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IDO-14672
February 1966

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LEACHABILITY OF GLASS PREPARED FROM HIGHLY
RADIOACTIVE CALCINED ALUMINA WASTE

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

B. E. Paige

**PHILLIPS
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ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
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IDO-14672
AEC Research and Development Report
Waste Disposal and Processing
TID-4500, Ed. 47
Issued: February 1966

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A B S T R A C T

Alumina-phosphate glass was prepared from full-level radioactive calcine produced in the Waste Calcining Facility at the Idaho Chemical Processing Plant. The glass was prepared from 25 weight percent alumina calcine, 40.5 percent P_2O_5 and 18.6 percent Na_2O added as $NaH_2PO_4 \cdot H_2O$, and 15.9 percent PbO . The details of preparation and the effect of radiation and heat treatment on the glass are reported. Leaching data obtained for fission products and the glass components are compared for the glass in distilled water at 25 and 94°C. A specially designed apparatus which circulated the water continuously was used. The high level of activity made it feasible to use a single molded piece permitting the surface area and other experimental conditions to be defined to a far greater degree than is feasible with the crushed glass techniques required for low levels of activity. Devitrification by heating for 30 days at 450°C was found to have no effect on the leaching rate.

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LEACHABILITY OF GLASS PREPARED FROM HIGHLY RADIOACTIVE CALCINED ALUMINA WASTE

by

B. E. Paige

I. SUMMARY

The operation of the Waste Calcining Facility (WCF)⁽¹⁾ at the Idaho Chemical Processing Plant (ICPP) has demonstrated that fluidized bed calcination can convert aqueous wastes to granular solids for storage. Although the calcined alumina from the WCF can be stored safely for long periods of time in underground stainless steel tanks in generally dry areas, conversion of the calcine to a glass may be desirable in areas where ground water could conceivably contact the solid. Conversion of the WCF calcine to an alumina-phosphate glass was shown to be feasible in laboratory studies. The effect on the glass of radiation, heat treatment, and leaching with water at different temperatures was studied.

Alumina calcine (25 weight percent), sodium monobasic phosphate, and lead oxide were mixed dry, heated to 400°C for 2 hours, and fused at 900°C for 16 hours. No residual stresses were detected in glass which had been molded at 600°C and cooled slowly to anneal. Glass produced from non-radioactive calcine became black and opaque when irradiated to a total dose of 10^{10} R, but the glass did not devitrify. Glass prepared from highly radioactive calcine, however, was thoroughly devitrified by heating for 30 days at 450°C to simulate short-term storage.

The leaching rate was determined for various constituents of the alumina-phosphate glass using distilled water. The leaching rate after seven weeks of leaching was about 5×10^{-7} grams of glass/cm²-day. By comparing the leaching rates for several different fission products and for aluminum, the leaching was shown to be primarily due to dissolution of the glass at 25°C. This was only partially true at 94°C, however.

With the surface area of the glass and other experimental conditions carefully defined, the effect of devitrification on the leaching rate was determined for glass specimens which were identical except that two had been devitrified by heating. Devitrification did not increase the leaching rate of a good glass which had been produced by using the correct chemical composition and by fusing until the glass was completely homogeneous.

II. INTRODUCTION

Fixation of radioactive waste in an insoluble medium such as glass is being considered extensively as a method for long-term storage of highly radioactive waste. The bulk of the highly radioactive waste at the ICPP contains a high concentration of aluminum nitrate from the processing of aluminum alloy fuel. Approximately 500,000 gallons of this aqueous waste has been successfully converted to calcined alumina(1). This material is considered to be safe for permanent storage in stainless steel tanks at the National Reactor Testing Station (NRTS); however, in areas where shallow ground water tables or high annual rainfall may create storage hazards, it may be desirable to convert the waste to a more nearly non-leachable form such as a glass.

Alumina-phosphate glass has been made previously(2) by adding phosphate or phosphite compounds to aluminum nitrate solutions prior to calcination and subsequent fusion. In order to determine the feasibility of converting radioactive calcine produced in the WCF directly to an alumina-phosphate glass, an experimental program was planned and completed; the details and results are included in this report.

The term glass, as used in this report, refers to mixed inorganic oxides which have been fused to form an alumina-phosphate glass. All glass can be devitrified, ie crystallized, within a particular temperature range, and some of the glass in this work was devitrified by heat treatment. Composition and non-homogeneity can cause crystallization during cooling of mixtures of oxides and prevent formation of a true vitreous glass. This is also sometimes referred to as devitrification. An excellent description of the chemical nature of glass and long-term storage of fission products in glass is presented in a report by J. R. Grover and B. E. Chidley(3).

Radioactive glass will be stored so that it will not normally be contacted by ground water. From a safety standpoint, however, the leaching rate is of interest in case water inadvertently contacts the glass during long-term storage. The high-level activity of the glass prepared from the WCF calcine made it possible to determine experimentally the leaching rate for several different fission products and provided a much more sensitive measurement technique than is possible using radioactive tracers.

The effect of crystallization caused by varying the composition of glasses has been studied recently for phosphate glasses prepared from waste oxides(4). That work showed a marked increase in solubility for the devitrified glasses with compositions of M_2O/P_2O_5 in the range of 2.3 and 2.8 (where M refers to sodium, aluminum, iron, and nickel). Since glass will devitrify during storage due to the heat generated by fission products in the waste, the effect of devitrification upon the leaching rate is of particular interest. Consequently, the effect of devitrification or crystallization, caused by heating a homogeneous vitreous glass was studied, and the results are included in this report.

III. PREPARATION, COMPOSITION, AND BEHAVIOR OF GLASS

1. Preparation of Alumina-Phosphate Glass

The glass was prepared by remote handling techniques from full-level radioactive calcine from the WCF⁽¹⁾. The alumina calcine, sodium monobasic phosphate, and lead oxide were mixed dry and heated at 400°C to remove the water from the phosphate. They were then fused at 900°C for 16 hours in porcelain* crucibles. After fusing, the glass was molded in graphite crucibles at 600°C and cooled slowly from four to five hours to anneal the specimens. Molds of known dimension were used so that the surface area could be determined accurately. Details of the various techniques of preparation which were studied are discussed in Appendix A.

