Co., Richland, WA.

Smith, H. D. (1986a) "C-Ring" Stress Corrosion Cracking Scoping Experiment for Zircaloy Spent Fuel Cladding. HEDL-7546, Westinghouse Hanford Co., Richland, WA.

Smith, H. D. (1986b) Zircaloy Spent Fuel Cladding Electrochemical Corrosion Experiment at 170°C and 120 PSIA H_2O. HEDL-7545, Westinghouse Hanford Co., Richland, WA.

Smith, H. D. (1987) Electrochemical Corrosion Scoping Experiments - An Evaluation of the Results. HEDL-7637, Westinghouse Hanford Co., Richland, WA.

Van Konynenburg, R. A., Smith, C. F., Culham, H. W., and Smith, H. D. (1984) Behavior of Carbon-14 in Waste Packages for Spent Fuel in a Repository in Tuff. UCRL-90855 Rev. 1, Lawrence Livermore National Lab., Livermore, CA.

Van Konynenburg, R. A., Smith, C. F., Culham, H. W., and Smith, H. D. (1986) Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository. UCRL-94708, Lawrence Livermore National Lab., Livermore, CA.

Wilson, C. N. (1983) Test Plan for Cladding Containment Credit Tests. HEDL-TC-2352-2, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. (1983) Test Plan for Cladding Containment Credit Tests. HEDL-TC-2352-2, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. (1984) Test Plan for Series 2 Spent Fuel Cladding Containment Credit Tests. HEDL-TC-2353-3, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. (1985) Results from NNWSI Series 1 Spent Fuel Leach Tests. HEDL-TME 84-30, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. (1986) Test Plan for Series 3 NNWSI Spent Fuel Leaching/Dissolution Tests. HEDL-7577, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. (1987) Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests. HEDL-TME 85-22, Westinghouse Hanford Co., Richland, WA.

Wilson, C. N. and Shaw, H. F. (1986) Experimental Study of the Dissolution of Spent Fuel at 85ºC in Natural Groundwater. UCRL-94633, Lawrence Livermore National Lab., Livermore, CA.

Wolery, T. J. (1979) Calculation of the Chemical Equilibrium Between Aqueous Solutions and Minerals: The EQ3/6 Software Package. UCRL-52628, Lawrence Livermore National Lab., Livermore, CA.

Wolery, T. J. (1983) EQ3NR, A computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation. UCRL-53414, Lawrence Livermore National Lab., Livermore, CA.

Wolery, T. J. (1987) EQ6, A Computer Program for Reaction-Path Modeling of Aqueous Geochemical Systems: User's Guide and Documentation. (in prep) Lawrence Livermore National Lab., Livermore, CA.