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DURABILITY OF SIMULATED DWPF ANNEALED GLASSES

by

Mary K. Andrews, Connie A.Cicero, Sharon L. Marra, and D. Chris Beam

Westinghouse Savannah River Company
Aiken, SC 29808

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DURABILITY OF SIMULATED DWPF ANNEALED GLASSES

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ABSTRACT

Simulated high-level waste glass samples of the DWPF projected compositions were annealed at various times and temperatures in order to develop time-temperature-transformation diagrams. These heat treated glasses were subjected to the Product Consistency Test (PCT) to evaluate glass durability. The B, Li, and Na concentrations in the leachate (the PCT results) were compared to the PCT results of the Environmental Assessment benchmark glass. Durability as a function of glass composition and crystallinity was also examined.

INTRODUCTION

Approximately 130 million liters of high-level radioactive waste are currently stored in underground carbon steel tanks at the Savannah River Site (SRS). This high-level radioactive waste will be immobilized in a durable borosilicate glass and poured into stainless steel canisters in the Defense Waste Processing Facility (DWPF). The canistered waste forms will eventually be sent to the Civilian Radioactive Waste Management System for final disposal at a repository. The Department of Energy has defined requirements which these canistered waste forms must meet to be acceptable for disposal in the repository. These requirements are the Waste Acceptance Product Specifications (WAPS).[1] The WAPS requires that time-temperature-transformation (TTT) diagrams be developed for each of the DWPF projected high-level waste glass compositions.

Seven DWPF glass compositions have been projected and are described in the DWPF Waste Form Compliance Plan (WCP).[2] Four of these compositions (Batches 1, 2, 3, and 4) have been projected from existing high-level waste inventory while three of them are hypothetical glass compositions. The three hypothetical glasses are the design-basis waste (Blend), high aluminum (HM) waste which represents the upper design limit of glass viscosity, and high iron (Purex) waste which represents the lower design limit of glass viscosity.[2] The Purex composition is based on: maximum precipitate feed rate, minimum sludge feed rate and minimum removal of soluble salts during sludge processing. Thus, the Purex represents a possible worst-case composition. The Environmental Assessment glass[3] is the benchmark glass for the DWPF.

In order to develop the TTT diagrams, samples of the seven DWPF projected glass compositions were heat treated at various times and temperatures. These heat treated glasses were then subjected to the Product Consistency Test (PCT).[4]

In order to provide the necessary information required by the WAPS, Corning Inc. was contracted to supply large quantities of the seven simulated waste glasses from the WCP.[3] Corning Inc. was unable to handle uranium containing glasses and so the U_3O_8 component of the WCP glasses[2] was omitted and the glass compositions renormalized. Reference amounts of the minor Ru component were added as RuO_2. The Corning analysis of the seven glass compositions as fabricated is shown in Table 1.

Table 1. DWPF Projected Compositions

Glass Components Wt %	Blend	HM	Purex	Batch #1	Batch #2	Batch #3	Batch #4
Al_2O_3	4.16	7.15	2.99	4.88	4.63	3.44	3.43
B_2O_3	8.05	7.03	10.33	7.78	7.88	7.69	8.14
BaO	0.18	0.11	0.20	0.15	0.16	0.18	0.25
CaO	1.03	1.01	1.09	1.22	1.08	0.99	0.84
Cr_2O_3	0.13	0.09	0.15	0.11	0.13	0.14	0.14
Cs_2O	0.08	0.06	0.06	0.06	0.02	0.06	0.09
CuO	0.44	0.25	0.42	0.40	0.42	0.40	0.45
Fe_2O_3	10.91	7.78	13.25	12.84	11.12	11.71	11.71
K_2O	3.68	2.21	3.41	3.33	3.38	3.40	3.86
Li_2O	4.44	4.62	3.22	4.43	4.50	4.51	4.29
MgO	1.41	1.49	1.41	1.42	1.42	1.42	1.43
MnO_2	2.05	2.15	2.07	2.11	1.73	1.87	3.11
MoO_3	0.15	0.22	0.08	0.11	0.17	0.12	0.20
Na2O	9.13	8.56	12.62	9.00	9.21	9.01	9.16
Nd_2O_3	0.22	0.55	0.06	0.15	0.26	0.17	0.39
NiO	0.89	0.41	1.19	0.75	0.90	1.05	1.06
RuO_2	0.03	0.04	0.01	0.02	0.04	0.03	0.05
SiO_2	51.90	55.80	46.50	50.20	52.10	52.60	50.10
TiO_2	0.89	0.56	0.68	0.68	0.69	0.68	1.03
ZrO_2	0.14	0.33	0.05	0.10	0.17	0.12	0.22
Total	99.91	100.42	99.79	99.74	100.01	99.59	99.95

EXPERIMENTAL

Heat Treatment

The WCP glasses were exposed to various times and temperatures in order to determine the effect of time and temperature on durability results. Approximately 70 grams of glass was placed in a covered high purity (99.8%) alumina crucible. The crucibles were placed in a Lindberg programmable furnace and melted at the DWPF melt temperature of 1150°C for four hours. The glasses were heat treated at temperatures of 500, 600, 700, 800, 900, 1000, or 1100°C and times of 0.75, 3, 12, 48, 192, or 768 hours. For heat treatment at temperatures of 900°C and below, the crucibles were transferred to preheated Thermolyne muffle furnaces. For heat treatment at temperatures above 900°C, the crucibles remained in the Lindberg. Each glass sample was heat treated at a unique time and temperature. The 500 and 1100°C temperatures were chosen for conservatism. The 1100°C temperature being just below the melting temperature and the 500°C temperature being just above the glass transition temperature. Some samples were heat treated at 400°C to serve as controls. Additional samples were heat treated at 650°C to provide more information.

In order to simulate quenched glass (i.e. not heat treated), the as-received glass from Corning was remelted and quenched. Approximately 70 grams of each of the seven DWPF projected compositions was placed in a covered high purity (99.8%) alumina crucible. The crucibles were placed in the same Lindberg furnace discussed above and melted at 1150°C for four hours. After melting, the glasses were removed from the furnace and air cooled rapidly to room temperature.

