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Radiation Damage Studies Related to Nuclear Waste Forms

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December 1981

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

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

PNL-4145

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy
Pages Price Codes

001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

PNL--4145

DE82 010028

PNL-4145

UC-70

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Richland, Washington 99352

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SUMMARY

Two aspects of self-radiation damage have the greatest potential for degradation of high-level waste solids. One is the atomic displacements caused by alpha decay, and associated recoil nuclei, of actinide elements. The second is the transmutation of fission products which usually results in both valence and ionic size changes.

Much of the previously reported work on alpha radiation effects on crystalline phases of importance to nuclear waste forms has been derived from radiation effects studies of composite waste forms. In the present work, two single-phase crystalline materials, $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{CaZrTi}_2\text{O}_7$, of relative importance to current waste forms were studied independently by doping with ^{244}Cm at the 3 wt% level. Changes in the crystalline structure measured by x-ray diffraction as a function of dose show that damage ingrowth follows an expected exponential relationship of the form $\Delta V/V_0 = A[1 - \exp(-BD)]$. In both cases, the materials became x-ray amorphous before the estimated saturation value was reached. The predicted magnitudes of the unit cell volume changes at saturation are 5.4% and 3.5% respectively for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{CaZrTi}_2\text{O}_7$. The later material exhibited anisotropic behavior in which the expansion of the monoclinic cell in the " c_0 " direction was over five times that of the " a_0 " direction.

The effects of transmutations on the properties of high-level waste solids have not been studied until now because of the long half-lives of the important fission products. This problem was circumvented in the present study by preparing materials containing natural cesium and then irradiating them with neutrons to produce ^{134}Cs which has only a 2y half-life. The properties monitored at about one year intervals following irradiation have been density, leach rate and microstructure. A small amount of x-ray diffraction work has also been done. Small changes in density and leach rate have been observed for some of the materials, but they were not large enough to be of any consequence for the final disposal of high level wastes.

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RADIATION DAMAGE STUDIES RELATED TO NUCLEAR WASTE FORMS

W. J. Gray, J. W. Wald and R. P. Turcotte

I. INTRODUCTION

Besides chemical complexity, the dominant characteristic of nuclear high level waste (HLW) solids is their radioactivity. Beta decay of the fission products and alpha decay of the actinide elements are the primary sources of radiation. There is also spontaneous fission of some of the actinide isotopes and some alpha-neutron reactions, but the frequency of these events is very low compared to beta and alpha decay and can usually be ignored. Alpha decay is the primary source of atomic displacements in HLW solids although some displacements are also produced by beta decay. The latter generally occur via ionization processes. A potentially more important aspect of beta decay is the associated transmutation of fission products which usually results in both valence and ionic size changes, both of which may not be readily accommodated by HLW solids.

Studies of property changes resulting from the various types of radiation have been part of general studies in many laboratories, especially at PNL. In particular, PNL has been engaged in a study of the effects of transmutations since 1978, the first study of this nature ever conducted. As interest in waste forms other than borosilicate glass increased, work on the effects of alpha decay, which was originally limited to glass behavior (Roberts, Jenks and Bopp 1976) or to pure actinide oxides (Turcotte 1976) was expanded to include crystalline waste forms and single crystalline phases.

The present report is intended to briefly summarize important aspects of the radiation damage problem with respect to HLW forms, particularly emphasizing results of studies undertaken on the Alternate Waste Form Program at PNL during 1978-1981. Following a general review (Section II), results of actinide doping experiments on two titanate phases of relevance to SYNROC development (Ringwood 1978) are presented in Section III. Effects of transmutations on several glasses and crystalline materials are described in Section IV.

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II. REVIEW OF RADIATION DAMAGE EFFECTS

There have been a number of reviews related to effects of self-radiation damage in nuclear waste solids. These include, in particular, papers by Permar and McDonnell (1981) and by Battelle (PNL) authors. In particular the Materials Characterization Center at PNL has hosted several workshops with proceedings (Roberts, Turcotte and Weber 1981; Weber and Turcotte 1982) and has published "A State-of-the-Art Review of Material Properties of Nuclear Waste Forms," which includes a discussion of radiation effects (Mendel et al. 1981). Since these documents discuss the sources of radiation damage in some detail, we only summarize the problem as follows:

- The major source of damage arises from atomic displacements caused by alpha decay of actinides. The 100 keV recoil nucleus causes about 90% of the displacements but has a range $\lesssim 20$ nm. The 5 MeV alpha particles have a range $\lesssim 20 \mu\text{m}$ and, therefore, may bombard non-actinide phases in multi-phase waste forms. The rate at which damage from actinide-containing compounds accumulates decreases with increasing dose so that the damage generally saturates by $\lesssim 5 \times 10^{19}$ α -decays/cm³ in crystalline phases and by $\lesssim 5 \times 10^{18}$ α -decays/cm³ in glasses.
- A second concern is damage introduced by ionization processes. In this case, high energy beta particles, gamma rays, or alpha particles cause valence electrons in the solid to be promoted to higher energy levels. This can lead to broken chemical bonds or in some cases to atomic displacements. There is not sufficient information to conclude whether these phenomena are important relative to displacement damage from actinide decay since even simple materials have mainly been studied to doses $\lesssim 10^{10}$ R in a gamma field or to $\gtrsim 10^{12}$ R in electron microscope experiments. The questions concerning HLW forms, unfortunately, are precisely in the difficult-to-study range 10^{10} - 10^{12} R.
- The transmutation aspect of the radiation damage problem had never been studied prior to the present investigation. The reason for this neglect seems to have been due to the difficulty of performing a true transmutation experiment or of developing

a suitable simulation technique. Only 16% of the fission products in the high-level waste stream are radioactive and nearly half of these have half-lives $\geq 10^5$ y. Only a very few have half-lives ≤ 1 y. ^{137}Cs and ^{90}Sr comprise about 6% of the fission products and are the two isotopes of major concern with regard to transmutations. Since they both have half-lives of about 30y, however, it is not practical to use them to study the effects of transmutations. The long-decay problem was circumvented at PNL by neutron-irradiating samples containing natural Cs (100% ^{133}Cs) to produce ^{134}Cs which has only a 2y half-life and can, therefore, be used to study transmutation effects in a reasonable time.

There has been little work at any laboratory on the second of these three areas. The first and third areas have been emphasized by the Alternate Waste Forms Program and the studies have included collaboration with scientists at the University of New Mexico, the Hahn-Meitner Institute (Berlin) and the Oak Ridge National Laboratory. Results from much of the work on actinide decay effects (Turcotte 1982; Weber et al. 1979; Rusin, Gray and Wald 1979;) and geochemical considerations (Ewing and Haaker 1980; Haaker and Ewing 1979, 1981) have already been published and are only reviewed in this section. Results from a laboratory study of curium doped titanate phases are given in Section III and transmutation effects are described in Section IV.

Actinide Decay Effects in Crystalline Waste Forms

It has been recognized for several decades that, to a first approximation, any solid state radiation damage effects arising from actinide decay should follow a relatively simple exponential equation of the form $\Delta x/x = A(1 - e^{-BD})$, where x is some property and D is the cumulative radiation dose (α -decays/cm³). The constant A relates to the property saturation value as $D \rightarrow \infty$, and B is the rate constant for self-annealing. At this time there is no a priori method of knowing what $\Delta x/x$ might be, nor what magnitude the coefficients A and B have, even for single phases. Consequently, potential actinide host phases are being directly investigated. Figure 1 gives an example of the

FIGURE 1. Volume Change Versus Accumulated Alpha Dose

density changes observed in a variety of materials (adapted from Turcotte 1982); it is evident that saturation occurs at doses $\lesssim 5 \times 10^{19}$ α -decays/cm³. The volume change is small for the fluorite structure but very large for zircon. There is no significant effect below $\sim 10^{17}$ α -decays/cm³.

