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MARTIN MARIETTA

Physical and Chemical Characteristics of Lead-Iron Phosphate Nuclear Waste Glasses

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PHYSICAL AND CHEMICAL CHARACTERISTICS OF LEAD-IRON PHOSPHATE
NUCLEAR WASTE GLASSES

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PHYSICAL AND CHEMICAL CHARACTERISTICS OF LEAD-IRON PHOSPHATE NUCLEAR WASTE GLASSES*

B. C. Sales and L. A. Boatner

ABSTRACT

Experimental determinations of the properties of lead-iron phosphate glasses pertinent to their application to the problem of permanently disposing of high-level nuclear wastes have been carried out. These investigations included studies of the composition and physical properties of nuclear waste glasses (NWG), as well as the effect of preparation conditions. Lead-iron phosphate nuclear waste glasses were prepared by dissolving simulated U.S. defense wastes or simu-simulated commercial power reactor wastes in molten lead-iron phosphate melts at temperatures between 900 and 1050°C. The measured physical and chemical properties of the nuclear waste glasses formed by cooling these melts and annealing included the following: (1) aqueous corrosion resistance as a function of the solution pH, solution temperature, and glass composition, (2) glass density, (3) thermal expansion coefficient, (4) glass transition temperature and softening point, (5) heat capacity, (6) critical cooling rate (7) temperature for the maximum crystallization rate, (8) relative solubility of waste oxides in the glass melt, (9) reactions between the molten glass and the melting crucible (Pt, ZrO_2, Al_2O_3), and (10) studies of possible metal cannister materials. Experimental results for the lead-iron phosphate NWG are compared to available data for borosilicate NWG. Relative to borosilicate NWG, the lead-iron phosphate glasses have several distinct advantages which include a much lower aqueous corrosion rate, a lower preparation temperature, and the ability to immobilize many types of commercial and defense-related high-level radioactive wastes.

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1. INTRODUCTION

Studies of the properties of lead phosphate glasses have been carried out for over 25 years [1-4]. These glasses have been of interest primarily as a result of their low preparation temperatures and low softening points — properties that made them ideal materials for fundamental studies of glass devitrification and the glass transition [5,6]. Commercially, lead phosphate glasses have been of very limited interest because of their poor chemical durability when exposed to aqueous conditions. Recently, however, it was found that the addition of iron oxide to lead phosphate could drastically improve the chemical durability of the resulting glass without substantially raising either the preparation temperature or the melt viscosity [7,8]. The effect of iron on the corrosion characteristics of lead-iron phosphate glasses is illustrated in Fig. 1 where the ionic release into distilled water at 90°C is plotted versus time for several lead-iron phosphate glasses. Although the measured solution conductivity in Fig. 1 is only proportional to the total ionic concentration in the dilute limit (see Sec. 3), quantitative analysis of the lead-iron phosphate leachate solutions for Pb, P, and Fe yield comparable results (i.e., the addition of 9 wt. % iron oxide to lead metaphosphate glass [Pb(PO$_3$)$_2$] increases the chemical durability of the glass in water by a factor of about 10^4). The tendency of pure lead phosphate glasses to crystallize is also greatly suppressed by the addition of iron oxide. Lead metaphosphate glass can be completely crystallized by heating the glass in air at 300°C for several hours. Lead-iron phosphate glasses, however, can be heated in air for several hundred hours at 500°C without exhibiting any evidence of crystallization.

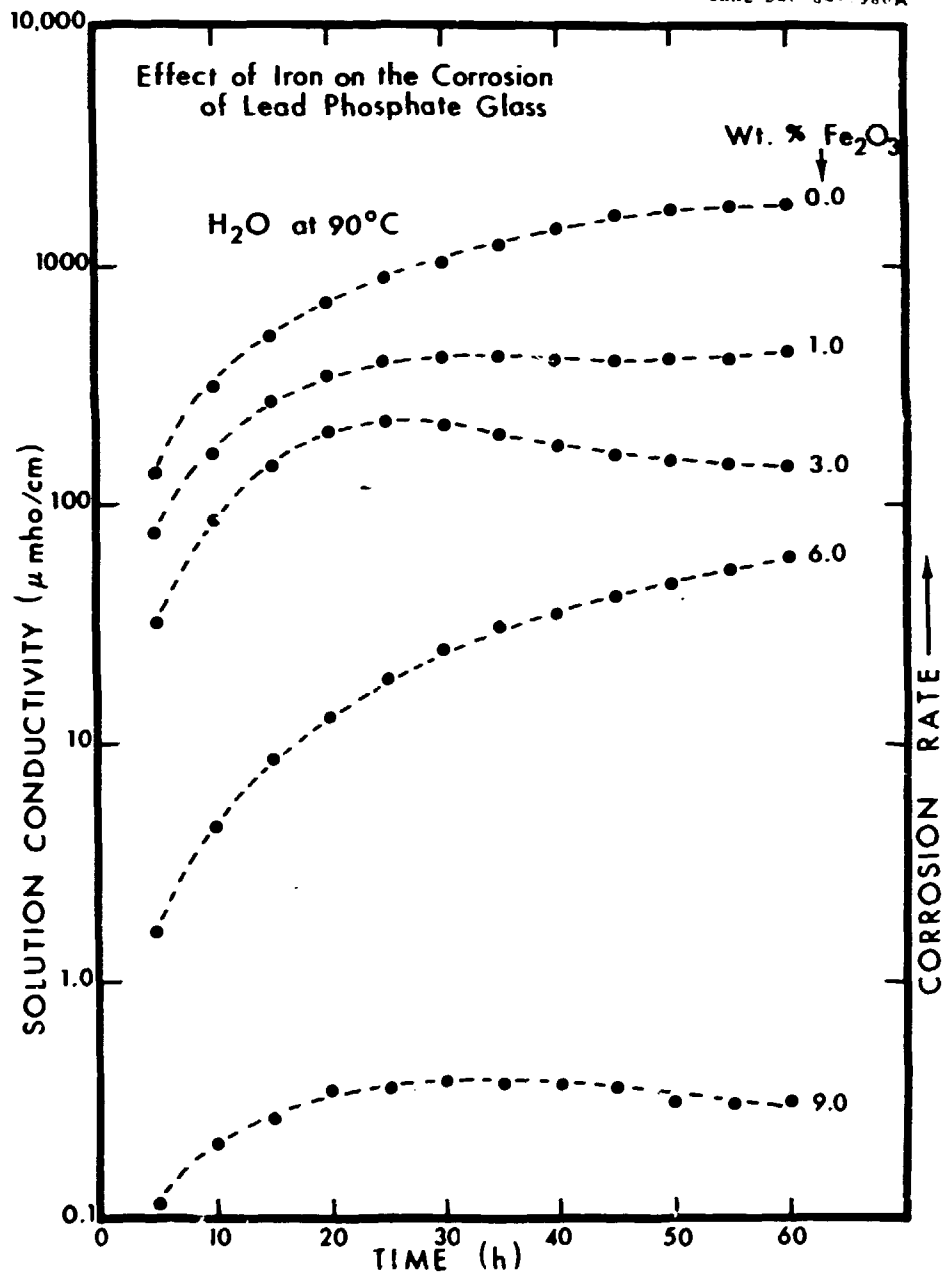Fig. 1. Leachate conductivity versus time for a lead metaphosphate glass [Pb(PO$_3$)$_2$] doped with 0.0, 1.0, 3.0, 6.0, 9.0 percent Fe$_2$O$_3$. The leachate conductivity is roughly proportional to the total ionic concentration released by the glass into solution.

The effects of iron oxide on the structural properties of lead-iron phosphate glasses are being investigated using the techniques of Mössbauer spectroscopy, electron paramagnetic resonance, Raman and infrared spectroscopy [9], EXAFS, low angle X-ray scattering, liquid chromatograry [10], and transmission electron microscopy. Preliminary results of these studies indicate that structurally pure lead metaphosphate glass [$Pb(PO_3)_2$] can be viewed as consisting of a distribution of long chains of PO_4 tetrahedra (average chain length > 15 PO_4 tetrahedra) bonded to adjacent tetrahedra by bridging oxygen atoms. Neighboring polyphosphate chains are then linked together by cross bonding between the metal cations (Pb) and the nonbridging oxygen atoms of each PO_4 tetrahedron. The in-chain P-O-P bond between PO_4 tetrahedra is generally much stronger than the cross bonding between chains via the metal cation.

As iron oxide is added to lead metaphosphate, the average polyphosphate chain length decreases from an average value which is greater than 15 for pure lead metaphosphate glass to an average value of 2.6 for a lead-iron phosphate glass with 9 wt. % Fe_2O_3. For glasses prepared below 900°C, all of the iron is incorporated in the glass as Fe^{+3} and appears to be located in one of two octahedral sites in the glass structure. The improved chemical durability of lead-iron phosphate glasses, therefore, is related to the ability of iron to strengthen the cross bonding between the polyphosphate chains and/or to strengthen the bonding of the ends of these chains to the surrounding glass structure.

A variety of metal oxides have been investigated as possible alternatives to iron oxide (e.g., MgO, Al_2O_3, CaO, Sc_2O_3, TiO_2, VO_2, Cr_2O_3, MnO_2, CoO, NiO, Cu_2O, ZnO, Ga_2O_3, Y_2O_3, ZrO_2, In_2O_3, La_2O_3, CeO_2, Gd_2O_3)

and, while some of these oxides produced an effect similar to that of iron oxide on the chemical durability of lead phosp. ate glasses, none of the metal oxides were as effective as iron oxide in stabilizing lead phosphate glass. Some of the oxides other than Fe_2O_3 were not sufficiently soluble in the lead phosphate melt at a reasonable temperature ($< 1100°C$), while others tended to increase the rate of crystallization or the melt viscosity.

In this article, experimental results associated with the potential use of lead-iron phosphate glasses as a storage medium for high-level nuclear waste are reported. All of the experimental studies reported here have been performed at the laboratory scale using glasses loaded with a chemically simulated nuclear waste (i.e., the wastes were simulated by using material that was chemically identical to the reported compositions of some types of commercial and U.S. defense wastes and differed only ir that radioactive isotopes were not employed).

2. EXPERIMENTAL

2.1 GLASS PREPARATION

Lead-iron phosphate nuclear waste glasses (NWG) were prepared by first thoroughly mixing the appropriate amounts of lead oxide (PbO), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and iron oxide (Fe_2O_3) with a powdered form of the simulated nuclear waste. Ammonium dihydrogen phosphate, which decomposes to P_2O_5 at about 450°C, was used in preference to P_2O_5 — a material that is extremely hydroscopic and more difficult to handle. The well-mixed powders were melted in either a platinum, alumina (Al_2O_3), or zirconia (ZrO_2) crucible at temperatures between 900 and 1050°C for 3–5 h. The molten glass, which could be poured at temperatures

as low as 800°C, was cast into a heated mold of either boron nitride or graphite. The glass was then annealed at 450°C for 1–2 h, and cooled to room temperature over the space of a few hours. Compositions of the lead-iron phosphate NWG investigated here are given in Tables 1–3.

All of the waste oxides and silicates contained in both the simulated U.S. defense waste [11,12] and in the simulated commercial waste [13,14] were completely dissolved in the lead-iron phosphate glass melt at 1050°C with the exception of ZrO_2 — a constituent of commercial waste (see Table 3). Depending on the preparation conditions, lead-iron phosphate glasses loaded with simulated commercial waste often had a Zr rich crystalline phase imbedded in the glass. The presence of this crystalline phase, however, was not found to degrade the physical or chemical durability of the waste glass (see Sec. 3). The Al_2O_3 and zeolites (Na-Al-silicate, Ca-Al-silicate), present in the simulated defense waste compositions investigated (see Table 3), were completely dissolved in the lead-iron phosphate melt, although it should be noted that there is a limited solubility for Al_2O_3 in lead-iron phosphate glasses of about 3–4 wt. % relative to the total weight of the glass. To use lead-iron phosphate glasses to immobilize defense wastes which contain large amounts of Al_2O_3 [11], either the "high Al_2O_3" waste would have to be mixed with a low Al_2O_3 waste to lower the aluminum oxide content to a value close to that present in the reported "composite" composition (see Table 3), or the overall waste loading would have to be reduced and additional iron oxide added to the lead-iron phosphate glass frit.

Most of the lead-iron phosphate NWG investigated here were prepared by melting in platinum crucibles. There appeared to be very little

Table 1. Compositions of Lead-Iron Phosphate Defense
Waste Glasses (wt. %)

Compound	1-D	2-D	3-D	4-D	5-D	6-D	7-D [**]
P_2O_5 (added as $NH_4H_2PO_4$)	32.9	32.9	39.5	35.6	43.5	29.3	25.5
PbO	51.6	51.6	41.4	45.8	36.9	56.3	60.1
Fe_2O_3	7.75	6.88	9.55	9.3	9.8	7.2	7.2
Al_2O_3	1.55	1.36	1.87	1.82	1.92	1.41	1.41
MnO_2	2.14	1.91	2.63	2.57	2.70	1.99	1.99
CaO	0.57	0.51	0.71	0.69	0.72	0.53	0.53
NiO	0.97	0.86	1.20	1.17	1.23	0.91	0.91
SiO_2	0.20	0.16	0.25	0.24	0.25	0.19	0.19
Na_2O (added as Na_2CO_3)	1.12	0.98	1.37	1.34	1.41	1.04	1.04
Na_2SO_4	0.20	0.18	0.25	0.24	0.25	0.19	0.19
U_3O_8	0.70	0.62	0.86	0.84	0.88	0.65	0.65
Cs_2O	0.155	0.15	0.19	0.19	0.20	0.14	0.14
SrO	0.155	0.15	0.19	0.19	0.20	0.14	0.14
Zeolite[*]	0.0	1.44	0.0	0.0	0.0	0.0	0.0
C	0.0	0.29	0.0	0.0	0.0	0.0	0.0
Total	100.01	99.99	99.97	99.99	99.96	99.99	99.99
Waste Loading (wt. %)	15.5	15.5	19.1	18.6	19.6	14.4	14.4
Glass Density (g/cm^3)	4.7	4.7	4.0	4.5	4.0	5.1	5.4
Waste/Volume Loading (g/cm^3)	0.73	0.73	0.76	0.83	0.78	0.73	0.78

[*]The zeolite used was a 50/50 mix by weight of Ca-Al-Silicate (Linde 5A) and Na-Al-Silicate (Linde 4A).

[**]Not a homogeneous glass — a large amount of crystalline material.