Product Consistency Test

The heat treated glasses and the seven as quenched glasses were subjected to the Product Consistency Test (PCT)[4] to assess the durability. Preparation for the PCT included crushing the glass to 100-200 mesh and washing it to remove fines. The glasses are then immersed in ASTM Type I water . Three and a half grams of glass and 35 grams of ASTM Type I water were placed in teflon vessels for 7 days at 90°C. Tests containing ASTM Type I water but no glass samples were run simultaneously with the glasses as "blanks." The use of blanks ensures that test vessel preparation was adequate and that the sample leachates can be corrected for elemental variation occurring independently of the glass-solution interactions. A standard glass, ARM-1 was used as a control to eliminate long term bias in the experimental analysis and in the analytical data. For several of the tests the Environmental Assessment (EA) glass was also run and used as a benchmark.

Following the seven day exposure, the leachates were filtered with a 45 um filter to remove colloids and/or particulates. The leachates were analyzed for pH and the elemental concentration of the glass species of interest. The normalized releases of B, Na, and Li were compared to the average normalized release of the

Environmental Assessment (EA) glass.

The leachate concentrations are reported as normalized elemental mass losses, NCi, released from the glass in grams of glass per L of leachant. This has the advantage that the release concentrations in parts per million are normalized by the weight fraction of that element present in the glass.

The expression below for normalized elemental mass loss, NCi has been used in this study.

$$NC_i = \frac{C_i}{F_i}$$

where NC_i = normalized elemental mass loss (gglass/L)

C_i = mass of element "i" in the solution corrected for the average mass of element "i" in the blanks (gi/m3)

F_i = fraction of element "i" in the glass (g_i/g_{glass})

RESULTS

The blanks and standards run simultaneously with the heat treated glasses during the performance of the PCT showed that no significant errors occurred during the testing. The normalized releases of the seven glass compositions were compared to the average normalized release of the Environmental Assessment (EA) glass.[4] For the majority of the glasses, the normalized release was significantly less than the EA glass. However, some of the samples heat-treated at 600 and 700°C for longer times did exceed the EA normalized release for boron and lithium. It should be noted that previous work by SRTC[5] has shown that under the conditions expected during cooling of a canister, all of the projected glasses were more durable than the EA glass.

Figure 1-7 show the normalized boron and lithium releases as a function of time for each of the seven glass compositions annealed at 600, 700, and 800°C. The other temperatures had less significant releases. Also included in these figures are the average normalized releases of boron and lithium for the EA glass. Batch 1 and HM glasses did not exceed the results of the EA glass even under extreme conditions. The lithium releases of the Batch 2 and Blend glasses exceeded the lithium release of the EA glass but were acceptable for boron and sodium. Batch 3, Batch 4 and Purex exceeded the boron and the lithium releases of the EA glass.

The normalized PCT results from the quenched glasses are compared to the normalized EA results in Table 2. Batch 4 and Purex had the least durable baseline because they contain the highest amounts of alkali (which decrease durability) and the lowest amount of glass formers (which increase durability). The higher