Simulated crystalline waste forms which have been studied by the actinide doping method have so far included only partially crystallized glasses (Weber et al. 1979), supercalcine (Rusin, Gray and Wald 1979;) and a celsian based glass-ceramic (this work). In all of these cases the actinide partitioned into only one or two of the phases and these actinide host phases eventually became x-ray amorphous. At the same time, volumetric changes measured by an immersion-density method were larger than could be accounted for by expansion of the actinide host phases, as measured by x-ray diffraction. This means either that the actinide-containing phases continue to expand after they have become x-ray amorphous or that α -particle bombardment of non-actinide-containing phases leads to significant changes that are not easily measured. Another possibility is the formation of cracks. Figure 2 shows the density changes measured for the parent (celsian) glass, for its crystallized-ceramic form and for supercalcine. Crystallite size is very small in both of the crystallized forms, generally $< 1 \mu\text{m}$. No cracking of the material or other obvious degradation was observed, in contrast to a glass which had been intentionally heat treated to form large ($> 10 \mu\text{m}$) crystals. In that case (Weber et al. 1979), radiation-induced microcracking was observed.

Other radiation-induced property changes (beyond structural effects) have been examined, though not in much detail. For glasses, leach rate changes appear to be small (Turcotte 1982). Dose dependent data for a crystallized glass suggest that effects may not be large even when crystalline phases become x-ray amorphous (Weber et al. 1979), though more work is needed before any general conclusion can be made. This is especially true since metamict minerals do show an increased reactivity in their natural environment, as discussed below.

FIGURE 2. Density Change Versus Accumulated Alpha Dose

Geologic Analogues

One of the primary motivations for development of a crystalline waste form was the observation that there are many stable crystalline phases found in nature, some of which contain actinides. It should, therefore, be possible to fabricate analogues that contain nuclear waste. A program was undertaken to examine crystalline phases in nature as a possible guide to understanding behavior of proposed synthetic forms. This work has been reported by Ewing and Haaker over the last several years (Haaker and Ewing 1979, 1981; Ewing and Haaker 1980). Table 1 was taken from Haaker and Ewing (1981-their Table 41) and summarizes their conclusions concerning geologic stability of SYNROC and supercalcine phases with respect to chemical alteration.

With respect to radiation stability, Haaker and Ewing (1981) conclude:

"Most actinide crystalline phases are susceptible to damage by alpha particles and recoil nuclei. It is notable that the monazite and UO_2 structures appear to be highly resistant to radiation effects. The apatite, perovskite and zirconolite structures are susceptible to alpha radiation damage and may become metamict. Meta-mict, natural apatite, perovskite and zirconolite have glass-like physical properties, decreased density and show enhanced hydration effects."

These observations have so far been exactly reproduced in accelerated laboratory work on these structure types. Apatite, perovskite and zirconolite all become x-ray amorphous in the laboratory, whereas the fluorite structure (UO_2) is stable, though with 1% volume expansion. The monazite phase has not been studied yet.

With respect to hydration effects, or more importantly, leach rate changes, few relevant studies on crystalline phases and ceramic waste forms have been reported yet. With regard to studies of mineral analogues, the work by Ewing et al. has most recently included etch rate measurements on natural zircons with different levels of self-radiation damage. Their results will be reported in detail later. They did observe a one order of magnitude increase in leachability of metamict over highly crystalline zircon.

TABLE 1. Durability of Natural Analogues to SYNROC and Supercalcine Phases. Criteria and Qualifications Listed in the Text Should be Noted.^(a)

Mineral	Durable	Durable(reducing) conditions only)	Not durable
Baddeleyite, ZrO_2	X	-	-
Nepheline, NaAlSiO_4	-	-	X
Pollucite, $\text{CsAlSi}_2\text{O}_6$	-	-	X
Scheelite Ca(W,Mo)O_4	X	-	-
Sodalite, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$	-	-	X
Apatite, $(\text{Ca,REE})_5(\text{SiO}_4)_3\text{OH}$	X ^(b)	-	-
Monazite, $(\text{Ce,Lu})\text{PO}_4$	X ^(b)	-	-
Uraninite, UO_2	-	X	-
Priderite ^(c) $(\text{K,Ba})_{2-x}(\text{Fe,Ti})_8\text{O}_{16}$	Rare occurrence, possibly quite durable		
Perovskite ^(c) $(\text{Ca,REE})_{1-x}\text{TiO}_3$	X	-	-
Zirconolite ^(c) $\text{CaZrTi}_2\text{O}_7$	X	-	-

(a). This table was reproduced from Table 41 of Haaker and Ewing (1981).

(b). Ce in these minerals is subject to oxidation

(c). SYNROC phases

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III. RADIATION EFFECTS IN CURIUM-DOPED

$\text{Gd}_2\text{Ti}_2\text{O}_7$ AND $\text{CaZrTi}_2\text{O}_7$ *

Background

Previous radiation effects studies in both intentionally devitrified glass and glass ceramic systems have identified a rare earth titanate phase of the general formula $(\text{R.E.})_2\text{Ti}_2\text{O}_7$ which was capable of acting as a host phase for the actinide dopant. In the case of the Celsian glass ceramic system, this phase was observed to become x-ray amorphous with dose. However, in the glass system the phase was reported as stable (i.e., crystalline) throughout the duration of the study (Weber et al. 1979). Because of these apparently conflicting results, the $(\text{R.E.})_2\text{Ti}_2\text{O}_7$ phase was selected for further study. The second phase selected in this study was also a titanate based material, $\text{CaZrTi}_2\text{O}_7$ (Zirconolite). It was selected because of structural similarity to the $(\text{R.E.})_2\text{Ti}_2\text{O}_7$, and because it was a phase of importance in the SYNROC waste system (Ringwood 1978).

Ewing and Haaker (1980) have reported that in investigations of naturally occurring metamict minerals, both $(\text{R.E.})_2\text{Ti}_2\text{O}_7$ (pyrochlore) and $\text{CaZrTi}_2\text{O}_7$ (Zirconolite/Zirkelite) occur as metamict but may be partially or completely crystalline as well. They have suggested that part of this inconsistency may lie in nomenclature but also may be a result of structural stability, cumulative dose, or dose rate among other factors.

Ringwood and coworkers (Oversby and Ringwood 1981) have suggested that the zirconolite phase in SYNROC will become metamict because it will accept actinide elements within its structure. They have concluded, however, that based upon mineralogical studies, this structural change should not effect the quantitative ability of the phase to retain actinide elements.

Sample Fabrication

The fabrication of actinide doped single phase compositions involved first identifying a technique which would yield the appropriate crystalline phase from starting materials and second, the addition of

* P. Offerman of the Hahn-Meitner Institut für Kernforschung, Berlin Germany, participated in this study.

the actinide species to this crystalline phase. Starting materials for the crystalline phases consisted of carbonates, nitrates and an organo-titanate which were wet milled in alcohol in an agate laboratory disc mill. The resulting mixture was air dried and the powder recovered.

The actinide species used in the doping work was ^{244}Cm with a half-life of 18.1 years. Curium was chosen because it was expected to easily substitute for gadolinium (3+) or as 2Cm^{3+} in place of $(\text{Ca}^{2+} + \text{Zr}^{4+})$. Curium is also capable of providing damage levels in the range of $10^{18} - 10^{19}$ α -events/ cm^3 in reasonable time periods (~ 1.5 years). Each crystalline phase was doped with 3 wt.% ^{244}Cm in an inert atmosphere glovebox. Curium oxide powder was dissolved in hot nitric acid and then added to the precalcined starting materials in the appropriate quantities. This slurry was dried on a hot plate and then processed to obtain the desired crystalline phases.

Preparation of the crystalline phase typically involved a two-step firing operation, the first step being a bulk calcining operation at $\sim 725^\circ\text{C}$ in air followed by a cool to room temperature and a mechanical grinding to -200 mesh. The second step involved cold pressing pellets of 0.5" diameter and firing in air at the desired conditions of time and temperature. The precise conditions used in this work are summarized in Table 2. X-ray diffraction, optical metallography and scanning electron microscopy (SEM) were used to establish the optimum formation conditions. The minimization or elimination of second phase and unreacted constituents, as well as the reduction of porosity were factors of prime concern. Porosity values for the two phases were 7% and 17% respectively for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{CaZrTi}_2\text{O}_7$ with only the latter material showing an indication (<1%) of a persistent second phase in the SEM.