Table 2. Compositions of Lead-Iron Phosphate Commercial Waste Glasses (wt. %)

Compound	1-C	2-C	3-C	4-C	5-C	6-C	7-C
P_2O_5 (added as $NH_4H_2PO_4$)	32.2	33.1	33.9	39.2	40.1	41.2	42.3
PbO	50.6	51.9	53.3	41.1	42.0	43.1	44.3
Fe_2O_3	10.8	8.4	6.1	13.1	11.2	8.8	6.3
Simulated commercial waste (see Table 3)	6.4	6.6	6.8	6.5	6.7	6.9	7.0
Total	100.0	100.0	100.1	99.9	100.0	100.0	99.9
Glass Density (g/cm^3)	5.0	4.9	4.9	4.6	4.4	4.3	4.3
Waste/Volume Loading (g/cm^3)	0.32	0.32	0.33	0.30	0.29	0.30	0.30

Table 3. Compositions of Simulated Nuclear Waste (wt. %)

| Compound | Defense[a] | | Commercial Waste[b] |
	D1	D2	C
Fe_2O_3	50.0	44.4	4.1
Al_2O_3	9.8	8.8	-
MnO_2	13.8	12.3	-
U_3O_8	4.5	4.0	6.2
CaO	3.7	3.3	-
Ni	6.3	5.6	0.3
SiO_2	1.3	1.0	-
Na_2O	7.2	6.3	-
Na_2SO_4	1.3	1.2	-
Cs_2O	1.0	0.9	7.8
SrO	1.0	0.9	2.9
Zeolite[c]	0.0	9.3	-
C	0.0	1.9	-
Total	99.9	99.9	
ZrO_2			13.4
MoO_3			14.1
CrO_3			0.6
P_2O_5			1.8
Rb_2O			0.5
Y_2O_3			1.6
RuO_2			5.0
PdO			1.8
Ag_2O			0.2
TeO_2			2.0
BaO			4.3
La_2O_3			4.0
CeO_2			9.0
PrO_2			4.0
ND_2O_3			12.3
Sm_2O_3			2.5
Eu_2O_3			0.5
Gd_2O_3			0.4
Total			99.8

a. The "composite" composition of U.S. Defense waste currently in
   interim storage at the Savannah River facility [11,12].
b. The "PW-4b" commercial waste composition [13,14] which is typical of
   the nuclear waste which results from the reprocessing of spent fuel
   rods from commercial light water power reactors.
c. The zeolite used was a 50/50 mix by weight of Ca-Al-Silicate
   (Linde 5A) and Na-Al-Silicate (Linde 4A).

reaction between the lead-iron phosphate melt and the Pt crucible — particularly when melting defense waste glasses. In an attempt to quantify this observation, a thin-walled Pt crucible was exposed to a molten lead-iron phosphate melt at 1050°C for several hundred hours. The glass was then removed from the crucible and analyzed for dissolved Pt using spark source mass spectrometry. These data indicate that in order for lead-iron phosphate glasses to dissolve a 1-mm thick Pt layer, a continuous exposure at 1050°C for over 10^4 h would be required.

Lead-iron phosphate glasses were also prepared in alumina (Al_2O_3) crucibles. Although it is possible to use these crucibles to melt lead-iron phosphate glasses loaded with both defense waste and commercial waste, it is necessary to adjust the lead-iron phosphate frit composition and the melt temperature so that most of the Al_2O_3 dissolved in the glass comes from the waste and not from the alumina crucible. If this is not done, undissolved pieces of alumina are imbedded in the glass. While this represents a problem when preparing glasses at the laboratory scale, it may not represent a significant problem in a large melter where the ratio of the surface area of the alumina crucible to the volume of molten glass is greatly reduced.

Lead-iron phosphate NWG was also prepared by melting in ZrO_2 crucibles. Although these crucibles were only used for a few preparations, it appeared that the reaction between the lead-iron phosphate glass melt and zirconia was considerably lower than that characteristic of alumina crucibles.

Lead-iron phosphate NWG can also be prepared by initially fusing only the components of the lead-iron phosphate glass frit (i.e., PbO,

$NH_4H_2PC_4$, and Fe_2O_3) to form a pure lead-iron phosphate glass. This pro-
cess does not involve radioactive material at this stage and, hence, could
be easily performed in a standard chemical processing facility. In the
final processing steps, preground lead-iron phosphate glass "frit" would
be mixed with the nuclear waste in a remote processing facility, melted in
an appropriately lined (stabilized ZrO_2, Pt, Al_2O_3, etc.) melter, and then
poured into a suitable metal cannister such as stainless steel. One
advantage of preparing the lead-iron phosphate glass frit in advance is
that the ammonia and water which are given off during the decomposition
of $NH_4H_2PO_4$ to P_2O_5 can be handled with a nonradioactive off-gas system.
Final melting and remote processing of the nuclear waste glass is also
simplified, since foaming of the melt is greatly reduced when the premade
lead-iron phosphate glass frit is employed.

2.2 OPTIMIZATION OF THE GLASS COMPOSITION

A pure lead phosphate glass that does not contain iron or nuclear
waste can be prepared by fusing PbO with P_2O_5 between 800 and 900°C; and
by adjusting the ratio of PbO to P_2O_5, the composition of the glass can be
varied. If the percentage of PbO exceeds about 66 wt. %, however, crys-
talline lead phosphate is formed rather than a glass. Hence, the crit-
ical limit for glass formation is 66 wt. % PbO. The lower limit on the
amount of PbO which can be melted with P_2O_5 for practical nuclear waste
glass formation is not as well defined. A composition of about 40 wt. %
PbO and 60 wt. % P_2O_5, however, appears to represent a lower limit for the
PbO content since the viscosity of the molten glass increases rapidly
as the PbO concentration is reduced below 40 percent. Increased melt
viscosity requires higher temperature processing, which is undesirable

for a variety of reasons (e.g., loss of volatile radioactive material, melter lifetime etc.).

The practical concentration ranges for formation of the lead-iron phosphate glass host, therefore, are as follows: PbO (40–66 wt. %), P_2O_5 (30–60 wt. %), and Fe_2O_3 (0–12 wt. %). The amount of iron oxide required for the lead-iron phosphate glass frit depends on the amount of iron oxide already present in the nuclear waste and on the PbO to P_2O_5 ratio used in the frit. A lower amount of PbO in the glass frit requires the addition of a higher percentage of iron oxide in order to produce the most corrosion resistant glass.

A low aqueous corrosion rate is perhaps the most desirable characteristic of a nuclear waste glass. The optimum lead-iron phosphate glass frit composition for each type of nuclear waste was defined as that composition which minimized the overall corrosion rate of the nuclear waste glass in water at 90°C. The relative corrosion resistance of each glass was first screened by measuring the electrical conductivity of the leachate solutions as a function of time [15]. As the nuclear waste glass corrodes in distilled water, mobile ions are released into solution resulting in an increase in the solution conductivity. For total concentrations lower than about 10^{-3} mole/ℓ, the effects of ion-ion interactions in solution can be neglected and the activity coefficients of all ions can be assumed to be unity [15-17]. In this dilute limit, the overall release of the major constituents from the waste glass into solution is roughly proportional to the solution conductivity [15,18]. This is illustrated in Fig. 2 for the case of a borosilicate waste glass. In this example the concentrations of the specific ions which contribute to

the conductivity have been measured using quantitative solution analyses. Most of the increase in leachate conductivity is due to Si, B, Na, and Li ions — the major components of the glass. The calculated conductivity of 140 μmho/cm based on a quantitative analysis of the leachate compares favorably with the measured value of 152 μmho/cm (Fig. 2).

Several compositions of lead-iron phosphate frit were prepared and loaded with either simulated defense waste (waste composition D1—Table 3) or simulated commercial waste (waste composition C — Table 3). Slices from these simulated nuclear waste glasses were placed in solution conductivity cells and the overall ionic release into solution was monitored. The solution conductivity versus time data are shown in Figs. 3—5 for both defense and commercial lead-iron phosphate nuclear waste glasses. On the basis of these and other data, the defense waste glass # 1-D (see Table 1) and the commercial waste glass # 1-C (see Table 2) were selected as the compositions to be used in most of the investigations of the properties of lead-iron phosphate nuclear waste glasses reported here.

3. EXPERIMENTAL RESULTS

3.1 CORROSION TESTS — GENERAL

Samples of lead-iron phosphate glasses loaded with either simulated defense waste or simulated commercial power reactor waste were subjected to a variety of aqueous corrosion tests. In most of the tests the glasses were exposed to triply distilled water at 90°C for times ranging from 14-270 d, with the ratio of the surface area of the glass sample to the volume of liquid fixed at about 0.1 cm^{-1}. At the conclusion of a given corrosion period, each solution was analyzed for the elements: Pb, P, Fe,
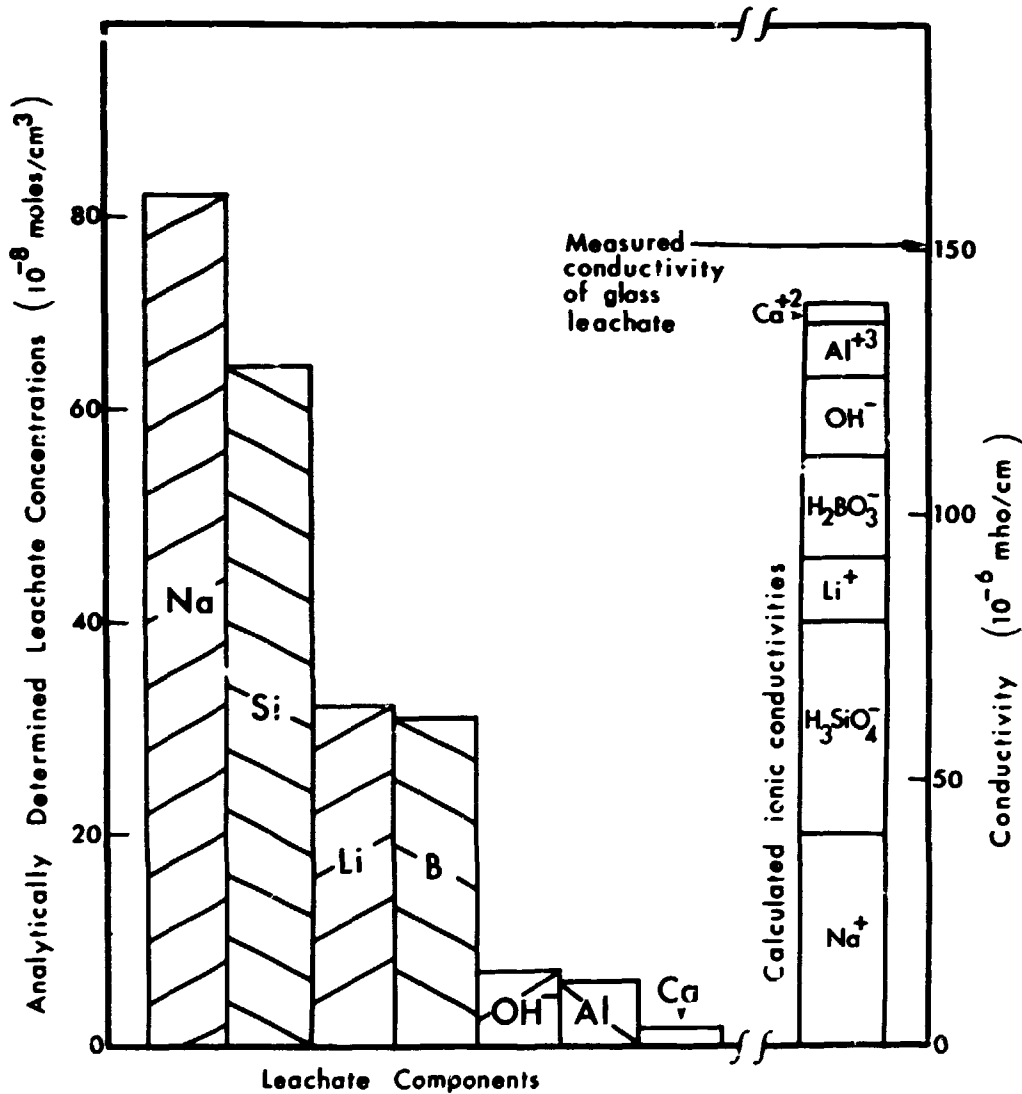
Fig. 2. A borosilicate glass (Frit 21 + 20 wt. % of waste composition D1) was corroded in distilled water at 90°C for 100 h. The analytically determined concentrations of the major elements in the leachate are shown in the left portion of the figure. The contribution of each element to the leachate conductivity was then calculated and is shown in the right portion of the figure. The calculated value for the leachate conductivity at room temperature ($\sim$140 µmho/cm) compares favorably with the measured value of 152 µmho/cm.

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Fig. 3. Leachate conductivity versus time at 90°C for a series of lead-iron phosphate glasses loaded with simulated defense waste (see Tables 1 and 3 for glass compositions). The homogeneous glasses 1-D through 6-D are roughly equivalent in performance with # 4-D exhibiting the lowest ionic release rate. Glass 7-D, which contained crystalline material, is clearly inferior to the other lead-iron phosphate compositions.

