Compatibility of Two Idaho Chemical Processing Plant Glasses with Electric Melting Processes

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**Pacific Northwest Laboratory
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COMPATIBILITY OF TWO IDAHO CHEMICAL
PROCESSING PLANT GLASSES WITH ELECTRIC
MELTING PROCESSES

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SUMMARY

The Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho, has converted high-level liquid nuclear wastes produced at the Idaho Chemical Processing Plant (ICPP) to a dry calcine powder. The feasibility of converting this calcine to a durable waste glass is being evaluated at ICPP. Candidate waste glass compositions were developed and plans were made to construct and operate a laboratory electric glass melter at INEL.

The Pacific Northwest Laboratory (PNL) examined the electric melter processing characteristics of two Idaho developed waste glasses, ICPP Zr-13 and ICPP Zr-51. This preliminary evaluation found both borosilicate glasses acceptable candidates for electric melting trials. The high temperature resistivity, viscosity, and corrosion behaviors are consistent with PNL melting experience. The ICPP calcine characteristics, waste glass volatility, and waste glass devitrification behavior have not been previously encountered at PNL. Several melter operation and design options are available to deal with all of these conditions. Additional work in three basic areas is, however, suggested for the final candidate waste glass composition:

- volatility - species identification
- corrosion behavior of electrodes at operating temperatures
- means of improving melting rates and glass homogeneity.

Reducing the devitrification tendency of the candidate waste glass will significantly improve the stability and control of an electric glass melting process.

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COMPATIBILITY OF TWO IDAHO CHEMICAL PROCESSING PLANT GLASSES WITH ELECTRIC MELTING PROCESSES

INTRODUCTION

Currently, the reference process for treatment of high-level liquid radioactive wastes is calcination followed by fixation in a glass. At the Idaho National Engineering Laboratory (INEL), near Idaho Falls, Idaho, high-level liquid nuclear wastes produced at the Idaho Chemical Processing Plant (ICPP) have been converted to a dry calcine by fluidized bed calcination since 1963. The feasibility of converting this calcine to a durable waste glass is being evaluated at ICPP. They plan to install and operate a laboratory electric glass melter with waste glasses containing simulated ICPP zirconia calcine.

The Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy, was contracted to assist the INEL vitrification program. Over the past two years, PNL has designed, constructed, and operated three electric glass melters that have processed a variety of simulated nuclear waste glasses. As a preliminary step in the design of an ICPP electric glass melter, PNL is evaluating the compatibility of two Idaho developed waste glass formulations with present electric melting processes.

This report presents the results of a preliminary study on two glasses proposed for the ICPP electric glass melter.

SAMPLE PREPARATION

Two proposed ICPP waste glasses evaluated at PNL incorporate a simulated fluidized-bed calcine into a borosilicate glass. The zirconia calcine waste (ICPP-Zr) was produced at ICPP and supplied to PNL. The Idaho-developed glass frits for incorporating the zirconia calcine are ICPP-13 and ICPP-51. The waste glasses which are produced by melting defined calcine/frit mixtures are ICPP Zr-13 and ICPP Zr-51.

SIMULATED CALCINE CHARACTERISTICS

The main chemical components of the ICPP zirconia calcine were Al_2O_3 , ZrO_2 , and CaF_2 . Table 1 lists the range of components in wt%, a "typical" composition, and the chemical analysis of the calcine material supplied to PNL. While some compositional variations are noted, they do not deviate significantly from general ranges. The only crystalline phase present was CaF_2 .

"Typical" Idaho zirconia calcine consists of two distinct particle size fractions. The "product" (60 to 70 wt%) is the direct product of fluidized-bed calcination, with particle diameters from 100μ to 600μ . The remaining 30 to 40 wt% are "fines", from 10μ to 100μ that are removed from the calciner off-gas system. The particle size distribution of ICPP-Zr was determined by screen and sedimentation analyses of representative calcine samples. Figure 1 clearly shows the bimodal particle size distribution with approximately 77 wt% being comprised of coarse "product" ($>100\mu$). The "fines", (1μ to 10μ), however, appear to be smaller in size than anticipated. The loose bulk density of the ICPP-Zr calcine was 1.2 g/cc. Tapping increased bulk density to 1.5 g/cc.

The response of ICPP-Zr calcine to increasing temperature was evaluated by thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and heating in a thermal gradient. Weight loss was gradual up to 850°C . Significant quantities of H_2O and NO_x were not present. Additional weight was lost above 850°C , as shown in Figure 2. The calcine began to sinter at 850°C . A minor unidentified exothermic reaction occurred at 230°C , as shown in Figure 3.