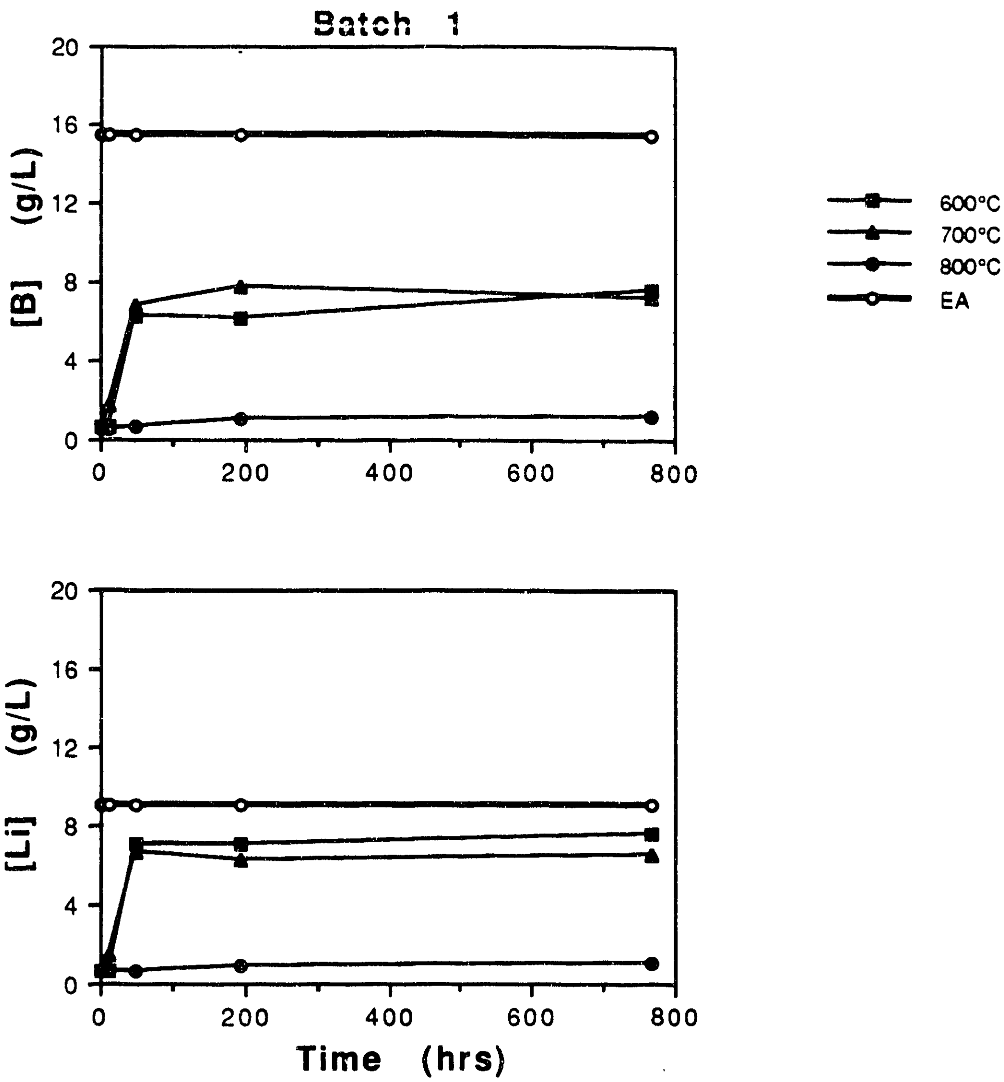


Figure 1

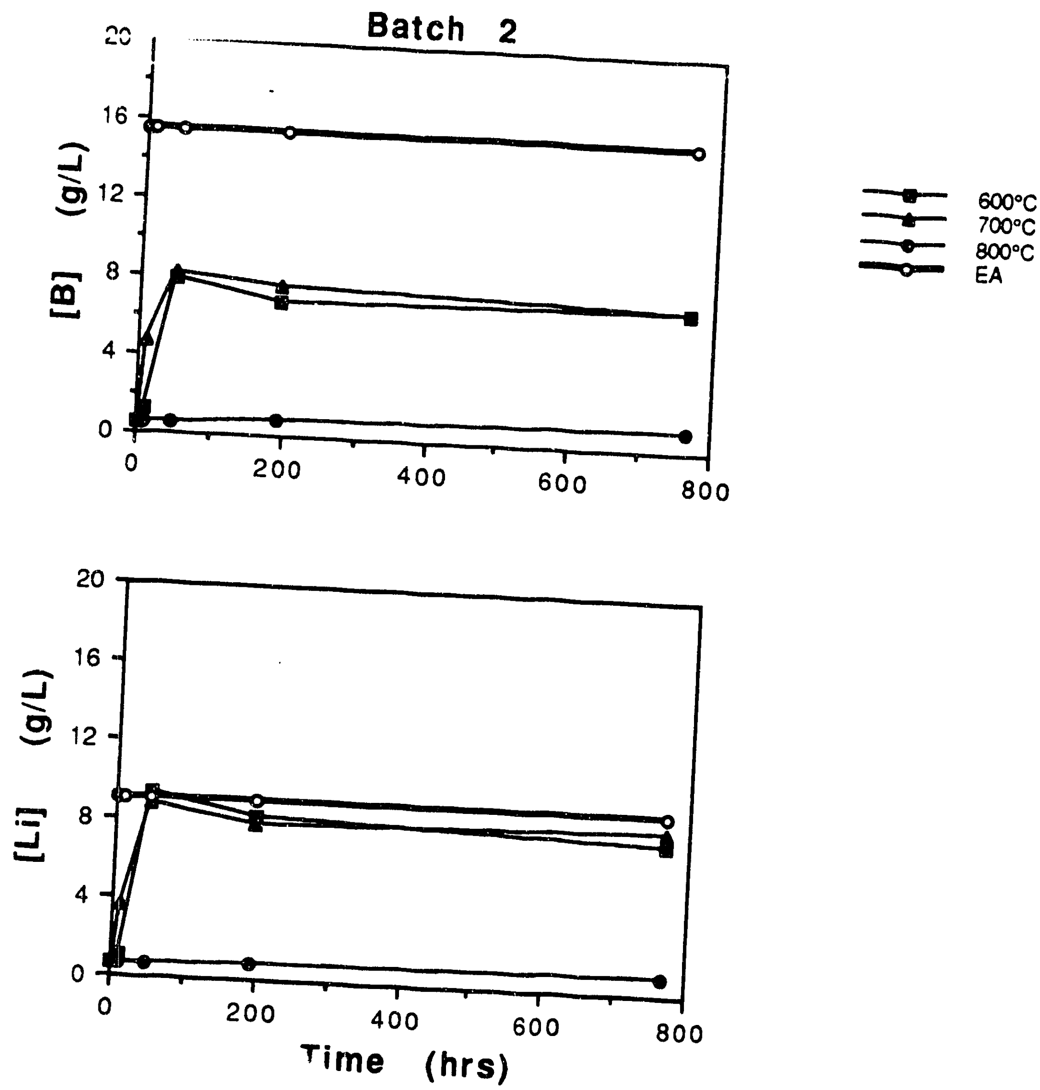

Batch 2
[B] (g/L)
0
4
8
12
16
20
0
200
400
600
800
600°C
700°C
800°C
EA
[Li] (g/L)
0
4
8
12
16
20
0
200
400
600
800
Time (hrs)