Sample Analysis

By nature of the high activity level in the curium doped samples and the associated hazards connected with their handling, sample size was kept to a minimum in both dimension and numbers. Typically, two samples are required for damage ingrowth studies by x-ray diffraction; one sample is required for density measurements and one additional

TABLE 2. Processing Conditions for the Fabrication
of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{CaZrTi}_2\text{O}_7$

	<u>$\text{Gd}_2\text{Ti}_2\text{O}_7$</u>	<u>$\text{CaZrTi}_2\text{O}_7$</u>
Calcine: Temperature	725°C	725°C
Time	1 hr.	1 hr.
Cold Press	20,000 psi	40,000 psi
Firing: Temperature	1400°C	1325°C
Time	46 hr	40 hr
Atmosphere	Air	Air

sample is required for optical microscopy or archive. In this work, only x-ray diffraction and density measurements were made on the samples. However, future work may include recrystallization studies on the damaged phases as well as leach studies.

X-ray diffraction measurements were made on the samples starting at time "zero" (just after firing) and were taken at regular intervals, depending on dose rate, until an x-ray amorphous state was reached. Two samples were required for this portion of the analysis so that surface contact could be made between the pellets during interim storage, thereby assuring that the surface analyzed by XRD was typical of the bulk. A conventional GE XRD-5/DIANO 8000 Diffractometer was used to slow scan selected peaks of the crystalline phases and the externally fixed silicon standard. Figure 3 illustrates the sample-standard-mount configuration that was used during analysis and storage.

Solid pellets with a flat ground surface were temporarily fixed in the aluminum mount by the use of set screws and spacer pins. Exact alignment in the diffractometer could be assured for each analysis in this fashion. The intent of the externally mounted silicon standard

FIGURE 3. Sample-Standard-Mount Configuration
or X-ray Diffraction Analysis

was to provide a reference material that would not become damaged by radiation during the course of the study. Since the major damage source under investigation was that due to α -decay events, this effect could be eliminated in the standard by this configuration. The NBS silicon (SRM-640) was mixed with a casting resin to form a thick paste which was filled and set in the specific cavity; there was some indication that gamma and neutron effects on the resin binder may have caused small variations in the standard during the course of the examination.

Apparent-density measurements were made by immersion techniques at the same time as the x-ray diffraction measurements using the procedure described in Procedure ASTM C-693-74. The standard used in this measurement was a disc of high purity Al_2O_3 ceramic with total porosity <2%. The standard disc was prepared to duplicate the approximate geometric size of the pellets to be measured. There were some difficulties in obtaining consistent density measurements on the doped ceramic pellets and it is believed that this is related to the porosity of the samples. Variation in the Al_2O_3 standard over the duration of about two years of measurements was $\pm 0.07\%$.

Results

At this time, curium doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ (pyrochlore) and $\text{CaZrTi}_2\text{O}_7$ (Zirconolite) have been monitored for approximately two years and one and a half years respectively and have experienced a cumulative alpha-recoil dose of 17×10^{18} and 16×10^{18} α -decays/cm³. Figure 4 illustrates the percent change in apparent density versus dose for the two phases studied. The curves through the respective data points were generated by a computer fit of an exponential equation. The data fit the curves far better in the case of $\text{Gd}_2\text{Ti}_2\text{O}_7$ than for the $\text{CaZrTi}_2\text{O}_7$ phase, as noted, most likely as a result of the errors generated in the measurements due to porosity of the samples. Both phases exhibited a decrease in density as a function of dose indicating an expansion of the lattice with cumulative damage. The $\text{Gd}_2\text{Ti}_2\text{O}_7$ phase, which was x-ray amorphous at the last dose level measured, has decreased in density by about 4.2%. The $\text{CaZrTi}_2\text{O}_7$ phase, on the other hand, still has about 5% crystallinity remaining (determined from the presence of the main diffraction peak) and has decreased in density by 4.9%.

The x-ray diffraction data was refined by computer, using the Appleman-Evans (1973) routine for least squares unit cell refinement and indexing. Figure 5 illustrates the change in unit cell volume versus cumulative dose for both phases. The curves fit through the respective data points, again, were generated by fit of an exponential relationship. Consistent with the density data, the $\text{Gd}_2\text{Ti}_2\text{O}_7$ phase has experienced the largest expansion in the unit cell at about 4.2%, while the $\text{CaZrTi}_2\text{O}_7$ phase had only shown an increase of about 2.1% at the last measurable dose level. Figure 6 illustrates the integrated intensity ratio changes of some of the main x-ray diffraction peaks, referenced to the silicon standard. Both phases have shown general decreases in diffracted intensities at about the same rates. In the $\text{Gd}_2\text{Ti}_2\text{O}_7$ material, the anisotropic decreases observed in the Celsian glass ceramic study, do not seem to exist. The $\text{CaZrTi}_2\text{O}_7$ phase, on the other hand, exhibits rather marked anisotropic changes in unit cell parameters as illustrated in Figure 7. The structure of this system is monoclinic with initial cell parameters of $a_0 = 12.456 \text{ \AA}$, $b_0 = 7.271 \text{ \AA}$, $c_0 = 11.387 \text{ \AA}$ and $\beta = 100.556^\circ$. At a dose of 10×10^{18} α -decays/cm³,

FIGURE 4. Percent Change in Density for $\text{Gd}_2\text{Ti}_2\text{O}_7$ (a), and $\text{CaZrTi}_2\text{O}_7$ (b) Versus Accumulated Alpha Dose

FIGURE 5. Percent Change in Unit Cell Volume for $\text{Gd}_2\text{Ti}_2\text{O}_7$ (a) and $\text{CaZrTi}_2\text{O}_7$ (b) Versus Accumulated Alpha Doses

FIGURE 6. Percent Change in X-Ray Intensity of Selected Diffraction Peaks for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{CaZrTi}_2\text{O}_7$ as a Function of Accumulated Alpha Dose

the a_0 parameter has expanded by about 0.3%, the b_0 parameter has not significantly changed, and the c_0 parameter has increased by about 1.6%. There is also some indication of anisotropic behavior noted in the intensity data illustrated in Figures 6-c and d.

The ingrowth and saturation of radiation induced damage can be expected to follow an exponential relationship of the form:

$$\frac{\Delta V}{V_0} = A(1 - e^{-BD})$$

The parameters A and B are constants; A is the saturation property change at infinite dose (D), and B is the rate of change. In the present case, $\Delta V/V_0$ is the change in unit cell volume measured by x-ray diffraction. Table 3 gives values for the constants A and B as determined by regression analyses of the data from this work; and it also gives values of A and B for selected materials studied elsewhere. Saturation dose values listed in Table 3 were obtained from the above equation by setting $\Delta V/V_0$ equal to 99% of its value at infinite dose. For both the $Gd_2Ti_2O_7$ and $CaZrTi_2O_7$ phases studied here, it would appear that expansion of the unit cell has not completely saturated before the onset of x-ray amorphization. This is a similar result to that reported by Mosley (1971) for the $CmAlO_3$ system (Perovskite structure). For the other materials in Table 3, although the approach to saturation follows a similar relationship, amorphization does not. For example, saturation of damage effects in $ZrSiO_4$ (Zircon) occurs prior to actual x-ray amorphization while in actinide dioxides, such as PuO_2 , saturation occurs with no tendency toward x-ray amorphization being reported. In the Zircon system, it was not possible to readily fit the reported data to the damage ingrowth equation given above, but for simple comparison purposes, the listed values were calculated using the saturation values given.

