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VITRIFICATION OF HIGH-LEVEL ALUMINA NUCLEAR WASTE

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ABSTRACT

Borophosphate glass compositions have been developed for the vitrification of a high-alumina calcined defense waste. The effect of substituting SiO_2 , P_2O_5 and CuO for B_2O_3 on the viscosity and leach resistance was measured. The effect of the alkali to borate ratio and the $\text{Li}_2\text{O}:\text{Na}_2\text{O}$ ratio on the melt viscosity and leach resistance was also measured.

INTRODUCTION

Vitrification of high-level nuclear waste is one of the waste management alternatives being investigated at the Idaho Chemical Processing Plant (ICPP). 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 , 15% Al_2O_3 , and 52% CaF_2 , and alumina calcine consisting of approximately 90% Al_2O_3 , 3% Na_2O , 3% B_2O_3 , 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 >1:1 in alumina calcine. Because of this, formulations to vitrify the alumina calcine were developed. Although both borophosphate and borosilicate frits were evaluated, only the borophosphate frits reported on here resulted in practical alumina waste glasses.

Each of the glass compositions were evaluated on the basis of melt viscosity and leach resistance. These two criteria were used because glasses with melt viscosities of 50-200 poise at temperatures of 1050-1200°C are desired for 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.

EXPERIMENTAL METHOD

Glass Preparation

Experimental glasses were melted at 1100°C in either 100 mL platinum or high-fired alumina crucibles. Glasses were made using reagent grade oxides and carbonates, and a simulated alumina calcine.⁵ A 20-24 h 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 scale for viscosity ranging from 1=25-75 poise, 2=75-150, 3=150-300, 4=300-500, and 5=not pourable, as estimated from standard viscosity fluids. The actual viscosity of selected melts was measured with a Brookfield viscometer.

Numerous compositions developed a meltable borophosphate glass containing 23 mol% calcine which was then used as a base glass for further study (Table 2). The glass was evaluated in the four leach solutions shown in Table 1. The solutions were designed to evaluate the glass over a wide range of pH conditions. The soxhlet test was used because it measured the corrosion rates of the glasses in a neutral pH region at a elevated temperature. Preliminary experiments showed that the borophosphate glasses varied most in the soxhlet leach test and had good leach resistance in the other leach solutions. Thus, the Soxhlet leach test was used to compare the modifications made to the base borophosphate glass. The modified glasses were checked periodically for both acid and Soxhlet leach resistance.

Leach Tests

Experimental procedures previously used at the ICPP² were followed in leaching the glasses. Four grams of the ground glass sample was weighed and placed in either a 100 mL leachant solution (Table 1) 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

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 1. Types of Leaching Solutions and Conditions

<u>Solution</u>	<u>pH</u>	<u>Temperature, °C</u>	<u>Time, h</u>	<u>Description</u>
A	3.6-3.8	25	19	1M acetic acid, buffered
B	7	95	72	distilled water, Soxhlet test
C	9	25	19	1M NH ₄ OH, buffered
D	7.5	25	19	WIPP brine water, 306 g/L dissolved solids

Table 2. Base Borophosphate Glass Composition and Properties

<u>Glass No.</u>	<u>Composition, mol%</u>						
	<u>SiO₂</u>	<u>B₂O₃</u>	<u>P₂O₅</u>	<u>Li₂O</u>	<u>Na₂O</u>	<u>CuO</u>	<u>Al₂O₃ Calcine</u>
178	4	40	10	10	10	3	23

Properties

Viscosity at 1100°C : 25-75
(poise)

Acid Leach, wt% lost/
19 h (25°C) 0.5

Soxhlet Leach, wt%
lost/72 h (95°C) 6

BOROPHOSPHATE GLASS DEVELOPMENT

Single Substitutions of SiO₂ or P₂O₅ for B₂O₃

The base borophosphate glass (No. 178) has a high Soxhlet leach rate and a low melt viscosity. Individual substitutions of SiO₂ and P₂O₅ were made for B₂O₃ in this base glass (Table 3) to improve the Soxhlet leach rate. The substitution of SiO₂ (8-20 mol%) decreased the Soxhlet leach rate to only 1.5 wt% while only moderately increasing the melt viscosity. The substitution of (15 mol%) P₂O₅ also lowered the Soxhlet leach rate without

