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VITRIFICATION OF HIGH-LEVEL ALUMINA NUCLEAR WASTE

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ABSTRACT

Borosilicate and borophosphate glass compositions have been developed to vitrify simulated high-alumina calcined nuclear defense waste. The effects of the alkali (Li_2O , Na_2O) to borate ratio and the Li_2O to Na_2O ratio on the glass melt viscosity and leach resistance were measured. The effects on the same properties of substituting CaO and P_2O_5 for SiO_2 and of substituting SiO_2 , P_2O_5 and CuO for B_2O_3 were measured in the borosilicate and borophosphate glass, respectively.

SUMMARY

Alumina calcine, produced by a fluidized-bed calcination process from the liquid waste of reprocessed nuclear fuel, is stored at the Idaho Chemical Processing Plant. Future regulations may require that the calcine be converted to an alternative waste form. Vitrification is one of the processes currently being considered. Two types of glass formulations, borosilicate and borophosphate, were developed to vitrify the alumina calcine. Each type of glass was developed by varying ratios of glass additives in a base borosilicate and borophosphate composition. The glasses were evaluated for acid and Soxhlet leach resistance, melt viscosity at 1100°C, and glass homogeneity.

Variation of the Li₂O to Na₂O ratio, substitutions of CaO and P₂O₅ for SiO₂, and of alkali and B₂O₃ for SiO₂ were made in a base borosilicate glass composed of 43 mol% SiO₂, 10% B₂O₃, 14% Li₂O, 14% Na₂O, 3% CuO, and 16% Al₂O₃ calcine. Increases in the Li₂O to Na₂O ratio lower the melt viscosity, but do not improve the relatively high acid leach rate of the borosilicate glass. Substituting CaO and P₂O₅ for SiO₂ in two of the mixed alkali glasses decreases the acid leach rate from about 40 wt% to 30 wt% without increasing viscosity. Increasing the borate or alkali content produces lower viscosity glasses, but no improvement in the acid leach rate was observed.

The borosilicate glasses generally have low Soxhlet leach rates (1-1.5 wt% lost in 72 h). Based upon the above experiments, a borosilicate glass high in Na₂O (18 mol%) or high in Li₂O (18 mol%) is recommended for further study.

Substitutions of SiO₂ and P₂O₅ for B₂O₃ were made in a base borophosphate glass consisting of 4 mol% SiO₂, 40% B₂O₃, 10% P₂O₅, 10% Na₂O, 10% Li₂O, 3% CuO, and 23% Al₂O₃ calcine. Both of the additives increase the melt viscosity and decrease the Soxhlet leach rate. Substituting 4-15 mol% SiO₂ in a 15 mol% P₂O₅ base glass also lowers the leach rate and increases the viscosity, but these glasses are more viscous when compared at Soxhlet leach rates equal to the base glass. The viscosity of the glasses low in silica (0-6%) is slightly decreased by increasing the alkali to borate ratio and by substituting CuO for B₂O₃. These modifications produce variable effects on the Soxhlet leach rates.

The viscosity of glasses high in silica (10-15%), is decreased by increasing the alkali to borate ratio, increasing the Li₂O to Na₂O ratio, and by substituting CuO for B₂O₃. These modifications cause only slight changes in the Soxhlet leach rate. The acid leach rates (19 h) of these high and low silica glasses are quite low (0.5 wt%).

Based on Soxhlet and acid leach rate, melt viscosity, and glass meltability, there are a number of borophosphate glasses suitable to vitrify the alumina calcine. The high silica glasses have Soxhlet leach rates approximately one half that of the low silica glasses, and meet the viscosity requirements of proposed vitrification processes. It is recommended that borophosphate glasses high in silica with 10 and 15 mol% P₂O₅ be examined further.

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I. INTRODUCTION

Vitrification of high-level nuclear waste is one of the alternatives being investigated at the Idaho Chemical Processing Plant (ICPP) for final disposal of the waste. Currently the nuclear waste solutions are calcined to a mixture of granules and powder by a fluidized-bed calcination process.¹ The calcined waste has been produced since 1963 and is currently stored in near-surface stainless steel bins within concrete vaults. The two most abundant wastes produced are zirconia calcine, consisting of approximately 24% ZrO_2 , 17% Al_2O_3 , and 55% CaF_2 , and alumina calcine consisting of approximately 90% Al_2O_3 , 3% Na_2O , 3% B_2O_3 . Both calcines contain 0.5% fission products and 3.5% miscellaneous. Glass compositions have been developed for the zirconia calcine.² The flux developed for the zirconia waste does not readily vitrify the alumina calcine, nor does it vitrify mixtures of the two wastes containing more than 15 wt% alumina calcine. Because of this, several different types of frits were prepared and tested for ability to melt the simulated alumina calcine.

Two basic glass compositions, a borophosphate and a borosilicate, were selected on the basis of melt viscosity and leach resistance for further testing and evaluation. These two criteria were used because glasses with melt viscosities of 50-200 poise at temperatures of 1050-1200°C are desired for the proposed nuclear waste vitrification processes of in-can melting³ or joule heated melting^{3,4} and glasses with high leach resistance are desired for environmental safety.