While the compounds listed in Table 3 represent only a few materials, they also represent a wide range in generic structure types. In general these are pyrochlore, distorted pyrochlore (Monoclinic), perovskite, zircon and fluorite. The data for these phases indicate

FIGURE 7. Unit Cell Constant Changes for Monoclinic $\text{CaZrTi}_2\text{O}_7$ as a Function of Accumulated Alpha Dose

TABLE 3. Radiation Damage Ingrowth Parameters

Phase	A (a)	B (a)	DOSE		Reference
			X-Ray Amorphous	Saturation (99%)	
$Gd_2Ti_2O_7$	0.054	$1.01 \times 10^{-19} \text{ cm}^3$	$\sim 1.7 \times 10^{19} \frac{\alpha\text{-decays}}{\text{cm}^3}$	$\sim 4.6 \times 10^{19} \frac{\alpha\text{-decays}}{\text{cm}^3}$	This work
$CaZrTi_2O_7$	0.035	8.69×10^{-20}	$\sim 1.6 \times 10^{19}$	$\sim 5.3 \times 10^{19}$	This work
$CaAlO_3$	0.096	7.88×10^{-20}	$\sim 1.4 \times 10^{19}$	$\sim 5.8 \times 10^{19}$	Mosley (1971)
$ZrSiO_4$	0.0502	$\sim 3.2 \times 10^{-19}$ (b)	$\sim 2.4 \times 10^{19}$	$\sim 2.1 \times 10^{19}$	Holland and Gottfried (1955)
PuO_2	0.0096	4.27×10^{-19}	---	$\sim 1.1 \times 10^{19}$	Chikalla and Turcotte (1973)

(a) A + B are constants of the equation: $\Delta V/V_0 = A[1 - \exp(-BD)]$

(b) Calculated from values at saturation only

that while the approach to saturation of damage ingrowth and the absolute magnitude of the changes may vary measurably, the dose values required to reach these saturation values (assumed at 99%) are all in the range $\sim 1-6 \times 10^{19} \alpha\text{-decay/cm}^3$.

Weber et al.(1981), have discussed in detail the principal sources of nuclear radiations present in high level waste forms resulting from both defense and commercial waste streams, as well as the mechanisms and potential for damage effects. They have concluded that, for a defense waste stream, there is only a slight concern for radiation induced changes in ceramic waste forms for time periods less than 10,000 years. If the waste stream consists of commercial nuclear fuel waste, however, data suggest a potential exists for significant radiation induced changes in time periods less than a thousand years. The two crystal systems studied here illustrate the magnitudes and rates at which damage ingrowth might be expected in the most severe case. This work also illustrates that marked anisotropic expansion can occur in non-cubic structures as a function of accumulated radiation dose. Although it was not observed macroscopically in the present case, this nonuniform swelling might result in microcracking of the waste form host with a potential for increase in leach rates due to increased surface area.

IV. EFFECTS OF FISSION PRODUCT TRANSMUTATIONS ON CRYSTALLINE AND NON-CRYSTALLINE SOLIDS

Background

Changes in valence and ionic size that result from transmutation of fission products have the potential to disrupt both crystalline and noncrystalline solids. Possible adverse effects of transmutations have not been studied until now, however, because of the very long times involved.

Table 4 lists the fission products that will exist in the high-level waste stream, the decay product of each, and the resulting ionic size and valence changes. It can be seen that very long times would be required to study transmutation effects using actual radioactive wastes since only a few isotopes have reasonably short half-lives, and these are present only in minor quantities. The effects of transmutations could be studied by making a simulated waste using particular short-lived radioactive isotopes or by making the waste with non-radioactive material and then neutron irradiating it to generate suitable short-lived isotopes. The first method would be prohibitively expensive; the second method is feasible but essentially only with cesium. Fortunately, cesium is also one of the more abundant fission products and one that is highly radioactive with a large biological hazard potential. Its transmutation to barium includes a change of valence from +1 to +2 and a reduction in ionic radius of 20%, both of which may be difficult to accommodate in solid materials.

Natural Cs is 100% ^{133}Cs which has a fairly large thermal neutron capture cross section. Therefore, a reasonable fraction of the Cs can be converted via neutron irradiation to ^{134}Cs which decays to Ba with a 2.06 year half-life. An experimental program was, therefore, established to evaluate the effects of Cs transmutations on several glasses and crystalline materials.

^{134}Cs Production: A series of calculations were made using the ORIGEN computer code (Bell 1973) to optimize ^{134}Cs production in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The code

TABLE 4. Fission Products and Their Decay Products

Element	Ionic Radius (A)	Valence	Relative Abundance(a) (%)	Radioactive Fraction (%)	Half-Life	Product	Ionic Radius (A)	Valence
Rb	1.48	+1	1.15	0.0	Stable			
Sr	1.13	+2	3.07	60.6	29Y	Zr	0.80	+4
Y	0.93	+3	1.62	1.4	59D	Zr	0.80	+4
Zr	0.80	+4	12.60	20.0	9.5×10^5 y	Nb	0.70	+5
Mo	0.62	+6	11.78	0.0	Stable			
Tc	0.98	+7	2.89	100.0	2.1×10^5 y	Ru	0.67	+4
Ru	0.67	+4	7.81	5.3	369D	Pd	0.86	+2
Rh	0.68	+3	1.34	0.0	Stable			
Pd	0.86	+2	4.38	17.9	6.5×10^6 y	Ag	1.26	+1
Ag	1.26	+1	0.20	0.8	252D	Cd	0.97	+2
Cd	0.97	+2	0.28	0.0	Stable			
Sn	1.12	+2	0.18	36.8	$\sim 10^5$ y	Te	0.70	+4
Te	0.70	+4	1.92	0.0	Stable			
Cs	1.69	+1	9.38	5.9	2.06Y	Ba	1.35	+2
				12.2	2.3×10^6 y	Ba	1.35	+2
				44.9	30.1Y	Ba	1.35	+2
Ba	1.35	+2	4.76	0.0	Stable			
La	1.15	+3	4.35	0.0	Stable			
Ce	1.01	+4	9.32	8.9	284D	Nd	1.08	+3
Pr	1.09	+3	4.11	0.0	Stable			
Nd	1.08	+3	13.29	0.0	Stable			
Pm	1.06	+3	0.37	100.0	2.6Y	Sm	1.04	+3
Sm	1.04	+3	2.82	5.8	93Y	Eu	1.03	+3
Eu	1.03	+3	0.63	25.9	8.6Y	Gd	1.02	+3
				2.8	4.8Y	Gd	1.02	+3
Gd	1.02	+3	0.34	0.0	Stable			
			98.59					

(a) I and Se and the Noble gases are not included.

was also used to verify that HFIR was, indeed, the most efficient available reactor for production of ^{134}Cs . Because ^{134}Cs also has a large thermal neutron capture cross section that yields the very long-lived ^{135}Cs isotope, the amount of ^{134}Cs produced does not increase with time as fast as might be expected. This is reflected in Table 5 which shows the fraction of Cs that is transmuted to Ba after different irradiation and decay times.

One other factor reduces the amount of useful Cs→Ba transmutations that can be achieved. During irradiation, the waste form undergoes neutron damage which must be annealed out after irradiation so that its effects don't mask those caused by the transmutations. However, transmutations have already occurred during irradiation, and the effects of these will also be annealed out. Table 5, therefore, lists the fraction of Cs originally present that transmutes to Ba following the anneal which was assumed to occur ten days after the end of the irradiation. It is shown that the maximum amount of Cs→Ba transmutations are achieved with an irradiation time of about 100 days. Table 5 also lists the amount of ^{134}Cs remaining after 700 days decay time as well as the amount of ^{135}Cs produced. Additional details on the irradiation are given in a following section.

Materials Studied

Table 6 shows both the nominal and analyzed composition of the materials irradiated in this test. Those materials that contain actinides were analyzed only for Cs. Some of the Cs probably vaporized during fabrication resulting in concentrations somewhat lower than the nominal value in most cases.

The identity of the seven materials studied and the rationale for their inclusion is given below followed by fabrication details.

- 1) Nominally 76-68 glass but with Cs_2O increased from ~1.0 to 3.23% so that the total number of Cs→Ba transmutations after four years decay time would be about equal to those in an actual 76-68 waste glass after all the ^{134}Cs and ^{137}Cs had decayed. The extra Cs_2O was substituted for Na_2O on a molar basis. ^{244}Cm was added in sufficient quantity so that the ratio of

TABLE 5. Calculated Buildup of Barium After Irradiation of ^{133}Cs in HFIR

Decay Time (Days)	Irradiation Time (Days)				
	60	80	100	120	140
	Ba (%) (a)				
0	0.91	1.59	2.45	3.49	4.70
10	1.18	1.93	2.86	3.97	5.23
20	1.40	2.21	3.18	4.33	5.62
30	1.61	2.45	3.45	4.61	5.91
100	2.84	3.80	4.84	6.00	7.27
300	5.86	7.03	8.10	9.16	10.3
700	10.5	12.0	13.1	14.0	14.8

^{134}Cs remaining after 700 days (%) (a)				
10.3	11.1	11.2	10.8	10.3

^{135}Cs produced (%) (a)				
11.3	17.3	23.3	29.1	34.4

Cs $\rightarrow$ Ba Transmutations occurring after initial 10-day decay time (%) (a)				
300	4.68	5.10	5.24	5.19
700	9.3	10.1	10.2	10.0
	19.6	21.2	21.4	20.8
				19.9

(a) All percentages are relative to amount of ^{133}Cs originally present.

