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MCC

Materials Characterization Center Second Workshop on Irradiation Effects in Nuclear Waste Forms

Summary Report

W. J. Weber
R. P. Turcotte

January 1982

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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MATERIALS CHARACTERIZATION CENTER SECOND WORKSHOP ON IRRADIATION EFFECTS IN NUCLEAR WASTE FORMS

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Pacific Northwest Laboratory
Richland, Washington 99352

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MATERIALS CHARACTERIZATION CENTER
SECOND WORKSHOP ON IRRADIATION EFFECTS
IN NUCLEAR WASTE FORMS

1.0 SUMMARY

A workshop on irradiation effects in nuclear waste forms, sponsored by the Materials Characterization Center (MCC), was conducted August 13 and 14, 1981, at the Battelle Seattle Research Center. The purpose of this second workshop on irradiation effects was to continue the discussions initiated at the first workshop (Roberts, Turcotte, and Weber 1981) and to obtain guidance for the MCC in developing test methods. The workshop brought together 21 experts in radiation damage in materials and nuclear waste technology representing Department of Energy (DOE) laboratories, the National Bureau of Standards, universities, and private industry.

The following major conclusions were reached:

- Ion or neutron irradiations are not substitutes for the actinide-doping technique, as described by the MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms, in the final evaluation of any waste form with respect to the radiation effects from actinide decay.
- Ion or neutron irradiations may be useful for screening tests or more fundamental studies. The use of these simulation techniques as screening tests for actinide decay requires that a correlation between ion or neutron irradiations and actinide decay be established. Such a correlation has not yet been established and experimental programs in this area are highly recommended.
- There is a need for more fundamental studies on dose-rate effects, temperature dependence, and the nature and importance of alpha-particle effects relative to the recoil nucleus in actinide decay.

- There are insufficient data presently available to evaluate the potential for damage from ionizing radiation in nuclear waste forms.
- No additional test methods were recommended for using ion or neutron irradiations to simulate actinide decay or for testing ionization damage in nuclear waste forms. It was recognized that additional test methods may be required and developed as more data become available.
- An American Society for Testing and Materials (ASTM) Task Group on the Simulation of Radiation Effects in Nuclear Waste Forms (E 10.08.03) was organized to act as a continuing vehicle for discussions and development of procedures, particularly with regard to ion irradiations.

2.0 INTRODUCTION

The MCC, established by the DOE and managed by the Pacific Northwest Laboratory (PNL), is responsible for ensuring the availability of reliable data on the properties of materials associated with the management of nuclear wastes. The data are needed for analytical models for safety analyses and licensing and for decisions regarding the selection of materials. To fulfill this responsibility, the MCC will collect and analyze existing data, perform additional tests where necessary, and develop and document procedures. The resulting data and procedures will be included in a Nuclear Waste Materials Handbook after approval by the Materials Review Board (MRB).

Since the procedures published in the Nuclear Waste Materials Handbook will have some of the characteristics of national standards, the scientific and technical communities are included in a review process to ensure that the proposed procedures are generally acceptable. As part of the review process, the MCC organizes workshops at which technical experts from DOE laboratories, universities, and private industry are invited to discuss issues relevant to data requirements and methodology and to critique procedures proposed by the MCC. The first workshop on "Leaching of Radioactive Waste Forms" was held in February 1980 (Mendel et al. 1980), followed by a second meeting to examine leaching models. Another workshop was held in July 1980 on "Irradiation Effects in Nuclear Waste Forms" (Roberts, Turcotte, and Weber 1981). Two other workshops on the "Corrosion of Engineered Barriers" (Merz et al. 1981) and on the "Compositional and Microstructural Analysis of Nuclear Waste Materials" (Daniel et al. 1981) were also held during 1980.

2.1 PURPOSE OF THE WORKSHOP

An important consideration in nuclear-waste management is the effects of the energetic nuclear radiations from radioactive decay on the durability of nuclear waste forms over geologic time periods. Laboratory evaluation of the anticipated effects must rely on accelerated testing to generate data that can be extrapolated to long time periods. The first workshop on "Irradiation

Effects in Nuclear Waste Forms" (Roberts, Turcotte, and Weber 1981) provided a forum for scientific and technical experts to examine the issues related to irradiation effects and to provide input on a draft procedure (MCC-6) to evaluate the effects of alpha decay on waste forms. The workshop was also intended to initiate continuing communication between the MCC and other scientists in this field. The second workshop on irradiation effects, which is summarized in this report, was organized to continue the discussions initiated at the first workshop. In particular, this workshop examined the issues associated with other techniques to simulate actinide decay (ion or neutron irradiations), discussed the potential for both solid-state damage and enhanced leaching from ionizing radiation, and considered the need for additional test procedures (besides MCC-6) for evaluating irradiation effects.

2.2 ORGANIZATION OF THE WORKSHOP

Scientific experts from various laboratories and universities studying irradiation effects in either nuclear waste forms or ceramic materials in general were invited to participate in the workshop. The workshop was structured around two working groups that met concurrently. The assigned topics for the two working groups were as follows:

- Group I was to evaluate the merits and limitations of ion and neutron irradiations as techniques to simulate the displacement damage induced by alpha decay. Group I was also assigned the topic of transmutation effects.
- Group II was assigned the task of addressing the potential effects of ionizing radiation on solid-state damage and on enhanced solid/water interactions due to radiolysis.

2.3 ARRANGEMENT OF THIS REPORT

The objective of this report is to summarize the workshop proceedings. Background information presented at the workshop is summarized in Section 3. Summary reports of the working groups are given in Section 4. The participants and their addresses are listed in Appendix A and the workshop agenda is

presented in Appendix B. Appendix C is a list of the members of the ASTM Task Group on the Simulation of Radiation Effects in Nuclear Waste Forms. The MRB provisionally approved version of the MCC-6 Method for the Preparation and Characterization of Actinide-Doped Waste Forms is given in Appendix D.

3.0 BACKGROUND INFORMATION

This section summarizes some of the pertinent information presented at the workshop on 1) the sources of irradiation effects, 2) the effects of irradiation on waste-form properties, 3) the conclusions of the first workshop on irradiation effects, and 4) the status of the MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms.

3.1 SOURCES OF IRRADIATION EFFECTS

The chief sources of radiation in high-level nuclear waste (HLW) forms are beta decay of the fission products and alpha decay of the actinide elements. Projected numbers of beta-decay and alpha-decay events for both commercial (Roberts, Turcotte, and Weber 1981; Weber and Roberts 1981) and defense (Baxter 1981; Bibler 1981) HLW forms are shown in Figure 1 for storage times up to 10^6 years. In general, beta decay of the fission products predominates during the first 500 years with high radioactivities and high waste-form heat generation, while alpha decay predominates at longer times with a much lower heat-generation rate.

Radiation damage in the waste forms results primarily from 1) the displacement of waste-form constituent atoms from their normal sites by elastic collisions of the nuclear projectiles with the atoms, 2) ionization effects, and 3) the transmutation of radioactive parent nuclei into different elements.

It is generally accepted that the primary source for irradiation effects in nuclear waste forms is from displacement damage. Since alpha decay produces several orders of magnitude more displacements than any other radiation source, as illustrated in Figure 2, most studies on irradiation in nuclear waste forms have emphasized alpha-decay effects.

The effects of ionization from beta-gamma interaction with the waste-form solids include covalent-bond rupture, valence changes, H_2O and OH^- decomposition (an important consideration for waste forms with a high water content), and decomposition of unstable molecular ions. Additionally, a radiation-induced change in the leach rate can result from radiolysis of the

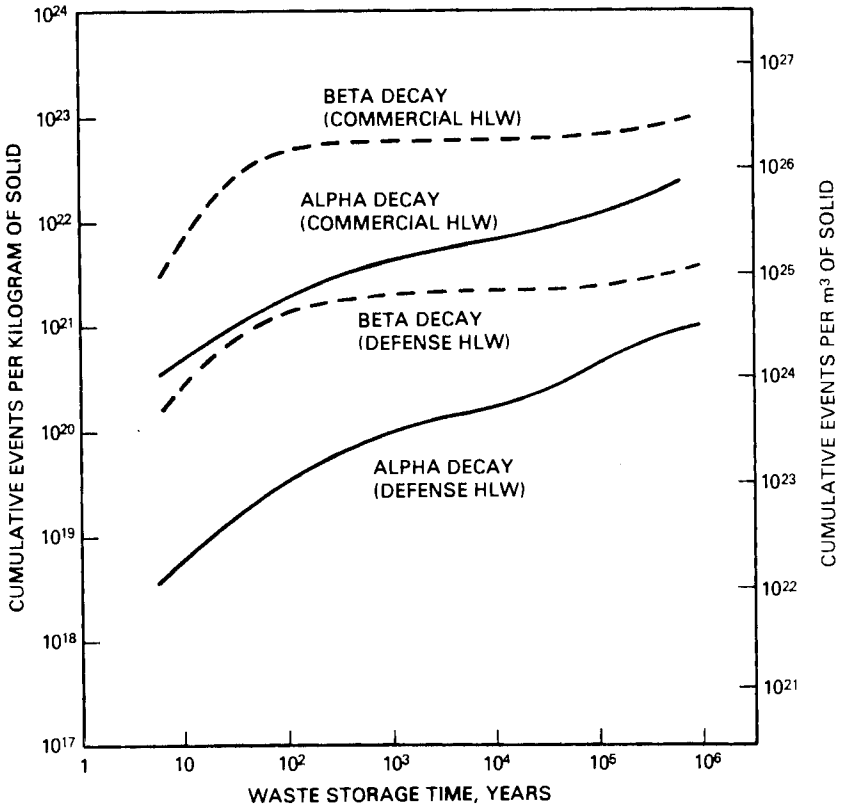

FIGURE 1. Cumulative Number of Decay Events Per Unit Mass and Per Unit Volume for Commercial and Defense HLW Forms (Basis: Commercial HLW-3.3% enriched UO_2 fuel, burnup of 33,000 MWd/MTHM, cooled 5 years before reprocessing and solidification, 25 wt% waste loading; defense HLW-Savannah River Plant waste, 25 wt% waste loading.)

atmosphere and ground water in the presence of the intense ionizing radiation field associated with beta decay (McVay and Pederson 1981). The ionization dose from the alpha particles is also significant and eventually exceeds the ionization dose from beta-gamma radiation, as illustrated in Figure 3.

