DP-MS-75-94

EFFECT OF INTERNAL ALPHA RADIATION ON BOROSILICATE GLASS CONTAINING SIMULATED RADIOACTIVE WASTE

by

N. E. Bibler and J. A. Kelley

Savannah River Laboratory
E. I. du Pont de Nemours and Company
Aiken, South Carolina 29801

A paper proposed for publication in *Nuclear Technology*.

This document was prepared in conjunction with work accomplished under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

DISCLAIMER

DP-MS-75-94

EFFECT OF INTERNAL ALPHA RADIATION ON BOROSILICATE GLASS CONTAINING SIMULATED RADIOACTIVE WASTE

N. E. Bibler and J. A. Kelley

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

ABSTRACT

To evaluate borosilicate glass as a matrix for long-term storage of radioactive waste, samples containing 45 wt % simulated waste [$Fe(OH)_3$-MnO_2] along with either 0.5 wt % ^{244}Cm or 1 wt % ^{238}Pu as alpha particle emitters were synthesized. A glass containing ^{238}Pu without simulated waste was also made. Effects of internal alpha radiolysis from ^{244}Cm and ^{238}Pu on physical stability, leachability, and dilatation of the glasses were examined. Dose rates ranged from 3.1×10^{11} to 8.9×10^{11} alpha dis/(min)(g), equivalent to 1.6×10^{6} to 5.0×10^{6} rad/hr. After 420 days, no macrostructural damage to the glasses was observed. Leachabilities for ^{244}Cm and ^{238}Pu were $< 7 \times 10^{-8}$ g/(cm^2)(day) and were not significantly affected by radiolysis. Continuous leaching by water for 5 days removed $<10^{-5}$% of the isotopes. Alpha radiolysis caused expansion of the simulated-waste glasses, in contrast to the

The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration.

effect observed with pure silica or borosilicate glasses. Positive dilatations varied linearly with dose up to a maximum of 40 Grads. Glasses with simulated waste could be dissolved in 8M HNO_3.

INTRODUCTION

Borosilicate glass is currently being evaluated[1,2] as a possible long-term storage matrix for radioactive waste generated at Savannah River Plant (SRP). For incorporation in glass, this waste will be a dry mixture of hydrous oxides of primarily iron, manganese, and aluminum contaminated with fission products, uranium, and transuranium elements.[3] Properties of glass that make it an attractive matrix are high strength and low leachability. This latter property ensures that only a small fraction of the total radioactivity would be released should the glass be accidentally exposed to environmental water. Processes using glass as a matrix for radioactive waste have been in operation[4,5] or are being tested.[6,7]

Previous studies were concerned with external radiation and revealed no adverse effects on leachability.[1,4] However, studies of the effects of internal alpha radiolysis on glasses during long-term storage have begun only recently. Stored energy from internal alpha radiolysis has been shown to saturate at $\sim$25 cal/g at an alpha dose of $\sim 10^{18}$ alpha dis/g.[8] We have examined the effect of internal alpha radiation on dilatation of the glass, and on leachability of the alpha-emitting isotopes. To accelerate

the effects of alpha damage during long-term storage, relatively large amounts of ^{244}Cm or ^{238}Pu were incorporated in the glasses.

EXPERIMENTAL

Description of Materials

Oxide composition (by wt %) of the glass-forming mixture for the three glasses was: 52.5% SiO_2, 10% B_2O_3, 22.5% Na_2O, 10% TiO_2, and 5% CaO. Previous experiments[1] have shown that this glass composition is acceptable for incorporation of solid SRP radioactive waste.[2] Simulated dry waste [50 mol % $Fe(OH)_3$ and 50 mol % MnO_2] was added to portions of glass-forming mixture for two of the glasses to the level of 45 wt % waste. ^{244}Cm was added to one waste-oxide mixture and ^{238}Pu to the other. These isotopes were added as small volumes of nitrate solutions and were thoroughly dispersed in the respective mixes. Another glass containing ^{238}Pu, but no simulated waste, was also made. The final mixes were slowly heated to 1150°C in ceramic crucibles and held at that temperature for 3 hours. The melts were poured into graphite molds and annealed at 500°C for 1 hour.