Fig. 4. Leachate conductivity versus time at 90°C for a series of lead-iron phosphate glasses loaded with simulated commercial waste (see Tables 2 and 3 for class compositions). Compositions 1—C and 2—C give comparable results while the ionic release rate for glass 3—C is slightly higher.
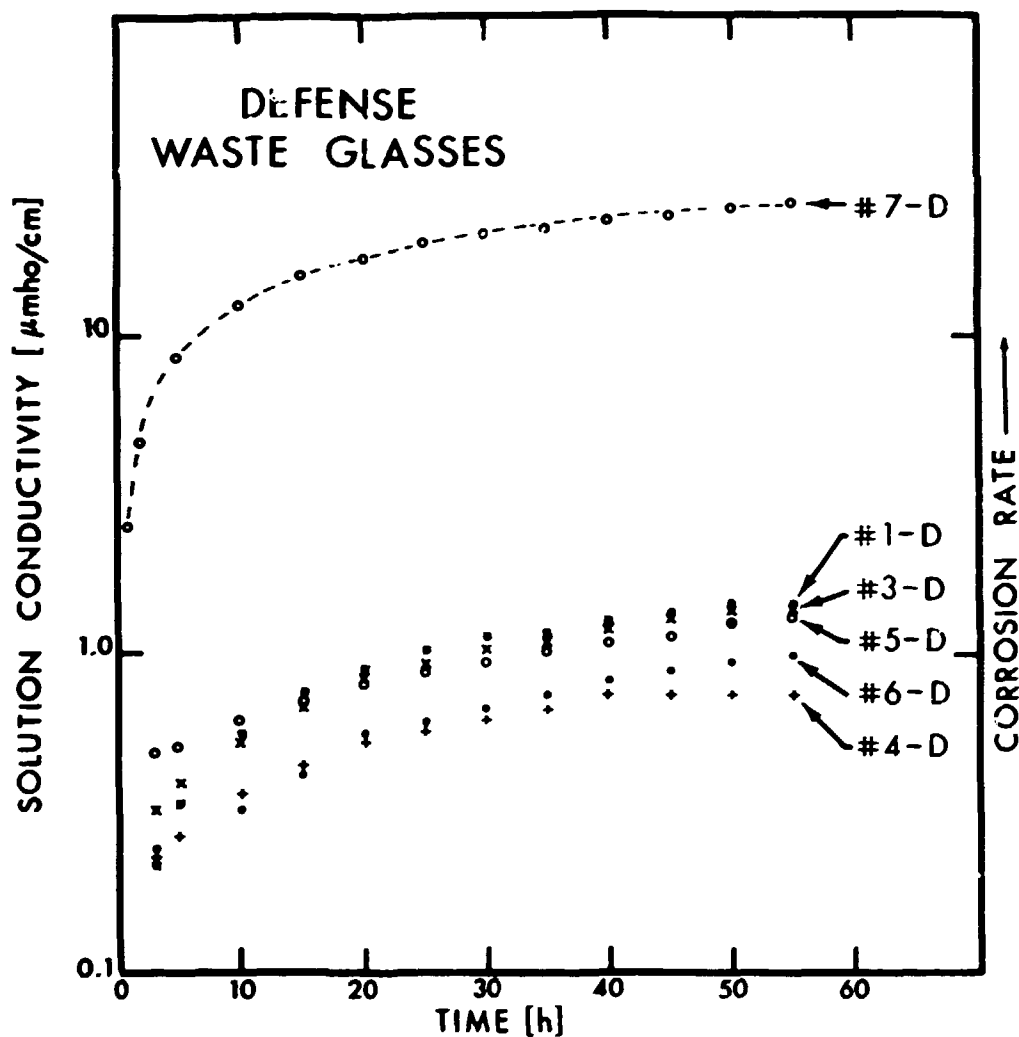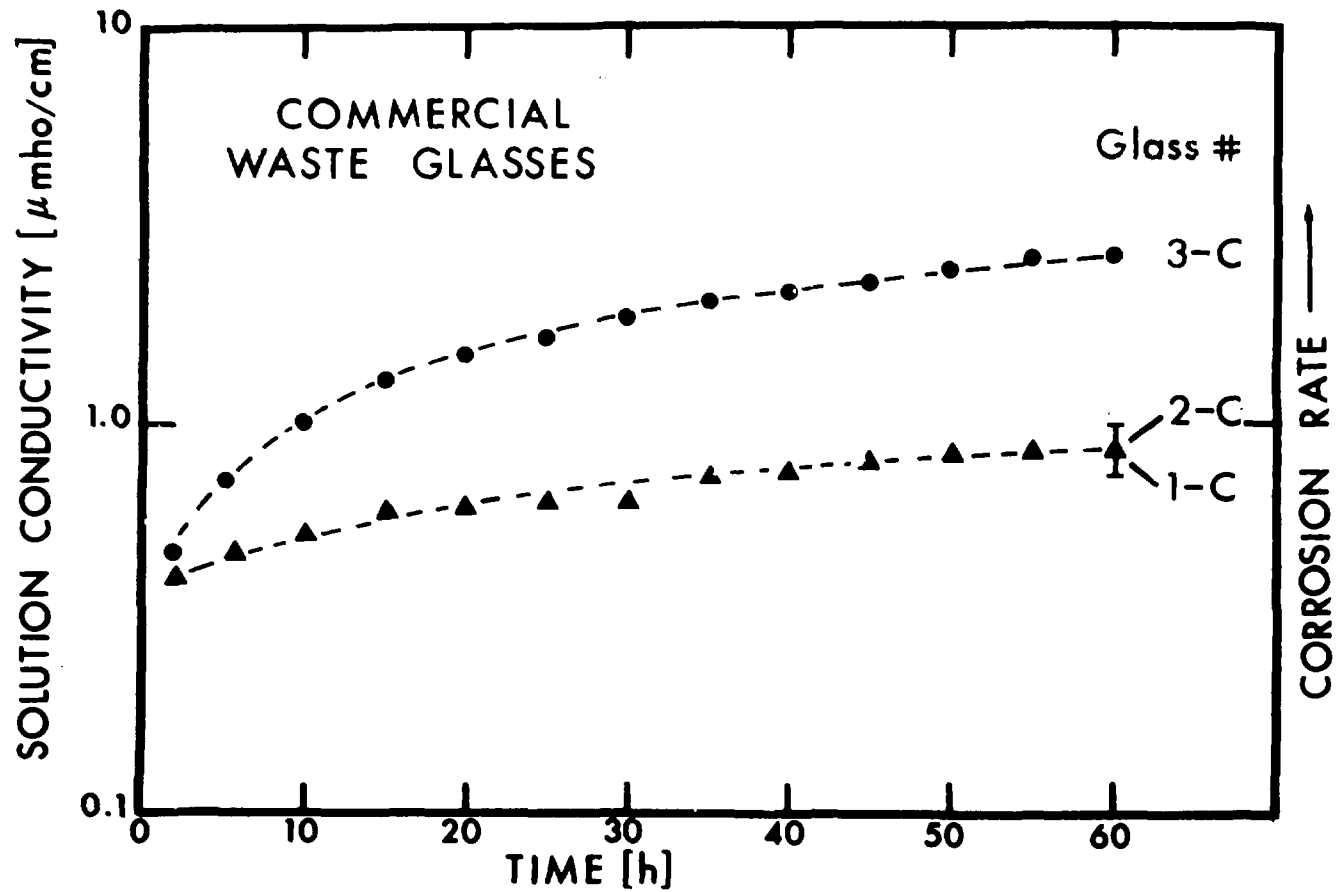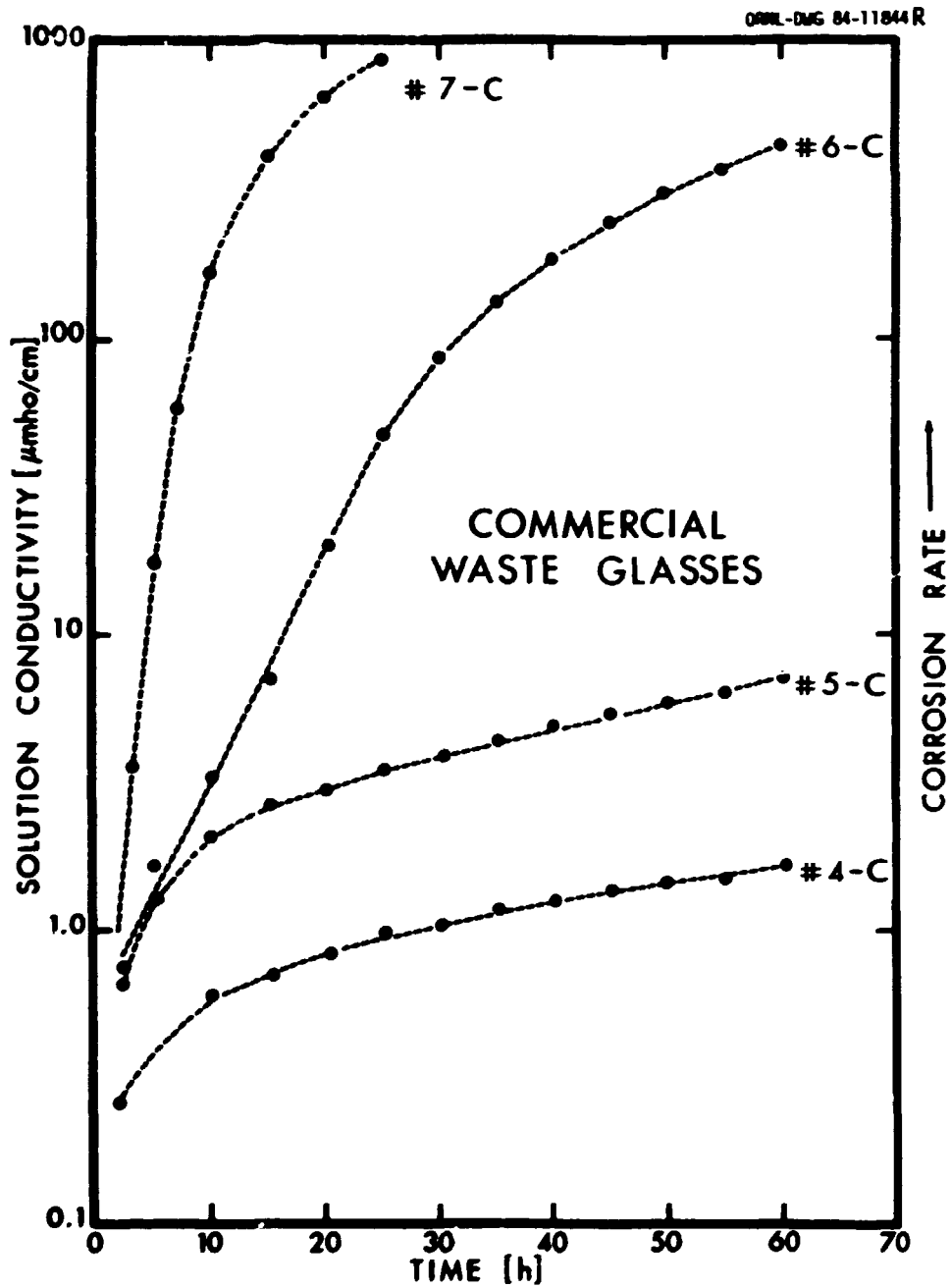
Fig. 5. Leachate conductivity versus time for a series of lead-iron phosphate glasses loaded with simulated commercial waste (see Tables 2 and 3 for glass compositions).

U, Sr, Cs, Mo, Zr, Na, Cr, Mn, Ni, and Al. The concentrations of all the elements in solution were determined using inductively coupled plasma (ICP) emission analyses with the exception of the Cs and U concentrations, which were determined using atomic absorption spectroscopy and fluorimetry, respectively.

In order to facilitate comparisons with the data from other nuclear waste glasses, the concentration of each element found in solution has been converted to a normalized corrosion rate, $R = A_i \cdot v/(F_i \cdot S \cdot t)$ where A_i is the concentration (g/ml) of species i found in solution, v the volume (ml) of solution, S the geometric surface area (m^2) of the glass, t, the amount of time (days) the sample was exposed to the solution, and F_i the mass fraction of element i present in the uncorroded glass.

3.2 CORROSION TEST RESULTS — DEFENSE WASTE GLASSES

A lead-iron phosphate nuclear waste glass (composition # 1-D, see Table 1) was exposed to distilled water at 90°C for 30 days. The leachate was then analyzed quantitatively and the corrosion rate, R, was calculated for selected elements in the glass. A borosilicate glass (Frit 131 [11,19]) loaded with the same simulated defense waste composition (D1, see Table 3) was prepared and corroded using test conditions that were identical to those used for the defense waste loaded lead-iron phosphate glass. This borosilicate glass is one of the reference waste glasses developed for the disposal of defense waste currently in interim storage at the Savannah River Facility. A comparison of the corrosion data for the lead-iron phosphate defense waste glass and the borosilicate defense waste glass is shown in Fig. 6. The results of these experiments show that, under the specified corrosion conditions, the net release of all
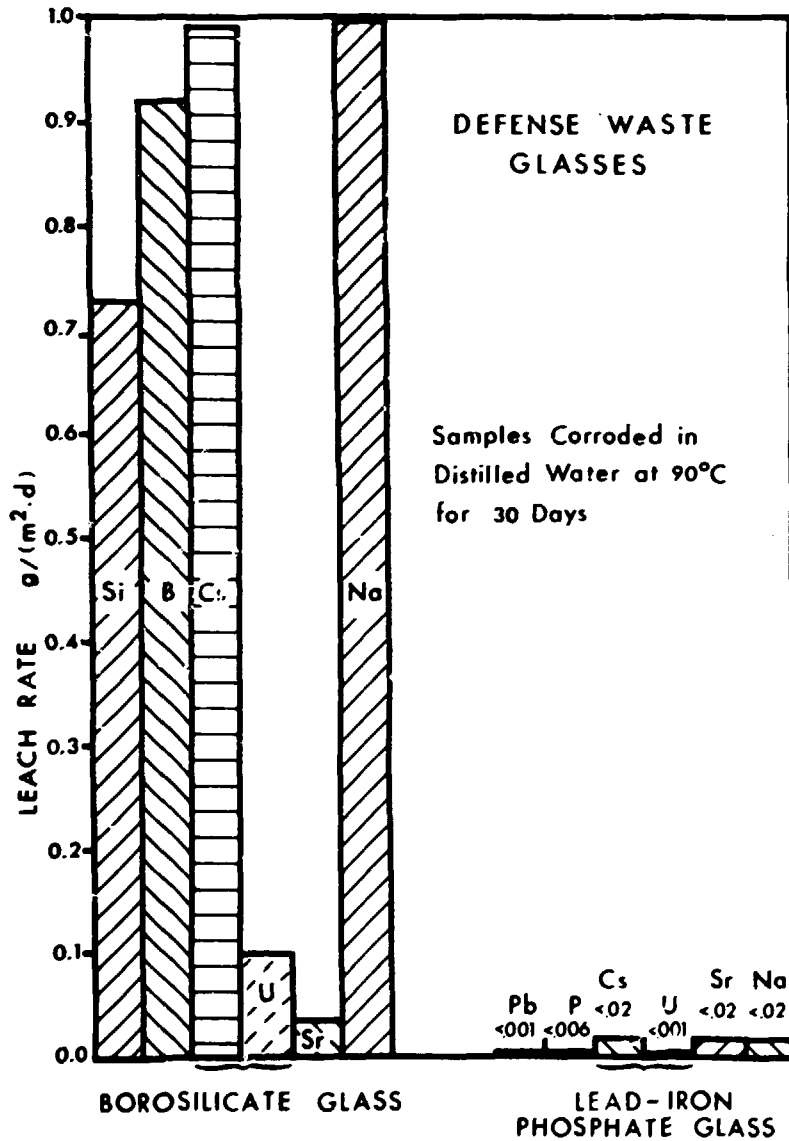
Fig. 6. The 30-day corrosion rates at 90°C in distilled water for a lead-iron phosphate (glass # 1-D) and a borosilicate (Frit 131 + 29 % of waste composition D1) nuclear waste glass loaded with simulated defense waste. The concentrations of all elements present in the lead-iron phosphate leachate were below the detectability limits of standard analytical chemical techniques. Lead-iron phosphate and borosilicate nuclear waste glasses had the same waste-per-volume loading.

elements from the lead-iron phosphate glass was less by at least 100–1000 times than the corresponding release from a comparable borosilicate nuclear waste glass.

The effect of the corroding solution pH on the corrosion rate of lead-iron phosphate defense waste glass # 1–D was also investigated and comparisons were made to the corrosion behavior of a defense-waste-loaded borosilicate glass. The solution pH was varied by adding the appropriate amounts of either hydrochloric acid (HCl) or sodium hydroxide (NaOH) to distilled water. No buffering agent was used and the pH value quoted refers to the initial pH of the corroding solution. The results of these investigations are shown in Fig. 7. For solution pH values between 5 and 9, which bracket the pH range of most natural ground waters [20], the corrosion rates of the lead-iron phosphate glass were smaller by at least 100 to 1000 times than the corrosion rates of the borosilicate glass. At the pH extremes of 2 and 12, the corrosion rates of the lead-iron phosphate glass approach but do not exceed those of the borosilicate nuclear waste glass.