II. EXPERIMENTAL METHOD

A. Glass Preparation

Experimental glasses were melted at 1100°C in 100 mL platinum or high-fired alumina crucibles. Glasses were made using reagent grade oxides or carbonates and a simulated alumina calcine.⁵ A 20 to 24 hour fining period was used after the charging of the glass additives was completed. The glass samples were poured into graphite molds, cooled, and then ground to a -16+30 mesh size for leach testing.

Upon pouring, each glass was judged on a relative viscosity scale as follows; 1=25-75 poise, 2=75-150, 3=150-300, 4=300-500, and 5=not pourable, as estimated by comparison with standard viscosity fluids. The actual viscosity of selected melts was measured with a Brookfield viscometer.

B. Leach Tests

Experimental procedures previously used at the ICPP² were followed in leaching the glasses. Four grams of the glass sample were weighed and placed in either a 100 mL leachant solution (Table I) at 25°C or in a Soxhlet apparatus at 95°C. After 19 hours on a magnetic stirrer or 72 hours in the Soxhlet apparatus, the sample was removed, dried, and then weighed. The gross weight percent lost was then calculated. All leach rates referred to in this report are expressed as weight percent lost in either a 19 hour or 72 hour period.

TABLE I. LEACHING SOLUTIONS AND CONDITIONS

Solution	pH	Temperature, °C	Time, h	Description
Acid	3.6-3.8	25	19	1M buffered acetic acid
Distilled Water	7	95	72	Distilled Water, Soxhlet test
Base	9	25	19	1M NH ₄ OH, buffered
Brine	7.5	25	19	WIPP ^a brine water, 306 g/L dissolved solids

^a WIPP=100 mg/L Na⁺, 200 Mg⁺², 600 Ca⁺², 200 Cl⁻, 1750 SO₄²⁻, 145 miscellaneous.

III. GLASS DEVELOPMENT

A. Introduction

The preliminary experiments to develop a low melting temperature glass to vitrify alumina calcine resulted in two glasses of basically different compositions (Table II). The borosilicate glass (No. 171) is limited in its ability to vitrify alumina calcine and also has poor leach resistance to an acid media (Table III). The borophosphate glass (No. 178) incorporates a larger amount of calcine and has generally better properties than glass 171 (Table III).

Experimentation with glass compositions made before the selection of glass 171 and 178 showed that the leach resistance of the borosilicate glasses varies most in the acid leach test while the leach resistance of the borophosphate glass varies most in the Soxhlet leach test (Table IV). The leach solutions which resulted in the largest variations in leach resistance were used as the test solutions for the modified glasses examined in this report.

Glass modifications tested here were periodically checked for both acid and Soxhlet leach resistance, since some glass additives improve leach resistance in one pH range while decreasing it in another.^{6,7}

Modifications were made to the base borosilicate (No. 171) and borophosphate (No. 178) compositions to improve the glass properties. The borosilicate glass was modified by first varying the Li_2O to Na_2O ratio and substituting CaO and/or P_2O_5 for SiO_2 , and then substituting B_2O_3 and alkali for SiO_2 . Glasses were selected from each experiment and used as base glasses in the succeeding experiment. The borophosphate glass was modified by first substituting SiO_2 and P_2O_5 for B_2O_3 , and then substituting SiO_2 for B_2O_3 in the base glass with a higher P_2O_5 content. The Li_2O to Na_2O ratio, the alkali to borate ratio, and the CuO content were then varied in selected glasses. All glasses were evaluated for leach resistance and melt viscosity.

TABLE II. BASE BOROSILICATE AND BOROPHOSPHATE GLASS COMPOSITIONS AND PROPERTIES

Glass Type	Glass No.	Glass Composition						
		SiO_2	B_2O_3	P_2O_5	Li_2O	Na_2O	CuO	Al_2O_3 Calcine
Borosilicate	171							
wt%		40	11	-	7	14	3	25
mol%		43	10	-	14	14	3	16
Borophosphate	178							
wt%		3	35	18	4	8	3	29
mol%		4	40	10	10	10	3	23

TABLE III. VISCOSITY AND LEACH RATES OF BASE BOROSILICATE AND BOROPHOSPHATE GLASSES

Property	Glass	
	Borosilicate No. 171	Borophosphate No. 178
Viscosity at 1100°C, poise	200-300	25-75
Acid leach rate, wt% lost/19 h (25°C)	35	0.5
Soxhlet leach rate, wt% lost/72 h (95°C)	3	6

Table IV. Range of Leach Rates of Preliminary Glass Compositions

Glass	Leach Rate, wt% lost			
	Acid	Soxhlet	Base	Brine
	19 h	72 h	19 h	19 h
Borosilicate	20-40	1-3	>.05	>.05
Borophosphate	0.5-15	5-15	>.05	>.05

B. Borosilicate Glass

1. Variation of Alkali Ratio

The Li_2O to Na_2O ratio was varied in the base glass to improve the acid leach resistance and melt viscosity (Table V). The variations produced some glasses with a lower melt viscosity, but did not improve the leach rate in an acid solution. Of the five glasses tested, a high Li_2O glass and a high Na_2O glass, No.'s 190 and 183, respectively, were chosen for further testing.