TABLE 6. Composition of Test Materials in Weight Percent

Oxide	1		2		3		4		5		7		8	
	N ^(a)	A ^(b)	N	A	N	A	N	A	N	A	N	A	N	A
Li ₂ O	--	--	--	--	--	--	1.94	2.02	2.95	3.07	--	--	--	--
B ₂ O ₃	9.28	--	11.93	--	12.65	12.3	9.69	9.57	11.80	11.4	--	--	--	--
Na ₂ O	11.82	--	--	--	--	--	16.73	15.9	10.32	10.1	--	--	0.14	--
Al ₂ O ₃	--	--	--	--	--	--	5.68	5.96	15.12	15.0	16.35	--	3.42	--
SiO ₂	39.02	--	25.08	--	26.59	29.2	61.02	61.0	37.29	37.6	38.47	--	14.37	--
P ₂ O ₅	0.48	--	0.31	--	0.32	--	--	--	--	--	--	--	3.22	--
CaO	1.96	--	1.26	--	1.34	1.63	--	--	4.49	4.61	--	--	3.18	--
TiO ₂	2.91	--	1.87	--	1.98	2.20	0.92	1.09	--	--	--	--	--	--
Cr ₂ O ₃	0.41	--	0.26	--	0.28	0.32	--	--	--	--	--	--	0.41	--
MnO ₂	--	--	--	--	--	--	--	--	3.36	3.42	--	--	--	--
Fe ₂ O ₃	9.66	--	6.21	--	6.58	7.58	--	--	10.30	10.4	--	--	3.62	--
NiO	0.20	--	0.13	--	0.14	0.18	--	--	0.75	0.70	--	--	0.17	--
ZnO	4.87	--	3.13	--	3.32	4.07	--	--	--	--	--	--	--	--
Rb ₂ O	0.12	--	0.08	--	0.09	--	--	--	--	--	--	--	0.42	--
SrO	0.37	--	0.24	--	0.26	0.32	--	--	--	--	--	--	4.23	--
Y ₂ O ₃	0.21	--	0.14	--	0.14	--	--	--	--	--	--	--	0.72	--
ZrO ₂	1.75	--	1.13	--	1.20	1.31	--	--	--	--	--	--	5.93	--
MoO ₃	2.26	--	1.45	--	1.54	1.24	--	--	--	--	--	--	7.64	--
RuO ₂	1.05	--	0.67	--	0.72	0.57	--	--	--	--	--	--	3.56	--
Rh ₂ O ₃	0.17	--	0.11	--	0.12	--	--	--	--	--	--	--	0.58	--
PdO	0.53	--	0.34	--	0.36	--	--	--	--	--	--	--	1.78	--
Ag ₂ O	0.03	--	0.02	--	0.02	--	--	--	--	--	--	--	0.11	--
CdO	0.03	--	0.02	--	0.02	0.05	--	--	--	--	--	--	0.12	--
TeO ₂	0.26	--	0.16	--	0.18	0.13	--	--	--	--	--	--	0.87	--
Cs ₂ O	3.23	2.79	36.62	30.5	38.83	33.0	4.03	3.87	3.62	3.47	45.17	45.3	3.45	3.35
BaO	0.56	--	0.36	--	0.38	0.43	--	--	--	--	--	--	1.88	--
La ₂ O ₃	0.52	--	0.33	--	0.36	0.47	--	--	--	--	--	--	1.77	--
CeO ₂	1.18	--	0.76	--	0.80	0.86	--	--	--	--	--	--	3.78	--
Pr ₆ O ₁₁	0.53	--	0.34	--	0.36	--	--	--	--	--	--	--	1.78	--
Nd ₂ O ₃	1.70	--	1.09	--	1.13	1.26	--	--	--	--	--	--	17.12	--
Sm ₂ O ₃	0.33	--	0.21	--	0.22	--	--	--	--	--	--	--	1.11	--
Eu ₂ O ₃	0.07	--	0.05	--	0.05	0.05	--	--	--	--	--	--	0.24	--
Gd ₂ O ₃	0.05	--	0.03	--	0.03	0.02	--	--	--	--	--	--	0.16	--
U ₃ O ₈ ^(c)	4.15	--	2.66	--	--	--	--	--	--	--	--	--	14.01	--
²⁴⁰ PuO ₂	0.07	--	0.65	--	--	--	--	--	--	--	--	--	--	--
²⁴³ Am ₂ O ₃	--	--	0.04	--	--	--	--	--	--	--	--	--	--	--
²⁴³ Am ₂ O ₃	--	--	0.04	--	--	--	--	--	--	--	--	--	--	--
²⁴⁴ Cm ₂ O ₃	0.22	--	2.30	--	--	--	--	--	--	--	--	--	--	--
Total	100.00	--	99.98	--	100.01	99.41	100.01	99.41	100.00	99.77	99.99	--	99.9	--

(a) Nominal

(b) Analyzed

(c) U₃O₈ is depleted (0.25% U-235).

alpha-decay events to Cs transmutations would be about the same as that in actual waste during the first 20 years (assuming 1% of the U and Pu remain in the waste stream). ^{244}Cm was added because it was felt that the alpha-decay might modify the effects of the Cs $\rightarrow$ Ba transmutations, perhaps by providing the energy necessary for the atoms to rearrange to a more suitable configuration following a transmutation.

- 2) Nominally 76-68 glass except that all the Na_2O was replaced by Cs_2O on a molar basis, and the amount of B_2O_3 was doubled to aid in melting. The large increase in Cs_2O content was employed so that any effects due to Cs $\rightarrow$ Ba transmutations would be more readily detectable than in glass No. 1. Again, ^{244}Cm was added so that the ratio of alpha-decay events to Cs $\rightarrow$ Ba transmutations would be the same as it initially is in actual waste.
- 3) Same as material No. 2 except no actinides were added so that the effect of Cs $\rightarrow$ Ba transmutations with and without accompanying alpha-decay could be determined.
- 4&5) Two other glasses with compositions substantially different than glasses 1, 2 and 3 as shown by the composition diagram in Figure 8. Note that Figure 8 also shows composition ranges of waste glasses being studied by PNL, Savannah River, and Rockwell as well as a generic study of glasses conducted at PNL (Chick et al. 1981). Glasses 4 and 5 were included so that the relative effect of Cs $\rightarrow$ Ba transmutations on different types of glasses could be determined.
- 7&8) Material 8 is supercalcine (SPC-2 formulation) which is a possible ceramic alternative to glass as a waste form. Material 7 is pollucite ($\text{CsAlSi}_2\text{O}_6$) which is the phase in supercalcine that contains the Cs.

Fabrication Details: All the glasses were made up by mixing the components together as carbonates, nitrates, and oxides. The simulated fission products for glasses 1, 2 and 3 were added as calcined oxides.

- FORMERS INCLUDE SiO_2 , B_2O_3 , P_2O_5 , Al_2O_3
- MODIFIERS INCLUDE ALKALI AND ALKALINE EARTHS
- INTERMEDIATES INCLUDE EVERYTHING ELSE

FIGURE 8. Composition Diagram of Potential Waste Glasses

The mixtures were melted in platinum crucibles at 1050 to 1150°C for three hours. Glasses 1 and 2 were then finely ground up, powdered $^{244}\text{Cm}_2\text{O}_3$ was mixed in, and the glasses were remelted for two hours.