Glass specimens prepared from 25 weight percent of non-radioactive calcine are shown in Figure 1. These specimens contained no cavitations and were homogeneous except for small amounts of residual sand which had been used as a bed material for startup of the WCF. The reduction in waste volume produced by calcining to alumina in the WCF is approximately 9.3, whereas there is a volume increase of about 1.3 produced by converting alumina to glass. This gives an overall volume reduction of about 7.2, in agreement with results reported for direct vitrification starting with a waste solution.

2. Composition of the Glass

Fig. 1 Alumina-phosphate glass prepared from non-radioactive WCF calcine

The same composition, which was based on earlier work with alumina-phosphate glasses at Oak Ridge National Laboratory⁽²⁾, was used throughout most of this study. The glass was prepared to contain 25 weight percent alumina calcine, 15.9 percent PbO, and with sufficient $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ added to obtain 40.5 percent P_2O_5 and 18.5 percent Na_2O . The calcine contains less than 100 percent alumina, so the radioactive glass was dissolved and analyzed to determine the exact composition. The chemical composition of the glass was 19.5 percent aluminum oxide, 41.8 percent phosphorus pentoxide, 18.4 percent sodium oxide, and 16.7

* The discoloration in the lower specimen shown in Figure 1 was caused by fusing it in a platinum crucible.

percent lead oxide. The glass specimens contained 0.2 to 2 percent silicon dioxide, which was apparently dissolved from the porcelain crucibles during fusion. The material balance for the sum of these components in the glass was greater than 95 percent. Mercury, which was present in the calcine, was volatilized during the fusion. Non-radioactive specimens of glass were cut into vertical segments and analyzed to determine the degree of homogeneity. The glass was completely homogeneous (see Appendix A).

A small number of fusions were also made using higher concentrations of amorphous alumina produced in the WCF. When 33 weight percent calcine was used, the alumina was fused, but it did not form a homogeneous glass (see Appendix A). This shows that higher concentrations of alumina calcine can be incorporated into the phosphate matrix. This type of materials was not studied in detail because it can not be expected to have the same characteristics of durability as a glass.

Each gram of the WCF calcine used to prepare the radioactive glass contained 10.5 mCi of cesium-137, 7.6 mCi of strontium-90, 25 mCi of cerium-144, and 1.4 mCi of ruthenium-106. Detailed data on the fission product content of the glass is given in Appendix A. Essentially all of the cesium, strontium, and cerium in the original calcine remained in the glass during formation. Most of the ruthenium apparently volatilized during the formation of the glass. This phenomenon, characteristic of most high temperature waste processes, was not studied in detail in the current work. Presumably, the volatile ruthenium can be adequately absorbed because it has been removed from off-gas streams in the WCF to levels which are well below the Radiation Concentration Guide (RCG) limit. Other fission products, such as zirconium-95 and niobium-95, were present in the glass, but the concentration in the leachate was too low, relative to the other fission products, to be determined accurately.

3. Effect of Treatments on Glass

To prepare uniform specimens of the glass for testing, the specimens were annealed by cooling slowly. The samples were examined with a polaroscope, and no residual stresses were found. Similar glass, prepared from non-radioactive calcine, which was cooled by quenching in air to room temperature, had considerable residual stress. Details of cooling and annealing are discussed in Appendix A.

Prior to the formation of radioactive glass, a non-radioactive glass was irradiated in the MTR Gamma Facility to determine the effect of irradiation. Segments of four specimens of glass were irradiated in an air-filled tube at an equilibrium temperature of about 200°C to a total dose of 10^{10} R. The non-irradiated and irradiated portions of these specimens are shown in Figure 2. These specimens varied in composition, degree of fusion, and quantities of alpha alumina in the original calcine, but in all cases, the glass was darkened by radiation. At an initial dose of 2×10^7 R, the specimens were only slightly brown, but the discoloration increased with irradiation dosage until they were

Fig. 2 Effect of irradiation on alumina-phosphate glasses:
 (A & D) Glass containing 25 weight percent amorphous alumina calcine,
 (B) Glass containing 33 weight percent amorphous alumina calcine,
 (C) Glass containing 25 weight percent calcine prepared from calcine
 containing 58 percent alpha alumina. Darkened specimens are those
 irradiated at 200°C to a total dose of 10^{10} R.

entirely black and opaque at 10^{10} R. X-ray diffraction analysis of the irradiated glass specimens indicated no crystallinity, showing that the glass had not devitrified during the irradiation period.

Two of the radioactive specimens of glass prepared from full-level calcine from the WCF were heat-treated at 450°C for 30 days to simulate short-term storage. The vitreous glass formed by molding is shown on the left in Figure 3, and the heat treated specimen is shown on the right. The heat treatment thoroughly devitrified the glass. X-ray diffraction analysis showed that lead phosphate was the predominant crystalline component in the devitrified specimen, but that the original molded specimen was vitreous. Since devitrification will probably occur during storage due to heat generated by fission products in the waste, determination of the effect of devitrification on the leachability of the glass was included as a prime objective of this study.

IV. LEACHING STUDIES

1. Experimental Technique

The leaching apparatus was specially designed to circulate the liquid and to minimize erosion of the solids, and is described in detail in Appendix B. The radioactive glass specimens, which had about 35 cm^2 of surface area and weighed about 40 grams, were placed in the apparatus, and 500 ml of distilled water was circulated at approximately 100 ml per minute with an air lift. At the end of the leaching period, the leachate

Fig. 3 Vitreous (on the left) and devitrified alumina-phosphate glass prepared from WCF radioactive calcine. The sample on the right was devitrified by heating 30 days at 450°C .

Fig. 4 Relative leachability of aluminum, cesium, and strontium at 25°C

Fig. 5 Effect of devitrification on leachability of alumina-phosphate glass

was completely removed and replaced with fresh distilled water. The leachate was adjusted to a known volume and aluminum was determined by spectroscopy, cesium by gamma spectrometry, and strontium and cerium by radiochemical separation techniques.