Another potential source of radiation-induced changes is the transmutation of the fission products. The two main sources of transmutations are the intermediate-lived fission products, ^{137}Cs (30.2 years half-life) and ^{90}Sr (28.1 years half-life), which undergo the following decay schemes:

$$^{137}Cs \rightarrow {}^{137m}Ba + \beta^- \rightarrow {}^{137}Ba$$

$$^{90}Sr \rightarrow {}^{90}Y + \beta^- \rightarrow {}^{90}Zr + \beta^-$$

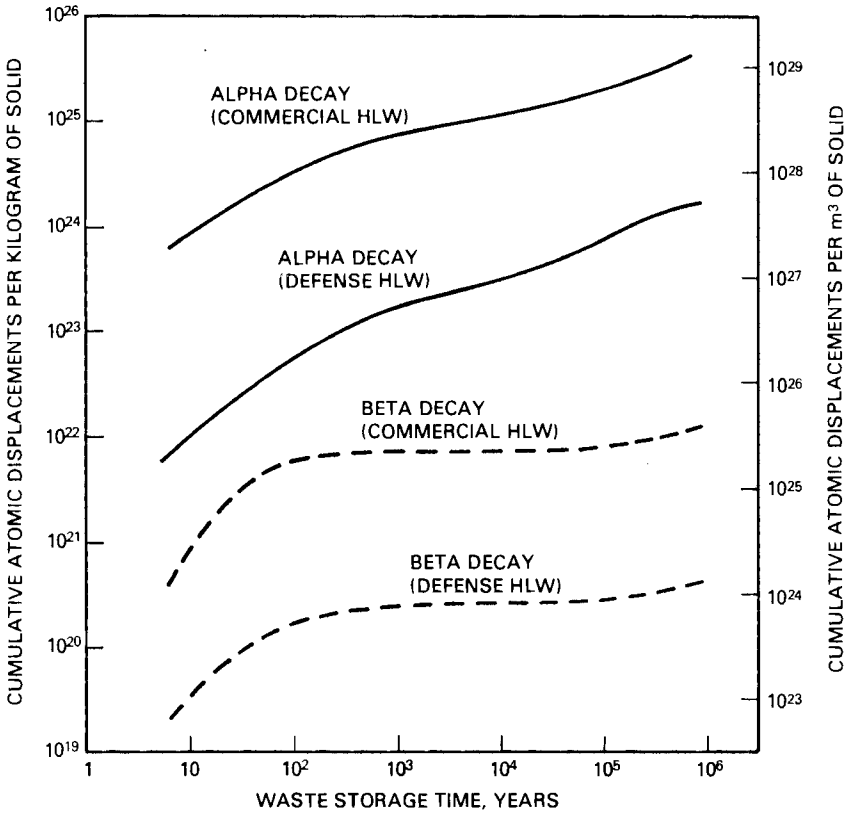

FIGURE 2. Cumulative Number of Displacements Per Unit Mass and Per Unit Volume of Commercial and Defense HLW Forms

Transmutations can involve valence changes and large changes in atomic radii. Glass waste forms are more likely to tolerate these changes because they already have 10 to 25 elements present, including substantial concentrations of barium and zirconium. The crystalline phases in ceramic waste forms have ordered structures and are less likely to accomodate these kinds of changes.

3.2 EFFECTS OF IRRADIATION

Both the simulation techniques employed and the data obtained from studies of irradiation effects in nuclear waste forms have been extensively reviewed and reported elsewhere (Weber and Roberts 1981). The majority of the data available have been obtained by actinide-doping techniques and, as such, simulate the long-term effects due to alpha decay. Few data are available on the effects of ionization from the beta-gamma radiation produced by fission-product

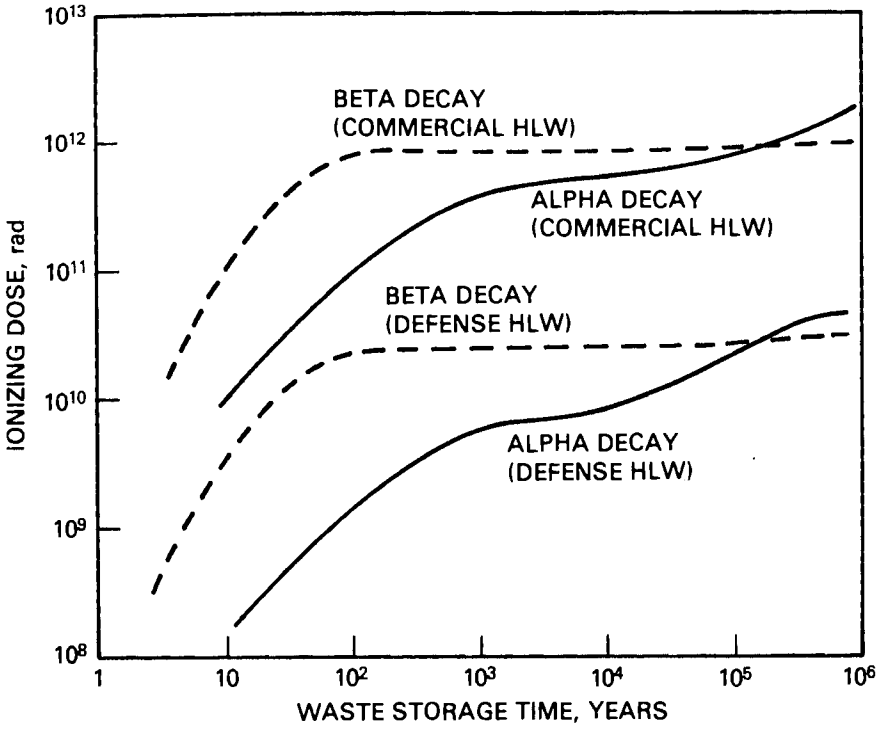

FIGURE 3. Ionizing Radiation Dose in Commercial and Defense HLW Forms

decay. In general, saturation of structural damage, as indicated by volume changes, occurs at a dose on the order of 5×10^{24} alpha decays/m^3 (averaged over the total waste-form volume).

3.3 SUMMARY OF PREVIOUS WORKSHOP

The first workshop on "Irradiation Effects in Nuclear Waste Forms" (July 29-30, 1980) sponsored by the MCC brought together experts in radiation damage in materials and waste-management technology to review the problems associated with irradiation effects on waste-form integrity and to evaluate standard methods for generating data to be included in the Nuclear Waste Materials Handbook.

The workshop reached the following conclusions:

- The concept of MCC-6 (actinide doping) for evaluating the effects of alpha decay is valid and useful. As a result of the workshop,

modifications to the proposed procedure were incorporated in a revised version of MCC-6, which was subsequently submitted to the MRB for consideration.

- The MCC-6 test is not applicable to the evaluation of radiation damage in spent fuel.
- Plutonium-238 was recommended as the dopant for transuranic and defense HLW waste forms. When high doses are required, as in the case of commercial HLW forms, ^{244}Cm can be used.
- Among the important property changes caused by irradiation are those that lead to greater leachability, e.g., chemical changes that reduce durability and physical changes that increase surface area. Additionally, radiolysis of the leachant may increase leach rates; research in this area was recommended.
- Ionization-induced changes in physical properties can be as important as displacement damage in some materials. A synergism is also likely to exist from the combined effects of ionization and displacement damage.
- The effect of changing the temperature and dose rates on property changes induced by radiation damage should be determined.

3.4 STATUS OF MCC-6

The MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms was provisionally approved by the MRB on October 6, 1981. The provisionally approved version of this test method is given in Appendix D.