Table 3. Substitution of SiO_2 or P_2O_5 for B_2O_3

Base Glass 178

A. Substitution of SiO_2

Glass No.	Mol% $\text{SiO}_2\text{-B}_2\text{O}_3$	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
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

B. Substitution of P_2O_5

Glass No.	Mol% $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3$	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
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	-

Base Glass 185

A. Substitution of SiO_2

Glass No.	Mol% $\text{SiO}_2\text{-B}_2\text{O}_3$	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
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

significantly raising the melt viscosity. At levels above 15 mol% P_2O_5 , the glasses become very viscous, melted with heavy surface scums, and had a high Soxhlet leach rate.

Having observed a useful range of 10-15 mol% P_2O_5 in the base glass, it was decided to substitute SiO_2 for B_2O_3 in glass 185 which contained 15 mol% P_2O_5 (Table 3). Substitutions of 4-14 mol% SiO_2 had little effect on the Soxhlet leach rate, and only moderately increased the melt viscosity. It was not until substitutions of 14-16 mol% SiO_2 were made that the leach rate decreased and increased the viscosity to 75-150 poise. The Li_2O to Na_2O ratio, alkali to borate ratio, and CuO content was then varied in the selected glasses (Table 4) to improve the melt viscosity and Soxhlet leach resistance.

Table 4. Selected Low and High Silica Borophosphate Glasses

Glass No.	Composition, mol%						
	SiO_2	B_2O_3	P_2O_5	Na_2O	Li_2O	CuO	Al_2O_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

Variation of the Alkali Ratio

The alkali ratio was varied in a low silica glass (No. 178) and a high silica glass (No. 271). The effect of variation in the alkali ratio on the viscosity and Soxhlet leach rate of glass 178 was markedly different from that of glass 271 (Tables 4 and 5).

All of the low silica glasses with a $Li_2O:Na_2O$ ratio of 1:1 or greater had leach rates of 6-9 wt% while glasses with less Li_2O present had leach rates of 25-30 wt%. The variation of the $Li_2O:Na_2O$ ratio had no effect on melt viscosity. This glass was not improved by changing the alkali ratio.

All of the high silica mixed alkali glasses (Table 5) had leach rates between 1-2 wt% but the viscosity of the glasses decreased with increasing Li_2O content. As an example, glass 301, which contains only Li_2O had the lowest viscosity (50 poise) and leach rate (1 wt%).

Table 5. Effect of Variation of Alkali Ratio on Viscosity and Leach Rate

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

Glass 271			
Glass No.	Mol% Li ₂ O-Na ₂ O	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
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

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 6). It was observed that the viscosity of the glasses decreased as the alkali content increased, and that the effect became more pronounced as the SiO₂ and P₂O₅ content in the glass increased. For example, the most significant decrease in viscosity occurred in glass 274, a high SiO₂, high P₂O₅ glass.

The low silica glass 178 had acid leach rates of 25 to 40 wt% when the alkali content was other than 20 mol% (alkali:borate=1:2). The low P₂O₅ and SiO₂ contents of the glass are the cause for the high leach rates. The other glasses showed no major changes in leach rate if the alkali content was between 18-24 mol%. Thus, improvements of the glasses (other than 178) can be made by increasing the alkali to borate ratio of the glass.

Table 6. Effect of Variation of Alkali to Borate Ratio on Viscosity and Leach Rates

Base 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
Base Glass 185			
Glass No.	Mol% Alkali-B ₂ O ₃	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
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	20-31	1	2.0
Base Glass 272			
Glass No.	Mol% Alkali-B ₂ O ₃	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
272	20-24	2	1.3
305	22-22	2	1.4
306	24-20	2	1.4
Base Glass 274			
Glass No.	Mol% Alkali-B ₂ O ₃	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
281	16-27	3	4.7
282	18-25	2	1.3
274	20-23	2	1.3
283	22-21	1	.85
284	24-19	1	1.8

Substitutions of CuO for B₂O₃

Substitutions of CuO for B₂O₃ were made in a low silica glass (178) and a high silica glass (272) (Table 7). Both glasses were affected by CuO in a similar manner. Glass 178 without CuO did not dissolve the Al₂O₃ calcine. The glasses with 3 and 5 mol%

CuO produced good melts and had leach rates of 6-7 wt%. The viscosity of the glasses slightly decreased as the CuO content increased.