Isotopic analysis of the curium and plutonium indicated that >99.9% of the alpha activity resulted from ^{244}Cm and ^{238}Pu, respectively. ^{244}Cm and ^{238}Pu contents of the final glass buttons were measured calorimetrically to 0.1%. Specific activites and alpha particle energies used for dose rate calculations were taken from the literature.[9]

Leachability and Density Measurements

Leachabilities were measured in 150 ml of stirred, distilled water at 25°C. Leach water was changed daily. Leachabilities, L, were calculated from

$$L = f(M/A)(1/t)$$

where f is the fraction of ^{244}Cm or ^{238}Pu leached during time t, and M/A is the mass-to-surface area ratio of the sample. The amount of isotope leached was based on measurements of alpha activity of leach water.

Glass densities were determined at 22 ±1°C by weighing samples in air and in carbon tetrachloride. Each determination included a density measurement of a silicon standard. Reproducibility of standards indicated that errors due to experimental technique were negligible.

RESULTS AND DISCUSSION

Effect of Alpha Radiation on Glass Volume

Initial densities and other properties of the three glasses are shown in Table I. The glasses were shiny, opaque, and brownish-blue in color. Glasses containing simulated waste had much larger densities than normal glass because oxides of iron or manganese fill vacancies in the glass network.

Internal alpha radiation caused positive dilatations of all three glasses (Fig. 1). Such dilatation must be considered as a stress-producing mechanism if glass forms containing radioactive waste are to be stored in tight-fitting steel primary containers.

Borosilicate glasses containing small quantities of network modifiers and vitreous silica exhibit negative dilatations when externally irradiated.[10,11] This compaction has been explained by radiolytic displacement of bonded oxygen into the free volume of the glass network.[11] In glasses containing waste, this free volume is no longer present, and bond breakage leads to network expansion. Such expansion has been observed in vitreous silica containing aluminum as an impurity when the glass is irradiated externally with x-rays, γ-rays, or electrons.[12] The hypothesis that expansion results when the network free volume is filled with waste is supported by a lower rate of expansion for the glass containing ^{238}Pu but no simulated waste. This glass still expands, apparently because of the effect of the relatively large amount of ions of sodium, calcium, and titanium in the glass. For the three glasses, expansion rates in volume percent per Grad are 0.017 for the ^{238}Pu glass with waste, 0.012 for the ^{244}Cm glass with waste, and only 0.0043 for the ^{238}Pu glass with no waste.

Effect of Heat on Volume of Irradiated Glass

To test the effect of heat on irradiated glass, a sample of the glass containing ^{238}Pu and waste was heated 362 days after preparation from 23°C to 400°C in approximately 3.5 hours and then allowed to cool slowly. No physical damage was evident, but a density measurement indicated that the volume had decreased by 0.14%. Total dilatation prior to heating was 0.28%. Apparently

at least part of the positive dilatation can be annealed out at 400°C. This has also been observed in impure vitreous silica.[11]

Leachabilities of ^{244}Cm and ^{238}Pu from Glass

Results for leachability of ^{244}Cm and ^{238}Pu from the glasses are shown in Table II. Before these leachabilities were determined, the glasses were lightly wiped or washed to remove ^{244}Cm or ^{238}Pu not held in the glass network. Preliminary experiments showed that this was 10^{-6} to 10^{-5} of the total activity. Results in Table II agree with data for leaching of alpha activity from test samples of borosilicate glasses containing actual SRP radioactive waste.[2] Leachabilities in Table II are 10^{2} to 10^{3} lower than those found for cesium and strontium from glass.[2] Data in Table II indicate that internal alpha radiolysis up to at least 40 Grads does not significantly affect leachability. Moreover, after the loosely held ^{244}Cm or ^{238}Pu is removed, leachability does not significantly change with leach time. Over a 4-day leach period, the fractions of activity leached are 2×10^{-8} for ^{244}Cm and 2×10^{-7} for ^{238}Pu. Consistently higher values for ^{238}Pu indicate that it is not held in the matrix as strongly as is ^{244}Cm.