TABLE 1. Simulated Zirconia Waste Calcine

	General/Range Wt%	Typical Wt%	Chemical Analysis, wt%
Al_2O_3	17-22	18	13.7
ZrO_2	18-22	20	24.6
CaF_2	50-55	55	52.0
Ca(OH)_2	5- 8	5	2.2
H_2O	0- 0.5	0.2	1.0
B_2O_3	0- 2	0.7	(a)
NO_x	2- 4	1.0	1.0
Cs	0- 0.1	0.1	(a)
Sr	0- 0.1	0.1	(a)
Rare earths	0- 0.2	0.1	(a)

(a) Not analyzed.

FIGURE 1. Particle Size Distribution of ICPP Zr Calcine

SAMPLES HEATED IN AIR AT 10°C/min

FIGURE 2. TGA Results for ICPP Zr

GLASS FRIT CHARACTERISTICS (ICPP-13 and ICPP-51)

Glass frits are convenient forms in which the necessary glass-forming constituents can be added to the waste for vitrification. Two Idaho-developed frits, ICPP-13 and ICPP-51, were prepared and evaluated at PNL. Table 2 lists the composition of both borosilicate glass frits.

Three kilograms of each frit were produced. The chemical constituents were weighed to the nearest 0.1 g and thoroughly mixed in a ball mill before they were melted. After melting for one hour at 1100°C in platinum crucibles, the molten glass was quenched into a water bath to duplicate commercial frit preparation practice. After it was dried, the glass frit was crushed to -60 mesh to ensure chemical homogeneity. Frit ICPP-13 was a clear, transparent glass with a density of 2.576 ± 0.001 g/cc. Frit ICPP-51 was deep blue in color with a density of 2.521 ± 0.001 g/cc.

SIMULATED WASTE GLASS PREPARATION (ICPP Zr-13 and ICPP Zr-51)

The two Idaho-developed simulated waste glasses were prepared by melting a 1:2 weight mixture of ICPP Zr calcine and frit ICPP-13 or ICPP-51. Table 3 lists the theoretical and actual compositions of ICPP Zr-13 and ICPP Zr-51 waste glasses.

SAMPLES HEATED IN AIR AT 10°C/min

FIGURE 3. DTA Results for ICPP Zr

TABLE 2. ICPP Frit Compositions (wt%)

<u>Oxide</u>	<u>ICPP-13</u>	<u>ICPP-51</u>
SiO ₂	51.8	66.0
Na ₂ O	28.3	24.0
B ₂ O ₃	12.9	8.0
Li ₂ O	2.1	--
CaO	2.8	--
ZnO	2.1	--
CuO	--	2.0
	<u>100.0</u>	<u>100.0</u>

TABLE 3. ICPP Waste Glass Compositions, wt%
(2:1 Frit:Zr Calcine wt Ratio)

	ICPP Zr-13		ICPP Zr-51	
	Theoretical	Wet Chemical Analysis	Theoretical	Wet Chemical Analysis
SiO ₂	34.8	32.0	44.4	40.6
Na ₂ O	19.0	18.1	16.1	14.0
B ₂ O ₃	9.0	--	5.5	--
Li ₂ O	1.4	--	--	--
CaO	3.1	3.4	1.2	3.8
ZnO	1.4	--	--	--
CuO	--	--	1.3	--
Al ₂ O ₃	6.0	4.7	6.0	4.8
ZrO ₂	6.8	8.6	6.8	9.6
CaF ₂	18.5	15.6	18.5	12.8
Cs ₂ O, SrO	0.1	--	0.1	--
R E oxides	—	—	—	—
		100.0		100.0

The calcine/frit mixture, or batch, was melted in platinum crucibles at 1100°C for two hours. Then the molten glass was quenched onto stainless steel plate to eliminate any possibility of selective leaching caused by quenching into water. Unlike the glass frits, both ICPP Zr-13 and ICPP Zr-51 waste glasses had obvious inhomogeneities. Composition ICPP Zr-13, a yellow transparent glass, left a small amount of a white crystalline phase, identified as ZrO₂, at the top of the crucible. In the bulk of ICPP Zr-13, no crystalline phases were found by x-ray diffraction. Waste glass ICPP Zr-51, an opaque turquoise-colored glass, showed slight variations in color. A considerable quantity of crystalline CaF₂ was identified by x-ray diffraction but could not be observed with the optical microscope. The densities of both waste glasses showed considerably more variation with ICPP Zr-13 at 2.771 ± 0.003 g/cc and ICPP Zr-51 at 2.766 ± 0.018 g/cc. Both glasses were crushed to -10 mesh in a tool steel mortar to improve representative sampling before they were distributed to individual researchers for further evaluations.