2. Leachability of Alumina-Phosphate Glass

The leaching rate of alumina-phosphate glass prepared from full-level radioactive calcine was determined with distilled water at 25° and 94°C using two of the vitreous specimens and the two heat-treated specimens. In order to compare the leaching rate for the various components, the leaching results are normalized to grams of glass leached per square centimeter of surface area per day of leaching. Throughout this report g/cm²-day refers to this unit. Distilled water was used as the leaching liquor for these experiments and measurements of pH showed that the pH remained at 7.0 throughout these experiments, possibly due to a buffering action of the dissolved phosphate glass. The leaching rate was determined for the fission products cesium, strontium, and cerium, and for the glass components aluminum and lead, to determine if a fission product was leached by dissolving the glass or by preferential leaching of the fission product. The high-level of activity made it feasible to use a single molded specimen with a measured surface area rather than crushed glass with the associated difficulties in determining the surface area accurately.

The leaching rate was first determined at 25° ± 1°C using distilled water, and average leaching rates were calculated using data for both the vitreous and devitrified specimens. Figure 4 shows the relative leaching rates for aluminum, cesium, and strontium from the glass. The curve shown in this figure represents the aluminum data. The leaching rate of strontium agrees well with the aluminum leaching rate. The leaching rate for cesium is also similar to that of aluminum although it may be slightly higher during this short-term leaching. The leaching rate determined for cerium-144 in these studies was somewhat lower due to surface treatment of the test specimens, but it was not drastically different from the other leaching rates at 25°C with distilled water (see Appendix B).

The effect of devitrification on leaching was determined using glass specimens which were identical except that two had been devitrified by heating. Figure 5 shows the average leaching curve together with the data points for the vitreous glass and the devitrified glass. These points are average values for the cesium, strontium, and aluminum data. As can be seen on Figure 5, the glass which was devitrified by heating for one month at 450°C has the same leaching rate as the vitreous glass.

The glass also was leached at 94°C ± 1°C (boiling point) in distilled water. As shown in Figure 6, the leaching rate for aluminum at this higher temperature was approximately two orders of magnitude higher than at 25°C. No initial accelerated leaching rate occurred at 94°C because the same specimens were used that had been used in the 25°C experiments. The leaching rates of the fission products strontium, cerium and cesium relative to the leaching rates of the glass components aluminum and lead at 94°C are shown in Figure 7. At this temperature,

Fig. 6 Effect of temperature on leachability of aluminum from glass

Fig. 7 Relative leachability of fission products and glass components at 94°C

the leaching rate for cesium is approximately four times as high as the leaching rate for aluminum. A long-term leaching study is needed to determine whether this higher rate continues or whether it levels off once the surface is depleted of the cesium. The leaching rates for cerium and strontium are similar to the leaching rate of the glass component, lead. This is probably related to the low solubility of the phosphates of these metal ions.

The leaching rates for vitreous and devitrified glass were compared at 94°C for aluminum, cesium, cerium, and strontium (see Appendix B). Although there is considerable scatter in the data, apparently no difference exists between the vitreous and the devitrified glass, even at 94°C.

3. Comparison of Leachability of Alumina-Phosphate Glass and WCF Calcine

The leaching rate for some solid forms of waste, such as WCF calcine, is determined as percent leached per day because the surface area is not known and the rate cannot be determined as g/cm²-day. In order to compare the leaching rate for glass to the leaching rate of other solid wastes, the rate for the glass was also calculated as the percent of either fission product or glass component leached per day. This value is, of course, dependent upon the surface area of the glass. However, glass will probably be stored in larger volumes than the test

Fig. 8 Relative leachability of cesium and strontium from calcine and glass

specimens, and therefore the surface area-to-weight ratio will be lower and the percent leached per day will be less than the values reported.

Approximately 95 percent of the cesium and 35 percent of the strontium were leached from the WCF calcine in seven weeks⁽⁵⁾ at 25°C with distilled water while only 0.005 to 0.01 percent of the cesium and strontium were leached from the glass using the same conditions, as shown in detail in Appendix B. In Figure 8, the leaching rate of the glass is compared to the leaching rates of the WCF calcine for both cesium and strontium⁽⁵⁾. This curve shows that even after 95 percent of the cesium and 35 percent of the strontium are leached, the leaching rate of the calcine is still much higher than the leaching rate for the glass.

V. CONCLUSIONS

The following conclusions have been made from this work:

- (1) Alumina-phosphate glass can be prepared from radioactive calcined alumina produced by the fluidized bed calcination process. A vitreous and homogeneous glass can be formed, and by cooling slowly, it can be thoroughly annealed.
- (2) Irradiation per se does not cause devitrification up to a total dose of 10^{10} R; however, heating for 30 days at 450°C thoroughly devitrifies the alumina-phosphate glass.
- (3) At 25°C, distilled water leaches the cesium and the strontium at the same rate as the aluminum; ie, the leach rate is dependent on the rate of dissolution of the glass.
- (4) At 94°C, cesium is leached faster than the aluminum, while the strontium, the cerium and the lead component of the glass are leached at a considerably slower rate than aluminum. Long-term leaching studies are needed to determine if this trend continues.
- (5) Devitrification of alumina-phosphate glass by heating at 450°C for one month does not increase the leaching rate with distilled water at either 25°C or 94°C provided a good vitreous glass was formed initially by using the correct composition and by fusing until the glass is homogeneous.
- (6) Because the fission products are leached at a much lower rate from the glass than from the calcine, the glass would undoubtedly be a more suitable form for storage of highly radioactive waste in areas where a reasonable possibility exists that ground water may contact the waste.

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APPENDIX A

PREPARATION AND EXAMINATION OF ALUMINA-PHOSPHATE GLASS

PREPARATION AND EXAMINATION OF ALUMINA-PHOSPHATE GLASS

1. Preparation of Alumina Phosphate Glass

Various compositions for alumina-phosphate glasses, containing lead oxide to lower the fusion temperature, have been studied previously at Oak Ridge National Laboratory⁽²⁾. In addition, a ternary plot has been published for the glass forming range of the Al_2O_3 - P_2O_5 - Na_2O system⁽⁶⁾. The optimum composition for alumina-phosphate glass was selected from these earlier works. Most of the earlier work involved the addition of sodium hypophosphite to aluminum nitrate solution prior to calcination and fusion. In the current work with WCF calcine, a technique was devised for producing glass directly from the calcined alumina by preparing a number of glass specimens from non-radioactive calcine produced in the final WCF cold run. Sodium monobasic phosphate was used as a source of phosphate for the direct fusion of the calcined alumina.