Lead-iron phosphate glasses (# 1–D) were also exposed to J–13 well water, a concentrated brine solution, and distilled water with a low amount of dissolved oxygen (low eH) for 1 month at 90°C. The J–13 well water is the reference water type for waste disposal in a tuff geological formation (pH$\approx$8.2) [21], the brine solution was similar to the WIPP B (Waste Isolation Pilot Project) brine composition which is primarily a nearly saturated sodium chloride solution, and the low eH solution was maintained by bubbling a 4 % H_2/96 % Ar gas mixture through distilled water. The brine leachate was not analyzed, but the lead-iron phosphate
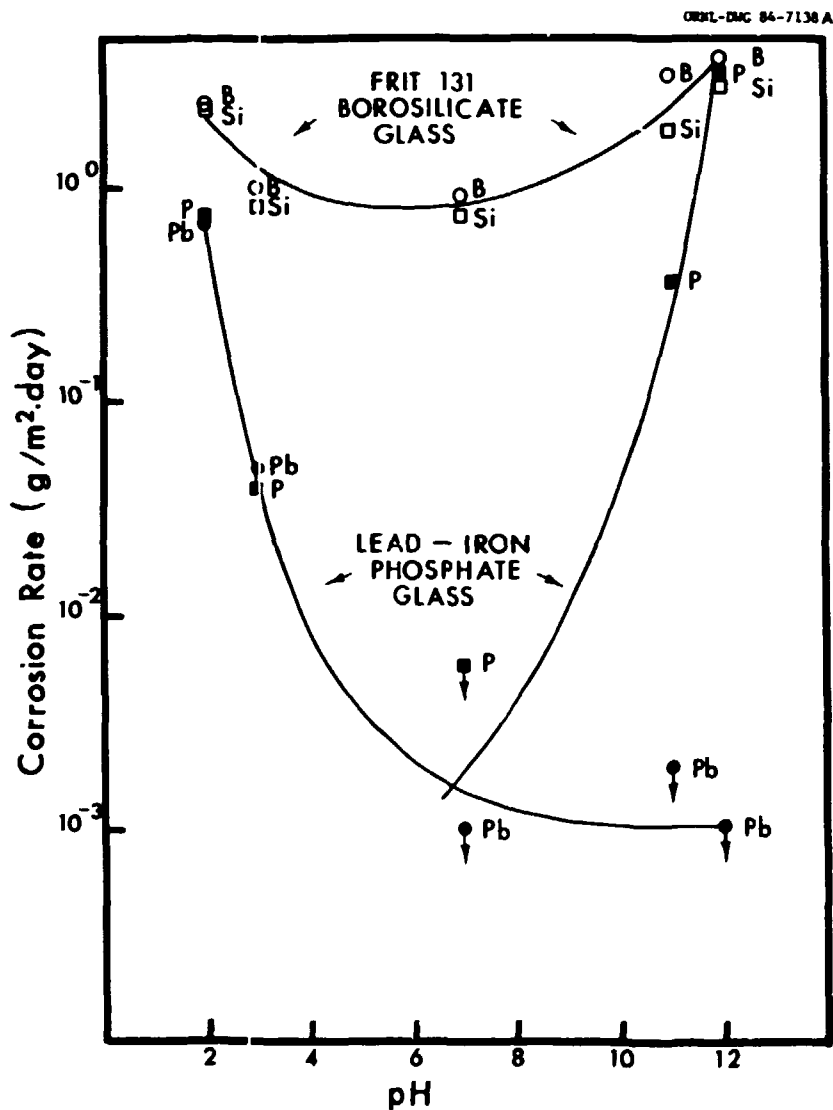
Fig. 7. The 30-day corrosion rates of lead-iron phosphate (# 1—D) and borosilicate (Frit 131 + 29 wt. % of waste composition D1) nuclear waste glasses at 90°C as a function of the solution pH. The solution pH was varied by adding the appropriate amounts of either hydrochloric acid (HCl) or sodium hydroxide (NaOH) to distilled water. No buffering agent was used and the pH value quoted refers to the initial pH of the corroding solution. For clarity, the corrosion rates of only the major constituents of each glass are shown.

glass exhibited no evidence of corrosion and had no measurable weight loss. For the other two leachates there were no components of the glass in solution at concentrations above the analytical detectability limits (Table 4) following a one-month exposure at 90°C.

A nuclear waste form, after it is placed in a deep geologic repository, will be subjected to large doses of gamma radiation during the first several hundred years of storage. In order to study the corrosion behavior of a lead-iron phosphate NWG (# 1-D) under simulated operating conditions of this type, samples were simultaneously exposed to J-13 well water at 115°C in a gamma radiation field of 10^6 R/h for a period of one week. This dose rate is about 100 to 1000 times that experienced by a U.S. defense waste form during the initial storage period. No measurable weight loss of the glass was found after this corrosion test, an indication that the corrosion behavior of lead-iron phosphate glass is not significantly affected by the combination of large doses of gamma radiation and tuff ground water corrosion at 115°C.

Corrosion tests on lead-iron phosphate glasses loaded with simulated defense waste (# 1-D) in essentially neutral solutions (distilled water, J-13 well water, and low eH distilled water) indicate that the aqueous corrosion rates of these glasses are very low — at least at 90°C (Table 4). For acidic solutions with low pH values (pH=2), the glasses appear to dissolve congruently since all components of the glass corrode at about the same rate (Table 4). In basic solutions with high pH values (pH=12), the corrosion is highly incongruent since phosphorus, aluminum, and the alkalis are selectively leached from the glass while lead is not removed (see Fig. 7).

Table 4. Corrosion Rates (g/m^2-d) for Lead-Iron Phosphate Glasses Loaded with Simulated Defense Waste — Glass # 1–D.

All samples were corroded at 90°C for 1 month in a sealed Teflon container.

Corroding solution	Distilled water	J-13 Well[a] water	Low eH[b] water	pH 3[c]	pH 11[d]	pH 2[e]	pH 12[f]
Pb	<0.001	<0.001	<0.001	0.05	<0.001	0.79	<0.001
P	<0.006	<0.006	<0.01	0.04	0.36	0.76	4.46
Fe	<0.001	<0.001	<0.001	<0.001	<0.001	0.19	<0.001
Mn	<0.001	<0.001	<0.001	0.03	<0.001	0.72	<0.001
Al	<0.02	<0.02	<0.09	0.04	0.4	0.77	5.4
Na	<0.02	<0.1	<0.04	<0.02	-	0.96	-
Cs	<0.02	<0.1	-	<0.1	<0.2	1.2	3.5
Sr	<0.02	<0.02	<0.01	<0.02	<0.02	0.72	<0.02
U	<0.001	<0.001	<0.001	0.02	<0.001	0.67	<0.01

[a]J–13 well water (which has a pH of about 8.2) is the reference water type for disposal in a tuff formation [21].

[b]The low eH solution (low amount of dissolved oxygen) was maintained by bubbling a 4% hydrogen/96% argon gas mixture through distilled water. The eH of this type of solution is about 0.0 [34].

[c]A 0.001 N HCl solution.

[d]A 0.001 N NaOH solution.

[e]A 0.01 N HCl solution.

[f]A 0.01 N NaOH solution.

Two long-term corrosion experiments were performed on defense waste loaded lead-iron phosphate glasses (# 1-D). Glass samples were exposed to distilled water at 90°C for 270 days or to J-13 well water at 90°C for 210 days. With the exception of a small amount of P and possibly Na and Cs in the leachate solutions, there was no measurable corrosion of these glasses by either solution (see Table 5).

The temperature dependence of the corrosion rates of lead-iron phosphate glasses loaded with simulated defense waste was investigated in two sets of experiments. In the first experiments, glass samples were exposed to distilled water for one month at temperatures of 60, 90, 125, and 150°C. The leachate solutions were then analyzed and corrosion rates calculated for selected elements in the glass (see Table 6). The corrosion rate for these lead-iron phosphate glasses becomes measurable at 125°C and appears to increase significantly as the temperature is raised further. From these measurements, it is concluded that if defense waste loaded lead-iron phosphate nuclear waste glasses were exposed to extreme hydrothermal conditions (water at temperatures greater than about 200°C) the glasses would not provide an effective barrier to the release of the radioactive nuclei into the water.

In the second set of experiments, the temperature dependence of the corrosion rate was investigated at temperatures below 100°C. Since no corrosion of the glass could be detected with a sample surface area to solution volume ratio of 0.1 cm^{-1}, powdered samples were used in an attempt to increase the amount of dissolved glass in solution. Samples weighing 0.6 g were powdered and placed in 40 cc of water at 23, 56, 70, and 90°C for 24 h. From scanning electron microscope photographs, the

Table 5. Long-Term Corrosion Rates (g/m²-d) for Lead-Iron Phosphate Glasses Loaded with Simulated Defense Waste — Glass # 1-D.

All samples were corroded at 90°C in a sealed Teflon container.

Corroding Solution	Distilled Water for 270 days	J-13 Well Water[a] for 210 days
Pb	<0.00007	<0.0001
P	0.004	0.03
Fe	<0.0001	<0.0001
Mn	<0.0005	<0.0005
Al	<0.001	0.02
Na	0.01	<0.06
Cs	0.003	0.05
Sr	<0.001	<0.001
U	<0.0003	<0.0003

[a]J-13 well water (which has a pH of about 8.2) is the reference water type for disposal in a tuff formation [21].

Table 6. Corrosion Rates (g/m²-d) of Lead-Iron Phosphate Glasses Loaded with Simulated Defense Waste: Temperature Dependence.

All glasses were corroded for 1 month in distilled water.

Temperature	60°C	90°C	125°C[a]	150°C[a]
Pb	<0.001	<0.001	<0.001	0.05
P	<0.006	<0.00	0.11	10.7
Fe	<0.001	<0.001	0.04	0.013
Mn	<0.0001	<0.001	0.14	4.0
Al	<0.02	<0.02	<0.02	0.13
Na	<0.02	<0.02	4.0	60
Cs	<0.001	<0.01	-	-
Sr	<0.02	<0.02	<0.02	4.4
U	<0.001	<0.001	<0.001	0.04

[a]Part of the corrosion cells were made of stainless steel and Inconel. It is not known how much of the Fe, Mn, and P detected in solution was due to the corrosion of the container.

average particle size was found to be about 0.1 microns. Since there was a substantial amount of colloidal material suspended in the solution, a quantitative analysis of the solution was not attempted. Instead, the solution conductivity was measured before and after each corrosion experiment and the difference in conductivity was assumed to be proportional to the concentration of dissolved glass ions actually in solution. To check this assumption, the same experiment was carried out with a defense-waste-loaded borosilicate glass, since for these glasses the temperature dependence of the corrosion rate is well established [22]. Since the density of the borosilicate glass was about half that of the lead-iron phosphate glass, only 0.3 g of glass was powdered and placed in solution. The average particle size for the borosilicate glass powder was about 1—10 microns as determined from SEM photographs. The corrosion data for the lead-iron phosphate and borosilicate glasses are shown in Fig. 8. Because of the uncertainty in particle sizes and the effect this has on the corrosion rates, no statement can be made about the absolute value of the corrosion rate. The correct temperature dependence of the overall corrosion rate, however, should be reflected in the data. For the lead-iron phosphate glass, there does not appear to be any substantial temperature dependence in the overall corrosion rate at temperatures between 23 and 90°C. The borosilicate glass, however, exhibits an apparent activation energy for corrosion of 11 ± 1 kcal/mole — a value that is typical of borosilicate nuclear waste glasses in this temperature region [22].

3.3 RUTHERFORD BACKSCATTERING STUDIES OF CORRODED GLASS SURFACES

The surfaces of several corroded lead-iron phosphate nuclear waste glasses loaded with simulated defense waste were examined using the

ORNL-DWG 85-8311

**TEMPERATURE DEPENDENCE
OF CORROSION RATE**
(Glass Powder)

Borosilicate
NWG

Lead-Iron
Phosphate
NWG

10^4

10^3

10^2

10^1

10^0

SOLUTION CONDUCTIVITY $\sigma(\mu mho/cm)$
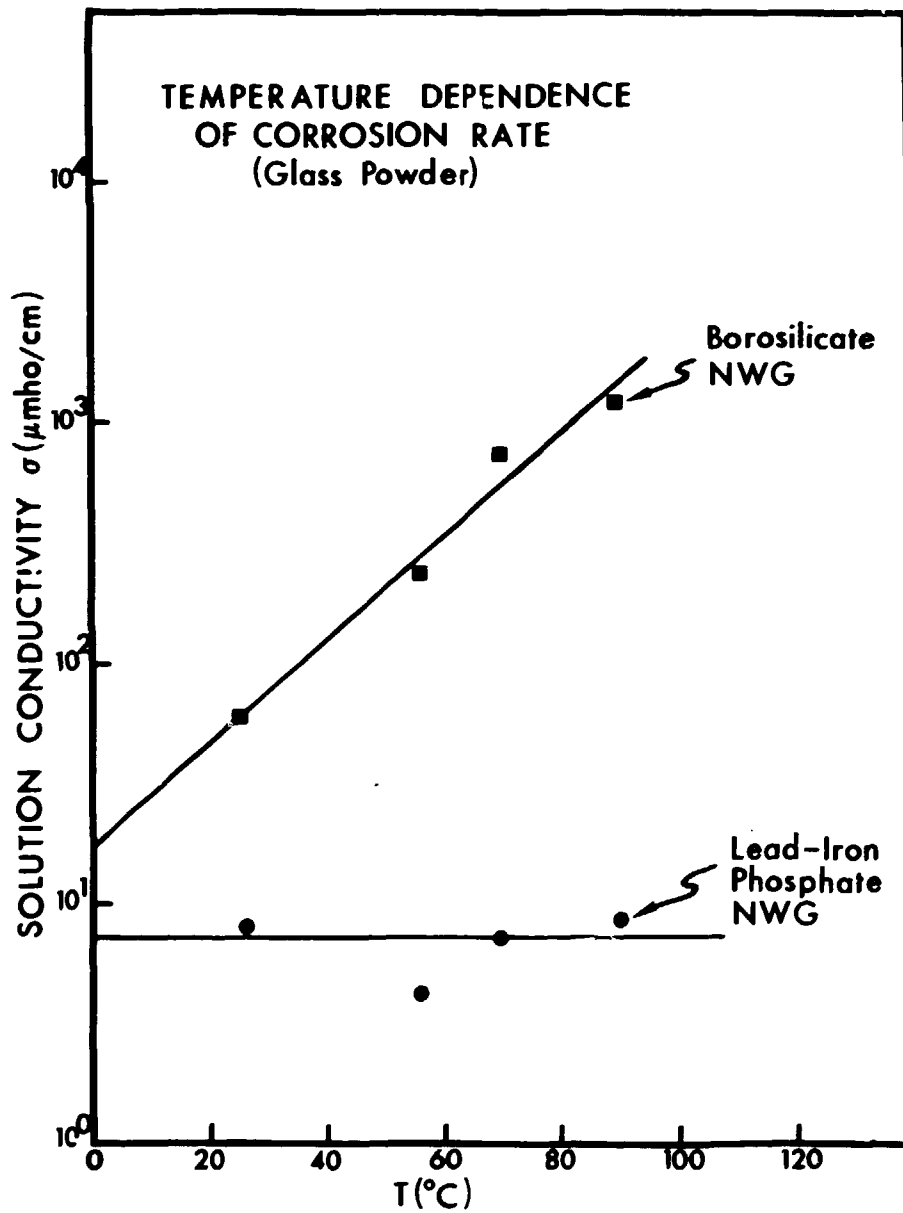
0   20   40   60   80   100   120

T(°C)

Fig. 8. Temperature dependence of the corrosion rate in water for a
lead-iron phosphate glass # 1-D and a borosilicate glass (Frit 131 + 29
wt. % of waste composition D1) as determined from solution conductivity
measurements on glass powders (see Sec. 3.2).

technique of Rutherford backscattering (RBS). The general theory of Rutherford backscattering is described in several excellent review articles [23,24]. The application of the technique of RBS to the study of nuclear waste glass corrosion has been treated in some detail in previous articles [19,25–27] so that only a brief description of the technique will be given here. After allowing the corroded glass samples to dry in air, a 10 nm thick Al film was evaporated onto the glass surface to prevent charging during the subsequent backscattering measurements. The Al coated glass was then placed in a vacuum chamber and bombarded by a 2 MeV beam of He^+ ions. By analyzing the energy distribution of the scattered He^+ ions which arrived at a solid state detector placed at a scattering angle of about 160 degrees, concentration vs depth profiles could be determined for most elements in the glass. Concentration profiles could be probed to a maximum depth of 1–2 microns below the surface with a depth resolution of 0.01–0.02 microns.