Glass 272 without CuO melted well and had a Soxhlet leach rate similar to the glasses with 3 and 5 mol% CuO (1.5 wt%). The viscosity decreased as the CuO content decreased, but all were still within the viscosity range of 75-150 poise. Thus, the low silica and high silica glass were improved by substitutions of CuO for B₂O₃.

Table 7. Effect of Substituting CuO for B₂O₃ on Viscosity and Leach Rate.

Base Glass 178			
Glass No.	Mol% CuO-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
Base Glass 272			
Glass No.	Mol% CuO-B ₂ O ₃	Relative Viscosity	Soxhlet Leach Rate, wt% lost/72 h
307	0-27	2	1.3
272	3-24	2	1.4
308	5-22	2	1.4

Brookfield Viscosity Measurements

Actual 1000-1100°C viscosities, as measured by a Brookfield viscometer were determined for four glasses containing 10% P₂O₅ and 20% alkali and for two glasses containing 15% P₂O₅ and 20% alkali. In addition, the reduction in viscosity achieved in these glasses by increasing the alkali to borate ratio and the Li₂O to Na₂O ratio was measured (Table 8).

Glasses with leach rates of about 1.5 wt% (glasses 271, 272, and 274) and 3 wt% (glasses 185 and 212) were measured for viscosity. All of the 10% P₂O₅ glasses have better viscosity ranges than the corresponding 15% P₂O₅ glasses. The former glasses appear more suitable for calcine vitrification.

Reductions of 30-50 poise were achieved by increasing the alkali to borate ratio of the glasses. A similar reduction in viscosity (about 30 poise) occurred when Li₂O was replaced for Na₂O in the glass. As stated earlier, it appears that high alkali, high Li₂O glasses are improvements over the base compositions.

Table 8. The Viscosity-Temperature Profile of Selected Borophosphate Glasses

Condition	Glass No.	Glass Viscosity (poise)		
		1000°C	1050°C	1100°C
Comparison of 10%, 15% P ₂ O ₅ Glasses	185	175	105	30
	212	110	60	40
	272	275	150	90
	274	580	250	120
Alkali to Borate Ratio	272	275	150	90
	306	210	120	70
	274	580	150	120
	283	180	100	70
Use of Li ₂ O	271	210	130	80
	301	160	90	50

SUMMARY AND RECOMMENDATIONS

Substitutions of SiO₂ and P₂O₅ for B₂O₃ were made using a base borophosphate (10 mol% P₂O₅) composition. Both of the additives increased the melt viscosity and decreased the Soxhlet leach rate. Substitutions of 4-15 mol% SiO₂ in a 15 mol% P₂O₅ base glass also lowered the leach rate and increased the viscosity, but these glasses are more viscous when compared at equal leach rates. The viscosity of the low silica glasses, such as No.'s 178 and 185, is slightly decreased by increasing the alkali to borate ratio and by the substitution of CuO for B₂O₃. These modifications produced variable effect on the leach rates.

The viscosity of the high silica glasses, such as No.'s 272 and 274, 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 of these high and low silica glass are quite low (0.5 wt%).

Based on Soxhlet leach rate, melt viscosity, and glass melt-ability, there are a number of borophosphate glasses suitable for vitrification of the alumina calcine. High silica glasses with 10-15 mol% P₂O₅ and 20-24 mol% alkali (with a Li₂O to Na₂O ratio

of 1:1 or greater) have soxhlet leach rates approximately one half that of the low silica glasses. All glasses meet the viscosity requirements of joule heated melting or "in-can" melting. These experiments demonstrate that leach resistant glasses containing alumina calcine can be made at temperatures compatible to the proposed vitrification processes.

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