Metallography, including energy dispersive x-ray analysis, was performed on archives of all the glass samples. The data are not necessarily pertinent, however, since all the glasses were remelted following irradiation to remove neutron damage. The archive samples of glasses 1, 2 and 3 contain small metallic-looking inclusions of Pt or Pd. No inhomogeneities at all were found in glass 4. Glass 5 has several small crystals that are apparently spinel since they contain primarily Fe, Ni and Mn. Autoradiographs of glasses 1 and 2 show the Cm is distributed somewhat non-uniformly. Remelting following irradiation would be expected to homogenize the samples somewhat although no redistribution of the Cm between samples would have been possible.

The supercalcine and pollucite were prepared from carbonates and nitrates, when available; otherwise, oxides were used. Silica was added as LUDOX which is an ammonia-stablized colloidal suspension of SiO_2 in water. The materials were dissolved to the extent possible in water and then evaporated to dryness. They were then cold pressed and sintered. The supercalcine was sintered one and one half hours at 1200°C; the pollucite was sintered overnight at 1000°C, four hours at 1200°C and two hours at 1575°C.

X-ray diffraction data on the pollucite were in good agreement with those of Gallagher (1979) and there was no evidence of phases other than pollucite. A small amount (perhaps 5%) of disilicate (CsAlSiO_4) always remained after firing at 1200 to 1400°C, but this was eliminated by the firing at 1575°C.

Table 7 lists the phases one normally expects to find in supercalcine (McCarthy, et al. 1979). Only the phases so indicated were identified in archive samples of the supercalcine used in this study as established by scanning electron microscopy (SEM) with energy dispersive x-ray (EDX) analysis. The other phases may have been present but in quantities too small to detect. In particular, McCarthy, et al. (1979; Quarterly Report 1979) found that the amount of apatite phase is reduced in supercalcine containing uranium, as do the samples in the present study.

TABLE 7. Crystalline Phases Present in Supercalcine

<u>Nominal Composition</u>	<u>Structure Type</u>	<u>Phases Identified with SEM and EDX</u>
$(\text{Ca}, \text{Sr})_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (a)	Apatite	
REPO_4	Monazite	
$(\text{U}, \text{Ce}, \text{Zr}, \text{RE})\text{O}_{2\pm x}$	Fluorite	X
$(\text{Cs}, \text{Rb}, \text{Na})\text{AlSi}_2\text{O}_6$	Pollucite	X
$(\text{Ca}, \text{Sr}, \text{Ba})\text{MoO}_4$	Scheelite	X
$(\text{Fe}, \text{Cr})_2\text{O}_3$	Corundum	
$(\text{Ni}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	Spinel	
RuO_2	Rutile	X

(a) RE = Rare Earths La, Ce, Pr, Nd, Sm, Gd, Y.

The crystalline materials, supercalcine and pollucite, were fabricated as pellets 0.100 in. long with diameters of 0.138 in and 0.187 in. respectively after sintering. All the glass samples were core drilled to a diameter of 0.138 in. from a larger melt and then cut into lengths nominally 0.100 in. long.

Irradiation Details

Twenty samples of each of the seven materials were placed in subcapsules shown schematically in Figure 9. The seven subcapsules were then placed in an aluminum irradiation capsule, together with two subcapsules supplied by Sandia Laboratories, for insertion in the HFIR. Prior to final closure welding of the irradiation capsule, it was evacuated and backfilled with helium. This procedure also filled the subcapsules with helium via the small hole in the bottom of each. Figure 10 shows the location of each of the subcapsules relative to the reactor midplane. The subcapsules supplied by Sandia contained materials for their own transmutation study. However, those samples have never been examined following irradiation because of insufficient funds.

NOTES:

**ALL DIMENSIONS ARE IN INCHES
SUBCAPSULE MATERIAL IS 6061 ALUMINUM**

FIGURE 9. Irradiation Subcapsule

FIGURE 10. Schematic Diagram of Irradiation Capsule

All the PNL materials except pollucite had very high heat-generation rates in the reactor. There were four basic sources of heat generation: 1) normal gamma heating, which was assumed to have a peak value of 15 W/g; 2) radiation decay heat, which was conservatively estimated to be 5 W/g; 3) nuclear reactions with Li and B according to

and

and 4) fissioning of uranium and other actinides. In the latter case, substantial fractions of the ${}^{238}\text{U}$ and ${}^{244}\text{Cm}$ were converted to ${}^{239}\text{Pu}$ and ${}^{245}\text{Cm}$ respectively, and it was the latter isotopes that underwent most of the fission reactions. Heat generation rates from fission and the nuclear reactions were calculated using the ORIGEN computer code (Bell 1973).

The nuclear reaction with B produced Li as well as heat. To minimize the effects of both, boron enriched to 98.5% ${}^{11}\text{B}$ was used in all five glasses. Nevertheless, the remaining 1.5% ${}^{10}\text{B}$ generated a substantial amount of heat. The heat generated in glasses 4 and 5 by the nuclear reaction with Li was judged to be acceptable.

Both the ${}^{10}\text{B}$ and the ${}^6\text{Li}$ were largely burned out in the first few days of irradiation. Thus, the peak heat generation rate occurred for these two isotopes during the first few hours. The ${}^{235}\text{U}$ also burned out fast. Heat generated from fissioning of the other actinides peaked after a few days of irradiation. Two values for heat generation rates are listed in Table 8, one for the first few hours and the second for a few days later when the rate peaked for some of the actinides. Maximum centerline temperatures for the different materials were calculated using the HEATING 5 computer code (Turner, Elrod and Simon-Tov 1977) and are also listed in Table 8. Both the heat generation rates and temperatures listed take into account the position of the material within the capsule. Thus, they were modified in proportion to the thermal flux profile shown in Figure 11.

TABLE 8. Heat Generation Rates and Maximum Centerline Temperatures

Material(a)	Heat Generation Rate W/g(b)						Temperature (°C)	
	Li-6	B-10	U-235	Other Actinides	Gamma	Decay		Total
1	--	50 (9)	3 (1)	11 (15)	12	5	81 (42)	280
2	--	41 (7)	2 (1)	29 (105)	8	5	95 (126)	560
3	--	82 (14)	--	--	15	5	102 (34)	450
4	43 (12)	54 (9)	--	--	13	5	115 (39)	400
5	53 (15)	53 (9)	--	--	10	5	121 (39)	420
7	--	--	--	--	15	5	20 (20)	200
8	--	--	13 (6)	35 (35)	14	5	67 (60)	390

(a) See "Materials Studied" Section and Table 6 for description of materials.

(b) The first number applies to the first few hours of irradiation, while the number in parenthesis applies after a few days. Gamma and decay heat generation rates are relatively uniform throughout the 4-cycle irradiation.

The heat generation rates listed in Table 8 are to be compared with an average value of about 30 W/g that is generated in a light water reactor fuel pellet. Despite these large heat generation rates, temperatures were maintained relatively low by making sample diameters small, by making the gas gap between samples and subcapsules as small as possible, and by filling the gap with helium for improved thermal conduction.

Figure 11 shows thermal neutron flux in HFIR as a function of axial position. Although the flux at the ends of the capsule was only about 50% of the peak flux, Figure 12 shows that the amount of useful Cs→Ba transmutations at these positions was calculated to be about 75% of the peak values listed in Table 5.

Post-Irradiation Examinations and Procedures

The following observations were made during disassembly of the irradiation capsule and unloading of the samples. Materials 3, 4, 5 and 7 were easily removed from the subcapsules and looked very much the same as before irradiation; this, despite the large thermal gradients (due to the high heat generation rates) which were expected to cause fracture due to thermal stress. Material 8 (supercalcine) was fractured; each pellet appeared to be in four or five pieces. However, they were also stuck to the aluminum subcapsule and were broken up much more extensively getting them out. Thermal stresses are likely responsible for the fracturing, but the reason the pellets were stuck to the aluminum is not clear. Materials 1 and 2 also stuck to the aluminum subcapsule and had to be broken up somewhat to get them out. They did not, however, appear to be fractured due to thermal stress as expected.

All materials were annealed to remove neutron radiation damage effects about 15 days after the end of irradiation and before beginning post-irradiation analyses. Materials 1-5 (all glass) were annealed at 900° to 1000°C in graphite crucibles. An inert atmosphere was used to keep the graphite from oxidizing. At this temperature, all the samples melted into roughly spherical pellets. The samples were cooled to room temperature in about 30 min. Materials 7 and 8 were annealed at 1150°C in air and then furnace cooled.