Three samples of lead-iron phosphate nuclear waste glass # 1–D were exposed for 26 h at 90°C to either distilled water, a 0.01 N HCl (pH=2) solution, or a 0.01 N NaOH (pH=12) solution. The backscattering spectra for the glasses corroded in the acidic or basic solutions are shown in Figures 9 and 10, respectively (closed circles), along with the backscattering spectrum from an uncorroded glass (open circles). The backscattering spectrum from the lead-iron phosphate glass corroded in distilled water was identical to the uncorroded glass spectrum and hence is not shown. Because of the very strong ion scattering from the lead in these materials, RBS measurements on lead-iron phosphate glasses are not as informative as, for example, RBS measurements on borosilicate glasses.

Fig. 9. Energy spectra of 2.0 MeV He$^+$ ions backscattered from uncorroded (O) and corroded (●) samples of lead-iron phosphate nuclear waste glass # 1-D. The lack of ion scattering at energies of about 1.8 MeV is caused by a depletion of lead from the surface region (about 200 nm) of the corroded glass. The lead-iron phosphate glass # 1-D was corroded at 90°C for 26 h in a solution with a pH of 2.
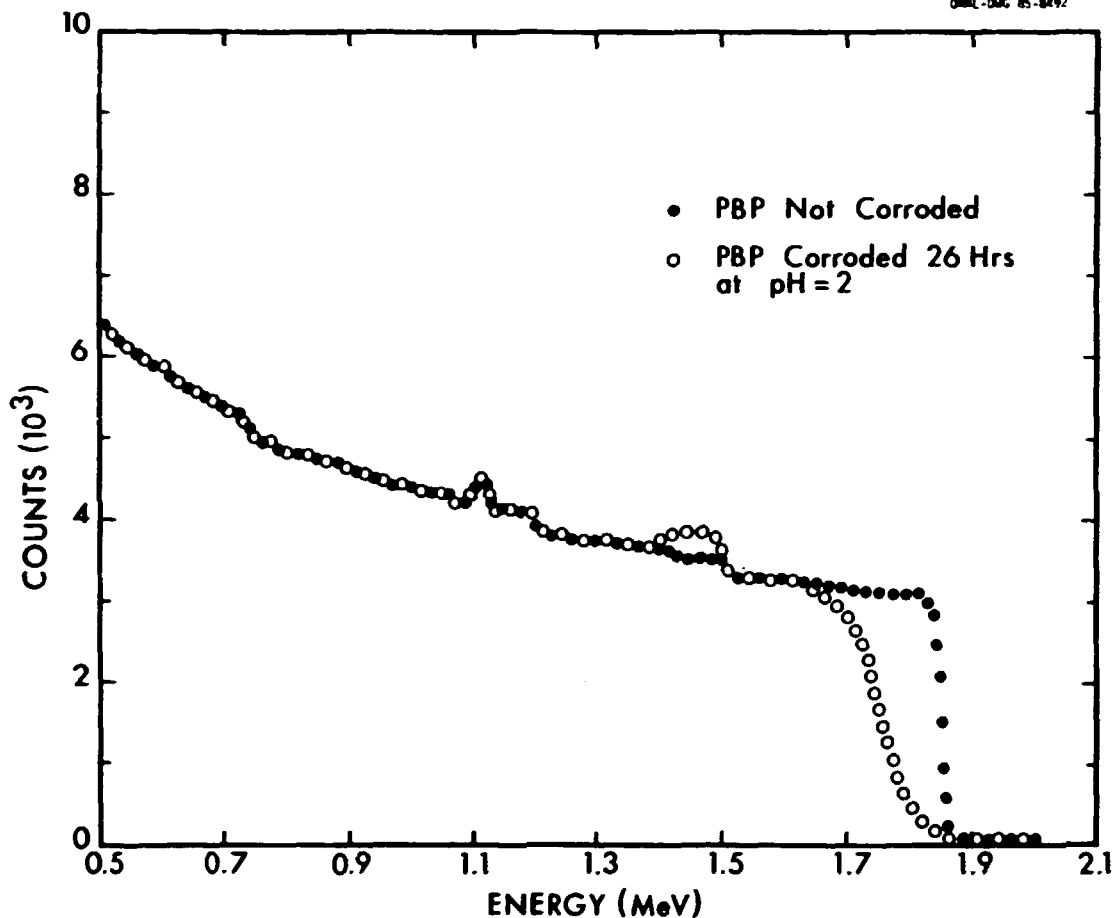
Fig. 10.   Energy spectra of 2.0 MeV He$^+$ ions backscattered from uncorroded (O) and corroded (●) samples of lead-iron phosphate nuclear waste glass # 1-D.   The increase in the ion scattering at energies between 1.1 and 1.5 MeV is probably caused by the presence of excess Fe, Mn, and Ni in the altered surface layer (about 200 nm thick) of the corroded glass.   The lead-iron phosphate glass # 1-D was corroded at 90°C for 26 h in a solution with a pH of 12.
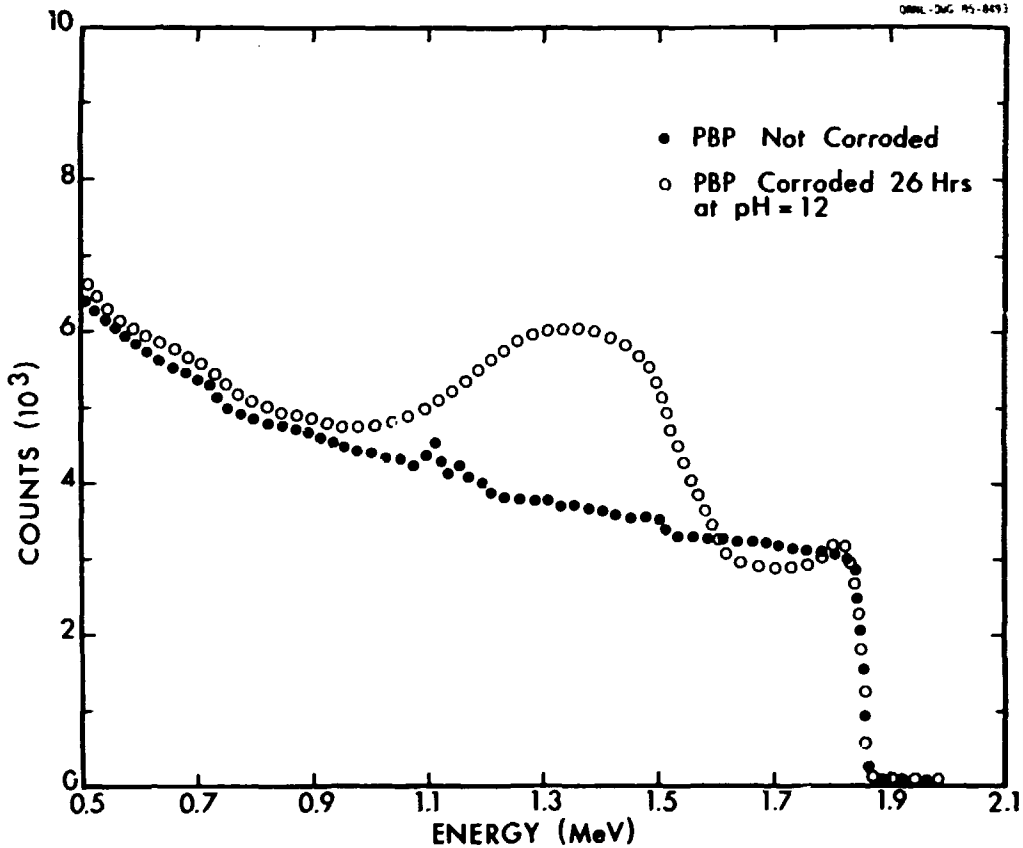
The RBS spectrum from the glass corroded in the pH=2 solution, however, showed a depletion of lead from the near-surface region (about 100 nm), but otherwise was very similar to the spectrum for the uncorroded glass. This indicates the corrosion of this glass in an acidic solution is primarily via congruent dissolution, in qualitative agreement with the solution analysis results (Table 4). After corroding the lead-iron phosphate glass in a basic solution, the RBS spectrum exhibited a substantial change in the surface composition which is indicative of incongruent dissolution. This result is also in agreement with the findings from solution analysis (Table 4). The increase in the ion scattering at energies between 1.1 and 1.5 MeV evident in Fig. 9 is believed to be due to the presence of excess Fe, Mn, and Ni in an altered surface layer which is approximately 200 nm thick.

3.4 CORROSION RESULTS — DEFENSE WASTE GLASSES WITH ZEOLITE AND CARBON

The defense waste composition D1 was used (see Table 3) in all of the previously described corrosion experiments (Sec. 3.2) employing lead-iron phosphate glasses loaded with simulated defense waste. This composition did not include zeolite and carbon, however, two components that are present in some types of defense waste. In the handling of the actual radioactive waste in storage at the Savannah River Facility, for example, zeolites are to be used to separate the radioactive Cs from the other components in the waste. At a later step in the waste processing, the zeolite and Cs may be combined with the rest of the waste for processing into a glass. The zeolites used in the Cs fixation are composed of Na-Al-silicates and Ca-Al-silicates [12]. During the melting process, these zeolites should decompose to Na_2O, CaO, Al_2O_3, and SiO_2. Since all

of these oxides were already present in the defense waste composition D1, it was considered unlikley that the addition of zeolite would significantly alter the performance of the glass. To test this hypotheses, lead-iron phosphate glasses were prepared and loaded with defense waste plus crushed zeolites and carbon (i.e., defense waste composition D2 in Table 3). Carbon is another constituent in some types of defense waste that could conceivably alter the performance of the glass. Lead-iron phosphate melt temperatures of about 1050°C were necessary to completely dissolve the crushed zeolite in the glass presumably because part of the zeolite decomposed to Al_2O_3 (see Sec. 2).

Samples of lead-iron phosphate and borosilicate glass loaded with defense waste composition D2 (see Table 3) were prepared. The glasses were placed in distilled water at 90°C and the increase in the solution conductivity as a function of time was measured. The results from this experiment (Fig. 11) indicate that the presence of zeolite and carbon in lead-iron phosphate glasses loaded with defense waste produces no measurable change in the aqueous corrosion rate. The overall corrosion rate of lead-iron phosphate nuclear waste glass containing both zeolites and carbon is still about 1000 times lower than the corrosion rate from a comparably loaded borosilicate glass under the specified corrosion conditions.

3.5 CORROSION RESULTS — COMMERCIAL WASTE GLASSES

A lead-iron phosphate glass loaded with simulated commercial waste (glass composition # 1-C, see Table 2) was exposed to distilled water at 90°C for 1 month. The leachate solution was then analyzed and the corrosion rate, R, was calculated for selected elements in the glass. A well characterized borosilicate glass (PNL 76-68) [28], loaded with a similar
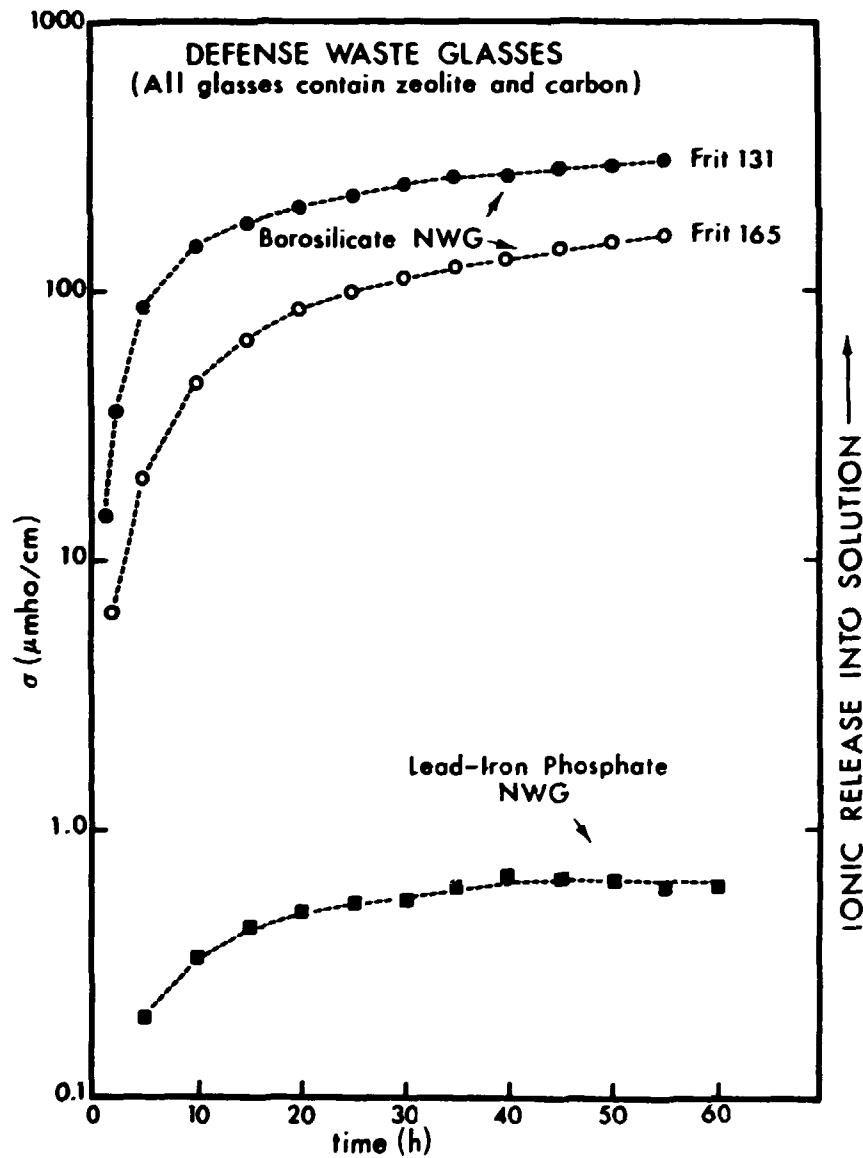
Fig. 11. Solution conductivity versus time plots for lead-iron phosphate glass # 2-D and borosilicate (Frit 131 and Frit 165 glasses loaded with 29 wt. % of waste composition D2) nuclear waste glasses. The lead-iron phosphate and borosilicate nuclear waste glasses had the same waste per volume loading.

composition of simulated commercial waste was corroded using the same test conditions as those employed for the lead-iron phosphate commercial waste glass. A comparison of the corrosion data for the lead-iron phosphate commercial waste glass and the borosilicate commercial waste glass [28] is shown in Fig. 12. No elements in the lead-iron phosphate leachate were present at concentrations above the analytical detectability limits which are indicated in the figure. The net release of all elements from the lead-iron phosphate glass was at least 100 to 1000 times smaller than the corresponding release from the borosilicate nuclear waste glass.