In the technique developed, sodium monobasic phosphate, lead oxide, and alumina calcine are mixed as dry solids. The mixture is heated for two hours at 400°C to dehydrate and convert the phosphate to sodium metaphosphate. The mixture is then heated at 600°C for another two hours to enable the phosphate to react slowly with small amounts of residual nitrate in the calcined alumina. This stepwise heating is necessary to avoid excessive foaming which occurred when the mixture was heated rapidly to fusion temperature. The foaming was not as evident using the radioactive calcine. The mixture is then fused at 900°C for 16 hours. Mixing is not required during the heating cycle to form a homogeneous glass.

1.1 Conversion of Sodium Monobasic Phosphate to Sodium Metaphosphate

Studies of the stepwise heating and fusion of the mixed alumina calcine, lead oxide, and sodium monobasic phosphate showed that unconverted sodium monobasic phosphate remained after heating for one hour at 400°C . No further change occurred upon heating for an additional 20 hours. In the intermediate heating step at 600°C , the sodium monobasic phosphate was entirely converted to amorphous sodium metaphosphate in two hours. Converting sodium monobasic phosphate to sodium metaphosphate prior to mixing with the oxides did not eliminate the need for an intermediate heating step at 600°C .

1.2 Fusion of Glass

In fusions made at 900°C with amorphous alumina produced in the WCF, unfused amorphous alumina remained in the bottom of the crucible after 6 hours, but the fusion was complete in 16 hours. Fusions using calcine from the pilot plant containing 58 percent alpha alumina were not homogeneous in 16 hours at 900°C , and an additional 50 hours of heating resulted in no further change. Exhibit C in Figure 2 in the text shows the glass produced by fusion of calcine containing 58 percent alpha alumina. Exhibit B in Figure 2 in the text shows the specimen

produced using 33 weight percent amorphous calcine instead of the usual 25 weight percent and fusing a total of 42 hours. Although the fusions were not homogeneous, apparently no alumina remained since both samples darkened uniformly during the irradiation test.

Fusion vessels made from a number of different materials were used. Porcelain crucibles were the most satisfactory for the fusion, but analysis of the glass indicated that some silica from the crucible had reacted with the glass. Iron and nickel crucibles were unsuitable because of high corrosion. Platinum crucibles corroded slightly and caused the discoloration shown in Figure 1 in the text, a phenomenon caused by most impurities. Graphite crucibles were tried for fusing to find a single material in which the glass could be both fused and molded. The glass components were placed in a graphite crucible and covered with a layer of powdered graphite to create an inert atmosphere during part of the fusion. Figure A-1 shows the graphite crucible and glass after fusion. Oxidation consumed the upper portion of the crucible and created an indentation in the crucible which prevented the release of the glass from the mold after cooling. In addition, the glass was cracked from stresses created during the cooling.

1.3 Molding of Glass Specimens

Small discs of glass were molded on cold stainless steel surfaces. Discs of this type were prepared from each fusion for analysis. Nickel, iron, platinum, or porcelain crucibles can be used as molds,

provided an adequate mold release is used. A thin coat of thorium oxide was tried as a mold release, but it migrated through the glass during the cooling and caused cracking. Aquadag, a colloidal suspension of graphite in water, worked well when it was applied to the mold and dried before use. However, pouring glass into the mold at temperatures higher than 600°C destroyed the mold release properties of the Aquadag, and pouring glass into molds at 400°C caused an excessive amount of residual stresses. At 600°C, a sufficient layer of Aquadag remained on the mold to function as a mold release, but the surface of the glass contained small pits such as those on the bottom surface of exhibit D in Figure 2 in the text. This was probably caused by oxidation of the Aquadag. Crucibles fabricated to known dimensions from reactor grade graphite were used to mold radioactive specimens remotely; the graphite molds did not retain their

Fig. A-1 Alumina-phosphate glass fused and cooled in a graphite crucible

mold release characteristics for a second use.

1.4 Annealing of Glass

All glass specimens were examined polariscopically for residual stresses. Glass quenched to room temperature in air was highly stressed and in some cases disintegrated spontaneously. Glass which had been stressed was not successfully annealed by heating because devitrification occurred too readily. Glass cooled from 900°C to 600°C during the molding was thoroughly annealed by cooling from 600°C to room temperature over a 4 to 5 hour period in a crucible furnace. Due to the high coefficient of expansion, the glass sometimes cracked when the temperature was changed rapidly between 100°C and room temperature. Even though the radioactive glass was quite dark in color due to impurities and radiation effects, a strong beam of light could be seen through the glass specimens making it possible to examine the radioactive glass with a polariscope. No residual stresses were detected in the radioactive specimens.

1.5 Preparation and Heat Treatment of Radioactive Glass

Six glass specimens were prepared remotely from full-level radioactive calcine from the WCF(1). Two of the glass specimens were heated at 450°C for 30 days in new graphite crucibles in a crucible furnace. This treatment was intended to devitrify the glass and to simulate short-term storage. A small amount of graphite from the molding crucibles adhered to the glass specimens, and was removed from the non-heat treated specimens by immersing in 6M nitric acid for approximately 10 minutes. The surface of the heat treated glass was clean and did not require washing. Some of the characteristics of the six radioactive specimens and fission product concentrations are presented in Table A-I.

2. Composition of the Glass

The glass was prepared from 25 weight percent WCF calcine so as to contain approximately 40.5 percent P_2O_5 , 25 weight percent Al_2O_3 , 18.6 percent Na_2O , and 15.9 PbO . According to previous work(2) using aluminum nitrate waste solution, this was the most satisfactory composition for alumina-phosphate glass with respect to physical properties. Since the calcine contained less than 100 percent alumina, the glass was dissolved and analyzed to determine the exact composition of the glass. Table A-II presents the analysis for the six radioactive specimens together with the material balance for the glass components. The average composition of the specimens was 19.5 percent Al_2O_3 , 41.8 percent P_2O_5 , 16.7 percent PbO , and 18.4 percent Na_2O . Mercury, which was present in the calcined alumina at 2.0 weight percent, was volatilized during the fusion and less than 0.1 percent of the original mercury remained in the glass.