FIGURE 11. Thermal Neutron Flux Profile in SRB Test Position in HFIR

FIGURE 12. Percentage of Cs $\rightarrow$ Ba Transmutations after Various Decay Times Versus Axial Position in HFIR

Post-irradiation analyses have included optical and scanning electron microscopy, leach tests, density measurements, and x-ray diffraction analyses. The goal in all cases was to measure changes in the properties of these particular samples, but not necessarily to compare their properties with other materials. All the tests were developed with that in mind.

The leach tests were conducted for seven days at 90°C in deionized water. The ratio of leachate volume to sample surface area was made the same for each leach test for a given material. This ratio was 30 cm in some cases and 40 cm in others. Leaching was done in sealed polypropylene containers of about 50 ml volume. Following the leach tests, the leachate solutions were analyzed for ^{134}Cs activity using a high resolution intrinsic germanium diode x-ray spectrometer. The spectrometer was calibrated with a ^{134}Cs standard traceable to the National Bureau of Standards. Care was taken to insure that the standard and sample environments were the same. That is, the standard was dissolved in 20 ml of water and placed in the same type of polypropylene bottle as the samples. Small size and geometry differences between standard and samples were negligible because both were counted at a distance of about 6 m.

After the leachate solutions were analyzed for Cs activity, the level of radioactivity was reduced by passing the solutions through ion exchange columns to remove the Cs. The solutions could then be analyzed by Inductively Coupled Plasma Spectroscopy for most other cations except alkali and alkaline earths which were altered by the ion exchange resins.

Density measurements were made by immersion in a liquid fluorocarbon, FC-75, made by 3M Company. Its density is about 1.78 g/cm^3 , but its precise density was determined each time using a sapphire standard whose density was taken to be 3.986 g/cm^3 independent of temperature over the range used. Archive samples of materials 3 and 5 were also measured each time for reference. Any or all of the samples may have bubbles or other inclusions. Therefore, the densities cannot be taken as absolute, and there can even be some variation between different samples of the same material. This does not preclude measurement of density changes on a given sample, however.

X-ray diffraction results have been unsatisfactory until recently when a new shielded diffractometer became operational at PNL. Only preliminary results have been obtained so far, but these suggest that accurate lattice parameters and degree of crystallinity data should be readily obtainable.

Results

^{134}Cs Concentration: The ^{134}Cs activity was measured for two or three samples of each material except for Material 8 which was in powder form and, therefore, less easily measured. The fraction of cesium converted to ^{134}Cs was based on the amount of Cs originally present as given by the analytical results shown in Table 6. Average measured values are listed in Table 9 along with the calculated ones. The data are quite scattered; still the result for material 2 appears out of line with the others and it is probably in error. For reasons described in Table 9, the decision was made to simply average the results uniformly for the seven materials, ignoring the result for Material 2.

Density: Results for materials irradiated in HFIR together with results for two non-radioactive reference materials are listed in Table 10. Densities have increased slightly for four of the materials including pollucite (7). The largest increases are for the two high-cesium glasses (2 and 3), particularly the one without curium (3). Increases for the other two materials (4 and 7) are statistically significant, but just barely; additional measurements a year or so from now will be required to definitely establish a trend.

Leach Rates: Three samples of each material were leach tested in May 1979, three different samples of each were leached during April 1980, and so on. Only those elements listed in Table 11 were found in appreciable quantities. A few comments regarding these results are in order. Several results from the second leach test and one from the first test appear to be in error. If that is true, then the leach

TABLE 9. Conversion of Cesium to ^{134}Cs

Material(a)	Distance from HMP (cm)	Percent of ^{134}Cs on 4/20/79(b)	
		Calculated	Measured
2	22.9	16.3	5.1 (ignored in average)
1	12.6	20.4	14.0
3	6.1	21.0	10.6
7	-0.4	21.2	10.6
8	-6.8	21.0	--
4	-13.3	20.4	12.8
5	-19.8	18.2	12.2
			$12.0 \pm 1.3^{(c)}$

(a) See "Materials Studied" Section and Table 6 for description of materials.

(b) Based on total cesium originally present as determined by chemical analysis after fabrication.

(c) The measured results are quite scattered and their correlation with position in the reactor bears little resemblance to the calculated one. However, there is also considerable uncertainty in the calculated values, so the decrease near the ends of the capsule is not well established. Therefore, the measured values were simply averaged ignoring the results for material 2. The error listed is two times the standard deviation of the mean.

TABLE 10. Density of HFIR Samples and Non-Radioactive Standards

Material(a)	Density (g/cm^3)(b)		
	6/79	2/80	6/81
Std. #3	3.209 ± 0.007	3.203 ± 0.004	3.214 ± 0.007
Std. #5	2.689 ± 0.009	2.690 ± 0.000	2.691 ± 0.007
1	1.993 ± 0.018	1.990 ± 0.010	1.992 ± 0.004
2	2.704 ± 0.015	2.727 ± 0.007	2.731 ± 0.005
3	2.835 ± 0.021	2.857 ± 0.018	2.911 ± 0.028
4	2.362 ± 0.005	2.360 ± 0.000	2.381 ± 0.015
5	2.315 ± 0.004	2.310 ± 0.000	2.309 ± 0.007
7	2.970 ± 0.020	2.970 ± 0.000	2.994 ± 0.003
8	4.207 ± 0.022	4.208 ± 0.010	4.199 ± 0.010

(a) See "Materials Studied" Section and Table 6 for description of materials.

(b) Errors listed represent two times the standard deviation of the mean.

TABLE 11. Leach Values of Materials Irradiated in HFIR

Material(b)	Percentage of Element Leached in 7 Days at 90°C in Deionized Water(a)					
	Boron			Silicon		
	5/79	4/80	8/81	5/79	4/80	8/81
1	ND ^(c)	0.93 $\pm$ 0.17	1.61 $\pm$ 0.22	0.57 $\pm$ 0.36	1.00 $\pm$ 0.12	1.36 $\pm$ 0.31
2	23.6 $\pm$ 17.6	15.0 $\pm$ 6.6 ^(e)	22.7 $\pm$ 3.0	7.8 $\pm$ 3.4	5.7 $\pm$ 2.3 ^(e)	10.3 $\pm$ 0.4
3	27.6 $\pm$ 2.6	14.5 $\pm$ 2.8 ^(e)	24.3 $\pm$ 8.9	7.0 $\pm$ 0.7	6.5 $\pm$ 1.9 ^(e)	7.6 $\pm$ 0.6
4	ND	0.46 $\pm$ 0.20	0.61 $\pm$ 0.07	0.13 $\pm$ 0.00	0.15 $\pm$ 0.03	0.12 $\pm$ 0.03
5	ND	0.31 $\pm$ 0.33	0.31 $\pm$ 0.15	0.43 $\pm$ 0.22	0.61 $\pm$ 0.19	0.57 $\pm$ 0.22
7	---(d)	---	---	0.70 $\pm$ 0.30	1.15 $\pm$ 0.06	1.25 $\pm$ 0.12
8	---	---	---	3.1 $\pm$ 0.3	2.23 $\pm$ 0.07 ^(e)	2.97 $\pm$ 0.14

Material	Percentage of Element Leached in 7 Days at 90°C in Deionized Water(a)					
	Molybdenum			Cesium		
	5/79	4/80	8/81	5/79	4/80	8/81
1	0.11 $\pm$ 0.04	ND	0.62 $\pm$ 0.26	0.52 $\pm$ 0.12	0.89 $\pm$ 0.19	1.56 $\pm$ 0.22
2	16.5 $\pm$ 15.8	9.5 $\pm$ 3.6 ^(e)	14.1 $\pm$ 3.1	15.3 $\pm$ 9.5	5.59 $\pm$ 2.21 ^(e)	16.5 $\pm$ 3.6
3	18.6 $\pm$ 0.9	8.8 $\pm$ 1.9 ^(e)	16.4 $\pm$ 7.5	29.9 $\pm$ 1.3	13.8 $\pm$ 2.8 ^(e)	28.6 $\pm$ 6.2
4	---	---	---	0.36 $\pm$ 0.03	0.38 $\pm$ 0.02	0.58 $\pm$ 0.07
5	---	---	---	0.53 $\pm$ 0.24	0.34 $\pm$ 0.10	0.38 $\pm$ 0.14
7	---	---	---	1.25 $\pm$ 0.51	1.68 $\pm$ 0.36	2.58 $\pm$ 0.34
8	0.71 $\pm$ 0.11 ^(e)	0.09 $\pm$ 0.02	0.08 $\pm$ 0.04	2.95 $\pm$ 0.16	0.57 $\pm$ 0.26 ^(e)	1.98 $\pm$ 0.65

(a) Errors listed represent two times the standard deviation of the mean.