Lead-iron phosphate glasses loaded with simulated commercial waste were also exposed for 1 month to: J-13 well water at 90°C, a 0.01 N HCl solution at 90°C, a 0.01 N NaOH solution at 90°C, distilled water at 125°C, and distilled water at 150°C. The results from these corrosion experiments are tabulated in Table 7. In general, the corrosion results for lead-iron phosphate glasses loaded with commercial waste are similar to the results obtained with defense waste loaded lead-iron phosphate glasses (see Sec. 3.2). The commercial waste glasses, however, appear to be more corrosion resistant in acidic solutions and in water at 150°C. This is probably due to the low amount of alkali oxides in commercial waste, the presence of rare-earth elements, and the lower waste loading appropriate to the disposal of commercial high-level wastes.

3.6 CRYSTALLIZATION RESULTS

One of the major reasons that phosphate glasses were abandoned during the early stages of nuclear waste form development was that most of the phosphate glasses investigated at that time tended to crystallize either during the cooling of large glass blocks or during moderate
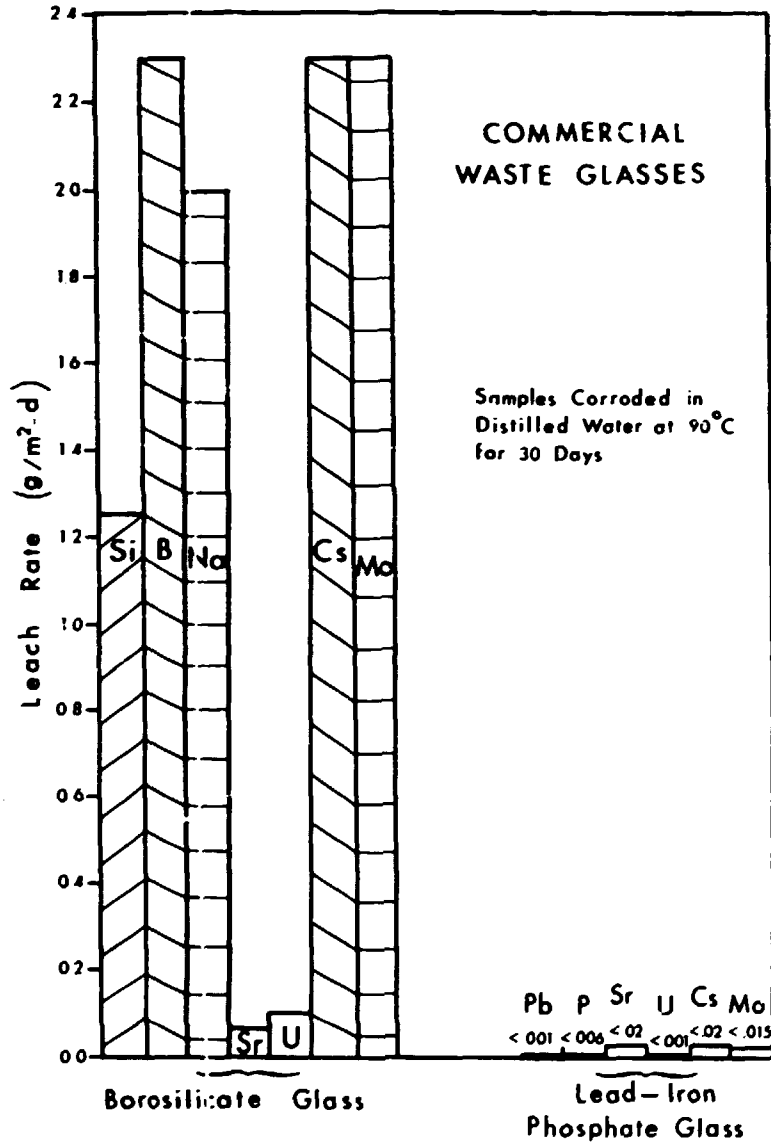
ORNL-DWG. 86-16753

Fig. 12. The 30-day corrosion rates at 90°C in distilled water for a lead-iron phosphate glass (# 1-C) and a borosilicate glass (PNL 76-68 [28]) loaded with simulated commercial waste. The concentrations of all elements present in the lead-iron phosphate leachate were below the detectability limits of standard analytical chemical techniques.

Table 7. Corrosion Rates $(g/m^2\text{-}d)$ for Lead-Iron Phosphate Glasses
Loaded with Simulated Commercial Waste — Glass # 1-C.

All glasses were corroded for 1 month.

Corroding Solution	Water 90°C	J-13 Water[a] 90°C	pH 2[b] 90°C	pH 12[c] 90°C	Water[d] 125°C	Water[d] 150°C
Pb	<0.001	<0.001	<0.11	<0.001	<0.002	0.008
P	<0.005	<0.005	0.1	1.5	0.04	1.5
Fe	<0.004	<0.0004	0.04	<0.0004	<0.009	<0.009
Sr	<0.004	<0.004	0.118	<0.0001	0.15	0.57
Cs	<0.005	<0.04	0.05	1.2	-	
Zr	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mo	<0.01	<0.04	<0.1	2.3	0.04	0.02
U	<0.001	<0.001	0.1	0.02	<0.002	0.03

[a]J-13 well water (which has a pH of about 8.2) is the reference water type for disposal in a tuff formation [21].

[b]A 0.01 N HCl solution.

[c]A 0.01 N NaOH solution.

[d]Part of the corrosion cells were made of stainless steel and inconel. It is not known how much of the phosphorus detected in solution was due to corrosion of the container.

reheating of the phosphate glass [29]. The crystallization of any nuclear waste glass can increase the surface area of the glass and tends to produce crystalline phases which may be soluble in water. Most often the net result of crystallization is to increase the aqueous corrosion rate of the glass which is obviously highly undesirable.

Although studies were not made to optimize the crystallization characteristics of lead-iron phosphate nuclear waste glasses by adjusting the composition, several crystallization tests were conducted on glasses loaded with either simulated defense waste (glass # 1-D, see Table 1) or simulated commercial waste (glass # 1-C, see Table 2). In one set of

tests the lead-iron phosphate nuclear waste glasses were heated to 1000°C
in air and then cooled to room temperature at a constant rate using a
programmable furnace controller. As is the case for most glasses, the
nucleation and growth of crystalline material in lead-iron phosphate
glasses began on the surface of the melt in contact with the air. The
cooling rate for which crystalline material was first observed on the sur-
face of the melt was defined to be the critical cooling rate for the
glass. For both the commercial and defense waste loaded lead-iron
phosphate glasses the critical cooling rate was between 5 and 10°C/min.
This means that if the glass melts are cooled slower than 5-10°C/min some
fraction of the resulting solid will be crystalline, whereas if the glass
melts are cooled faster than 5-10°C/min, a homogeneous glass will be
formed. It is important to realize that the cooling of the glass melt
only has to exceed the critical cooling rate in a narrow temperature range
in order to form a homogeneous glass. At temperatures above the ther-
modynamic melting point of the glass (above about 820°C for lead-iron
phosphate NWG), the glass can be cooled at any rate since there is no
driving force for crystallization, while at temperatures below about 550°C
the glass can be cooled at very low rates (less than 0.001°C/min) since
the high viscosity of the glass effectively blocks crystallization. To
determine over what temperature range the cooling rate of lead-iron
phosphate nuclear waste glasses must exceed 5-10°C/min to avoid crystalli-
zation, another set of experiments was performed. A lead-iron phosphate
glass loaded with simulated commercial waste (glass # 1-C) was placed in a
Perkin-Elmer DTA-1700 differential thermal analysis system and heated to
1050°C in a platinum cup in a nitrogen atmosphere. After holding the

glass melt at 1050°C for 30 min, the glass was cooled at rates near or below the critical cooling rate and the DTA signal was recorded. The presence of a small exothermic peak centered at about 680°C was an indication of crystallization occurring for a portion of the sample, and observations of this peak indicated that the temperature range through which the glass must be cooled faster than the critical cooling rate was between 650 and 710°C (see Fig. 13). When the same glass (# 1-C) was cooled in air, rather than in a pure nitrogen atmosphere, the measured critical cooling rate was about 5°C/min rather than 10°C/min.

Differential thermal analysis data were also taken while heating the glass at a constant rate of 10°C/min. These data were more difficult to interpret since the qualitative features of the DTA curve depended not only on the heating rate but also on the details of the previous cooling curve. If the glass was first heated at about 1050°C for about 30 min followed by cooling to room temperature at a rate greater than 10°C/min, the subsequent DTA heating curve was found to be reproducible. A typical DTA heating curve for glass # 1-C is shown in Fig. 14. The glass transition, glass crystallization temperature, and melting point are noted in the figure.

By comparing the critical cooling rates of 5-10°C/min with the measured air-cooled rates for large cylinders of molten borosilicate glass [30], it is estimated that lead-iron phosphate nuclear waste glasses could be cast into cylinders 15-30 cm in diameter by 300 cm long without encountering significant crystallization problems, particularly if metal cooling fins are inserted into the metal cannister to accelerate the cooling of the glass through the critical temperature region. The largest cylinder
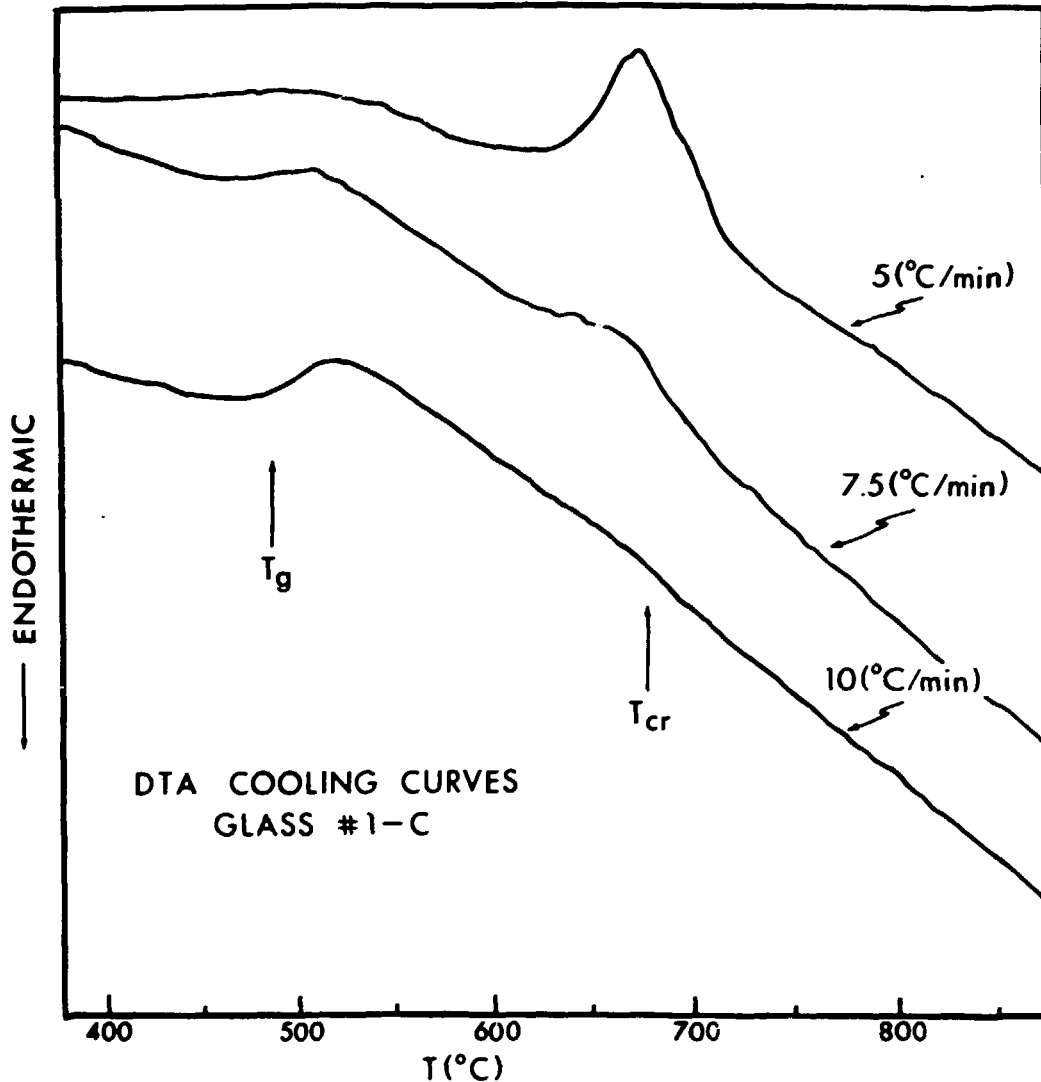
OPNL-DWG 85-8828