4.0 WORKING GROUP REPORTS

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

4.1 WORKING GROUP I - ION AND NEUTRON IRRADIATIONS

The primary assignment for Working Group I was to evaluate the merits and limitations of ion and neutron irradiations as techniques to simulate the displacement damage induced by alpha decay in radioactive waste forms. The motive for considering ion and neutron irradiations is that they can produce irradiation effects at lower costs and in relatively shorter times as compared to the actinide-doping technique (MCC-6), which was discussed at the previous workshop and is the generally accepted method for studying the effects of alpha decay in HLW forms. The simulation of transmutation effects was also discussed, and key experiments for ion irradiations were identified. The participants in this working group were as follows:

Bill Weber, MCC, Discussion Leader

George Arnold, Sandia Laboratories
Louis Cartz, Marquette University
Frank Clinard, Los Alamos National Laboratory
Mike Guinan, Lawrence Livermore National Laboratory
Dennis Kneff, Rockwell International
Bill McDonell, Savannah River Laboratory
Nick Packan, Oak Ridge National Laboratory
Mark Robinson, Oak Ridge National Laboratory
Vijay Sethi, Argonne National Laboratory
Karl Swyler, Brookhaven National Laboratory
Grady White, National Bureau of Standards

4.1.1 Introduction

The working group discussions began with presentations by the group participants on both the irradiation techniques employed and the results obtained

in their laboratories. The presentations dealt primarily with updated results from actinide-doping experiments or data obtained from ion irradiations. No data was presented from neutron irradiations, although two participants did describe planned experiments involving the use of the $^{10}B(n,\alpha)^{7}Li$ or $^{6}Li(n,\alpha)^{3}H$ reactions to study transmutation effects or mechanical properties. Other presentations generally summarized planned irradiation procedures, the application of existing ASTM standards (particularly ASTM E 521-77, Standard Recommended Practice for Neutron Radiation Damage Simulation by Charged-Particle Irradiation), numerical simulation of the atomic-displacement processes in polyatomic materials, ion irradiations of nonwaste-form materials, and general issues relevant to the understanding of irradiation effects in nuclear waste forms. The presentations generated discussions that focussed on five major topics. These were

- the general applicability of either ion or neutron irradiations to evaluating waste forms
- the need for correlation of both ion and neutron irradiation damage to damage induced from alpha decay of actinides
- the use of ion and neutron irradiations for fundamental studies
- the problems associated with leach testing ion-irradiated materials
- identifying the key experiments to be performed by ion and neutron irradiations.

4.1.2 Evaluation of Waste Forms

A major conclusion of the working group was that neither ion irradiations nor neutron irradiations are substitutes for actinide doping in the final evaluation of radiation damage from alpha decay in a nuclear waste form. The general consensus of the working goup was that the most useful applications of both ion and neutron irradiations may be as screening tests for waste forms or as research tools for more fundamental studies. Ion irradiations are perhaps a more powerful technique for screening and research because of the amount of flexibility inherent in this technique; however, neutron irradiations do allow the production of uniformly damaged specimens of sufficient size for bulk property measurements (including leach testing). Several fundamental issues in

the area of radiation effects were discussed which could be answered by carefully designed experiments utilizing ion irradiations. These fundamental questions deal primarily with dose-rate effects, temperature dependence, and the nature and importance of alpha-particle effects relative to the recoil nucleus in alpha decay. Results obtained from such experiments would provide complementary information to results obtained with the actinide-doping technique (MCC-6).

4.1.3 Correlation to Alpha Decay

The validity of either ion irradiation or neutron irradiation as a screening test or research tool for studying the effects of alpha decay must be established based on correlation experiments with actinide-doping studies. One possible correlation experiment involves ion irradiation of several different types of glasses and single-phase crystalline materials that have also been studied by actinide doping. Specifically, the cross sections (proportionality constants) for amorphization would be measured, and the hierarchies of results for this set of materials would be compared for both actinide doping and ion irradiation. It was also suggested that comparisons of lattice-parameter changes, stored energy, and leach rates under both actinide doping and ion irradiation would provide beneficial correlations; that other single-phase compounds need to be doped with actinides and investigated in order to add to the range of materials studied for possible correlation; and that the doses received in such correlation experiments should be compared based on damage energy (amount of energy that goes into displacements).

4.1.4 Fundamental Studies

The working group identified several fundamental issues concerning the simulation of irradiation effects in nuclear waste forms for which sufficient data are currently lacking to provide the necessary degree of understanding. These issues were concerned with dose-rate effects, temperature dependence, the role of the alpha particle, radiation-induced surface segregation, and the unit best suited for intercomparison of data obtained by different irradiation techniques.

The question of dose-rate effects is an important concern in radiation-damage studies of nuclear waste forms. Actinide doping, which is accepted as the best simulation technique, accelerates the dose rate by several orders of magnitude; ion and neutron irradiations accelerate the dose rate even more. Ion irradiations are the extreme case where the damage rate is accelerated by six to nine orders of magnitude over what is expected in the actual case. The effect of dose rate is not expected to be a linear function. The behavior can be expected to be such that at some limiting low dose rate (perhaps higher than the dose rate of actinide doping?) the effects will be minimal and the observed behavior can predict the behavior of the actual waste forms. The dose-rate effect is related to the amount of annealing or relaxation that occurs between subsequent events (including alpha decays, passing ions, and collision cascades) and is thus temperature dependent. Ion irradiations offer a very powerful tool to study dose-rate effects and may provide the understanding to evaluate the magnitude of any such effects. Additionally, carefully planned experiments with ion irradiations and radioactive actinide sources (either internal or external) may provide data over the range of dose rates necessary to understand the dependence of any effects.

Temperature dependence is another important issue because it is related to dose-rate effects. Most irradiations are carried out at or near room temperature, which is considered by some to be a conservative condition. It is recognized that a higher irradiation temperature might be a means of reducing potential dose-rate effects by accelerating annealing or relaxation following an ion or neutron collision; however, growth of macroscopic defects could also be enhanced at higher temperatures. An upper temperature limit of 300°C was suggested for studies in this area. Ion irradiations, because of their short irradiation times, can provide substantial data for many materials over the temperature range of concern. In-situ ion irradiations in an electron microscope with a hot stage would allow observation of the microstructural changes as a function of temperature and perhaps even dose rate.

Both an alpha particle and a recoil nucleus are emitted in alpha decay. Ion and neutron irradiation have generally been used to simulate only the effects of the recoil nucleus. The alpha particle may enhance annealing

during irradiation, produce isolated defects that interact differently than the defects produced in the collision cascade of a heavier particle, affect defect mobility by forming helium-defect complexes, result in gas bubbles, etc. Several facilities now exist that provide a means for simultaneous irradiation with alpha particles and heavier ions. These facilities could be used in experiments to further understand the role of the alpha particle in detail.

External irradiations can induce surface segregation of some elemental species. If surface segregation does occur, then the irradiated region does not represent bulk material damaged by self-irradiation. This is an area requiring further investigation if external irradiations are to be correlated with self-irradiation from actinide decay. It was recommended that single crystals of relevant materials be used to study surface segregation under external ion irradiation. It was also suggested that backscattering techniques, which are nondestructive, be employed.

It was suggested that more realistic experiments that closely followed the thermal and radiation history of a waste form may be desirable. Such experiments would require elevated temperatures in the presence of beta and gamma radiation, followed by actinide doping at lower (near ambient) temperatures. It was recognized that, although such experiments may be ideal, they are probably impractical.

A final point discussed by the working group was that fundamental studies should be carried out on single-phase materials to provide data that are more easily interpreted.

Although the dpa (displacements per atom) is the generally accepted unit for intercomparison of data from metals irradiated by different sources, this unit may not be acceptable for ceramics or glasses due to basic structural differences. It was suggested that the damage energy (the amount of energy that goes into displacing atoms) is a better unit; but even in this case, sophisticated codes for numerical computation of the damage energy in complex multielement ceramics do not exist. This is an area where much effort is needed. More theoretical and numerical studies on cascade development are required.

4.1.5 Leach Testing

There are many concerns over the leach testing of ion-irradiated surfaces, where the damage often varies with depth and is confined to a very narrow region near the surface. Accepted leach tests generally require a long leach period which would normally remove the damaged region. It was suggested that irradiations be carried out in such a manner that the damage is uniformly produced over much greater depths (several microns or more) in order to allow longer leach times. An example would be to use a higher energy ion beam and either interpose a variable energy degrader or rock the specimen.

Enhanced leaching in brine of ion-irradiated glasses, which has received considerable attention because of recent publications (Dran et al. 1980), was also discussed. It was recommended that leaching in brine of actinide-doped materials should be carried out to provide data under these conditions. Additional data in this area were presented that indicated insignificant changes in leach rates of simulated waste forms in deionized water after ion irradiation. Some of the data were obtained on specimens uniformly damaged to greater depths, which allowed 28-day leach testing.

4.1.6 Transmutation Studies

It was recognized that transmutation studies are very difficult to perform. Three types of experiments have been identified that will produce information on transmutation effects: slow-neutron irradiation of ^{133}Cs-bearing materials to induce $^{134}Cs \rightarrow {}^{134}Ba$ transmutations, slow-neutron irradiation of ^{6}Li or ^{10}B-containing materials to produce transmutation effects by (n,α) reactions, and examination of spent radioisotope heat sources. Currently, only one direct experimental study is being carried out on fission-product transmutation effects, namely, the study of W. J. Gray at PNL involving the $^{134}Cs \rightarrow {}^{134}Ba$ transmutation. It was suggested that, if possible, temperature dependence should be a consideration in future studies of this kind. Other experiments have recently been initiated at Rockwell International utilizing ^{6}Li-doped crystalline materials.