(b) See "Materials Studied" Section and Table 6 for description of materials.

(c) ND = element not detected.

(d) --- = element not present.

(e) Results that are out-of-line with related results and are, therefore, probably in error.

rates of materials 2, 3, 4 and 5 have not changed noticeably. Material 8 also has not changed much except for a very small decrease in the leach rate of Cs. The leach rates of material 1 (similar to 76-68 waste glass) and material 7 (pollucite) have increased slightly. However, the increases are relatively unimportant from a waste management point of view since the changes are less than a factor of ten.

Microstructure: Both optical and scanning electron micrographs were taken of the same areas of all seven materials during each of the three postirradiation examinations. No changes have been detected. A typical series of micrographs is shown for one of the high cesium glasses in Figure 13.

Conclusions

About 6% of the total cesium had undergone transmutations at the time of the most recent examinations. In the high cesium glasses, this represents nearly twice as many transmutations as would occur in most commercial waste glasses. Still, no changes in properties were found that would be of any consequence from a waste management viewpoint. The crystalline materials were also relatively unaffected. However, the number of transmutations in these materials has been only about 13% of those expected for an actual waste.

FIGURE 13. Micrographs of Material 3 (High-Cs Glass Without Cm). The white specks are artifacts of a conductive carbon coating that was removed for these optical micrographs and, therefore, are a little different in the different photos.

ACKNOWLEDGEMENTS

The authors are indebted to numerous individuals at PNL who assisted in sample preparation, irradiation capsule preparation and disassembly, leach test design and conduct, ^{134}Cs analysis and shielded x-ray diffraction. The help of T. M. Fish, G. D. Maupin, R. W. Stephens, W. J. Weber, F. D. Hobbs, G. L. McVay, H. J. Cartmell, L. A. Bray, R. L. Brodzinski and H. E. Kissinger was greatly appreciated.

The assistance of C. L. Ottinger, under whose direction the irradiations in HFIR took place, as well as E. M. King and R. Crouse who were responsible for test capsule disassembly and microstructural examination at ORNL, along with C. E. Saari at Hanford Engineering Development Laboratory, who performed density measurements, is also acknowledged and appreciated.

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REFERENCES

- Appleman, D. E. and H. T. Evans, Jr. 1973. "Indexing and Least Squares Refinement of Powder Diffraction Data (Job 9214)", NTIS, PB-216-188.
- Bell, M. J. 1973. ORIGEN--The ORNL Isotope Generation and Depletion Code, ORNL-4628.
- Chick, L. A., et al. 1981. The Effects of Composition on Properties in an 11-Component Nuclear Waste Glass System. PNL-3188, Pacific Northwest Laboratory, Richland, Washington.
- Chikalla, T. D. and R. P. Turcotte. 1973. Rad. Effects, 19:93-98.
- Ewing, R. C. and R. F. Haaker. 1980. Nuc. Chem. Waste Mgmt., 1:51.
- Gallagher, S. A. 1979. Cesium Aluminosilicates for Nuclear Materials Applications, Ph.D. Thesis submitted to the Pennsylvania State University.
- Haaker, R. F. and R. C. Ewing. 1979. "The Metamict State-Radiation Damage in Crystalline Materials." Ceramics in Nuclear Waste Management. ed. T. D. Chikalla and J. E. Mendel. CONF-790420:305.
- Haaker, R. F. and R. C. Ewing. 1981. Naturally Occurring Crystalline Phases: Analogues for Radioactive Waste Forms. PNL-3505, Pacific Northwest Laboratory, Richland, Washington.
- Haaker, R. F. and R. C. Ewing. 1981. "Natural Analogues for Crystalline Radioactive Waste Forms, Part II: Non-Actinide Phases," in Scientific Basis for Nuclear Waste Management, Vol. 3:299. J. Moore, ed. Plenum Press, N.Y.
- Holland, H. D. and D. Gottfried. 1955. Acta. Cryst., 8, Part 6:291-300.
- McCarthy, G. J., J. G. Pepin, D. E. Pfoertsch and D. R. Clarke. 1979. "Crystal Chemistry of the Synthetic Minerals in Current Supercalcine-Ceramics," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, OH. CONF-790420, Technical Information Center, Oak Ridge, Tennessee.
- Mendel, J. E., et al. 1981. A State-of-the-Art Review of Material Properties of Nuclear Waste Forms. PNL-3802. Pacific Northwest Laboratory, Richland, Washington.
- Mosley, W. C. 1971. J. Am. Cer. Soc., 54, No. 10:475-479.
- Oversby, V. M. and A. E. Ringwood. 1981. Radioactive Waste Management 1(3):289-307.
- Permar, P. H. and W. R. McDonnell. 1981. "Significance of Radiation Effects in Solid Radioactive Waste." Proceedings of the 10th. International Symposium on Effects of Radiation on Materials, ed. Kramer/Bragen/Perrin. ASTM-04-725000-35:115.

Quarterly Progress Report Research and Development Activities Waste Fixation Program, October through December, 1977. 1979. PNL-2265-4:15. Pacific Northwest Laboratory, Richland, Washington.

Ringwood, A. E. 1978. Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy: Australian National University Press, Canberra, Australia.

Roberts, F. P., G. H. Jenks and C. D. Bopp. 1976. Radiation Effects in Solidified High Level Wastes - Part I, Stored Energy. BNWL-1944. Pacific Northwest Laboratory, Richland, Washington.

Roberts, F. P., R. P. Turcotte and W. J. Weber. 1981. Materials Characterization Center Workshop on the Irradiation Effects in Nuclear Waste Forms, Summary Report. PNL-3588. Pacific Northwest Laboratory, Richland, Washington.

Rusin, J. M., R. O. Lokken and J. W. Wald. 1979. "Characterization and Evaluation of Multibarrier Nuclear Waste Forms." In Ceramics in Nuclear Waste Management, Proc. Int. Symp. ACS, CONF-790420.

Rusin, J. M., W. J. Gray and J. W. Wald. 1979. Multibarrier Waste Forms, Part II: Characterization and Evaluation, PNL-2668-2, Pacific Northwest Laboratory, Richland, Washington.

Turcotte, R. P. 1976. "Alpha Radiation Damage in the Actinide Dioxides." Plutonium 1975 and Other Actinides. Ed. H. Blank and R. Lindner, North-Holland Publishing Co., p. 851.

Turcotte, R. P. 1982. "Radiation Effects in High Level Radioactive Waste Forms." Radioactive Waste Management, 2(2):169.

Turner, W. D., D. C. Elrod and I. I. Simon-Tov, 1977. HEATING 5--An IBM 360 Heat Conduction Code, ORNL/CSD/TM-15.

Weber, W. J., R. P. Turcotte, L. R. Bunnell, F. P. Roberts, and J. H. Westsik, Jr. 1979. "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass," in Ceramics in Nuclear Waste Management, Proc. Int. Symp. ACS, CONF-790420.

Weber, W. J. 1981. "A Review of Radiation Effects in Solid Nuclear Waste Forms." PNL-SA-9855, presented at the Third Argonne Workshop on Basic Problems in Nuclear Waste Management, October 1-2, 1981. Argonne National Laboratory.

Weber, W. J. and R. P. Turcotte. 1982. Materials Characterization Center Second Workshop on Irradiation Effects in Nuclear Waste Forms -- Summary Report. PNL-4121, Pacific Northwest Laboratory, Richland, Washington.

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