Each gram of calcine contained 10.5 millicuries of cesium-137, 7.6 millicuries of strontium-90, 26 millicuries of cerium-144, and 1.4 millicuries of ruthenium-106. The percent of fission products in the

Table A-I

SOME PHYSICAL CHARACTERISTICS AND FISSION PRODUCT COMPOSITIONS OF RADIOACTIVE SPECIMENS

Specimen Number	Weight Grams	Surface Area, cm ² (1)		Fission Product Concentration in the Glass, d/(min)(g)			
		Before Cracking	After Cracking	Cs-137	Sr-90	Ce-144 ⁽²⁾	Ru-106
1	35.4	33.8	-	5.80×10^9	5.67×10^9	1.33×10^{10}	-
2	42.9	36.6	-	5.45×10^9	5.29×10^9	1.35×10^{10}	-
3	45.1	37.2	43.0	5.54×10^9	5.75×10^9	1.23×10^{10}	1.0×10^7
4	48.8	38.5	44.0	5.74×10^9	5.62×10^9	1.27×10^{10}	6.2×10^6
5	48.9	44.4	Not Cracked	5.88×10^9	6.37×10^9	1.42×10^{10}	7.9×10^6
6	46.7	38.0	Not Cracked	5.73×10^9	5.67×10^9	1.30×10^{10}	6.0×10^6
Average				5.69×10^9	5.73×10^9	1.32×10^{10}	-

(1) Glass specimen cracked from thermal shock during leaching studies at 94°C.

(2) Ce-144 corrected for decay: 1.1×10^{10} d/(min)(g) for date of 25°C run
 9.6×10^9 d/(min)(g) for date of 94°C run.

Table A-II

CHEMICAL COMPOSITION OF RADIOACTIVE GLASS

Specimen Number	Weight Percent					Material Balance
	Al_2O_3	P_2O_5	PbO	Na_2O	SiO_2	Total Weight %
1	18.6	41.5	16.9	18.3	0.3	95.6
2	19.5	41.3	16.9	18.2	0.2	96.1
3	19.6	42.4	16.8	18.7	2.1	99.6
4	19.8	42.2	16.7	18.6	1.7	99.0
5	20.0	41.7	16.2	18.4	2.4	98.7
6	19.6	41.8	16.8	18.4	0.9	97.5
Average	19.5	41.8	16.7	18.4	1.3	97.8

original calcine which remain in the glass during formation of the glass is shown in Table A-III. Since the chemical analyses are so similar for the six specimens, the deviations in the fission product values are believed to be analytical errors. This data shows that essentially all of the cesium, strontium, and cerium remained in the glass during the formation of the glass. The value was high for strontium throughout most of this work, indicating that the strontium value for the original calcine was low. The data for ruthenium shown in Table A-III indicated that most of the ruthenium was volatilized, but a material balance during the formation of the glass is not available. Some of the ruthenium in the original liquid waste was volatilized during calcination, but it was successfully removed from the off-gas during the operation of the WCF. Presumably, the ruthenium which may be volatilized during the formation of the glass can be satisfactorily removed from the off-gas by the same procedure.

The homogeneity of the fused glass specimens was determined by slicing each of five non-radioactive specimens into six vertical segments. Two of the six segments were analyzed for lead oxide, phosphorus pentoxide, and aluminum oxide. Table A-IV shows the results of an analysis of two of the segments from each of the specimens. These data show that the glass was homogeneous in all three components.

Table A-III

PERCENT FISSION PRODUCTS REMAINING IN GLASS DURING FUSION

Based on 25 Weight Percent Calcine in Glass

Specimen Number	<u>Cs-137</u> (%)	<u>Sr-90</u> (%)	<u>Ce-144</u> (%)	<u>Ru-106</u> (%)
1	100	134	93	-
2	94	125	94	-
3	95	136	86	1.3
4	99	133	88	0.8
5	101	151	99	1
6	98	134	91	0.7
Average	98	136	92	-

Table A-IV

HOMOGENEITY OF EXPERIMENTAL GLASS

<u>Specimen Number</u>	<u>Slice No.*</u>	<u>PbO</u>	<u>P₂O₅</u>	<u>Al₂O₃</u>
1	1	17.0	43.1	19.1
	3	17.1	43.2	19.1
2	2	16.1	42.0	23.5
	6	16.6	41.6	23.2
3	2	16.9	42.0	20.6
	5	16.9	42.2	20.6
4	2	15.5	44.3	19.3
	5	15.5	44.3	19.4
5	2	16.9	42.8	20.5
	4	17.0	42.1	20.1

* Each non-radioactive specimen sliced vertically into six segments.

APPENDIX B

THE LEACHING OF ALUMINA-PHOSPHATE GLASS

THE LEACHING OF ALUMINA-PHOSPHATE GLASS

A pyrex apparatus was designed for leaching calcined alumina⁽⁵⁾ and glass. Figure B-1 shows the apparatus which was used to leach glass at 94°C. The glass specimens are placed in the reservoir and 500 ml of distilled water added. The air lift circulates the water at approximately 100 ml/min. The upper portion of the apparatus is a disengager which prevents excessive motion of leachate in the reservoir. The water in the reservoir is heated to boiling with the heating tape and a condenser is attached for high temperature runs. A simpler apparatus, which is an open system consisting of only the reservoir, air lift, and disengager, was used for the 25°C experiments. At the end of each leaching period, the leachate was removed through the side access lip, transferred to a calibrated vessel, and made to a known volume. The aluminum was determined by spectroscopy. In experiments at 25°C, where the aluminum concentrations were very low, the leachate was concentrated by evaporation before analysis. Lead was also analyzed by spectroscopy after concentrating the samples by evaporation. Cesium was analyzed with a gamma spectrometer using a spectrum stripping technique. Strontium was separated by radiochemical techniques for analysis, and cerium was also determined by radiochemical separations, because the quantity of cerium relative to cesium was too low to determine cerium accurately by a spectrum stripping technique.