4.1.7 Test Procedures

The consensus of the working group was that it is premature for standardized test procedures for either ion or neutron irradiations. It was suggested, however, that the existing ASTM procedure (ASTM E 521-77) on "Neutron Radiation Damage Simulation by Charged-Particle Irradiation" may provide some guidelines on how to standardize charged-particle irradiations of waste forms. It was recognized that high vacuum ($<10^6$ Torr) and accurate temperature measurements are required. An ASTM Task Group on the Simulation of Radiation Effects in Nuclear Waste Forms (E 10.08.03) has formed and will be developing a standardized procedure for ion irradiation of nuclear waste materials. This ASTM Task Group is concentrating on three subject areas: 1) charged-particle irradiation techniques, 2) post-irradiation analyses, and 3) calculated exposure parameter for comparison of doses from different irradiation sources. The members of this task group are identified in Appendix C.

4.1.8 Experimental Work Needed

As discussed above, experimental work is needed in the following areas:

- effects of dose rates
- effects of temperature
- dual-beam (alpha and heavy-ion) irradiations to investigate the role of alpha particle in detail
- correlation studies of same materials (glasses and ceramics) to compare heavy-ion irradiation damage with damage from actinide decay
- surface segregation of elemental species under external irradiation
- development of computer codes to calculate the damage energy in complex multielement ceramics.

4.2 WORKING GROUP II - IONIZATION DAMAGE/SOLUTION RADIOLYSIS

The assignment for Working Group II was to evaluate, if possible (based on current data), the potential effects of ionizing radiation on both solid-state damage and enhanced solid/water interaction due to radiolysis. The participants in this working group were as follows:

Ray Turcotte, PNL, Discussion Leader

Ned Bibler, Savannah River Laboratory
David Howitt, University of California - Davis
Vic Kelsey, EG&G Idaho, Inc.
Paul Levy, Brookhaven National Laboratory
Marina Pascucci, Case Western Reserve University
Frank Roberts, MCC
Lou Vance, Pennsylvania State University
Richard Van Konynenburg, Lawrence Livermore National Laboratory

4.2.1 Introduction

Most of the individuals made short presentations (ten minutes) describing current research activities and philosophies concerning ionizing radiation effects in nuclear waste forms. Some points made during these discussions are listed below--not in order of importance, but to give a general feeling for the discussions and the types of contributions. Of course, these are comments of individuals, not necessarily a consensus of the group.

- Experiments have been initiated to study SYNROC(D) following MCC-6, but also including some high-dose gamma irradiation using High Flux Isotope Reactor spent fuel. Doses to ~8 x 10^{10} rad should be reached.
- Gamma-field leach experiments on SRL-131 glass show no significant effect on leach rates until the pH decreases due to air radiolysis.
- It was pointed out that ionization damage to solids includes a combination of several features that seem to occur readily in NaCl (for example) but not in silicates:

- electron excitation process
- atomic motion to limit recombination
- a strong temperature dependence

- Some relatively simple experiments (e.g., high-dose gamma irradiation of relevant materials) are needed to demonstrate ionizing radiation effects. [This point was also made at the previous MCC workshop.]

- Electron microscopy/electron bombardment of glasses to $>10^{13}$ rad leads, in some cases, to the formation of oxygen-containing pores and phase separation. These effects are strongly temperature dependent.

- Single-phase materials rendered amorphous by fission-fragment bombardment show extensive alteration by hydrothermal treatment at 200°C, whereas this is not observed for the corresponding unirradiated materials.

- Electron microscopy/electron bombardment studies of α-quartz show rapid nucleation of amorphous inclusions at $\geq 10^{10}$ rad. Loss of short-range order is suggested to occur before loss of long-range order ($\geq 10^{12}$ rad).

It was clear to all of the group that there are relatively few studies with respect to either ionizing damage effects in waste solids or with regard to radiolytic (solution) effects on leaching/corrosion behavior. It was the consensus that further, relatively simple studies are necessary to define the magnitude of any radiation-related effects both with respect to solid-state damage and with regard to waste form/barrier/backfill-aquifer interactions in a radiation field. In some cases, appropriate studies are already in progress but, in general, adequate data are not now available to either exclude or include ionizing-damage effects in defining materials behavior.

4.2.2 Solid-State Ionization Damage

Nuclear waste solids undergo self-irradiation by high-energy particles, electrons, neutrons, and photons. The energy is absorbed by displacement of

the atom as a whole ("hard-sphere" collision) or by interaction with its electrons. The latter process can lead to molecular rearrangements, which involves atomic displacements over large distances in some systems. We refer to permanent changes to the material induced by the latter as ionization damage.

Although actinide-doping experiments on single phases or more complex waste solids do include a significant ionizing radiation component from the alpha particle, concurrent displacement damage from the recoil limits any simple interpretation. Ionization-damage studies of inorganic oxides using gamma rays or electrons in the dose range of interest (10^7 - 10^{12} rad) are limited. The two areas of general importance with respect to property changes center on (a) the structural effects, and (b) changes in chemical durability. It was the feeling of the group that changes in structure, including amorphization of crystalline phases or radiation-induced phase transformations would not be expected to lead to large changes in leach rate unless the creation of high-energy interfaces is involved. This is supported by the lack of radiation-induced changes in leach rates of actinide-doped glasses and glass ceramics in studies in the U.S. and Europe. With regard to the dose dependence for ionization damage, Figure 4 summarizes observations made during the group discussion. The figure does not entirely represent unanimous agreement, mainly because of the paucity of data rather than because of conflicting information. For example, only a few laboratories have undertaken studies using electron microscopes to irradiate and examine appropriate glasses and crystalline phases. Few data appear to be available concerning either structural changes or leach-rate changes in high-dose (e.g., 5×10^{11} rad), gamma-irradiated, waste-form materials. Studies at the Savannah River Laboratory have included irradiation of SRL-131 waste glass to 8.5×10^{10} rad with no significant effect on density (<0.1%) or leach rate. There have been other gamma-irradiation studies to doses of ~5×10^{10} rad, limited electron bombardment studies, and studies of aged, actual, high-level waste glass to doses of 1 to 5×10^{11} rad, which have shown only small effects.

Previous studies of pure silica by Primak and others (Primak 1975; Primak 1979) and recent gamma irradiation of commercial borosilicate glasses by

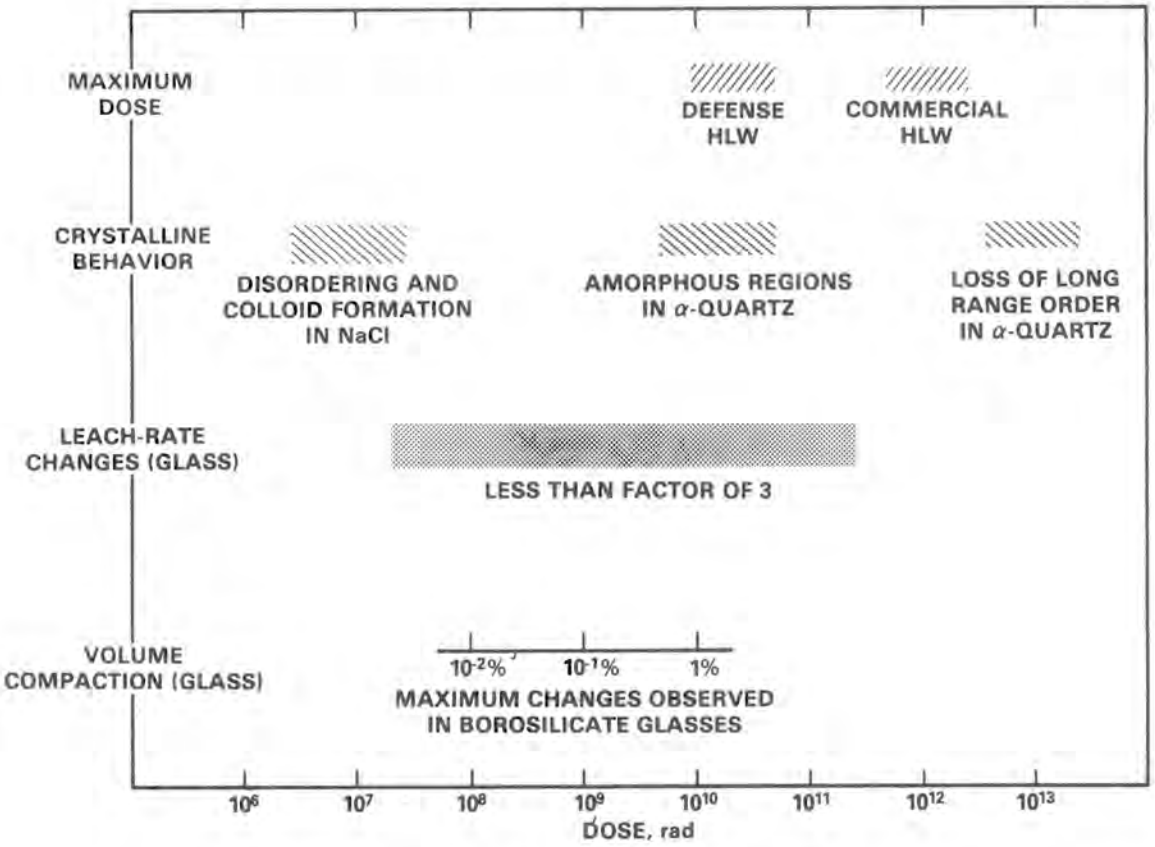

FIGURE 4. Summary of Ionizing Radiation Effects

Shelby (1980) nevertheless lead one to a concern that significant volumetric changes, at least, may occur in glass waste forms at high gamma doses. Figure 5 summarizes the data reported by Shelby (1980). Extrapolation to higher doses suggests that compaction into the 1% to 10% range may occur at doses that will be attained in high-level waste solids. There is no comparable information available for other crystalline phases of interest, nor have dose-dependent leach rate changes been reported for any material. It is therefore evident that gamma field and electron bombardment experiments are needed to evaluate effects up to ~10^{12} rad. The studies will of necessity require a time acceleration; hence, dose-rate and temperature-dependent properties must be ascertained. The objective should be to define property changes as a function of dose, as has been undertaken in evaluations of the alpha-recoil problem.