Helium in the Glass

Because of alpha decay of ^{244}Cm or ^{238}Pu, helium is continuously deposited internally in the glasses. If none of this helium has diffused from the glass, helium concentrations [cc He(STP)/cc glass] in the three glasses after 420 days are

0.061 for the ^{244}Cm glass, 0.025 for the ^{238}Pu glass with waste, and 0.018 for the ^{238}Pu glass without waste. These concentrations exceed estimates [$\sim 10^{-3}$ cc He(STP)/(atm)(cc glass)] for helium solubilities in glasses containing large amounts of network modifiers.[13] The actual concentration of helium in the sample glasses has not been measured, but helium generation has not caused damage at alpha doses simulating $>10^6$ years storage for wastes from SRP reactors and $\sim 10^2$ years for waste from power reactors.[7] Actual values for helium solubility and permeability are necessary to ascertain whether helium might damage larger glass samples.

Effect of Alpha Decay on Glass Microstructure

To determine the effects of alpha emitters on the glass microstructure, the three glasses were fractured, and fresh surfaces were examined by electron microscopy. A glass of composition identical to that containing the simulated waste but not containing ^{244}Cm or ^{238}Pu was also fractured and examined. Typical results are shown in Fig. 2. All three radioactive glasses exhibited randomly oriented microcracks that were not present in the nonradioactive glass. These microcracks may result from stresses produced by radiolytic bond breakage, which may account for the observed positive dilatation. Current data are insufficient to establish whether the cracks are due to alpha radiolysis or helium accumulation. Apparently, as evidenced in Table II, these microcracks did not significantly increase the leachabilities of ^{244}Cm or ^{238}Pu.

Another effect of alpha decay on glass microstructure observed only in the radioactive glasses was the blistering of portions of the glass surfaces after 20 to 30 seconds of exposure to the electron beam in an electron microscope. The blistering is shown in Fig. 3 where a square of blisters formed at a magnification of 2000X appears in the middle of an image photographed at 500X. All attempts to form these blisters on nonradioactive glass failed. In the two radioactive glasses, agglomeration of helium initiated by electron beam-heating of the surface could account for blister formation. Formation of bubbles and microcracks by dissolved gases in glasses have been reported previously;[14] heating a silicate glass containing ~3 mol % argon to 245°C caused bubble formation; when a similar glass containing 1 mol % helium was heated to 560°C, microcracks formed. Although the highest concentration of helium in the radioactive glasses was only 0.06 mol %, this mode of blister formation still appears reasonable since blisters could not be formed on the nonradioactive glass.

Effect of Nitric Acid on the Glass

Because radioactive waste glasses contain large amounts of non-glassforming oxides, they are poor glasses compared to Pyrex* or vitreous silica. Therefore, tests were performed to determine whether the waste glasses could be degraded by concentrated acids. When a 0.52-g sample of the ^{244}Cm glass was placed in 50 ml of

* Trademark of Corning Glass Works

8M HNO_3 at 60°C, almost all the glass dissolved in 4 hours. Only a slight amount of brown solids remained. After 2 days at ambient temperature, the solids in the solution became white. These solids were presumably silica. Absolute alpha counting of an aliquot of the solution indicated that ∿90% of the ^{244}Cm had dissolved. The remaining ^{244}Cm was probably sorbed on the white solids.

CONCLUSION

All the above results confirm that glass may be a desirable matrix for fixing SRP radioactive waste for long-term storage. Internal alpha radiolysis and helium accumulation in the small samples did not significantly damage the glass. Actual values for helium solubility and permeability would be necessary, however, to determine whether helium accumulation might eventually damage larger glass monoliths during long-term storage. Should it ever become desirable to retrieve or recycle the radioactive isotopes, the glass matrix can be destroyed easily by hot 8M HNO_3.