2. Substitution of CaO and/or P_2O_5 for SiO_2

Calcium oxide and P_2O_5 were substituted for SiO_2 in Glass 190 to lower the leach rate in acid. Each oxide was first added separately to evaluate the individual leach rate effect (Table VI). Substituting up to 9 mol% CaO for SiO_2 has little effect on the leach rate, but lowers melt viscosity by about 75 poise. Substituting up to 6 mol% P_2O_5 effectively decreases the leach rate to 2 wt%/19 h, but increases viscosity by about 100 poise.

Substitution of both 6% CaO and 6% P_2O_5 in glass 190 decreases both leach rate in acid and viscosity. This glass (No. 218), has an acid leach rate of 2.5 wt%/19 h, a significant improvement over the 31 to 35 wt%/19 h acid leach rates of glasses 171 and 190.

The 1:1 CaO to P_2O_5 ratio substituted in glass 218 (reference glass 190) was also used in glass 183 to determine if a similar decrease in leach rate in acid media would occur (Table VI). Although a more viscous glass (No. 259) was produced, a leach rate similar to glass 218 was observed. The alkali and borate contents of the low leach rate glasses (No.'s 218 and 259) were then varied to further improve glass properties, as reported below.

TABLE V. VARIATION OF ALKALI RATIO IN BOROSILICATE GLASS 171 (43 mol% SiO₂, 10% B₂O₃, 3% CuO, 16% Al₂O₃ CALCINE)

Glass No.	Mol%		Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	Li ₂ O	Na ₂ O		
191	28	0	2	26
190	21	7	2	31
171	14	14	3	34
183	7	21	3	31
189	0	28	3	41

Table VI. SUBSTITUTION OF CaO AND/OR P₂O₅ FOR SiO₂ IN BOROSILICATE GLASSES 190 AND 183^a

Substitution of CaO

Glass No.	Mol%		Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	CaO	SiO ₂		
190	0	43	2	34
201	3	40	2	32
202	6	37	1	40
203	9	34	1	40

Substitution of P₂O₅ for SiO₂

Glass No.	Mol%		Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	P ₂ O ₅	SiO ₂		
190	0	43	2	31
220	3	40	2	13
221	6	37	3	2

Substitution of CaO and P₂O₅ for SiO₂

Glass No.	Mol%			Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	CaO	P ₂ O ₅	SiO ₂		
190	0	0	43	2	34
277	3	6	34	2	2.8
219	6	3	34	1	4.4
218	6	6	31	1	2.5
222	6	9	28	2	8.1
183	0	0	43	2	31
259	6	6	31	2	3.0

^a Glass 190=10 mol% B₂O₃, 3% CuO, 21% Li₂O, 7% Na₂O, 16% Al₂O₃ calcine
 Glass 183=10 mol% B₂O₃, 3% CuO, 7% Li₂O, 21% Na₂O, 16% Al₂O₃ calcine

3. Variation of Borate and Alkali Content

The total alkali and borate content of borosilicate glass 218 was varied from 24-32 mol% and 8-14 mol%, respectively, by substituting for SiO₂ (Table VII). Decreasing the alkali content of glass 218 to 24 mol% slightly lowers the leach rate to 1.5 wt%, while increasing the

TABLE VII. SUBSTITUTION OF B₂O₃ OR ALKALI FOR SiO₂ IN BOROSILICATE GLASS 218 (6 mol% CaO, 6% P₂O₅, 16% Al₂O₃ CALCINE)

Substitution of B₂O₃ for SiO₂ (Li₂O=21 mol%, Na₂O=7%)

Glass No.	Mol% SiO ₂	Mol% B ₂ O ₃	Relative Viscosity	Acid Leach Rate, wt% lost/19 h
252	33	8	1	5.2
218	31	10	1	2.5
256	27	14	1	25.0

Substitution of Alkali for SiO₂ (B₂O₃=10 mol%)

Glass No.	Mol% SiO ₂	Mol% Alkali	Relative Viscosity	Acid Leach Rate, wt% lost/19 h
280	35	24	2	1.5
218	31	28	1	2.5
254	27	32	1	26

alkali content to 32 mol% greatly increases the leach rate to 25 wt%. The glass has a higher leach rate when the borate content is more or less than 10 mol%. The melt viscosity remains at less than 150 poise at 1100°C for all of these variations. However, if glasses with only 24 mol% alkali and 8 mol% borate are made, melting does not occur. Glasses 218 and 280 appear the most suitable of this group of glasses to vitrify alumina calcine, based on acid leach resistance and melt viscosity.

The effects of varying the alkali and borate content, by substituting for SiO₂, on the properties of glass 259 are significantly different from those of glass 218 (Tables VII and VIII). When the alkali content of this glass is lowered to 24 mol%, at 10 mol% B₂O₃, it does not melt at 1100°C. Increasing the alkali content to 32 mol% yields a low viscosity glass (25-75 poise) with a high leach rate (7 wt%). Thus, the best alkali content appears to be near 24 mol%. Varying the borate content between 8 and 14 mol%, though, does not change the acid leach rate as it does with glass 218. However, increasing the borate content from 10 to 14 mol% (glass 260) did lower the melt viscosity by about 50-75 poise (Table VIII), and appears to be the most suitable high Na₂O glass to vitrify alumina calcine.