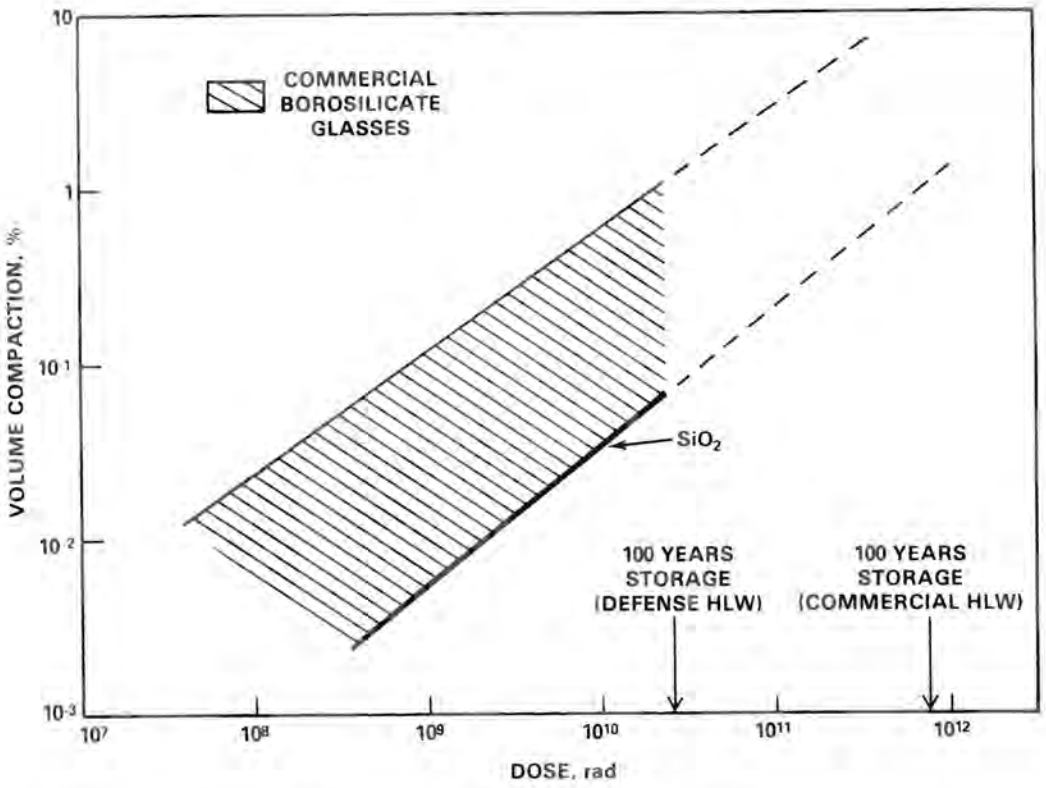

FIGURE 5. Volume Compaction in SiO_2 and Commercial Borosilicate Glasses as a Function of Dose (Shelby 1980)

4.2.3 Solution Radiolysis Effects

The group reviewed parts of a report on solution radiolysis effects by Burns et al. (1981), which is a good summary of the current state-of-the-art. The relatively limited studies now available concerning radiolysis show quantitative conversion of dissolved air to nitric acid. Other highly reactive products are well recognized and further work in the general field is needed. It was pointed out in the group discussion that a major limitation of current studies is the restriction to distilled water, but use of repository waters is planned in continued studies. The major conclusions were as follows:

- Formation of HNO_3 is a problem needing further study (Is dissolved N_2 or air required?).
- Effects on waste-form leaching so far appear to be relatively small (excluding acid effects).

4.2.4 Experimental Work Needed

Work is needed in the following experimental areas:

Solid-State Damage

- determination of damage mechanisms, radiolytic yields (G values), and displacement thresholds
- temperature- and dose-rate dependent studies
- gamma-field irradiations to as high a dose as possible with structural and leaching studies as a function of dose [f(dose rate, T)]
- overlap of quantitative data from gamma-field and electron-bombardment approaches.

Solution Radiolysis

- continued gamma-field studies as in progress [f(dose rate, T)] and extention to repository waters.

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APPENDIX A

WORKSHOP PARTICIPANTS

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APPENDIX B

WORKSHOP AGENDA

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WORKSHOP AGENDA

MATERIALS CHARACTERIZATION CENTER
SECOND WORKSHOP ON IRRADIATION EFFECTS IN NUCLEAR WASTE FORMS

Battelle Seattle Research Center
Seattle, Washington

August 13-14, 1981

AGENDA

Wednesday, August 12	8:00 pm	Informal Reception - Suite C-5
Thursday, August 13	7:45 am	Coffee - Seminar Lobby
	8:15	Welcome: R. D. Nelson
	8:25	Outline of Workshop Activities: W. J. Weber Role of MCC in Waste Management Overview - Irradiation Damage and Testing: W. J. Weber - Status of MCC-6 (Actinide Doping) - Ion Bombardment and Neutron Irradiation - Ionization Damage - Solution Radiolysis and Sample/Solution Interactions
	9:30	Introduction of Working Group Topics: W. J. Weber, R. P. Turcotte Organization of Working Groups
	10:15	Break
	10:30	Working Group Sessions (Establishment of Individual Working Group Agenda)
	12:15	Lunch
	1:00 pm	Working Group Sessions

	3:00-3:30	Group Chairman Schedule 15 min. Break
		Continuation of Working Group Sessions
	5:00	Cocktail Hour
	6:00	Dinner
	7:30	Group Leaders Prepare 1st Draft of Summary Reports
Friday, August 14	7:45 am	Coffee - Seminar Lobby
	8:15	Full Workshop Meeting: Brief Group Reports and Discussion
	8:45	Working Group Sessions: Continue Discussions, and Review and Revise Summary Reports
	10:30	Break
	10:45	Reconvene Full Workshop: Group Summary Reports - Ion Bombardment and Neutron Irradiation - Solid State Ionization Damage, Solution Radiolysis, and Sample/Solution Interactions
	12:15	Lunch
	1:00 pm	Full Workshop Meeting - General Discussion - ASTM's Role and Task Group Formation
	3:00	Coffee
	4:30	Adjourn

APPENDIX C

ASTM TASK GROUP MEMBERS

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ASTM Task Group E 10.08.03

Simulation of Radiation Effects in
Nuclear Waste Forms

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APPENDIX D

MCC-6P METHOD FOR PREPARATION AND CHARACTERIZATION OF ACTINIDE-DOPED WASTE FORMS

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MCC-6P METHOD FOR PREPARATION AND CHARACTERIZATION OF ACTINIDE-DOPED WASTE FORMS EXAMPLE REPORT 6-9

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APPENDIX

FACTORS AFFECTING APPROVAL STATUS OF MCC-6 METHOD FOR PREPARATION AND CHARACTERIZATION OF ACTINIDE-DOPED WASTE FORMS

This appendix identifies additional information that the MCC will provide the MRB before requesting full approval of MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms. Where feasible, an estimated schedule is also given.

A.1 Dose-Rate Effects (October 1982)

There has been some concern expressed regarding the validity of accelerated testing where the dose rates are increased by $\sim 10^3$ for commericial HLW forms and $\sim 10^6$ for defense HLW forms. Although the MCC is supporting some research in this area, a definitive resolution regarding the magnitude of this effect (if any) will require several years of experimental and theoretical research, much of which is not currently being supported by any government agency. Regardless of whether there is a dose-rate effect or not, accelerated testing is required if any data on irradiation effects on waste forms, simulating long storage periods, are to be obtained. If dose rate has an effect, then a theoretical understanding of the effect may allow prediction of behavior based on data obtained. All other simulation techniques increase the dose rate even more (by several orders of magnitude) than the actinide-doping technique and are less likely to produce the same type of damage as actinide decay. The MCC will keep the MRB abreast of developments in this area, but this issue may not be resolved for years.

A.2 Radiochemical Analysis (October 1982)

The MCC will develop or support the development of techniques and procedures for radiochemical analysis of the specific activity of actinide-doped waste forms.

A.3 Waste-Form Limits (October 1982)

MCC-6 requires that the actinide distribution be determined. In waste forms where the crystal sizes are $<5\ \mu m$ in average diameter, such as in the crystalline ceramic waste forms, the actinide distribution cannot be determined by the conventional techniques employed by MCC and other laboratories. The distribution and concentration of the actinide dopant under these conditions can be determined by using the analytical capabilities of a STEM. Until such a microscope is available for use on actinide-doped waste forms, MCC-6 will be limited to glass waste forms or waste forms containing large crystals ($>5\ \mu m$). Exceptions may be made on a case-by-case basis if, for instance, in the judgment of the MCC and MRB, the manufacturing technique reasonably assures a realistic distribution of the actinide dopant in the test specimens, even if it cannot be confirmed by actual measurement.