Due to the high-level of activity in the radioactive specimens, the leaching experiments were performed remotely. Four leaching apparatus were installed in a 34-inch wide cave equipped with Castle manipulators. The glass specimens were placed in the apparatus shown in Figure B-1, and the apparatus was assembled, and later disassembled, remotely. The operation of the apparatus during the leaching experiments was simple, and the cost of installing this type of circulating system was low. No difficulty was encountered with this type of apparatus during four separate experiments, each of which was of seven weeks duration.

The surface area of the glass specimen was determined quite accurately by using molds machined from reactor grade graphite and measuring the height of the molded specimen remotely. No allowance was made for surface roughness; however, the cold specimens molded in graphite molds showed only a very small degree of visible surface roughness. In any case, this was not a factor in making comparisons between samples, because the surface was uniform for all six radioactive specimens.

Leaching rates were determined as grams of glass per cm²-day for the glass using distilled water at 25° ± 1°C and 94°C. Detailed data are reported in Table B-I for these leaching experiments, and the results are discussed in the text. Specimens numbered 3 and 4 were vitreous while specimens numbered 5 and 6 were devitrified by the heat treatment. At 25°C, the first sampling was made at the end of 24 hours. At 94°C the first sampling was made at the end of seven days. There was insufficient sample for aluminum analysis in the first five leaching periods at 25°C. Samples from the 25°C leaching had too low a concentration of