C. Borophosphate Glass

1. Substitution of SiO₂ or P₂O₅ for B₂O₃

The base borophosphate glass (No. 178, Table II) used in this study has a high Soxhlet leach rate and a low melt viscosity. Substitution of SiO₂ or P₂O₅ was made for B₂O₃ in this base glass (Table IX) to improve the Soxhlet leach rate. The use of 20 mol% SiO₂ decreases the Soxhlet leach rate to only 1.3 wt% while only moderately increasing the melt viscosity. The use of 15 mol% P₂O₅ also lowers the Soxhlet leach rate without significantly raising the melt viscosity. At levels above 15 mol% P₂O₅, the glasses become very viscous, melt with heavy surface scums, and have high Soxhlet leach rates.

Table VIII. SUBSTITUTION OF B₂O₃ OR ALKALI FOR SiO₂ IN BOROSILICATE GLASS 259 (6 mol% CaO, 6% P₂O₅, 16% Al₂O₃ CALCINE)

Substitution of B₂O₃ for SiO₂ (Li₂O=7 mol%, Na₂O=21%)

Glass No.	Mol%		Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	SiO ₂	B ₂ O ₃		
258	33	8	3	4.0
259	31	10	2	3.0
260	27	14	1	2.7

Substitution of Alkali for SiO₂ (B₂O₃=10 mol%)

Glass No.	Mol%		Relative Viscosity	Acid Leach Rate, wt% lost/19 h
	SiO ₂	Alkali		
299	35	24	5	Glass does not melt
259	31	28	2	3.0
257	27	32	1	7.2

Having observed a useful range of 10-15 mol% P₂O₅ in the base glass (Table IX), it was decided to substitute SiO₂ for B₂O₃ in a glass (No. 185) which contained 15 mol% P₂O₅ (Table X). Substituting 14 mol% SiO₂ in the glass has little effect on the Soxhlet leach rate, and only moderately increases the melt viscosity. The leach rate is decreased to below 1.5% when the SiO₂ content in the glass is 14-16 mol%, which also increases the viscosity to 75-150 poise. Five glasses were then selected from the two groups for further improvement by varying the Li₂O to Na₂O ratio, alkali to borate ratio, and CuO content (Table XI).

Table IX. SUBSTITUTION OF SiO₂ OR P₂O₅ FOR B₂O₃ IN BOROPHOSPHATE GLASS 178^a

Substitution of SiO₂

Glass No.	Mol%		Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
	SiO ₂	B ₂ O ₃		
187	0	44	1	16.5
178	4	40	1	6.0
188	8	36	1	5.1
211	12	32	2	3.2
212	16	28	2	2.5
271	18	26	2	1.4
272	20	24	2	1.3

Substitution of P₂O₅

Glass No.	Mol%		Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
	P ₂ O ₅	B ₂ O ₃		
176	0	50	1	27
178	10	40	1	6
186	12.5	37.5	1	6
185	15	35	1	3
192	17.5	32.5	3	18
193	30	20	4	not reproducible
194	27.5	22.5	5	-

^a 10 mol% Li₂O, 10% Na₂O, 3% CuO, 23% Al₂O₃ calcine

Table X. SUBSTITUTION OF SiO₂ FOR B₂O₃ IN BOROPHOSPHATE GLASS 185^a

Glass No.	Mol%		Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
	SiO ₂	B ₂ O ₃		
185	4	35	1	3.0
231	6	33	1	3.4
232	8	31	1	3.0
233	10	29	1	3.6
234	12	27	1	3.0
273	14	25	2	1.3
274	16	23	2	1.4

^a 10 mol% Li₂O, 10% Na₂O, 3% CuO, 15% P₂O₅, 23% Al₂O₃ calcine

TABLE XI. COMPOSITIONS OF LOW AND HIGH SILICA BOROPHOSPHATE GLASSES SELECTED FOR FURTHER TESTING

Glass No.	Composition Mol%						
	SiO ₂	B ₂ O ₃	P ₂ O ₅	Na ₂ O	Li ₂ O	CuO	Al ₂ O ₃ Calcine
178	4	40	10	10	10	3	23
185	4	35	15	10	10	3	23
271	18	26	10	10	10	3	23
272	20	24	10	10	10	3	23
274	16	23	15	10	10	3	23

2. Variation of the Li₂O to Na₂O Ratio

The alkali ratio was varied in the base low silica glass (No. 178) and a high silica glass (No. 271). The effect of varying the alkali ratio on the viscosity and Soxhlet leach rate of glass 178 is markedly different from that of glass 271 (Table XII). The low silica glass with a Li₂O:Na₂O ratio of 1:1 or greater has a leach rate of 6-9 wt%, but when less Li₂O is present the leach rate increases to 25-30 wt%. The variation of the Li₂O:Na₂O ratio has no effect on melt viscosity and does not appear to improve leach rate.

Varying the alkali ratio in the high silica glass (Table XII) produces glasses with leach rates between 1-2 wt% but the viscosity of the glasses decreases with increasing Li₂O content. As an example, glass 301, which contains only Li₂O, has the lowest viscosity (50 poise) and leach rate (1 wt%).