A.4 Dose Threshold Effect (October 1982)

There has been some concern regarding results of Pb-ion irradiation studies (Dran et al. 1980. *Science* 209:1518), which suggested that a threshold in dose may exist for observance of radiation-enhanced leaching. Although no actinide-doping studies (in a wide range of materials) have observed this effect and there is considerable doubt in the scientific community concerning the validity of ion simulation, the MCC will keep the MRB informed of developments in this area. If it becomes apparent that thresholds for radiation effects have validity, then MCC-6 may be modified (higher required dose in commerical HLW forms) accordingly. This effect, if it exists, is not expected to impact MCC-6's (as written) applicability to either defense HLW forms or TRU waste forms.

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MCC-6 METHOD FOR PREPARATION AND CHARACTERIZATION OF ACTINIDE-DOPED WASTE FORMS

1.0 SCOPE

The MCC-6 Method for Preparation and Characterization of Actinide-Doped Waste Forms is used to prepare waste-form specimens in which the effect of alpha-emitting radionuclides is accelerated so that changes in waste-form properties induced by alpha decay can be measured in experimentally practicable times. Specimens prepared by this method are required for the measurement of alpha-decay-induced changes in such characteristics as leach rate, specific volume, and microstructure. The method is applicable to any HLW or TRU waste form, providing it is demonstrated that the distribution of actinide dopant in the waste-form specimens adequately reflects the expected distribution of actinides in the actual waste form.

2.0 SUMMARY

The method consists of incorporating short-lived actinides into specimens of simulated or actual nuclear waste forms to accelerate the radiation effects of alpha decay. Generally, ^{238}Pu ($t_{1/2}$ = 87.7 years) is used for TRU and defense HLW forms, and ^{244}Cm ($t_{1/2}$ = 18.1 years) is used for commercial HLW forms. Specimens are prepared in which an accumulated dose of at least 3×10^{18} alpha decays/cm^3 is achieved in a reasonable time, e.g., <2 years. The specimens are stored, and property measurements are made as a function of time (accumulated dose) using appropriate MCC procedures.

3.0 USES AND LIMITATIONS

It should be understood that the interpretation of the results of this test method may be limited by the extent to which the distribution of the actinide dopant can be shown to simulate the expected distribution of actinides in the chemical phases of the actual waste form.

Specimens prepared by this method are suitable only for the measurement of changes induced by alpha decay of actinides. Other MCC procedures may be developed to measure the changes induced by the spontaneous beta decay of the fission products.

Only limited data exist on the effect of accelerated dose rates. It is assumed that the effects produced in the waste-form specimens by the accelerated dose-rate methods described in this test method are equivalent to those that would occur over long time periods in an actual waste-form material under normal disposal conditions. The applicability of the test results depends on the validity of this assumption.

Self-heating due to the actinide dopant can increase specimen temperature during storage and testing. Thus, specimens should be made small enough (typically 1 to 3 g) so that self-heating of individual specimens does not significantly affect test results obtained by use of other MCC test methods. The heat generated in specimens containing 1-wt% dopant is 0.0056 and 0.0284 W/g for ^{238}Pu- and ^{244}Cm-doped specimens, respectively.

4.0 SAFETY PRECAUTIONS

Significant gamma and neutron radiation is associated with ^{244}Cm; therefore, adequate biological shielding must be provided for the protection of personnel. In addition, all preparation and testing must be performed in controlled-atmosphere gloveboxes because of the high biological hazard of airborne ^{238}Pu and ^{244}Cm.

Plutonium-238 and ^{244}Cm are hazardous and difficult to control. Personnel must be properly protected at all times against the possibility of skin contamination, inhalation, and ingestion. Guidelines to be followed when working with ^{238}Pu or ^{244}Cm or materials doped with these nuclides are as follows:

- Keep the material confined at all times.
- Avoid cross contamination with other alpha emitters and low-energy beta emitters.
- Avoid operations that could result in accidental airborne or surface contamination in occupied areas.
- In all cases, follow the radiation-protection procedures in effect at the laboratory performing the test.

5.0 EQUIPMENT AND CALIBRATION REQUIREMENTS

5.1 Equipment

The furnaces used in specimen fabrication must be capable of controlling the temperature of the specimens within ±25°C of the specified temperature. Provide a temperature recorder or other monitoring device to ensure that the desired temperatures have been maintained. Determine that self-heating does not interfere with maintaining the

desired specimen temperature, and report the results of such an evaluation.

Crucibles or dies used to contain the specimens during fabrication should not significantly react with the specimens. However, if significant reaction does occur, care must be taken that the reaction zone formed during specimen fabrication does not interfere with the subsequent testing of the specimens. Document the extent of the reaction zone.

Microstructural characterization requires the use of optical microscopy, powder XRD, SEM-EDX, and, in some cases, TEM or STEM. Microscopy techniques shall be capable of recording sample microstructures and phase morphology over a range of magnification, e.g., optical: 10 to 1000X; SEM: 100 to 10,000X. The XRD should preferably be equipped with a diffracted-beam monochromator and operated to obtain quantitative measurements of relative intensities and lattice parameters.

5.2 Calibration

Calibrate all instruments used in this test method initially and periodically to minimize possible errors due to drift. Table 1 shows the methods and minimum frequency of calibration required for the various devices used. Use standardization procedures that are published by recognized authorities such as the NBS or ASTM.

5.3 Quality Assurance

This test method must conform to all applicable quality assurance requirements of the laboratory performing the tests.

6.0 TEST-SPECIMEN PREPARATION

Prepare test specimens in which the required accumulated dose can be achieved in less than two years.

6.1 Choice of Actinide Dopant

Plutonium is the dominant alpha emitter in TRU wastes and defense HLW; therefore, ^{238}Pu is the preferred dopant for TRU waste and defense HLW forms. Likewise, ^{244}Cm is the preferred dopant for commercial HLW forms because it chemically simulates Am and Cm, the dominant alpha emitters in commercial HLW. Exceptions must be discussed in the submitted report. In special cases where the actinides contained in the waste partition into different host phases in the waste form according to valence state or some other criteria, it may be necessary to dope the waste form with appropriate amounts of both ^{238}Pu and ^{244}Cm.

Table 1. Required Calibration Schedule

Measurement	Device	Frequency Check and Method
Temperature	Thermocouple and thermocouple readout	6 mo NBS standards
Chemical analyses	Analytical method	3 mo NBS standards 2 times daily (routine) Secondary standards
Phase identification	XRD	3 mo NBS standard
	EDX	3 mo NBS standards Daily Secondary standards
Phase concentration	XRD	Daily Specially prepared in-house standards
	Optical-electronic scanning device for quantitative microscopy.	Daily Secondary standards

6.2 Actinide-Dopant Requirements

The required accumulated dose to be attained during the test period shall be at least 3 x 10^{18} alpha decays/cm^3. The required actinide-dopant concentration in the waste form is determined from the accumulated dose required and the length of the test period desired.

The required actinide-dopant concentration, C (wt%), needed to achieve a required dose, D (alpha decays/cm^3), in a specified time period, t (s), can be calculated from the expression

$$C = \frac{D\lambda}{\rho A\ (1-e^{-\lambda t})} \times 100 \qquad (1)$$

where ρ = specimen density (g/cm^3)

λ = decay constant of the dopant (s^{-1}) (1.2 x 10^{-9} s^{-1} for ^{244}Cm and 2.6 x 10^{-10} s^{-1} for ^{238}Pu)

A = specific activity of the dopant at time of preparation (Bq/g)

If some time, t_1, has elapsed since the specific activity, A_1, of the dopant was determined, then A is given by the expression

$$A = A_1\, e^{-\lambda t_1}. \qquad (2)$$

6.3 Specimen Requirements

Determine the tests to be performed on the doped solid waste form and quantity of specimens required by each test. Control specimens, that is, specimens from which the highly active actinide dopant is omitted, may also be required by the individual tests to be performed.

6.4 Specimen Composition

The composition of the test specimens shall be as near as possible to that produced by the prototypical waste-form-manufacturing process. For the actinide dopant to make the minimum alteration to the simulated waste-form chemistry, the actinide dopant is substituted, when possible, on an atom-for-atom basis for other actinides (e.g., uranium) and/or appropriate rare-earth elements in the simulated waste form. A complete discussion of the chemical basis and rationale for the substitution must be contained in the submitted report. General practice has been to limit the concentration of dopant to <5 wt% as oxide to minimize perturbation of waste-form chemistry, limit the amount of self-heating within the test specimens, and ensure solubility and uniform distribution of the dopant in the waste form.

6.5 Specimen Fabrication

Fabricate the specimens by following the procedures specified by the waste-form developers as closely as possible. The object is to add the actinide dopant to the waste form in a way that ensures solubility and a representative distribution of the actinide dopant during final fabrication. The method of adding the actinide dopant and final fabrication is waste-form dependent; therefore, a complete description of waste-form fabrication and verification of the desired distribution of the dopant are required in the report submitted to the MCC.