PROPERTIES OF ICPP WASTE GLASSES

For successful melter operation, the physical and chemical properties of the waste glasses must be compatible with equipment design and materials. Before beginning the ICPP melter design, PNL evaluated the following properties to determine potential glass processing problems related to:

- viscosity
- resistivity
- volatility
- phase behavior
- melting behavior
- corrosion.

All samples were produced as described previously.

VISCOSITY

The viscosity of molten glass is a measure of its resistance to flow. The nominal operating viscosity range for electric melters is below 200 poise at 1050⁰C. Experience has shown that melt homogeneity and equipment operation is satisfactory in this viscosity range.

The melt viscosity of both ICPP frits and simulated waste glasses were measured as a function of temperature using a rotating spindle Brookfield viscometer. The crucible and spindle were made of platinum to eliminate corrosion and prevent contamination of the sample glasses. Figures 4 and 5 illustrate the resulting viscosity data. Frit ICPP-13 is extremely fluid, having a viscosity of less than 30 poise at 1050⁰C. Frit ICPP-51 has a higher viscosity, 300 poise at 1050⁰C. This difference is attributable to the alkali/silica ratio, which is 0.59 for ICPP-13 and 0.36 for ICPP-51.

FIGURE 4. Viscosity vs Temperature for Frit ICPP-13 and Waste Glass ICPP Zr-13

The addition of 33 wt% of ICPP Zr calcine to either frit significantly lowers the resulting waste glass viscosity, as shown in Figures 3 and 4. The viscosity is reduced more in the case of the ICPP-51 frit, which has a higher initial viscosity. Both waste glasses have viscosities less than 200 poise at 1050°C. At temperatures between 950°C and 850°C, wide viscosity fluctuations are noted, apparently due to devitrification or growth of crystal phases.

FIGURE 5. Viscosity vs Temperature for Frit ICPP-51 and Waste Glass ICPP Zr-51

ELECTRICAL RESISTIVITY

Electrical resistivity or conductivity of molten glass is a fundamental consideration in electric glass melting. It is mainly a function of the glass composition and governs melter design. The apparatus and technique used to measure resistivity are described by J. L. Bates.⁽¹⁾

Table 4 lists the electrical conductivity ($\frac{1}{\text{cm}}$) and resistivities ($\Omega \text{ cm}$) determined for both frits and waste glasses. Figures 6 and 7 show resistivity as a function of temperature.

TABLE 4. Electrical Data for ICPP Glasses

Temperature °C	ICPP-13		ICPP Zr-13		ICPP-51		ICPP Zr-51	
	Electrical Conductivity (ohm ⁻¹ cm ⁻¹)	Electrical Resistivity (ohm-cm)	Electrical Conductivity (ohm ⁻¹ cm ⁻¹)	Electrical Resistivity (ohm-cm)	Electrical Conductivity (ohm ⁻¹ cm ⁻¹)	Electrical Resistivity (ohm-cm)	Electrical Conductivity (ohm ⁻¹ cm ⁻¹)	Electrical Resistivity (ohm-cm)
1250	1.49	0.67	0.843	1.19	0.823	1.22	0.347	2.88
1200	1.16	0.86	0.512	1.95	0.669	1.49	0.328	3.04
1100	1.03	0.97	0.323	3.10	0.545	1.83	0.245	4.08
1000	0.765	1.31	0.485	2.06	0.361	2.77	0.190	5.26
900	0.519	1.93	0.207	4.83	0.256	3.90	0.084	11.90
800	0.312	3.21	0.117	8.55	0.141	7.90	0.048	20.83
700	0.143	6.99	0.048	20.83	0.052	16.13	0.017	58.82
600	0.041	24.39	0.010	100.00	0.018	55.56	0.0041	243.3
700	0.113	8.85	0.041	24.39	0.062	16.13	0.016	62.5
800	0.251	3.98	0.087	11.49	0.131	7.63	0.044	22.73
900	0.490	2.04	0.178	5.62	0.254	3.93	0.101	9.90
1000	0.740	1.35	0.163	6.13	0.385	2.60	0.163	6.13
1100	1.06	0.94	0.256	3.91	0.575	1.75	0.289	3.47
1200	1.20	0.93	1.16	0.86	0.696	1.44	0.512	1.95
1250	1.49	0.67	1.38	0.72	0.823	1.22	0.629	1.59

Both frits, ICPP-13 and ICPP-51, show very gradual resistivity changes with temperature. The lower resistivity, 1.1 Ω -cm of ICPP-13, compared to 2.1 Ω -cm at 1050°C for ICPP-51, is consistent with its lower viscosity and higher alkali content. Since glass is an ionic conductor, the main charge carriers are alkali metal ions. The addition of waste to each frit dilutes the number of charge carriers present, and increases resistivity. The resistivity hysteresis observed during heating and cooling of both ICPP Zr-13 and ICPP Zr-51 is indicative of structural or phase changes occurring in the glass, such as devitrification or phase separation. Resistivity changes are much lower for ICPP Zr-51.