Fig. 13. Differential thermal analysis signal versus temperature for a lead-iron phosphate nuclear waste glass (# 1-C) which was cooled from 1050°C to 200°C at a constant cooling rate of 5, 7.5, or 10°C/min. These measurements were performed using a pure nitrogen atmosphere with the glass sample supported by a platinum cup. The glass transition temperature T_g, and the temperature of the maximum rate of crystallization T_{cr}, are noted in the figure. The temperature scale was calibrated using the melting point of pure aluminum metal.
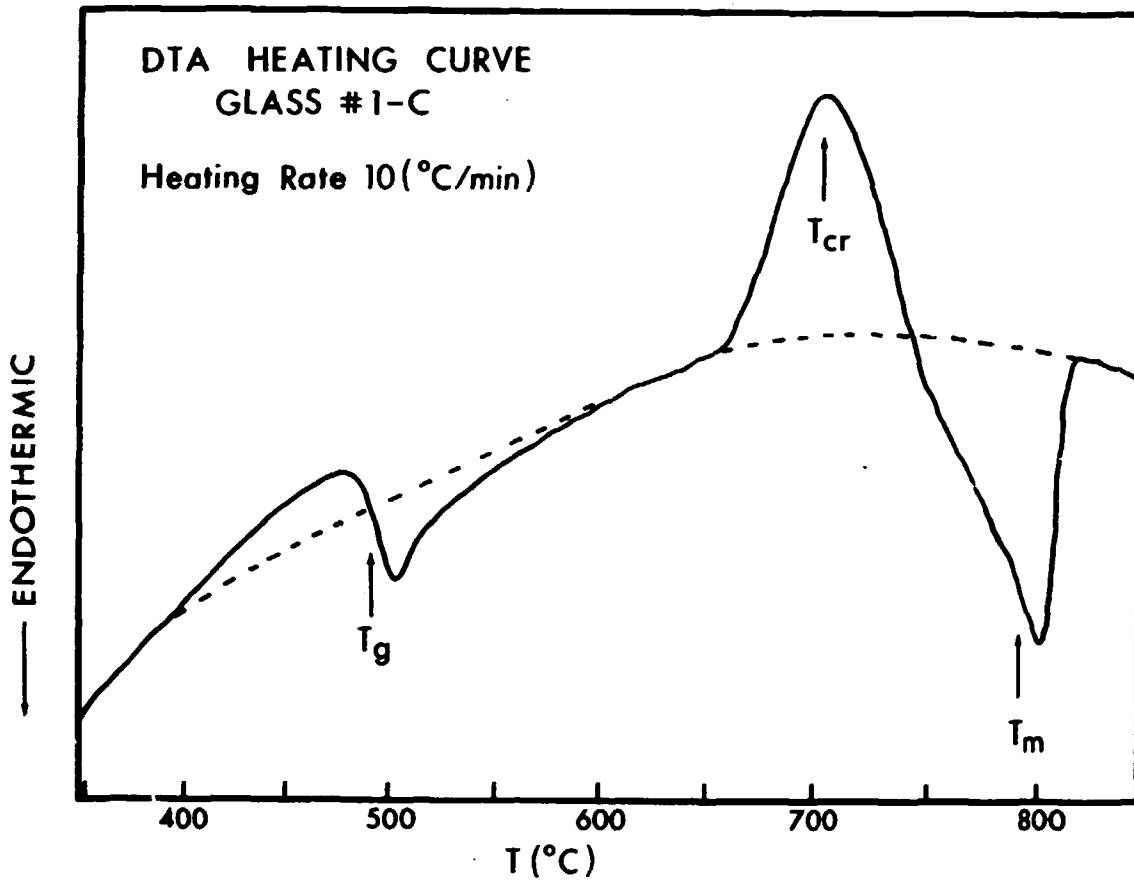
ORNL-DWG 85-8827

DTA HEATING CURVE
GLASS #1-C

Heating Rate 10(°C/min)

T_{cr}

ENDOTHERMIC

T_g

T_m

400   500   600   700   800

T (°C)

Fig. 14. Differential thermal analysis signal versus temperature for a lead-iron phosphate nuclear waste glass (# 1—C) which was heated from 200 to 1050°C at a constant rate of 10°C/min. Prior to this heating run, the glass was heated to 1050°C for 30 min and then cooled to 200°C at a rate of 20°C/min. These measurements were performed using a pure nitrogen atmosphere with the sample supported by a platinum cup. The glass transition temperature T_g, the temperature of the maximum rate of crystallizaton T_{cr}, and the melting point T_m, are noted in the figure. The dashed line shown is the normal baseline drift and was added as a guide to the eye. The temperature scale was calibrated using the melting point of pure aluminum metal.

of lead-iron phosphate NWG produced in our laboratory was 6 cm in diameter and 5 cm high.

Borosilicate nuclear waste glasses have very low critical cooling rates (about 0.1°C/min) which in general makes glass formation somewhat easier than in the case of lead-iron phosphate NWG. The temperature dependence of the viscosity for borosilicate glasses, however, is much weaker than for lead-iron phosphate glasses, which implies that for borosilicate glasses there is a larger temperature range where crystallization may occur. The importance of having a nuclear waste glass with a narrow temperature range for crystallization is illustrated by the results from the isothermal annealing experiments discussed below.

To assess the effects of prolonged annealing or reheating on the lead-iron phosphate and borosilicate nuclear waste glasses, a series of isothermal annealing and aqueous corrosion experiments were performed on both defense and commercial waste glasses. From thermal expansion measurements (see Sec. 3.7), it was determined that the optimum annealing temperature for both lead-iron phosphate and borosilicate NWG was about 450–500°C. Glasses which were heated at this temperature were sufficiently plastic to remove internal strains, which prevented the glasses from cracking on subsequent cooling to room temperature.

Samples of lead-iron phosphate (glass # 1–D and # 1–C) and borosilicate (Frit 131 + 29% SRW [18] and PNL 76-68 [28]) waste glasses were heated in air for 450 h at 500°C. After the heat treatment, the glasses were examined using scanning electron microscopy, energy dispersive x-ray analysis, and powder x-ray diffraction. For the lead-iron phosphate glasses, there was no evidence of crystallization or phase

separation as a result of the heat treatment. Subsequent corrosion tests on both defense and commercial waste loaded lead-iron phosphate glasses indicated no measurable change in the overall corrosion rate (Figs. 15,16). This null result is important because it implies that large blocks of lead-iron phosphate nuclear waste glasses can be annealed for prolonged periods of time thereby reducing the likelihood of glass cracking and, hence, increasing the chances of producing a large glass monolith with a small surface-to-volume ratio. Only the initial corrosion rate was investigated, since, as noted before, the crystallization of nuclear waste glasses usually begins at the air/glass interface. A measurement of the initial corrosion rate, therefore, should be most sensitive to any crystallization or phase separation which has occurred on the glass surface.

Following the same heat treatment, scanning electron microscopy and energy dispersive x-ray analysis indicated that substantial crystallization and phase separation had occurred on the surface of both the commercial and defense waste loaded borosilicate glasses. Subsequent measurements of the corrosion rate of these borosilicate glasses showed a 3—25 fold increase in the initial aqueous corrosion rate (Figs. 15,16).

If lead-iron phosphate nuclear waste glasses are heated at temperatures above 575°C for an extended period of time (greater than 1d), a substantial fraction of the glass will crystallize. This will result in a glass ceramic material which will have inferior physical and chemical characteristics. Hence, in the preparation of large monoliths of lead-iron phosphate NWG, care must be taken during the cooling of the glass to ensure that it does not remain at temperatures above 575°C for extended
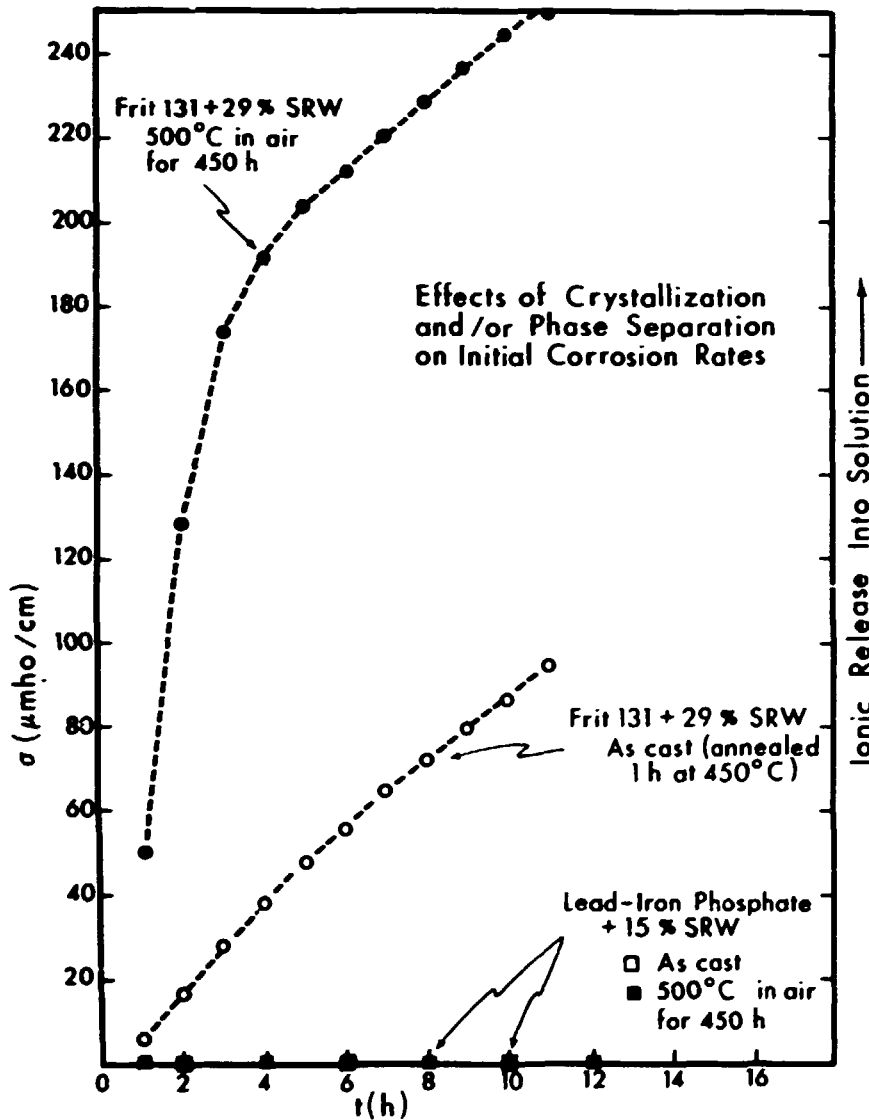
ORNL-DWG. 84-16746R

Fig. 15. Solution conductivity versus time data for lead-iron phosphate (# 1-D) and borosilicate (Frit 131 + 29 wt. % of waste composition D1) nuclear waste glasses loaded with simulated defense waste. The initial corrosion rates in water at 90°C were measured for "as cast" glasses and for glasses which had been heated in air at 500°C for 450 h. The increase in the initial corrosion rate of the borosilicate nuclear waste glass is due to the crystallization and/or phase separation which occurs on the glass surface. Following the same heat treatment, there was no detectable increase in the initial corrosion rate of the lead-iron phosphate glass.
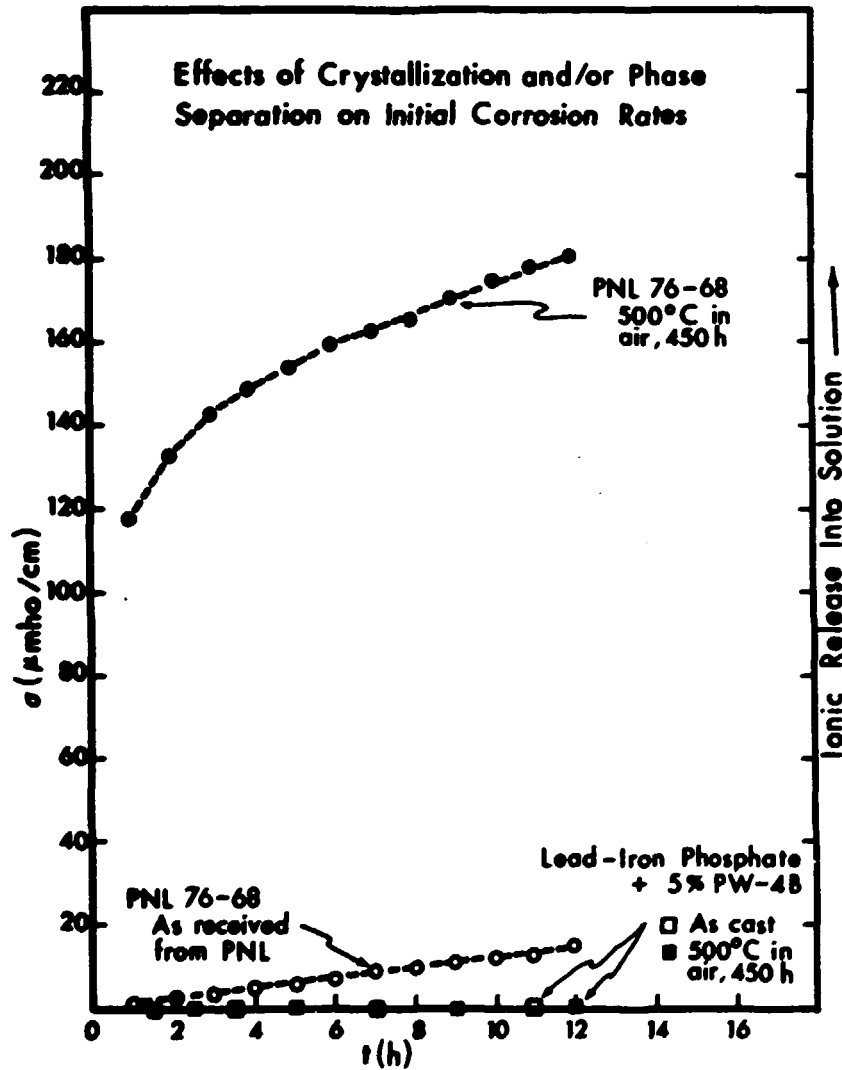
ORNL-DWG. 84-16745R

Fig. 16. Solution conductivity versus time data for lead-iron phosphate (# 1-C) and borosilicate (PNL 76-68, [28]) nuclear waste glasses loaded with simulated commercial waste. The initial corrosion rates in water at 90°C were measured for "as cast" glasses and for glasses which had been heated in air at 500°C for 450 h. The increase in the initial corrosion rate of the borosilicate nuclear waste glass is due to the crystallization and/or phase separation which occurs on the glass surface. Following the same heat treatment, there was no measurable increase in the initial corrosion rate of the lead-iron phosphate glass.

periods of time. It should be noted, however, that both of the borosilicate nuclear waste glasses investigated here (Frit 131 + 29 % of waste composition D1 and PNL 76-68) also rapidly crystallized when heated at temperatures higher than 575°C.

3.7 THERMAL PROPERTIES

To cast a large monolith of a nuclear waste glass in a metal cannister with a minimum of glass cracking, crystallization, and residual stress but with a maximum concentration of radioactive waste (which acts as a heat source) requires information about the fundamental thermal properties of the glass. Accordingly, the glass transition temperature, softening point, thermal expansion coefficient, thermal conductivity, and heat capacity were measured for several lead-iron phosphate nuclear waste glasses.