Figure 2

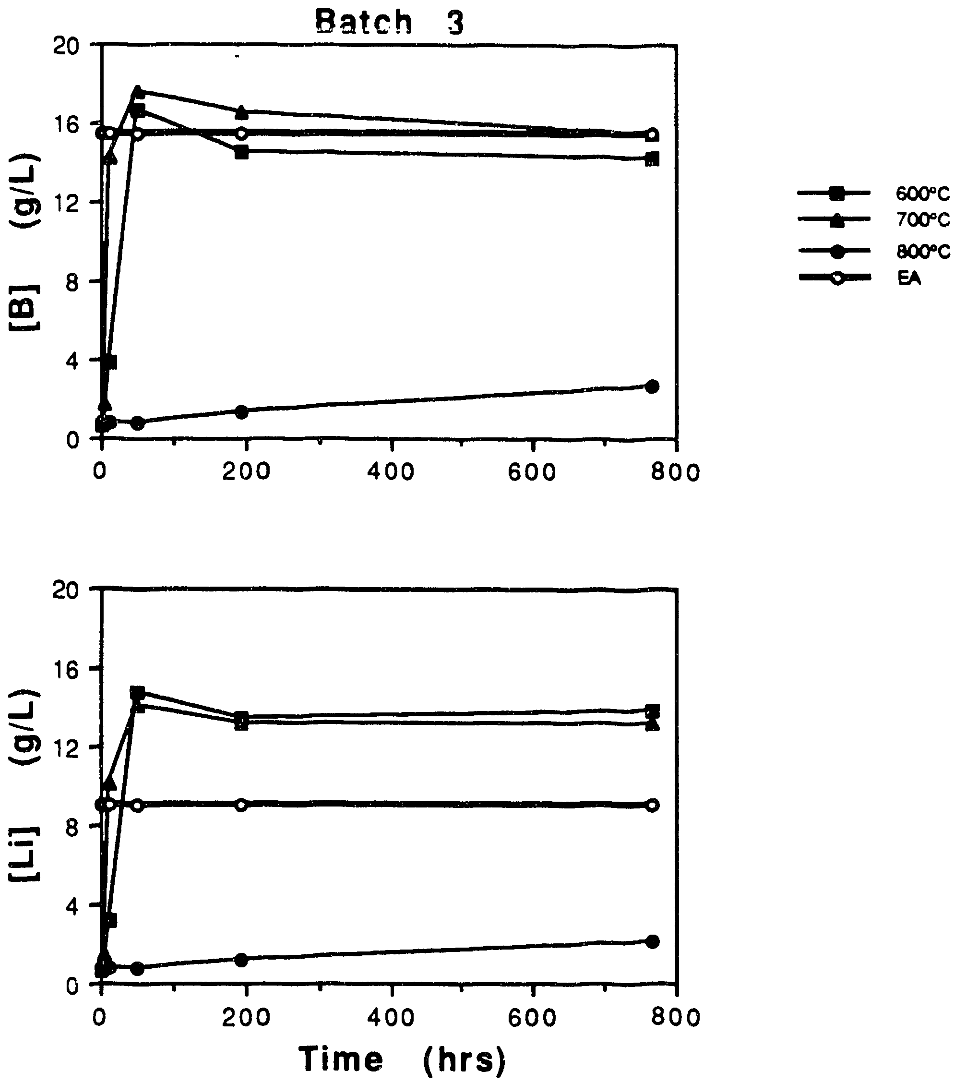
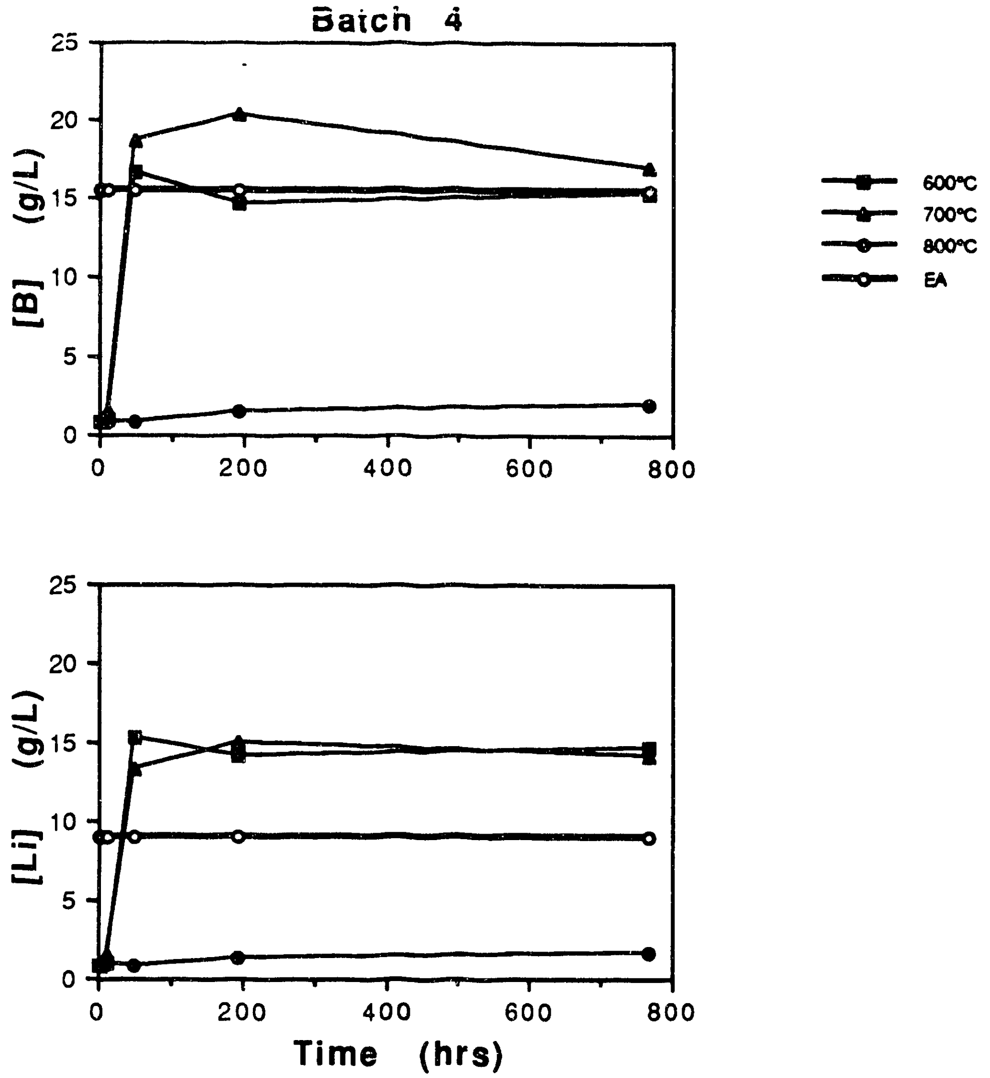

Batch 3
[B] (g/L)
20
16
12
8
4
0
0
200
400
600
800
600°C
700°C
800°C
EA
[Li] (g/L)
20
16
12
8
4
0
0
200
400
600
800
Time (hrs)

Figure 3



Batch 4
25
20
15
10
5
0
[B] (g/L)
0
200
400
600
800
600°C
700°C
800°C
EA
25
20
15
10
5
0
[Li] (g/L)
0
200
400
600
800
Time (hrs)