3. Variation of the Alkali to Borate Ratio

The alkali to borate ratio was varied in two low silica glasses (No.'s 178 and 185) and two high silica glasses (No.'s 272 and 274) (Table X). The viscosity of the glasses decreases as the alkali to borate ratio increases (Table XIII). This effect though, is often not sufficient to notice a change in the relative viscosity of the glasses. A decrease in relative viscosity was recorded only for glass 274, a high SiO₂, high P₂O₅ glass.

TABLE XII. EFFECT OF VARYING THE ALKALI RATIO ON VISCOSITY AND LEACH RATE IN BOROPHOSPHATE GLASSES 178 AND 271

Low Silica Glass 178

Glass No.	Mol% Li ₂ O Na ₂ O		Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
222	20	0	1	7.2
223	15	5	1	9.4
178	10	10	1	6.0
224	5	15	1	25.6
225	0	20	1	33.3

High Silica Glass 271

301	20	0	1	1.0
302	5	15	1	1.3
271	10	10	2	1.4
303	15	5	2	2.0
304	0	20	2	1.5

TABLE XIII. EFFECT OF VARYING ALKALI TO BORATE RATIO ON VISCOSITY AND LEACH RATE

Low Silica Glass 178

Glass No.	Mol% Alkali B ₂ O ₃		Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
248	16	44	1	43.3
249	18	42	1	23.6
178	20	40	1	6.0
250	22	38	1	22.0
251	24	36	1	18.9

Low Silica Glass 185

267	16	39	1	8.3
268	18	37	1	2.7
185	20	35	1	3.0
269	22	33	1	1.8
270	24	31	1	2.0

High Silica Glass 272

272	20	24	2	1.3
305	22	22	2	1.4
306	24	20	2	1.4

High Silica Glass 274

281	16	27	3	4.7
282	18	25	2	1.3
274	20	23	2	1.3
283	22	21	1	.8
284	24	19	1	1.8

The low silica glass 178 has acid leach rates of 25 to 40 wt% when the alkali content is other than 20 mol% (alkali:borate=1:2). The low total P₂O₅ and SiO₂ content of the glass is the probable cause for the high leach rates. The other glasses, including low silica glass No. 185, show no major changes in leach rate when the alkali content is between 18 and 24 mol%. Thus, an improved low silica glass can be produced by maintaining the alkali to borate ratio above 2:3.5 and using 15 mol% P₂O₅. The high silica glasses (No. 272, 274) with either 10 or 15% P₂O₅ can be improved by increasing the alkali to borate ratio.

4. Substitutions of CuO for B₂O₃

Substitutions of CuO for B₂O₃ were made in the base low silica glass (178) and a high silica glass (272) (Table XIV). Both glasses are affected by CuO in a similar manner. Without CuO present glass 178 does not dissolve the Al₂O₃ calcine at 1100°C. The glasses with 3 and 5 mol% CuO melt well and have Soxhlet leach rates of 6-7 wt%. Also, the viscosity of the glasses may decrease slightly as the CuO content increases.

TABLE XIV. EFFECT OF SUBSTITUTION CuO FOR B₂O₃ ON VISCOSITY AND LEACH RATE IN GLASS 178 AND 272

Glass 178

Glass No.	Mol% CuO	Mol% B ₂ O ₃	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
209	0	43	1	-
178	3	40	1	6.0
213	5	38	1	7.1

Glass 272

307	0	27	2	1.3
272	3	24	2	1.4
308	5	22	2	1.4

The high silica glass (No. 272) melts well without CuO and the Soxhlet leach rate is similar to the glasses with 3 and 5 mol% CuO (1.5 wt%). The viscosity decreases slightly as the CuO content decreases, but all glasses are still within the viscosity range of 75-150 poise. Thus, only the low silica glass is significantly improved by substituting CuO for B₂O₃.

5. Brookfield Viscosity Measurements

Viscosities at 1000-1100°C, as measured by a Brookfield viscometer, were determined for two glasses containing 10% P₂O₅ and 20% alkali (Table XV). Also shown is the reduction in viscosity achieved in the high silica glasses by increasing the alkali to borate ratio or the Li₂O to Na₂O ratio.

Figure 1 compares the viscosities of the glasses containing 10 and 15% P₂O₅ and having similar leach rates. The glasses containing 10% P₂O₅ have lower viscosities (at similar leach rates) than those glasses containing 15% P₂O₅ and appear more suitable to vitrify the alumina calcine.

Reductions of 30-50 poise are achieved by increasing the alkali to borate ratio of the high silica glasses (Figure 2). A similar reduction in viscosity (about 30 poise) occurs in the high silica glasses when Li₂O replaces Na₂O in the glass (Figure 3). As stated earlier, it appears that high alkali, high Li₂O concentrations result in glasses with reduced viscosity over the temperature range of 1000 to 1100°C.