A dilatometer (Theta Corp.—Dilatronic) with a linear variable differential transformer (LVDT) constant load sensor was used to determine the glass transition temperature T_g, softening point T_s, and thermal expansion coefficient α. The dilatometric measurements were made using a heating rate of 3°C/min, and during the experiment a 3-mm diameter quartz rod maintained a constant load of 10 g on the lead-iron phosphate sample. The glass transition temperature was taken to be the temperature at which a large increase occurred in the slope of the expansion vs temperature curve, and the softening point was defined as the temperature at which the thermal expansion curve passed through a maximum. Typical expansion vs temperature curves are shown in Figs. 17 and 18, respectively, for defense waste and commercial waste loaded lead-iron phosphate glasses.
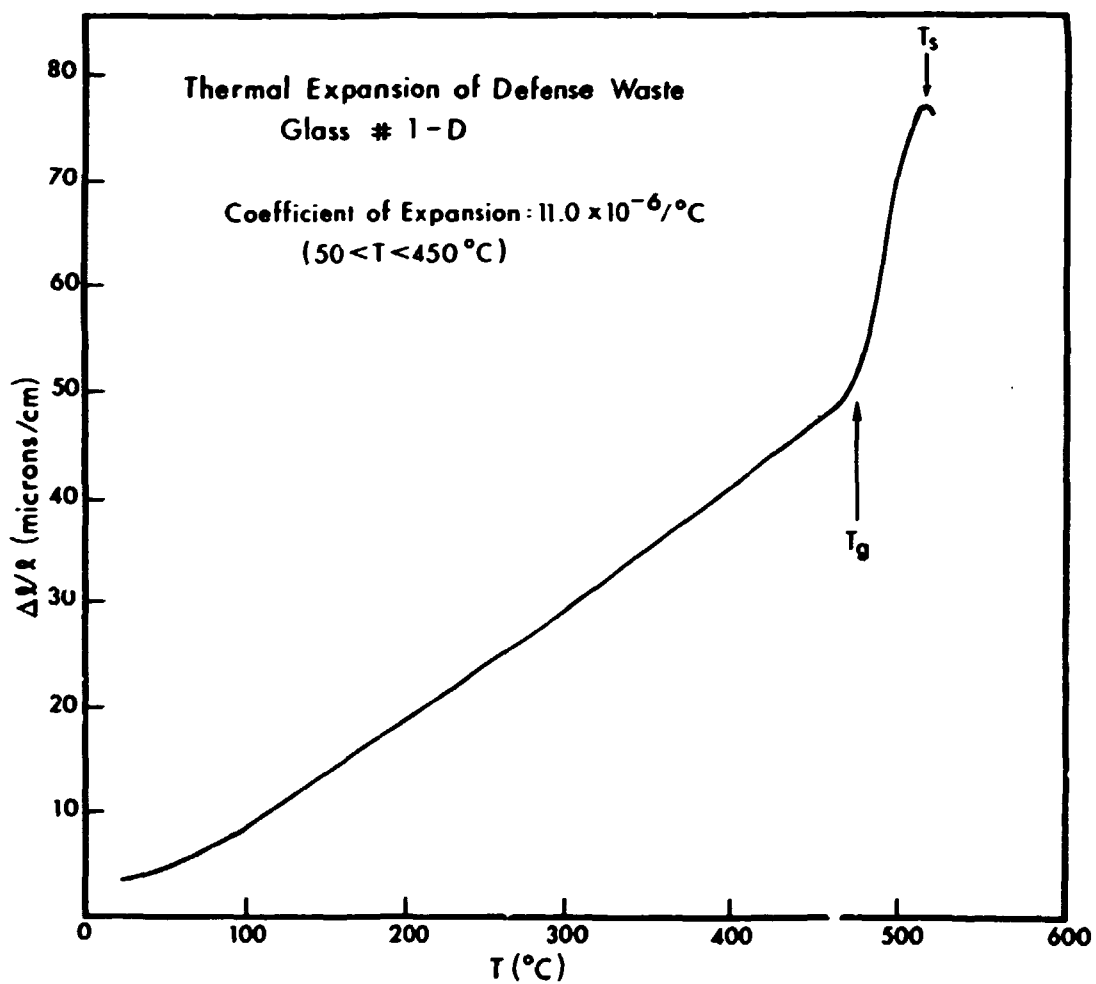
Fig. 17. Expansion versus temperature for lead-iron phosphate defense waste glass # 1-D. The glass transition temperature T_g and the softening temperature T_s are noted in the figur .
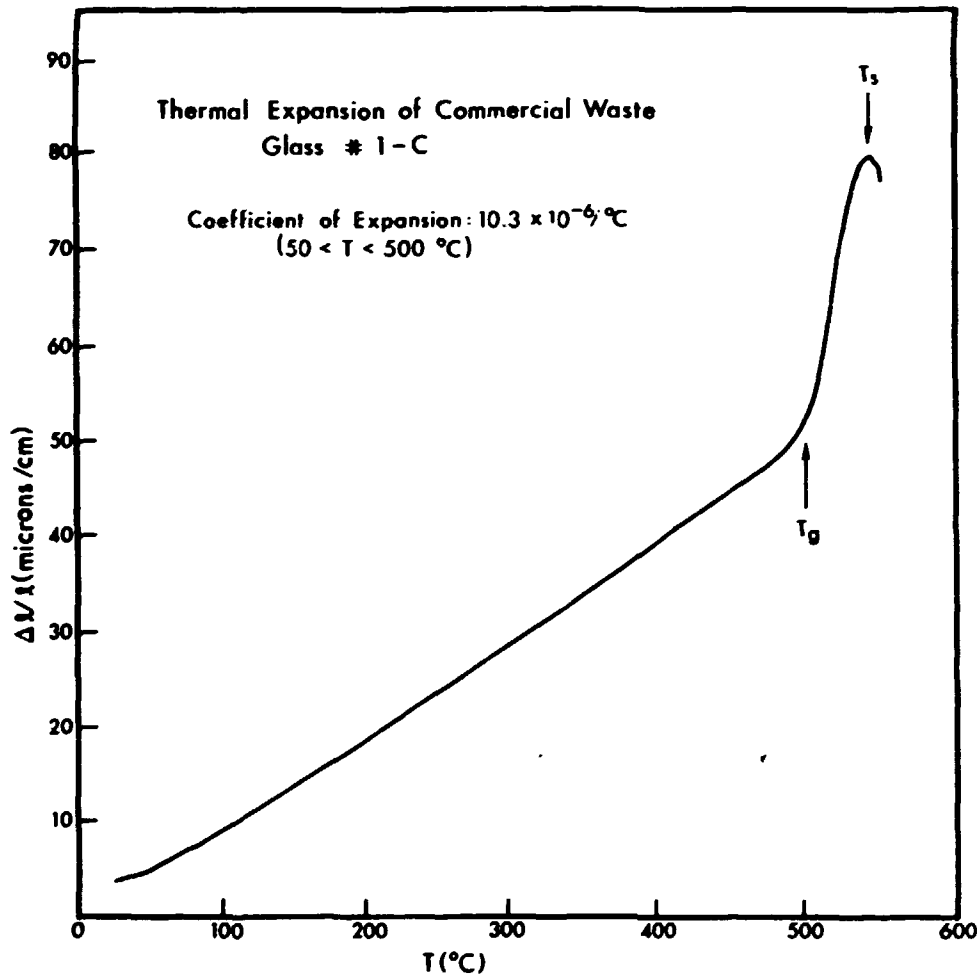
ORNL-DWG 85-8312

Fig. 18. Expansion versus temperature for lead-iron phosphate commercial waste glass # 1-C. The glass transition temperature T_g and the softening Temperature T_s are noted in the figure.

Heat capacity measurements on lead-iron phosphate NWG were made with a scanning calorimeter (Perkin-Elmer DSC-4) operated at a heating rate of 10°C/min. Quantitative heat capacity data was obtained by comparing the heat flow into the nuclear waste glass with the heat flow into a sapphire standard which had the same geometry and was measured under identical conditions. The heat capacity data for lead-iron phosphate glasses # 1-D and # 1-C are given in Table 8.

Thermal conductivity measurements were made [31] on samples of a defense-waste-loaded lead-iron phosphate glass # 3-D. The glass samples were cast in the form of right circular cylinders with a diameter of about 5 mm and a length of 1 cm. The end faces of the glass samples were cut parallel and polished flat. The thermal conductivity of these samples was measured at 30, 60, and 90°C and had values for K of 0.00585, 0.0060, 0.00622 watt/cm-K, respectively.

3.8 METAL CANNISTERS

Several metal containers were investigated as possible cannisters into which the molten lead-iron phosphate glasses could be poured. In the current plan for the disposal of U.S. defense wastes, for example, molten borosilicate glass will be poured into type 304 L stainless steel cannisters [12] and allowed to solidify. The cannisters will be then welded shut and transported to an underground repository for permanent storage. With the stainless steel cannister surrounding the waste glass, not only is the transportation of the glass from the processing facility to the repository greatly facilitated, but the cannister itself provides an additional barrier between the waste glass and the potential intrusion of groundwater.

Table 8. Heat Capacity of Lead-Iron Phosphate Nuclear Waste Glasses at
Constant Pressure versus Temperature.

Temperature°C	C_p (cal/gm-°C) for glass # 1-D	C_p (cal/gm-°C) for glass # 1-C
50	0.113	0.112
100	0.122	0.121
150	0.130	0.129
200	0.139	0.138
250	0.148	0.149
300	0.156	0.161
350	0.162	0.170
400	0.171	0.184

Samples of molten lead-iron phosphate NWG were poured into cans of aluminum, inconel, and type 430 stainless steel [32]. Molten lead-iron phosphate reacted violently with inconel, rapidly dissolving a good portion of the metal crucible. Inconel is not a suitable cannister material for lead-iron phosphate glasses. Before pouring the molten glass into the aluminum can, the temperature of the melt was reduced to 800°C (aluminum melts at 660°C). There appeared to be very little reaction between the lead-iron phosphate glass and the walls of the aluminum container and hence it was concluded that it would be possible to use an aluminum cannister. Some circumferential cracking of the glass in the aluminum container was observed that was presumably caused by the much larger thermal expansion coefficient of aluminum relative to lead-iron phosphate glass.

Samples of lead-iron phosphate glass were poured into type 430 stainless steel cans measuring 1.25 in. in diameter by 1.5 in. tall with a 0.025 in. wall thickness. There appeared to be very little reaction between the lead-iron phosphate glass and the metal walls and there was no observable circumferential fracturing of the glass. A type 400 series stainless steel was studied rather than a type 300 series stainless steel, because there is a very close match between the thermal expansion coefficient of lead-iron phosphate glasses and type 430 stainless steel [33]. The corrosion resistance of type 400 stainless steels is also comparable to steels of the 300 series [32].

4. SUMMARY

Lead-iron phosphate glasses appear to be a promising new storage medium for many major categories of defense and commercial high-level nuclear wastes. Relative to borosilicate nuclear waste glasses, which represent the current reference primary storage medium, lead-iron phosphate nucl· waste glasses have several distinct advantages which include: 1) an iqueous corrosion rate which is between 100 and 1000 times lower, 2) a formation temperature that is 100 to 250°C lower than the temperature (1150°C) required for a comparable borosilicate glass and, 3) a much lower melt viscosity in the temperature range between 800 and 1050°C. The processing technology for producing lead-iron phosphate nuclear waste glasses is also similar to that developed for processing borosilicate nuclear waste glasses in many respects.

The lead-iron phosphate nuclear waste glasses can be prepared by melting in either stabilized zirconia, platinum, or alumina crucibles.

For defense waste loaded glasses, platinum crucibles appear to be the preferred choice followed by zirconia, but for commercial waste loaded glasses zirconia crucibles may perform better. All of the waste oxides and silicates in both the simulated defense waste and in the simulated commercial waste were completely dissolved in the lead-iron phosphate melt at 1050°C with the exception of ZrO_2 — a constituent of commercial waste.

The results of extensive corrosion tests on lead-iron phosphate glasses indicate that these glasses are extremely resistant to aqueous corrosion when the solution pH is between about 5 and 9 and the solution temperature is below about 125°C. At temperatures above 125°C, the hydrothermal corrosion rate of defense-waste-loaded lead-iron phosphate glasses rapidly increases. Commercial-waste-loaded lead-iron phosphate glasses are resistant to corrosion for solution temperatures below 150°C.

Crystallization studies on lead-iron phosphate nuclear waste glasses indicate that these glasses can be annealed for prolonged periods of time (450 h at 500°C) without exhibiting any detectable crystallization or phase separation as a result of the heat treatment. Subsequent corrosion tests on heat treated glasses indicated no measurable change in the corrosion rate. In another set of crystallization experiments it was determined that at 680 ± 25°C the crystallization rate during cooling was a maximum for lead-iron phosphate glasses and that these glasses had to be cooled through this temperature region (680 ± 25°C) at a rate greater than 5—10°C/min to prevent crystallization from occurring. These crystallization studies indicate that it should be possible to produce a single uncracked cylindrical monolith of lead-iron phosphate nuclear waste glass approximately 15—30 cm in diameter by 300 cm long with a minimum of

crystallization. The largest cylinder of lead-iron phosphate nuclear waste glass produced in our laboratory was 6 cm in diameter and 5 cm high.

A summary of pertinent thermal, physical, and chemical characteristics of lead-iron phosphate nuclear waste glasses are given in Tables 9 and 10. Although all of the experimental results reported in this article were obtained on laboratory scale samples using glasses loaded with simulated nuclear waste, it is hoped that the results of the research will stimulate full scale evaluations of the possible use of lead-iron phosphate glass as primary storage medium for high-level nuclear waste.

Table 9. Summary of Thermal, Physical, and Chemical Properties of Lead-Iron Phosphate Glasses Loaded with Simulated Defense Waste.

Property	Measured Value	Temperature	Glass Compositions
Glass melting temperature	1050°C	—	1-D, 2-D
Glass pouring temperature	900°C	—	1-D, 2-D
Preferred melting crucible	Platinum		1-D, 2-D
Glass Density	4.7 ± 0.1 g/cm^3	25°C	1-D, 2-D
Waste Loading	0.73 g/cm^3	25°C	1-D, 2-D
Corrosion rate in water	< 0.001 g/m^2-d	90°C	1-D
Maximum hydrothermal temperature[a]	125°C	—	1-D
Critical cooling rate[b]	5-10°C/min	50-1000°C	1-D
Temperature of maximum rate of crystallization	680 ± 25°C	—	1-D
Annealing temperature	470°C	—	1-D
Glass transition temperature	477°C	—	1-D
Softening temperature	518°C	—	1-D
Thermal expansion coefficient	11.0×10^{-6}/°C	40-450°C	1-D
Heat capacity	0.1-0.16 cal/g-°C	50-350°C	1-D
Thermal conductivity	0.006 ± 0.001 W/cm-°C	30-90°C	3-D

[a]Above this temperature the corrosion rate rapidly increased with increasing temperature.

[b]The slowest rate at which the glass can be cooled without any bulk crystallization.

Table 10. Summary of Thermal, Physical, and Chemical Characteristics of Lead-Iron Phosphate Glasses Loaded with Simulated Commercial Waste.

Property	Measured Value	Temperature	Glass Compositions
Glass melting temperature	1050°C	—	1-C
Glass pouring temperature	900°C	—	1-C
Preferred melting crucibles	Zirconia, Pt	—	1-C
Glass Density	5.0 ± 0.1 g/cm^3	25°C	1-C
Waste Loading	0.32 g/cm^3	25°C	1-C
Corrosion rate in water	< 0.001 g/m^2-d	90°C	1-C
Maximum hydrothermal temperature[a]	150°C	—	1-C
Critical cooling rate[b]	5–10°C/min	50–1000°C	1-C
Temperature of maximum rate of crystallization	680 ± 25°C	—	1-C
Annealing temperature	490°C	—	1-C
Glass transition temperature	502°C	—	1-C
Softening temperature	544°C	—	1-C
Thermal expansion coefficient	10.3 x 10^{-6}/°C	50–500°C	1-C
Heat capacity	0.1–0.16 cal/g-°C	50–350°C	1-C

[a]This temperature is the maximum temperature at which aqueous corrosion tests were conducted.

[b]The slowest rate at which the glass can be cooled without any bulk crystallization.

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