Figure 4

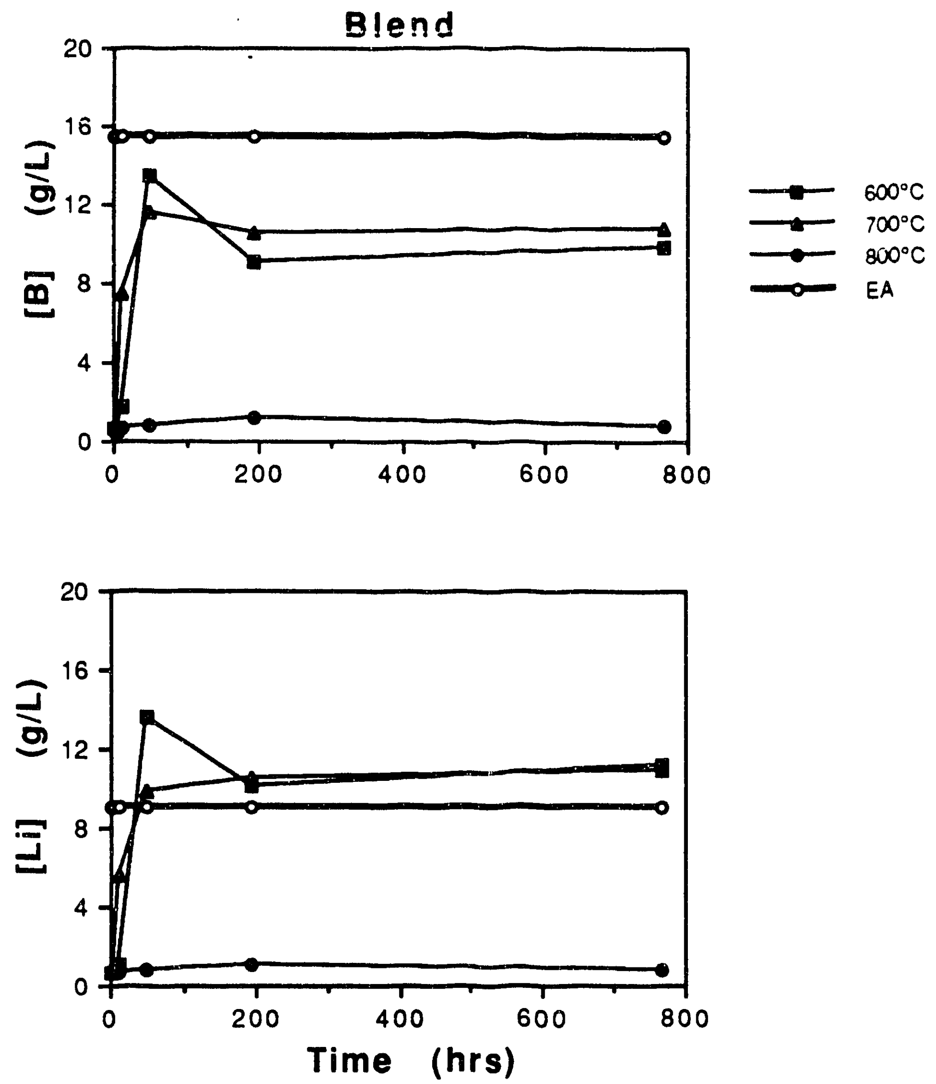

Blend
20
16
12
8
4
0
[B] (g/L)
0
200
400
600
800
600°C
700°C
800°C
EA
20
16
12
8
4
0
[Li] (g/L)
0
200
400
600
800
Time (hrs)

Figure 5

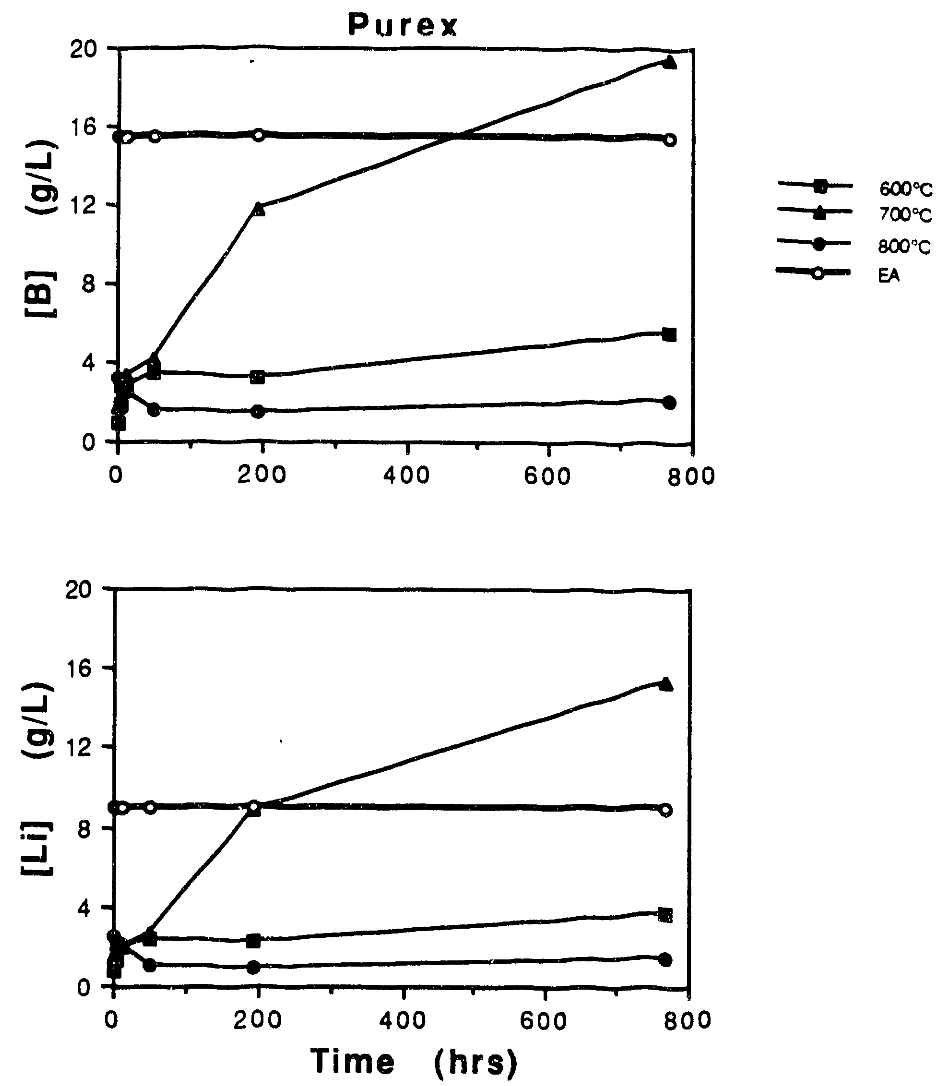

Purex
[B] (g/L)
600°C
700°C
800°C
EA
[Li] (g/L)
Time (hrs)
0
4
8
12
16
20
0
200
400
600
800