REFERENCES

1. J. A. KELLEY, "Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste," USERDA Report DP-1382, E. I. du Pont de Nemours and Company, Savannah River Laboratory (1975).
2. J. A. KELLEY, "Evaluation of Glass as a Waste Solidification Matrix - Radioactive Studies," USERDA Report DP-1397, E. I. du Pont de Nemours and Company, Savannah River Laboratory (1975).
3. R. M. WALLACE, H. L. HULL, and R. F. BRADLEY, "Solid Forms for Savannah River Plant High-Level Waste," USAEC Report DP-1335, E. I. du Pont de Nemours and Company, Savannah River Laboratory (1973).
4. J. R. GROVER, "Glasses for Fixation of High Level Radioactive Wastes." *Symposium on Management of Wastes from Fuel Reprocessing*, p 593, IAEA, Paris (1972).
5. C. SOMBRET and R. BONNIAUD. Presented at the 77th Annual Meeting of the American Ceramic Society, May 5-7, 1975, Washington, D. C. See also *Nature, 255*, 441 (1975).
6. J. L. McELROY, A. G. BLASEWITZ, and K. J. SCHNEIDER, "Status of the Waste Solidification Program," *Nucl. Technol. 12*, 69 (1971).

7. W. W. SCHULZ, A. L. DRESSEN, C. W. HOBBICK, and H. BABAD, "Glass Forms for Immobilization of Hanford Wastes," USERDA Report ARH-SA-210, Atlantic Richfield Hanford Co., Richland, WA (1975).

8. F. P. ROBERTS, "Waste Form Characterization - Stored Energy Measurements," *Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, October-December 1974.* J. L. McElroy, Ed., USERDA Report BNWL-1893, Battelle-Pacific Northwest Laboratory.

9. Y. A. ELLIS and A. H. WAPSTRA, *Nuclear Data Sheets*, Vol. 3, No. 2, Academic Press, New York (1969).

10. C. MYLONAS and R. TRUELL, *J. Appl. Phys. 29*, 1252 (1958).

11. W. PRIMAK and R. KAMPWIRTH, "The Radiation Compaction of Vitreous Silica." *J. Appl. Phys., 39*, 5651 (1968).

12. W. PRIMAK and R. KAMPWIRTH, "Impurity Effect in the Ionization of Vitreous Silica." *J. Appl. Phys., 39*, 6010 (1968).

13. J. F. SHACKELFORD, P. L. STUDT, and R. M. FULRATH, "Solubility of Gases in Glass II. He, Ne, and H_2 in Fused Silica." *J. Appl. Phys., 43*, 1619 (1972).

14. S. P. FAILE and D. M. ROY, "Solubilities of Ar, N_2, CO_2, and He in Glasses at Pressures to 10 Kbars," *J. Amer. Ceram. Soc., 49*, 638 (1966).

LIST OF TABLES

LIST OF FIGURES

TABLE I

Properties of Three Glasses Containing ^{244}Cm or ^{238}Pu

Glass Mass, g	16.4	14.5	7.93
Isotope Present	^{244}Cm	^{238}Pu	^{238}Pu
Wt % Simulated Waste	45	45	0
Wt % ^{244}Cm or ^{238}Pu	0.49	0.97	0.81
Density, g/cm^3	3.0474	3.1164	2.6187
Surface Area, cm^2	14.1	13.5	-
Radiation Intensity			
alpha activity, dis/(min)(g)	8.9×10^{11}	3.6×10^{11}	3.1×10^{11}
rads/(hr)(g)	5.0×10^{6}	2.0×10^{6}	1.6×10^{6}

TABLE II

Leachability of ^{244}Cm or ^{238}Pu from Borosilicate Glasses Containing Simulated Radioactive Waste[a]

Age of Glass, days[b]	*Leachability, g/(cm²)(day)*		*Fraction Leached*	
	^{244}Cm Glass	*^{238}Pu Glass*	*^{244}Cm Glass*	*^{238}Pu Glass*
6	0.16×10^{-8}	2.7×10^{-8}	0.14×10^{-8}	3.2×10^{-8}
274	0.34×10^{-8}	6.2×10^{-8}	0.29×10^{-8}	7.3×10^{-8}
275	0.98×10^{-8}	5.2×10^{-8}	0.84×10^{-8}	6.1×10^{-8}
276	0.70×10^{-8}	4.6×10^{-8}	0.60×10^{-8}	5.4×10^{-8}
277	0.56×10^{-8}	1.6×10^{-8}	0.48×10^{-8}	1.9×10^{-8}
278	0.21×10^{-8}	-	0.18×10^{-8}	-

a. Waste was 50 mol % each of $Fe(OH)_3$ and MnO_2.

b. Samples were leached in 150 ml of distilled water at ambient temperature for 24 hours. Fresh water was was added daily.