TABLE XV. THE VISCOSITY-TEMPERATURE PROFILES OF SELECTED BOROPHOSPHATE GLASSES

Glass No.	Mol% P ₂ O ₅	Condition		Glass Viscosity (poise)		
		Mol% Alkali	Mol% Li ₂ O	1000°C	1050°C	1100°C
185	15	20	10	175	105	30
212	10	20	10	110	60	40
272 ^a	10	20	10	275	150	90
274	15	20	10	580	250	120
272	10	20	10	275	150	90
306	10	24	12	210	120	70
274	15	20	10	580	150	120
283	15	24	12	180	100	70
271 ^b	10	20	10	210	130	80
301	10	20	20	160	90	50

^aSiO₂=20%

^bSiO₂=18%

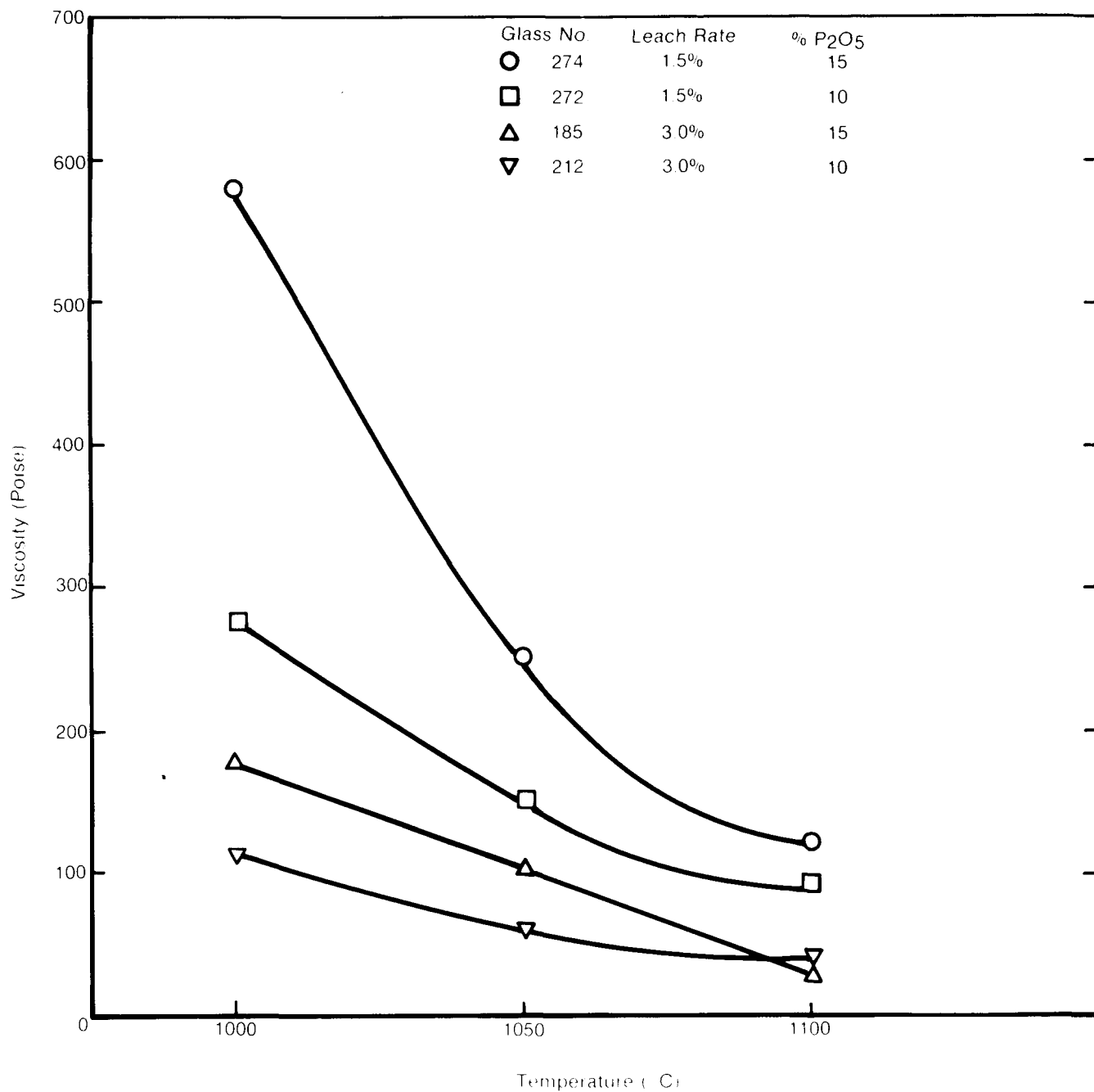
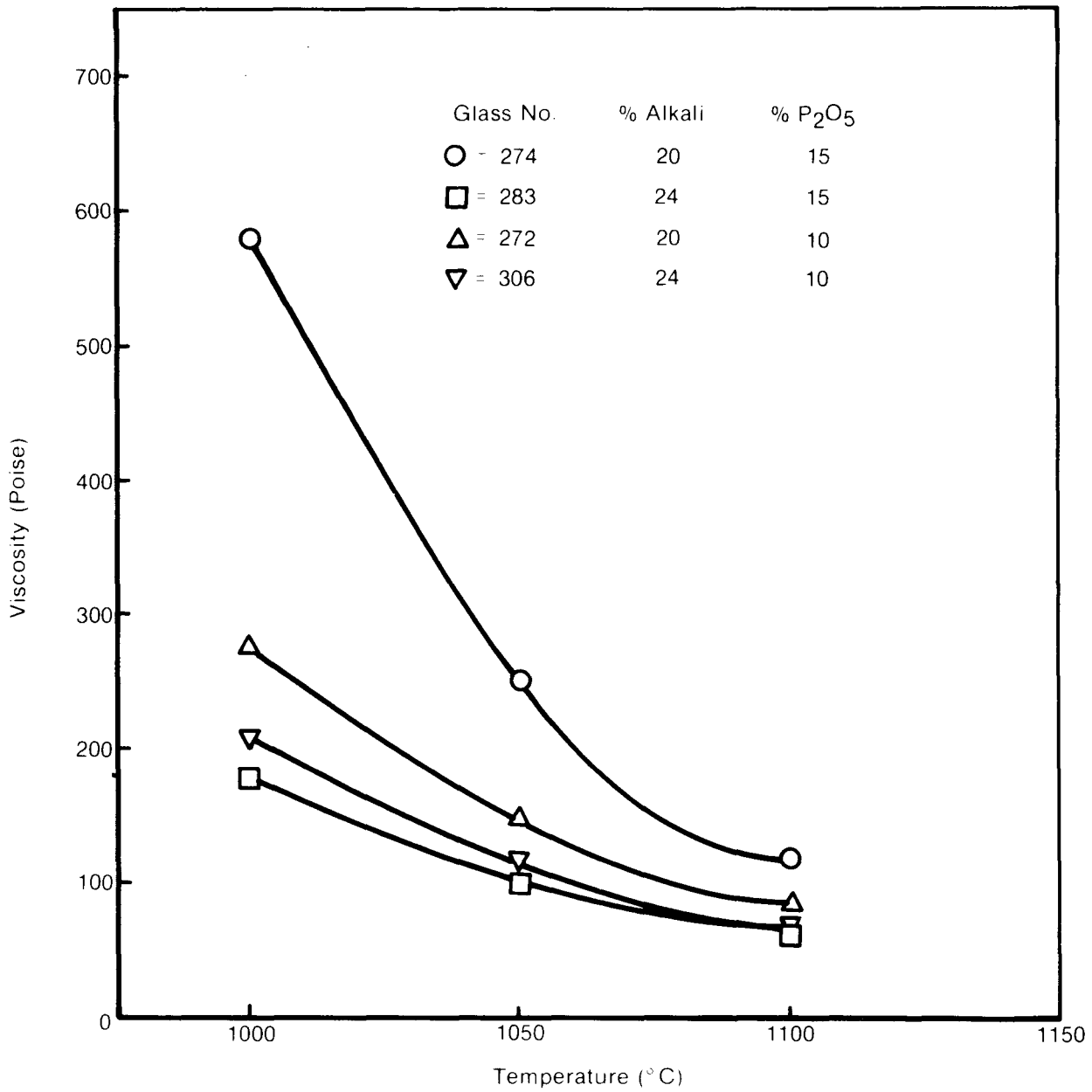
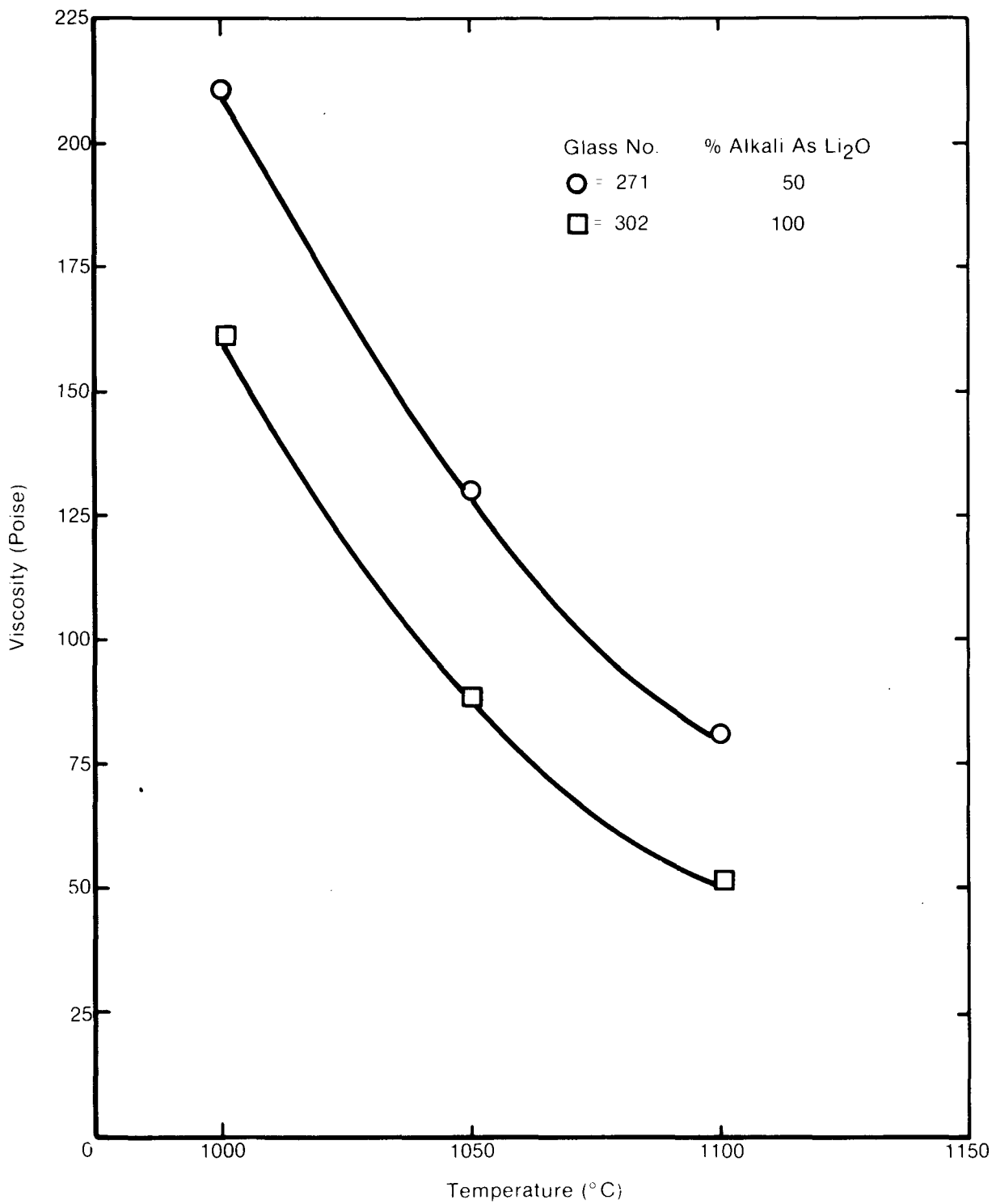