Figure 6

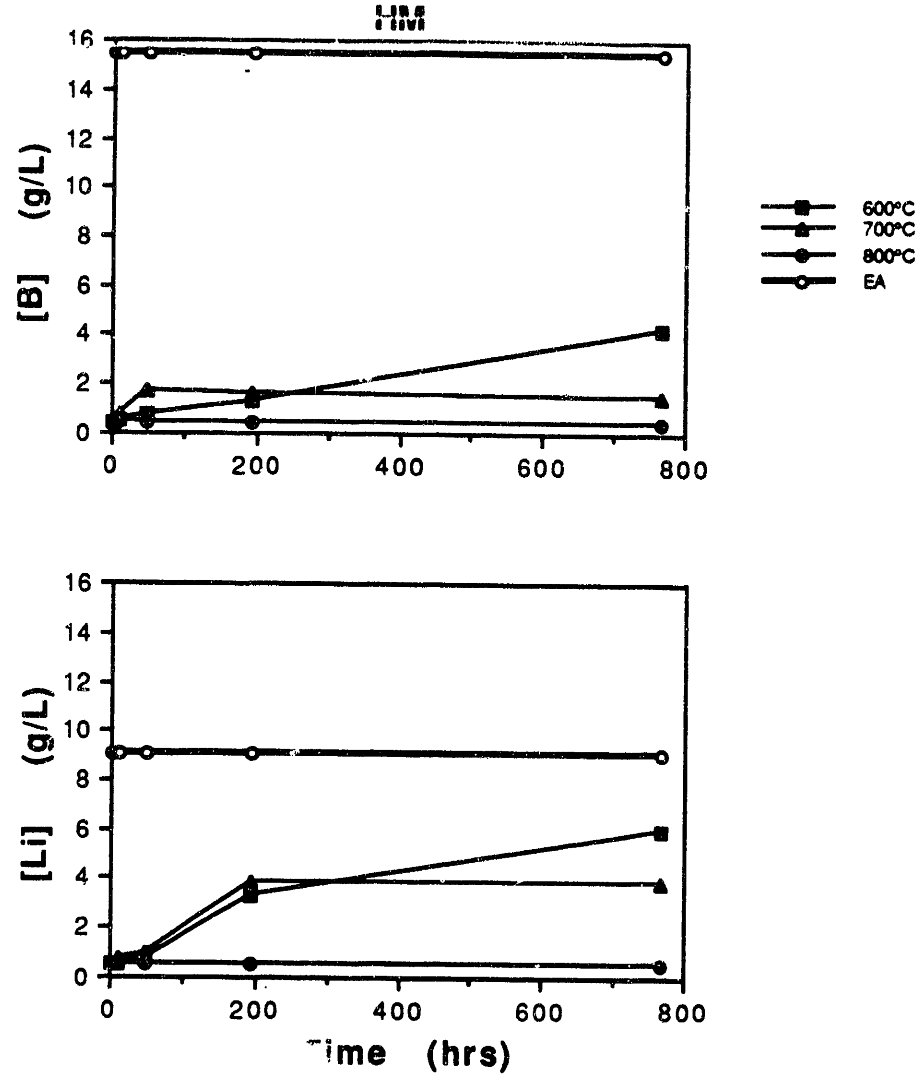


Figure 7

baseline releases for Batch 4 and Purex explain why these glasses exceeded both the boron and the lithium releases of the EA glass (Figures 4 and 6).

Table 2 - Normalized Releases of Boron, Sodium and Lithium in the Quenched Glasses and EA Glass.

Glass Type	B	Na	Li
Batch 1	0.64	0.66	0.73
Batch 2	0.54	0.56	0.61
Batch 3	0.74	0.71	0.75
Batch 4	0.83	0.81	0.84
HM	0.42	0.43	0.53
Purex	0.88	0.90	0.84
Blend	0.61	0.62	0.67
EA glass	15.48	12.85	9.05

The other glass compositions that exceeded the EA releases of boron and lithium, Batch 3, also had a high release for the quenched glass. When heat treated, this glass exceeded the lithium release of the EA glass before 12 hours at 700°C. The projected composition of Batch 3 contained more lithium and the heat treated glasses formed more lithium metasilicate crystals than most of the other glasses (see Table 1). The crystallization of this phase along with other alkali silicate phases tends to decrease durability, which explains why Batch 3 was less durable than the EA glass at a shorter heat treatment time than the other glasses.

The devitrification of three different alkali silicate phases, lithium metasilicate, acmite and nepheline, in some glasses caused additional loss of durability. Figures 8-11 show the normalized boron release for nearly all of the heat-treated glasses (the 400 and 650°C tests were not included in these graphs since they were not annealed for all of the six time periods). These figures show that the region of lowest durability (the highest release) can be found at the longer heat treatment times at 600 and 700°C. This corresponds to the region where acmite, lithium metasilicate, and nepheline were detected and where the most crystallization was observed.

Although crystallization of alkali silicate phases tended to decrease durability, crystallization of spinel had no affect on glass durability.[6] In the region of spinel devitrification, the concentration of boron released was virtually the same as in regions of no crystallization. This effect was also seen in earlier studies.[6]

Table 4 compares the boron release to the total crystallinity for selected glasses. In general, a higher boron release corresponds to a higher crystalline content.