For glass waste forms, the general practice has been to add the actinide dopant as either an oxide powder or nitric acid solution (both methods have been successful) to a finely crushed and sieved (<50 μm) glass frit of the as-received, waste-glass composition. If the actinide is added as an oxide powder, the mixture is melted as prescribed and then either poured into molds or cooled under the established conditions. The waste glass is generally held at 500°C for several hours to relieve thermal stresses. If the actinide dopant is added as a nitric acid solution, the mixture is dried at 100°C for several hours and then denitrated at 500°C for several more hours. The powder should be remixed before melting at the prescribed temperature.

In the case of ceramic waste forms, the actinide dopant may be added as either an oxide or nitric acid solution to the unreacted waste-form material received from the waste-form developers. The choice of oxide or nitric acid solution will depend on the form of the unreacted material received. Once the actinide has been added, the mixture is prepared according to the procedures and heat treatment prescribed by the waste-form developers.

6.6 Control-Specimen Fabrication

Prepare the control specimens required for any test methods following the procedure used to prepare the actinide-doped specimens. When more than 1% of the actinide dopant is required for the doped specimens, prepare the control specimens, if possible, using the same weight percent of a less-active isotope of the actinide (e.g., ^{239}Pu in the case of ^{238}Pu doping).

6.7 Specimen Characterization

6.7.1 Radiochemical Analysis

A radiochemical analysis of a representative test specimen of doped material from each preparation batch shall be

made to verify the specific activity of the prepared material. The specific activity is needed to calculate the accumulated dose. Specify the statistics of the analytical method used.

The accumulated dose, D, in alpha decays/cm³ can be calculated as a function of elapsed time from the expression

$$D = \frac{\rho A^*}{\lambda} (1-e^{-\lambda t}) \quad (3)$$

where ρ = specimen density (g/cm³)

A^* = specific activity of the specimen at time of preparation (Bq/g)

λ = decay constant of actinide dopant (s^{-1})

t = time elapsed after specimen preparation (s)

6.7.2 Chemical Analysis

A chemical analysis of a control specimen shall be made to verify the intended composition.

6.7.3 Homogeneity and Microstructure

Determine the distribution of actinide dopant in the specimens by analyzing polished cross sections of the specimens. Use alpha autoradiography, SEM-EDX, or equivalent technique, to define the distribution of the actinide dopant in the waste form and in specific phases for material of sufficiently large (>5 μm) grain sizes. Use optical microscopy and SEM-EDX in conjunction with powder XRD to identify crystalline phases and to obtain semiquantitative information on phase concentration. Also use optical microscopy to determine the extent of microcracking. Specify statistics of any analytical method used.

If the grain sizes in the waste form are <5 μm in average diameter, such as in crystalline-ceramic waste forms, the actinide distribution cannot be adequately determined using the conventional techniques described above. The distribution and concentration of the actinide dopant under these conditions can be determined by using the analytical capabilities of a STEM.

Characterization of the crystalline phases and microstructure of the control specimens is also required.

6.8 Specimen Storage

Store the specimens at room temperature. Store actinide-doped and control specimens at equivalent conditions, but in different containers.

7.0 TESTING OF SPECIMENS

The specimens prepared by this procedure should be tested for radiation-induced effects by approved MCC test methods in order for the property data to be certified for inclusion in the *Nuclear Waste Materials Handbook*. Several MCC test methods will be applicable for testing alpha-decay effects in radioactive waste forms. These will cover such characteristics as leaching behavior, density, microstructure, and tensile strength. The radiation flux at the surface of the specimens may be important to the applicability of a particular test and should be considered.

8.0 REPORTS

A standard format for reports appears below and is illustrated in the example report. Each report may then be inserted in the Specimen Preparation Section of the appropriate MCC property-measurement test report. Adherence to this format will allow the MCC and MRB to easily process the data submitted by the various laboratories for inclusion in the *Nuclear Waste Materials Handbook*. Each page of the report must contain the following information in the upper right-hand corner:

- Material tested and its identification number
- MCC test number (e.g., MCC-6P)
- Name of investigator
- Affiliation of investigator
- Date report submitted to MCC

STANDARD FORMAT

1.0 Chemical Composition

- Report actual composition of control specimens and how obtained.

2.0 Description of Actinide Dopant

- Discuss rationale in selection of dopant.
- Report chemical form of the dopant. Include quantitative chemical and radionuclide analyses, analytical methods utilized and the laboratory that performed the analyses, estimates of their precision, and date of radionuclide analysis.

3.0 Description of Specimen Preparation

- Detailed specimen preparation. Include description of equipment used, how dopant was added to the waste form, all heat treatments performed, and date of preparation.

4.0 Physical Description of Specimens

- Report dimensions, weight, and identification method (i.e., specimen number) for each specimen. The dimensions and weight are for descriptive purposes and need only be known to ±5%.

- Identify the specimens sectioned and the date of sectioning.

5.0 Characterization of Specimens

- Summarize results of actual and intended chemical analyses, radiochemical analysis, autoradiography, optical microscopy, XRD, SEM-EDX, or equivalent analyses. Preserve all autoradiographs, photomicrographs, and raw data from analyses of both actinide-doped and control specimens in archives.

- Provide a description of methods of calibration and estimates of precision and accuracy for all analytical methods. Also indicate the resolution capability of the instruments employed.

6.0 Storage of Specimens

- Describe method of storage.

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PNL-77-260 Glass
MCC-6S
J. R. Doe
Pacific Northwest Laboratory
Date Submitted 7/1/81

MCC-6P METHOD FOR PREPARATION AND CHARACTERIZATION OF ACTINIDE-DOPED WASTE FORMS EXAMPLE REPORT(a)

The purpose of this example report is to illustrate what the official report of MCC-6 results must contain. A full report of this type must be presented to the Materials Characterization Center for its review and subsequent submission to the Materials Review Board for approval for publication in the *Nuclear Waste Materials Handbook*.

1.0 CHEMICAL COMPOSITION

- Type of waste form—Partially devitrified borosilicate glass (PNL 77-260). This is a simulated commercial HLW glass.
- The chemical composition of the PNL 77-260 waste glass control specimen is given in Table 1.1; both the intended and actual (measured) composition are shown. The analysis was obtained by KOH fusion/ICP solution analysis of three separate specimens using a Jarrell-Ash Mark 8 ICP spectrometer. The Cs content was determined by AA using a Perkin Elmer Model 303 Atomic Absorption Spectrometer with a graphite furnace. The composition given in Table 1.1 is an average of these three analyses.

2.0 DESCRIPTION OF ACTINIDE DOPANT

- Isotope used—^{244}Cm was chosen as the dopant, since PNL 77-260 is a simulated commercial HLW glass and Cm and Am are the dominant alpha emitters.
- Chemical form—CmO_2 (verified by XRD)
- The calculated activity of the CmO_2 dopant was 1.88×10^{12} Bq/g on May 17, 1978. This is based on an original radiochemical analysis performed at the Oak Ridge National Laboratory on July 16, 1976. At that time the activity of the CmO_2 dopant was $2.02 \pm 0.01 \times 10^{12}$ Bq/g. The uncertainty is based on counting statistics. Complete documentation is maintained at the ORNL.

(a) Since this report is for illustrative purposes, only enough entries are shown to make the format clear. Many of the entries and data are fictitious.

Table 1.1. PNL 77-260 Waste Glass Control Specimen Composition

Constituent	Intended Wt% Oxide	Chemical Analysis Wt% Oxide
SiO_2	36.0	35.88
B_2O_3	9.0	9.05
Na_2O	11.2	11.18
K_2O	2.0	1.98
CaO	1.0	1.08
TiO_2	6.0	5.94
Al_2O_3	2.0	1.96
CuO	3.0	2.99
Fe_2O_3	1.2	1.22
P_2O_5	2.2	2.25
MnO_2	0.1	0.13
Gd_2O_3	10.3	10.25
Nd_2O_3	1.4	1.41
Sm_2O_3	0.3	0.32
ZrO_2	1.6	1.58
Rb_2O	0.1	0.11
SrO	0.3	0.28
Y_2O_3	0.2	0.21
MoO_3	1.9	1.92
RuO_2	0.9	0.89
Rh_2O_3	0.2	0.21
PdO	0.5	0.49
TeO_2	0.2	0.18
Cs_2O	0.8	0.81
BaO	0.5	0.52
La_2O_3	0.5	0.54
CeO_2	0.9	0.89
Pr_6O_{11}	0.4	0.41
U_3O_8	5.3	5.32
Total	100 wt%	100 wt%

- Three wt% of the CmO_2 dopant was substituted for 3 wt% U_3O_8 to achieve an activity of 5.5×10^{10} Bq/g.

3.0 DESCRIPTION OF SPECIMEN PREPARATION

- A simulated waste glass was prepared having the composition shown in Table 1.1 except that 3 wt% U_3O_8 was omitted.

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- The curium dopant and the simulated waste glass with the low U_3O_8 concentration (crushed to <50 μm) were thoroughly mixed in a mechanical mixer, melted in a platinum crucible, held at 1050° ± 25°C for 2 h, and air quenched.

- The glass was crushed (to <425 μm) and remelted at 1050° ± 25°C(a) for 2 h in a platinum crucible 13.3-mm diameter x 40-mm high.

- The melt was cooled at a controlled rate of 6°C/h.

- The test specimens were cooled to room temperature on May 17, 1978.