Figure 1 Viscosity-Temperature Profiles of Selected Glasses Containing 10 or 15 Mol % P₂O₅



ICPP-A-4972

Figure 2 Effect of Alkali to Borate Ratio on Viscosity of Glasses Containing 10 or 15 Mol % P₂O₅



ICPP-A-4971

Figure 3 Effect of Li₂O Content on Viscosity of Glasses Containing 10 Mol % P₂O₅

IV. CONCLUSIONS AND RECOMMENDATION FOR FURTHER TESTING

A. Conclusions

Leach resistant glasses containing alumina calcine can be made at temperatures compatible to the proposed vitrification processes of in-can melting or joule-heated melting. Based on melt viscosity, leach resistance, calcine content, and glass homogeneity, borophosphate glasses high in silica (18-20%) appear most suitable to vitrify the alumina calcine.

Based on the experimental data shown, the best of the borosilicate glasses (No. 218, 259) have melt viscosities similar to the best of the borophosphate glasses (No. 271, 283). The 19 h acid leach rates of the borosilicate glasses, though, are about six times higher (3.0 wt% vs. 0.5 wt%) than the borophosphate glasses, but the 72 h Soxhlet leach rates are very similar (1-1.5%) for both types of glasses. The borosilicate glasses accept less calcine than the borophosphate glasses. No problems occur in preparing a borosilicate frit while the borophosphate frits are water soluble and often form thick scums upon melting when Na_2O and P_2O_5 are included. Making the borophosphate frits without Na_2O and P_2O_5 (added to the frit as sodium phosphate) eliminates these problems. The use of two component frit mixtures should not be difficult, and forming waste glass using the batch chemicals also appears feasible.

B. Recommendations

Two borosilicate (218 and 259) and two borophosphate (271 and 283) glasses are recommended for further testing. Based on the criteria mentioned above, the tests should determine the calcine loading range of each glass. Secondly, the effect on the glass properties of mixing zirconia calcine and blended waste calcines or startup materials such as dolomite and fluorapatite with alumina calcine should be measured. The crystal species that may form in the glasses during processing should be identified and their effect on leach resistance should be determined. The effect of annealing rates on leach resistance and the corrosiveness of the glasses in the joule-heated melting and in-can melting production processes should also be investigated. The effects of long-term and hydrothermal leaching on the glass properties is another important area that should be investigated.

V. REFERENCES

1. G. F. Offutt and B. R. Wheeler, First Zirconium Alloyed Fuel Reprocessing Campaign Using Soluble Nuclear Poison, AEC-IN-1091 (March 1968).
2. D. Gombert, H. S. Cole, J. R. Berreth, Vitrification of High-Level ICPP Calcined Wastes, DOE-ICP-1177 (February 1979).
3. H. T. Blair, Vitrification of Nuclear Waste Calcines by In-Can Melting, DOE-BNWL-2061 (May 1976).
4. J. H. Valentine, B. J. Newby, et al., Calcination Flowsheet Development, DOE-ICP-1163 (October 1978).
5. S. A. Birrer, Pilot Plant Development of a Rover Waste Calcination Flowsheet, DOE-ICP-1148 (April 1978).
6. C. Hirayama, Properties of Aluminoborate Glasses of Group II Metal Oxides, J. Am. Chem. Soc., 44 (12) pp.602-606 (1961).
7. Ohta, Hironeri and Yoshiro Suzuki, Chemical Durability of Glasses in the System $\text{SiO}_2\text{-CaO Na}_2\text{-RmOn}$, Ceramic Bulletin, Vol. 57, No. 6 602-604 (1978).