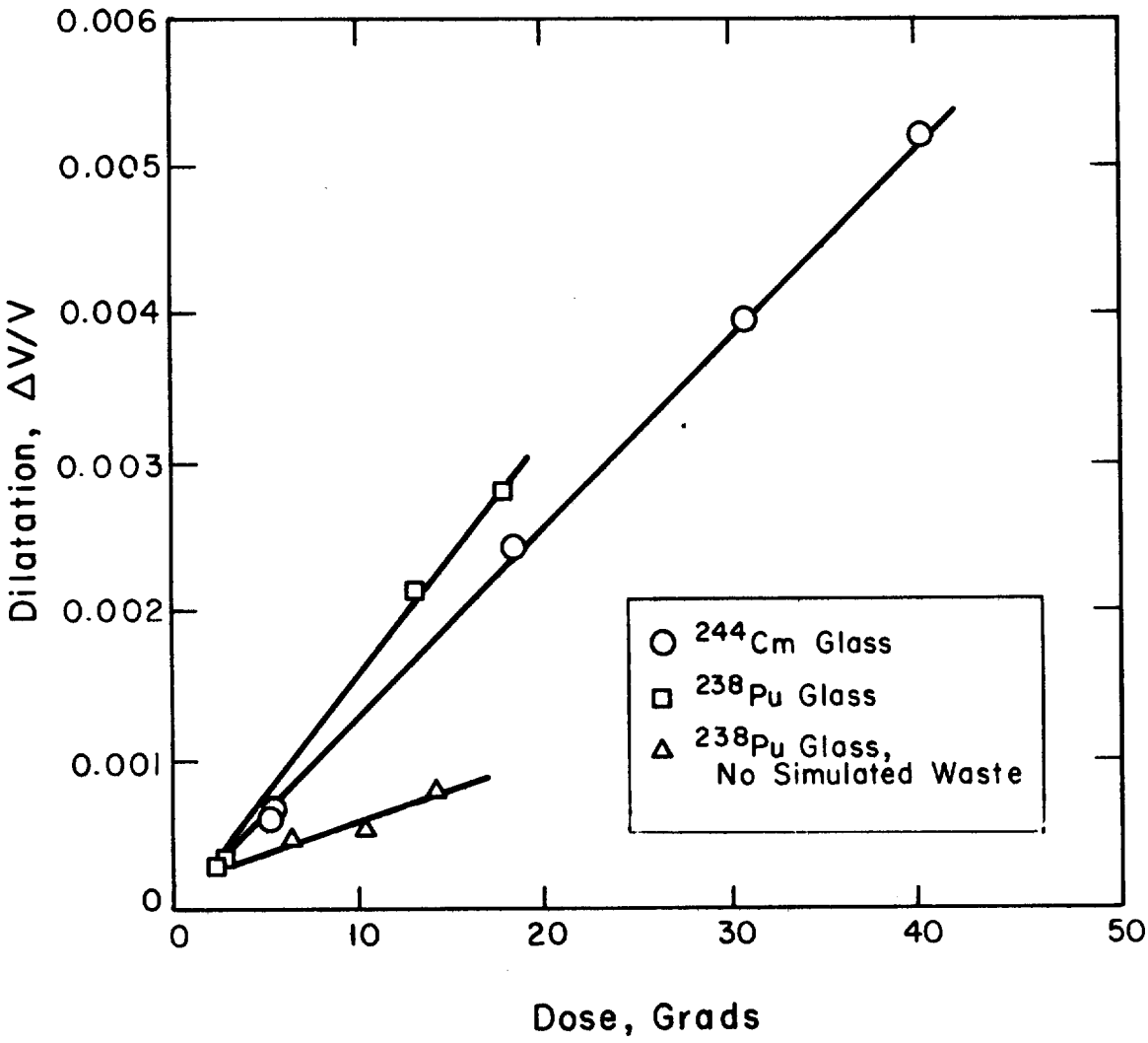
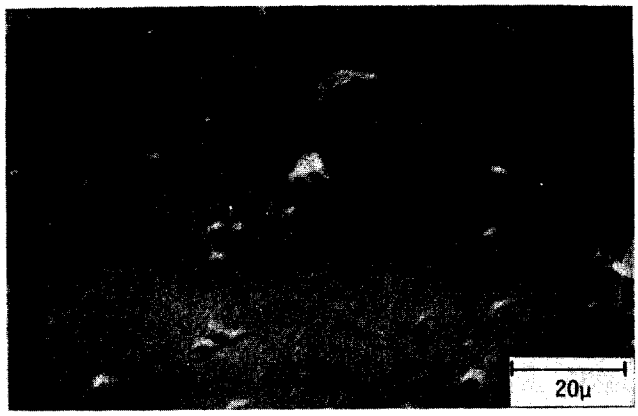
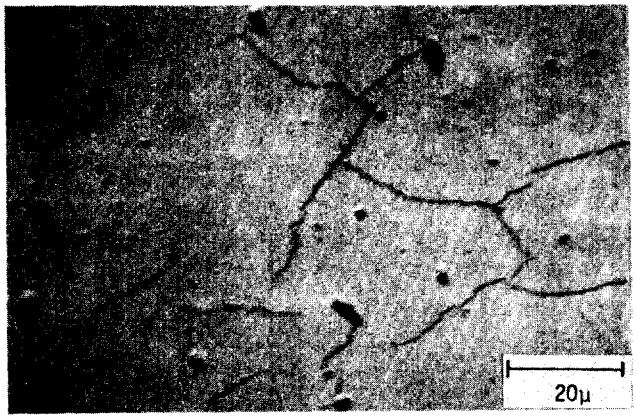