Fig. B-1 Apparatus for leaching glass at 94°C

Table B-I
LEACHING RATES FOR ALUMINA-PHOSPHATE GLASS WITH DISTILLED WATER

Time from Start of Test	Sample Numbers*	Grams of glass/cm ² -day									
		25°C ± 1°C					94°C ± 1°C				
		Al**	Cs-137	Sr-90	Ce-144	Al	Pb	Cs-137	Sr-90	Ce-144	
1 day	3	--	1.6 x 10 ⁻⁵	1.3 x 10 ⁻⁵	2.3 x 10 ⁻⁶	--	--	--	--	--	
	4	--	3.3 x 10 ⁻⁶	7.3 x 10 ⁻⁶	2.1 x 10 ⁻⁶	--	--	--	--	--	
	5	1.9 x 10 ⁻⁵	1.1 x 10 ⁻⁴	6.1 x 10 ⁻⁵	3.9 x 10 ⁻⁷	--	--	--	--	--	
	6	1.1 x 10 ⁻⁵	3.2 x 10 ⁻⁵	2.9 x 10 ⁻⁵	1.4 x 10 ⁻⁷	--	--	--	--	--	
2 days	3	--	1.0 x 10 ⁻⁵	1.2 x 10 ⁻⁵	1.0 x 10 ⁻⁶	--	--	--	--	--	
	4	5.7 x 10 ⁻⁶	2.5 x 10 ⁻⁶	3.3 x 10 ⁻⁶	1.2 x 10 ⁻⁶	--	--	--	--	--	
	5	--	1.2 x 10 ⁻⁵	4.4 x 10 ⁻⁶	1.7 x 10 ⁻⁷	--	--	--	--	--	
	6	1.4 x 10 ⁻⁵	7.7 x 10 ⁻⁶	1.9 x 10 ⁻⁶	1.9 x 10 ⁻⁷	--	--	--	--	--	
4 days	3	--	1.5 x 10 ⁻⁶	1.5 x 10 ⁻⁶	6.4 x 10 ⁻⁷	--	--	--	--	--	
	4	1.5 x 10 ⁻⁶	1.4 x 10 ⁻⁶	1.2 x 10 ⁻⁶	5.2 x 10 ⁻⁷	--	--	--	--	--	
	5	--	2.5 x 10 ⁻⁶	8.4 x 10 ⁻⁷	3.5 x 10 ⁻⁸	--	--	--	--	--	
	6	5.2 x 10 ⁻⁶	6.0 x 10 ⁻⁶	1.0 x 10 ⁻⁶	6.6 x 10 ⁻⁸	--	--	--	--	--	
1 week	3	--	8.2 x 10 ⁻⁶	9.8 x 10 ⁻⁶	--	1.3 x 10 ⁻⁵	4.1 x 10 ⁻⁶	3.1 x 10 ⁻⁵	1.4 x 10 ⁻⁶	1.6 x 10 ⁻⁶	
	4	3.3 x 10 ⁻⁶	2.3 x 10 ⁻⁶	2.9 x 10 ⁻⁶	1.5 x 10 ⁻⁶	2.7 x 10 ⁻⁵	6.0 x 10 ⁻⁶	8.6 x 10 ⁻⁵	1.3 x 10 ⁻⁶	3.3 x 10 ⁻⁶	
	5	--	4.4 x 10 ⁻⁶	7.3 x 10 ⁻⁷	3.8 x 10 ⁻⁸	1.0 x 10 ⁻⁴	2.1 x 10 ⁻⁶	1.4 x 10 ⁻⁴	7.1 x 10 ⁻⁷	1.1 x 10 ⁻⁶	
	6	3.7 x 10 ⁻⁶	5.7 x 10 ⁻⁶	1.1 x 10 ⁻⁶	1.5 x 10 ⁻⁷	1.0 x 10 ⁻⁵	1.2 x 10 ⁻⁶	7.5 x 10 ⁻⁵	2.7 x 10 ⁻⁶	2.0 x 10 ⁻⁷	
2 weeks	3	1.4 x 10 ⁻⁶	7.3 x 10 ⁻⁷	1.2 x 10 ⁻⁶	3.1 x 10 ⁻⁷	2.6 x 10 ⁻⁶	3.7 x 10 ⁻⁶	2.0 x 10 ⁻⁴	1.3 x 10 ⁻⁶	4.4 x 10 ⁻⁶	
	4	--	1.6 x 10 ⁻⁶	2.3 x 10 ⁻⁶	2.1 x 10 ⁻⁶	3.3 x 10 ⁻⁵	2.9 x 10 ⁻⁶	3.2 x 10 ⁻⁴	1.3 x 10 ⁻⁶	7.8 x 10 ⁻⁶	
	5	8.7 x 10 ⁻⁷	2.6 x 10 ⁻⁶	2.4 x 10 ⁻⁷	1.6 x 10 ⁻⁸	1.2 x 10 ⁻⁴	2.1 x 10 ⁻⁶	2.3 x 10 ⁻⁴	3.5 x 10 ⁻⁷	1.2 x 10 ⁻⁶	
	6	--	5.6 x 10 ⁻⁶	2.2 x 10 ⁻⁶	6.4 x 10 ⁻⁸	8.3 x 10 ⁻⁶	8.5 x 10 ⁻⁷	1.9 x 10 ⁻⁴	3.9 x 10 ⁻⁷	1.8 x 10 ⁻⁷	
3 weeks	3	9.9 x 10 ⁻⁷	1.1 x 10 ⁻⁶	3.6 x 10 ⁻⁷	1.1 x 10 ⁻⁷	--	--	--	--	--	
	4	5.4 x 10 ⁻⁷	4.8 x 10 ⁻⁷	4.7 x 10 ⁻⁷	2.2 x 10 ⁻⁷	3.6 x 10 ⁻⁵	1.0 x 10 ⁻⁶	4.1 x 10 ⁻⁴	1.6 x 10 ⁻⁷	7.7 x 10 ⁻⁶	
	5	3.9 x 10 ⁻⁷	1.7 x 10 ⁻⁶	2.0 x 10 ⁻⁷	1.0 x 10 ⁻⁸	9.8 x 10 ⁻⁵	1.8 x 10 ⁻⁶	2.3 x 10 ⁻⁴	4.2 x 10 ⁻⁷	2.9 x 10 ⁻⁷	
	6	5.5 x 10 ⁻⁷	1.9 x 10 ⁻⁶	7.2 x 10 ⁻⁷	1.4 x 10 ⁻⁸	1.8 x 10 ⁻⁵	7.3 x 10 ⁻⁷	1.7 x 10 ⁻⁵	1.8 x 10 ⁻⁷	--	
4 weeks	3	5.4 x 10 ⁻⁷	4.0 x 10 ⁻⁷	2.2 x 10 ⁻⁷	5.0 x 10 ⁻⁷	4.4 x 10 ⁻⁵	4.0 x 10 ⁻⁶	3.4 x 10 ⁻⁴	9.3 x 10 ⁻⁶	5.5 x 10 ⁻⁶	
	4	3.4 x 10 ⁻⁷	6.8 x 10 ⁻⁷	5.7 x 10 ⁻⁷	2.8 x 10 ⁻⁷	3.1 x 10 ⁻⁵	2.1 x 10 ⁻⁶	2.5 x 10 ⁻⁴	9.6 x 10 ⁻⁶	5.1 x 10 ⁻⁶	
	5	7.2 x 10 ⁻⁷	1.8 x 10 ⁻⁶	2.9 x 10 ⁻⁷	1.0 x 10 ⁻⁴	8.7 x 10 ⁻⁵	9.2 x 10 ⁻⁶	2.1 x 10 ⁻⁴	2.4 x 10 ⁻⁷	4.9 x 10 ⁻⁶	
	6	4.4 x 10 ⁻⁷	2.0 x 10 ⁻⁶	2.3 x 10 ⁻⁷	2.5 x 10 ⁻⁸	3.1 x 10 ⁻⁵	1.1 x 10 ⁻⁶	3.4 x 10 ⁻⁵	3.2 x 10 ⁻⁶	4.6 x 10 ⁻⁸	
5 weeks	3	4.5 x 10 ⁻⁷	1.3 x 10 ⁻⁶	2.9 x 10 ⁻⁷	1.4 x 10 ⁻⁷	--	--	--	--	--	
	4	5.4 x 10 ⁻⁷	3.5 x 10 ⁻⁷	5.2 x 10 ⁻⁷	1.0 x 10 ⁻⁷	6.6 x 10 ⁻⁵	1.7 x 10 ⁻⁶	4.7 x 10 ⁻⁴	6.2 x 10 ⁻⁷	1.1 x 10 ⁻⁶	
	5	3.9 x 10 ⁻⁷	5.1 x 10 ⁻⁷	1.1 x 10 ⁻⁷	1.2 x 10 ⁻⁸	1.2 x 10 ⁻⁴	6.6 x 10 ⁻⁶	2.5 x 10 ⁻⁴	4.0 x 10 ⁻⁶	9.8 x 10 ⁻⁷	
	6	5.1 x 10 ⁻⁷	3.0 x 10 ⁻⁶	1.3 x 10 ⁻⁷	2.3 x 10 ⁻⁸	3.7 x 10 ⁻⁵	1.2 x 10 ⁻⁶	4.5 x 10 ⁻⁴	8.6 x 10 ⁻⁷	1.4 x 10 ⁻⁶	
6 weeks	3	1.0 x 10 ⁻⁸	8.6 x 10 ⁻⁷	1.0 x 10 ⁻⁶	5.6 x 10 ⁻⁷	5.0 x 10 ⁻⁵	1.7 x 10 ⁻⁶	3.6 x 10 ⁻⁴	3.2 x 10 ⁻⁷	2.7 x 10 ⁻⁶	
	4	5.8 x 10 ⁻⁷	5.0 x 10 ⁻⁷	6.8 x 10 ⁻⁷	3.7 x 10 ⁻⁷	7.4 x 10 ⁻⁵	3.1 x 10 ⁻⁶	4.5 x 10 ⁻⁴	2.2 x 10 ⁻⁶	9.7 x 10 ⁻⁶	
	5	3.1 x 10 ⁻⁷	8.1 x 10 ⁻⁷	8.4 x 10 ⁻⁸	7.3 x 10 ⁻⁹	1.1 x 10 ⁻⁴	1.1 x 10 ⁻⁵	2.3 x 10 ⁻⁴	3.8 x 10 ⁻⁶	1.1 x 10 ⁻⁵	
	6	2.4 x 10 ⁻⁷	1.0 x 10 ⁻⁶	9.7 x 10 ⁻⁸	8.0 x 10 ⁻⁹	4.4 x 10 ⁻⁵	1.3 x 10 ⁻⁶	9.2 x 10 ⁻⁵	4.7 x 10 ⁻⁷	1.7 x 10 ⁻⁶	
7 weeks	3	3.7 x 10 ⁻⁷	8.0 x 10 ⁻⁷	9.8 x 10 ⁻⁷	2.3 x 10 ⁻⁷	3.1 x 10 ⁻⁵	7.0 x 10 ⁻⁶	2.6 x 10 ⁻⁵	2.0 x 10 ⁻⁶	5.1 x 10 ⁻⁶	
	4	2.9 x 10 ⁻⁷	3.9 x 10 ⁻⁷	5.7 x 10 ⁻⁷	8.1 x 10 ⁻⁸	4.7 x 10 ⁻⁵	3.0 x 10 ⁻⁶	4.1 x 10 ⁻⁴	1.8 x 10 ⁻⁶	2.5 x 10 ⁻⁶	
	5	1.9 x 10 ⁻⁷	7.3 x 10 ⁻⁷	8.9 x 10 ⁻⁸	< 10 ⁻⁸	5.3 x 10 ⁻⁵	6.9 x 10 ⁻⁶	1.3 x 10 ⁻⁴	2.3 x 10 ⁻⁶	4.3 x 10 ⁻⁶	
	6	3.3 x 10 ⁻⁷	8.5 x 10 ⁻⁷	1.1 x 10 ⁻⁷	< 10 ⁻⁸	2.9 x 10 ⁻⁵	2.9 x 10 ⁻⁶	6.8 x 10 ⁻⁵	7.2 x 10 ⁻⁷	1.6 x 10 ⁻⁶	