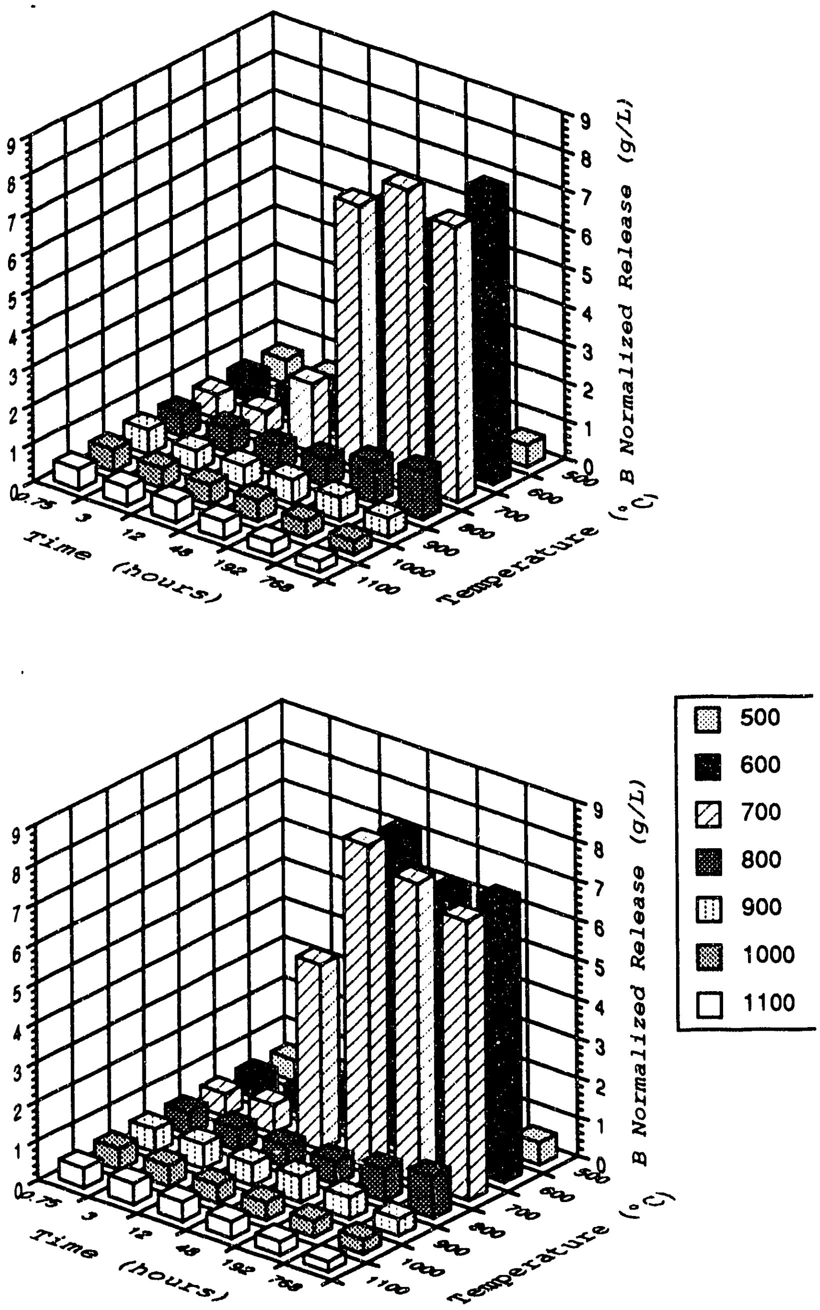


Figure 8. Normalized Boron Release for Batch 1 (top) and Batch 2 (bottom).

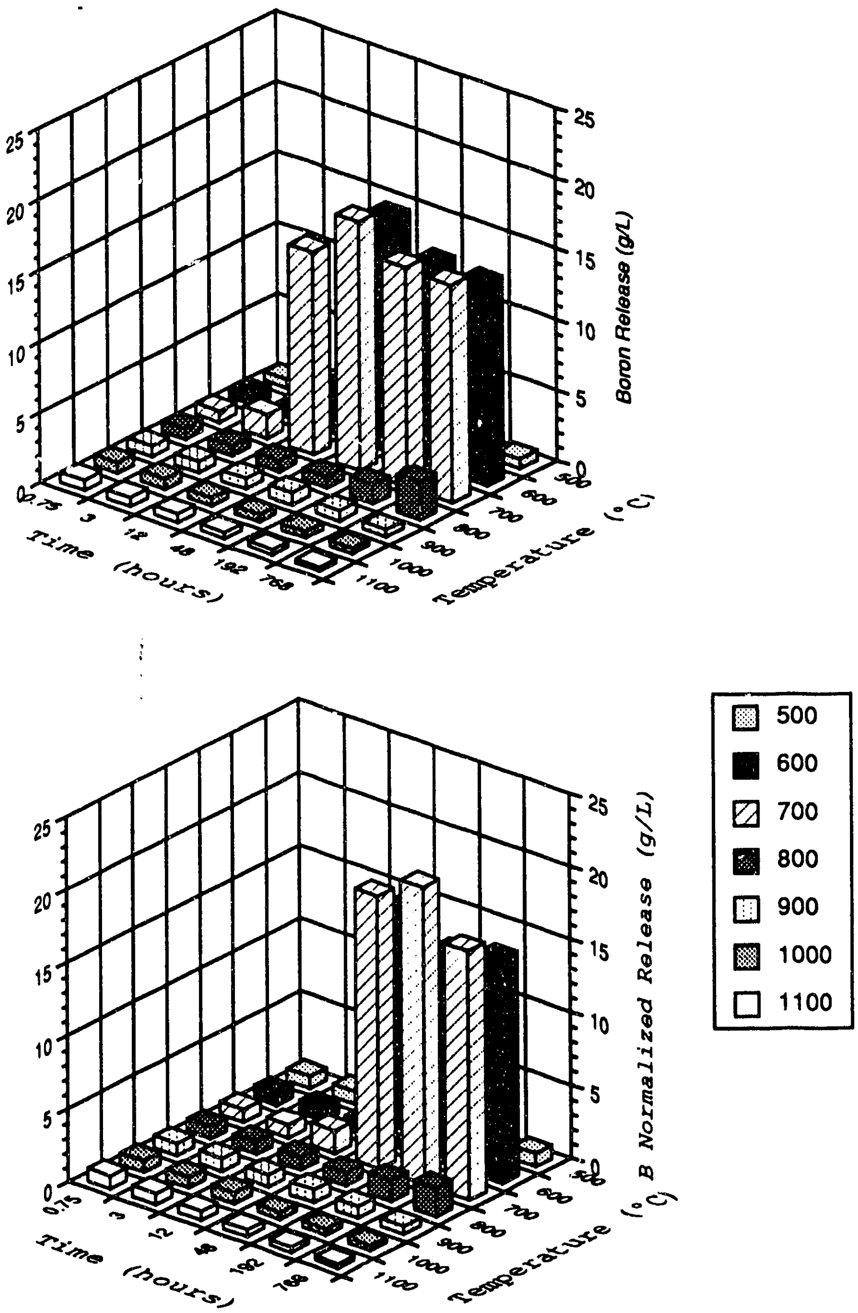


Figure 9. Normalized Boron Release for Batch 3 (top) and Batch 4 (bottom).