- The platinum crucible was removed from the glass rod which was cut into sections with a diamond saw, thus providing specimens for the individual measurements.

4.0 PHYSICAL DESCRIPTION OF SPECIMENS

All specimens were ~1.3 cm in diameter and the initial density was 3.200 ± 0.001(b) g/cm³, determined by buoyancy in distilled water (procedure similar to ASTM C 693-74, except smaller specimen). The specimens used for characterization were ~0.3-cm thick and weighed ~1.27 g. Specimens were numbered sequentially (1-14) as they were cut from the bottom of the glass rods.

5.0 CHARACTERIZATION OF SPECIMENS

5.1 Radiochemical Analysis

- The specific activity of the specimens was determined radiochemically by the dissolution of 100 ± 0.01(c) mg of sample by fusion in a 50-50 mixture of Na_2O-Na_2O_2. The cooled fusion solution was subsequently dissolved in water and acidified to 2 M HNO_3. Further dilution in 2 M HNO_3 was necessary to reduce the activity of the solution to ~2 Bq/ml. The specific activity and ^{244}Cm content of the solution were determined by total alpha counting and alpha-energy analysis of a small measured volume of solution. The specific activity of sample was then calculated based on specific activity of solution, total volume of solution, and the amount of sample dissolved in solution. The specific activity (>99% due to ^{244}Cm) of the specimens, based on the above analysis, was determined to be 5.6 ± 1.0(d) x 10^{10} Bq/g, which is in excellent agreement with calculated activity based on doping level and activity of dopant.

5.2 Chemical Analysis

- The actual chemical composition, given in Table 5.1, of the doped material was obtained by KOH fusion/ICP solution analysis of specimen number 10 using a Jarrell-Ash Mark 8 ICP spectrometer. The Cs content was determined by AA using a Perkin Elmer Model 303 atomic absorption spectrometer with a graphite furnace.

Table 5.1. Composition of ^{244}Cm-Doped PNL 77-260 Waste Glass(a)

Constituent	Wt% Oxide	Constituent	Wt% Oxide
SiO_2	35.88	SrO	0.28
B_2O_3	9.05	Y_2O_3	0.21
Na_2O	11.18	MoO_3	1.92
K_2O	1.98	RuO_2	0.89
CaO	1.08	Rh_2O_3	0.21
TiO_2	5.94	PdO	0.49
Al_2O_3	1.96	TeO_2	0.18
CuO	2.99	Cs_2O	0.81
Fe_2O_3	1.22	BaO	0.52
P_2O_5	2.25	La_2O_3	0.54
MnO_2	0.13	CeO_2	0.89
Gd_2O_3	10.25	Pr_6O_{11}	0.41
Nd_2O_3	1.41	U_3O_8	2.00
Sm_2O_3	0.32	CmO_2	2.87
ZrO_2	1.58	PuO_2	0.45
Rb_2O	0.11		

Total: 100 wt% of all oxides
(a) See Table 1.1 for the intended composition of PNL 77-260 waste glass.

5.3 Microstructural Characterization

- Microstructural examination included powder XRD of specimen number 9 (example shown in Figure 5.1), and SEM-EDX, alpha autoradiography and optical microscopy (examples of which are shown in Figure 5.2) of specimen number 7.

(a) The uncertainties are the absolute temperature limits within which the temperature is maintained.
b) The uncertainty in the density is plus or minus one standard deviation based on 10 individual measurements on specimen number 8.
(c) The uncertainty is plus or minus one standard deviation based on calibrated accuracy of balance used.
(d) The uncertainty is based on the counting statistics.

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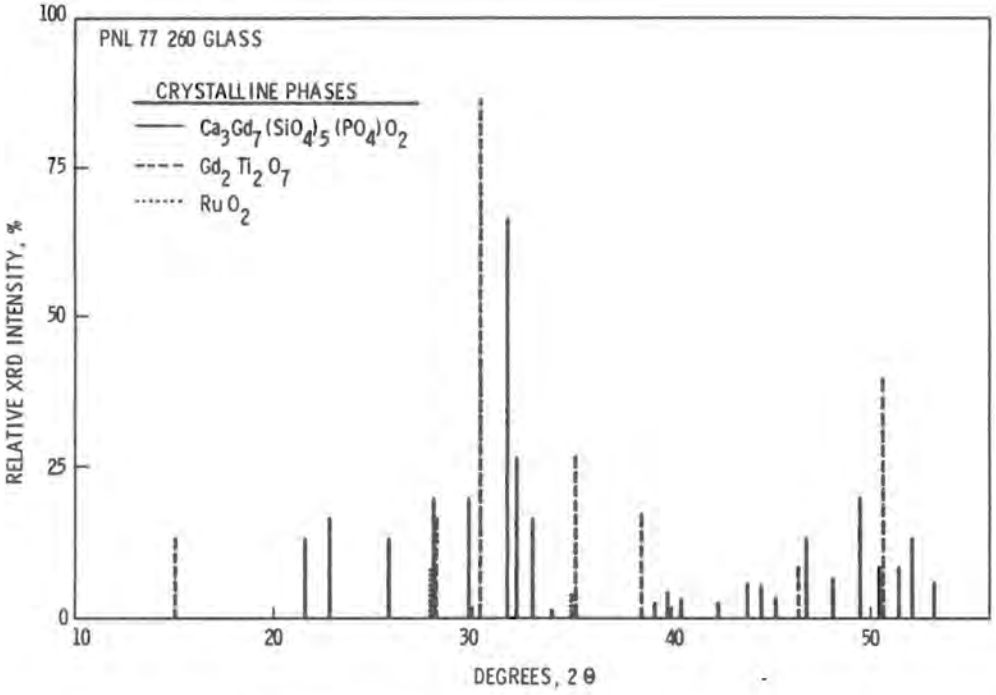

Figure 5.1 XRD Analysis of Crystalline Phases in Doped Specimen

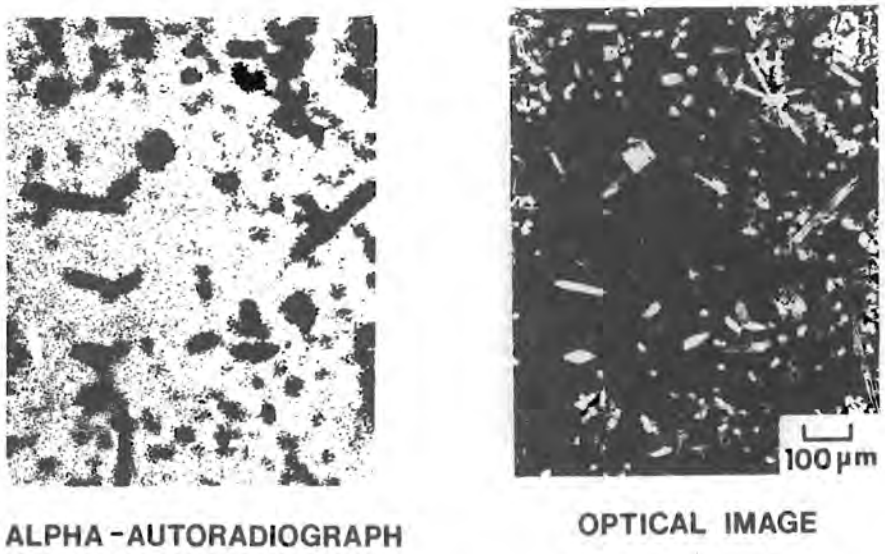

Figure 5.2. Alpha Autoradiography and Optical Microscopy of Doped Specimen

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- Degree of total crystallinity—~29 wt% (determined by quantitative optical microscopy).

- Approximate degree of total crystallinity—~30 wt% (determined semiquantitatively by comparison of XRD-integrated peak-intensity measurements with a suitably prepared set of standards containing known amounts of $Ca_3Gd_7(SiO_4)_5(PO_4)O_2$ and $Gd_2Ti_2O_7$. The estimated error of this technique is ± 10%.

- All crystalline phases observed in a planar section by optical and electron microscopy ranged from approximately 25 to 100 μm in size (longest dimension), as shown in Figure 5.2.

- Crystalline phases identified (see Figure 5.1):

  1. $Ca_3Gd_7(SiO_4)_5(PO_4)O_2$ with a hexagonal (apatite) structure (~15 wt%).
  2. $Gd_2Ti_2O_7$ with a cubic structure (~14 wt%).
  3. Trace amounts of RuO_2 (~1 wt%)

- The curium concentrated, as expected and shown in Figure 5.2, in the two crystalline phases present as a result of devitrification. The concentrations of curium in the two crystalline phases and in the glass matrix were estimated by alpha autoradiography (track counting) and are given in Table 5.1.

Table 5.2. Cm-244 Concentration

Phase	Concentration, wt%
$Ca_3Gd_7(SiO_4)_5(PO_4)O_2$	5.5 ± 1.2[a]
$Gd_2Ti_2O_7$	3.8 ± 1.0
Residual Glass	0.8 ± 0.4

(a) The uncertainties are plus or minus one standard deviation based on 10 individual observations for each phase.

- Optical microscopy revealed no microcracking in the as-prepared test specimens.

6.0 STORAGE OF SPECIMENS

- Atmospheric conditions—air (relative humidity ranged from 28% to 42%), except that the specimen for XRD analysis was stored in dry nitrogen.

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