* Numbers 3 and 4 were vitreous and 5 and 6 were devitrified by heating 1 month at 450°C.

** Insufficient sample for analysis in some cases.

lead to analyze by the lead method used. During two of the leaching periods at 94°C, data were not reported for sample 3 because the tape heater was not functioning properly.

As reported in the text, the leaching rates for cesium and strontium follow the leaching rate for aluminum at 25°C. Figure B-2 compares the cerium data with the aluminum leaching rate. The leaching rate for cerium from the devitrified samples is considerably lower than the leaching rate for aluminum. During the heat treatment the carbon crucibles became highly radioactive, apparently from cerium absorbed from the surface of these specimens. The vitreous samples, however, were washed with nitric acid which apparently removed most of the cerium deficient surface from the vitreous glass samples, and the cerium leaching rates are closer to the aluminum curve. At 94°C, the leaching rate for cerium followed the rate for lead and strontium. However, the leaching rate for cerium has not been included in the average leaching rates for the glass.

As reported in the text, the comparison of the average values for cesium, strontium, and aluminum for the vitreous and devitrified samples showed that the heat treatment did not affect the leaching rate at 25°C. Since the leaching rates are not the same for various fission products and aluminum at 94°C, a meaningful average value for the vitreous and for the devitrified samples could not be calculated. Figure B-3 shows a comparison of the data for the vitreous and the devitrified glass for each of the components and fission products in the glass. Although there

Fig. B-2 Relative leachability of cerium and aluminum from glass

Fig. B-3 Effect of devitrification on leaching rates at 94°C

is considerable scatter in the data at 94°C, there is no evidence of any effect of devitrifying the glass by heat treatment.

The cumulative percent of glass leached is presented in Table B-II for the glass components aluminum and lead and the fission products cesium, strontium, and cerium. The cumulative percent leached was calculated from the percent of the component leached per day. Since glass stored in larger volume will probably have a lower surface area-to-weight ratio than these test specimens, the radioactivity leached for a given period during actual storage of glass probably will be less than these reported values.

Table B-II
CUMULATIVE PERCENT OF GLASS COMPONENTS AND FISSION PRODUCTS LEACHED

Time from Start of Test	Average of Four Experiments with Distilled Water							
	25°C + 1°C			94°C + 1°C				
	Al	Cs-137	Sr-90	Al	Pb	Cs-137	Sr-90	Ce-144*
1 day	1.2×10^{-3}	3.5×10^{-3}	2.4×10^{-3}	--	--	--	--	--
2 days	2.0×10^{-3}	4.3×10^{-3}	2.9×10^{-3}	--	--	--	--	--
4 days	2.8×10^{-3}	4.7×10^{-3}	3.1×10^{-3}	--	--	--	--	--
1 week	3.6×10^{-3}	6.0×10^{-3}	4.0×10^{-3}	2.3×10^{-2}	2.0×10^{-3}	5.0×10^{-2}	9.1×10^{-4}	1.5×10^{-3}
2 weeks	4.3×10^{-3}	7.5×10^{-3}	4.7×10^{-3}	5.3×10^{-2}	3.4×10^{-3}	1.6×10^{-1}	1.4×10^{-3}	5.0×10^{-3}
3 weeks	5.7×10^{-3}	8.4×10^{-3}	4.9×10^{-3}	8.3×10^{-2}	4.2×10^{-3}	3.3×10^{-1}	2.0×10^{-3}	8.3×10^{-3}
4 weeks	6.9×10^{-3}	9.0×10^{-3}	5.1×10^{-3}	1.2×10^{-1}	6.8×10^{-3}	4.6×10^{-1}	5.6×10^{-3}	1.2×10^{-2}
5 weeks	8.0×10^{-3}	9.5×10^{-3}	5.3×10^{-3}	1.6×10^{-1}	8.8×10^{-3}	7.0×10^{-1}	6.8×10^{-3}	1.3×10^{-2}
6 weeks	9.2×10^{-3}	9.9×10^{-3}	5.5×10^{-3}	2.0×10^{-1}	1.3×10^{-2}	8.8×10^{-1}	8.6×10^{-3}	1.7×10^{-2}
7 weeks	9.9×10^{-3}	1.03×10^{-2}	5.8×10^{-3}	2.4×10^{-1}	1.6×10^{-2}	9.8×10^{-1}	1.06×10^{-2}	1.9×10^{-2}

* Average of two vitreous samples only.

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