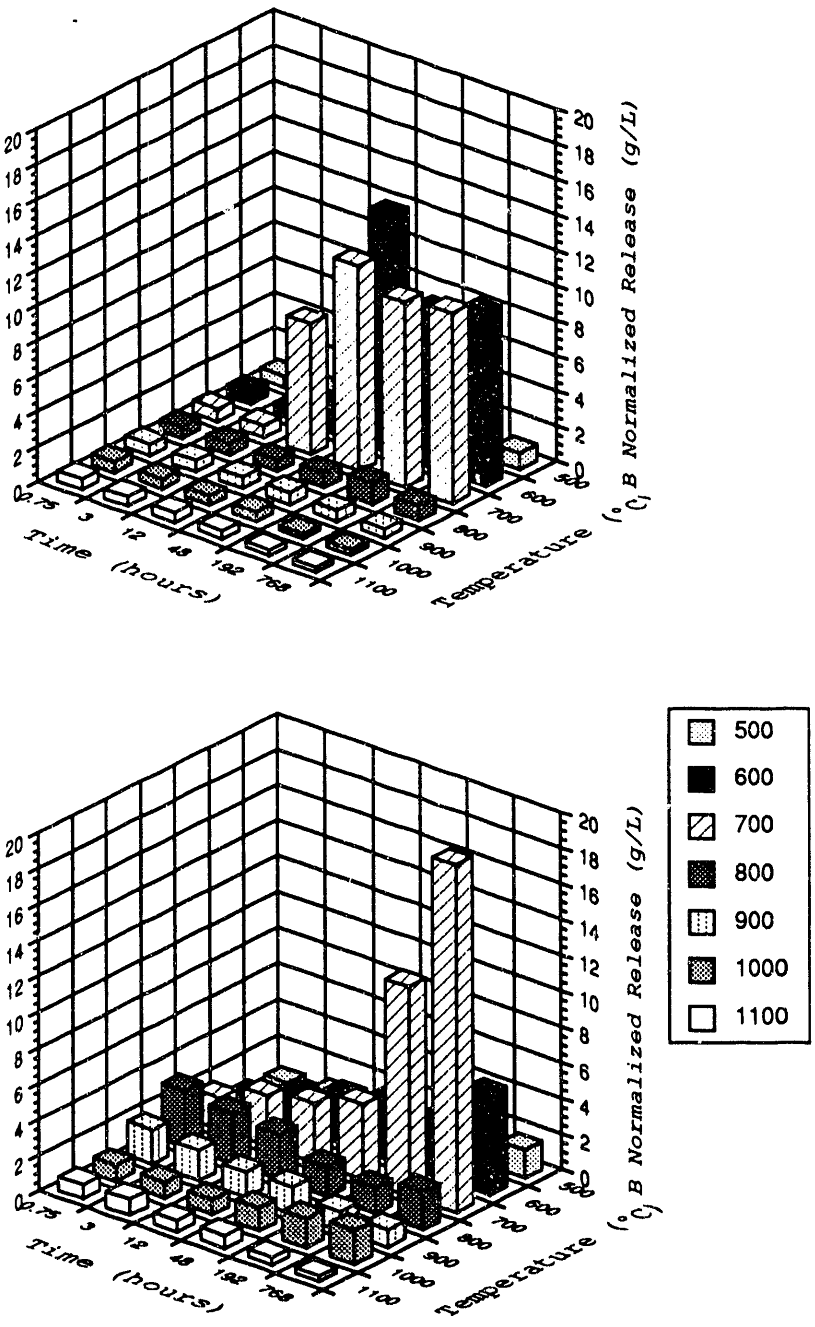


Figure 10. Normalized Boron Release for Blend (top) and Purex (bottom).

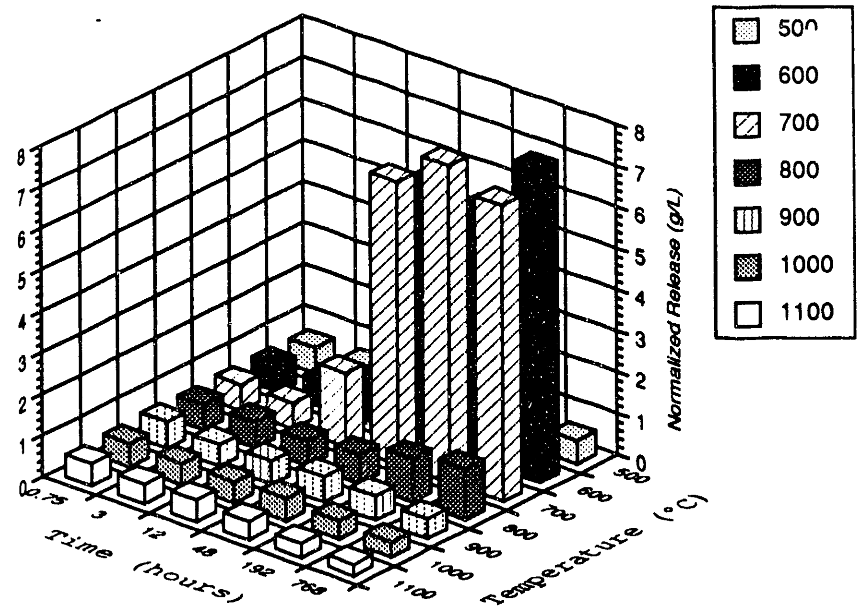


Figure 11. Normalized Boron Release for HM.

Table 4. Normalized boron results and total crystallinity.

Comp.	Temp.	Time	Boron	Total Crystallinity (Vol. %)
Batch 1	600	48	152.6	31.4
Batch 1	700	48	165.4	29.0
Batch 1	800	48	16.9	10.1
Batch 1	900	48	14.9	1.8
Batch 2	600	12	28.6	15.3
Batch 2	600	48	193.2	38.6
Batch 2	600	192	168.0	44.5
Batch 2	600	768	173.9	46.5
Batch 3	700	48	419.6	31.8
Batch 3	700	768	368.2	38.1
Batch 3	800	192	32.9	11.0
Batch 4	500	192	20.6	0.6
Batch 4	800	768	49.7	10.7
Batch 4	1000	768	9.6	1.5
Batch 4	1100	192	9.2	0.6
Blend	600	48	336.8	30.9
Blend	600	192	225.1	35.7
Blend	700	48	291.5	27.7
Blend	700	192	263.1	34.9
Purex	600	48	111.3	0.7
Purex	600	192	102.6	1.6
Purex	700	48	134.8	4.1
Purex	700	192	375.0	15.4
HM	600	192	28.7	25.0
HM	700	48	37.4	24.9
HM	700	192	36.1	27.9
HM	800	192	8.8	1.8

CONCLUSIONS

Although some glasses were less durable than the EA glass, these glasses were produced under conditions that are not expected to be encountered during normal operation and transportation. Temperatures of 600 and 700°C produced the most crystalline and the least durable glasses at longer annealing times. These annealing times were extreme (most were over 48 hours), so in an accident, this scenario would not be expected, although the required information is available should it become necessary.

A comparison of the x-ray diffraction results and PCT results show a relationship between the regions of highest crystallization and the regions of lowest durability. These are the regions where alkali silicate phases were found. The presence of lithium metasilicate and nepheline significantly reduced durability, while acmite by itself had less effect. The presence of trevorite had virtually no effect on the durability of the glasses.

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Contract No. DE-AC09-89SR18035 with U.S. Department of Energy.

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