Fig. 1. Positive dilatation due to internal alpha radiolysis of borosilicate glasses containing ^{244}Cm or ^{238}Pu.



a. Glass with no ^{244}Cm or ^{238}Pu

b. Glass with ^{244}Cm



c. Glass with ^{238}Pu

Fig. 2. Electron microscope images of borosilicate glasses containing simulated radioactive wastes.

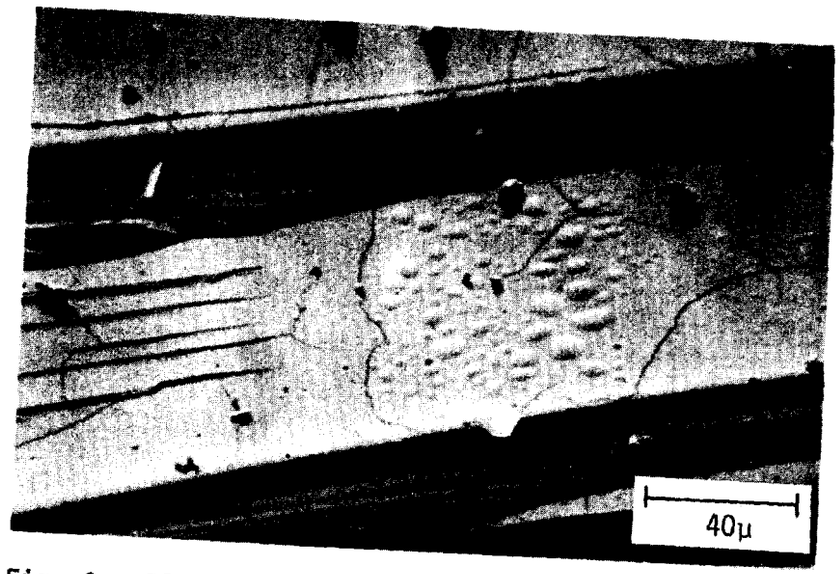


Fig. 3. Blister formation on a borosilicate glass containing ^{238}Pu due to exposure to a beam in an electron microscope.