Electric glass melters operated for over 18 months at PNL were designed for glass resistivities higher than 2.5 Ω cm at melting temperatures. Lower resistivity glasses require additional current for heating and could exceed electrode current density limits to maintain process temperatures. Both ICPP Zr-13 and ICPP Zr-51 waste glasses are compatible with present glass resistivity criteria for electric melting. The

FIGURE 6. Electrical Resistivity vs Temperature for Frit ICPP-13 and Waste Glass ICPP Zr-13

resistivity hysteresis observed on heating and cooling for both glasses could, however, present melter power control problems. Melter electrode resistance which is often a control parameter would then also be affected by devitrification, as well as glass composition and temperature.

VOLATILITY

Volatilization from molten waste glass becomes a problem when the material lost is corrosive to off-gas components, alters glass properties, or is a radioactive effluent to be removed in the off-gas stream. The high fluoride levels in both ICPP Zr-13 and ICPP Zr-51 waste glasses suggested that volatilization should be further studied. The apparatus

FIGURE 7. Electrical Resistivity vs Temperature for Frit ICPP-51 and Waste Glass ICPP Zr-51

and procedure used is described in a report by W. J. Gray.⁽²⁾ Twenty-gram samples of ICPP Zr-13 and ICPP Zr-51 were held at constant temperature for 24 hr in a platinum crucible with 2.00 cm² cross-sectional area. The sample weight was continuously monitored. This information was then converted to weight loss per unit surface area for each waste glass.

Results at 1000°C and above are shown in Figure 8. At 1200°C, weight-loss data for both glasses varies with the square root of time. This implies that diffusion is the rate-limiting mechanism of volatility in this temperature range. At lower temperatures, however, weight loss is a linear function of time, which implies that some surface reaction is rate limiting.

FIGURE 8. Weight Loss vs Time for Waste Glasses (ICPP Zr-13 and ICPP Zr-51)

Figure 9 shows weight loss after four hours as a function of temperature. Reproducibility is generally quite good. A linear relationship between the logarithm of weight loss versus the reciprocal of absolute temperature implies that one volatilization mechanism is occurring. Non-linearity of this relationship, on the other hand, suggests that different volatilization mechanisms occur within given temperature ranges. Waste glass ICPP Zr-51 appears to have a single volatilization mechanism. Above

FIGURE 9. Weight Loss vs Temperature for Waste Glasses ICPP Zr-13 and ICPP Zr-51

1000°C, waste glass ICPP Zr-13 shows similar weight loss behavior to ICPP Zr-51. Below 1000°C, however, ICPP Zr-13 loses significantly less weight than ICPP Zr-51. The different volatilization mechanism below 1000°C could be related to the presence of crystalline CaF_2 . The impact on process operation is not known. No attempt was made to identify the vaporizing species in the ICPP glasses.

MELTING BEHAVIOR

A glass melter supplies the energy to decompose and react the various constituents of a waste calcine/glass frit mixture, or batch, and thus produce a homogeneous waste glass product. The manner in which this occurs is a function of batch chemistry and behavior, as well as final glass composition. Data on the physical and chemical characteristics of batch materials at various temperatures can be used to predict melting problems.

Weight loss of the frit/calcine mixtures as a function of temperature for ICPP Zr-13 and ICPP Zr-51 batches are shown in Figure 10. Aside from some small variations, neither batch lost significant weight until above 950°C. No major chemical reactions were noted from DTA results.

The physical behavior of both batches as a function of temperature was evaluated after a sample of material was placed in a platinum boat inserted into a 100 to 1000°C thermal gradient for half an hour. The ICPP Zr-13 batch sintered extensively without apparent glass formation from 400°C to 620°C. Above 620°C until 930°C, calcine particles

SAMPLES HEATED IN AIR AT 10°C/min

FIGURE 10. Weight Loss vs Temperature for Waste Glass Batches (ICPP Zr-13 and ICPP Zr-51)

were dispersed in a glass matrix. An apparently homogeneous glass formed above 930°C. The ICPP Zr-51 batch reacted more slowly, sintering between 550 and 620°C. From 620 to 1000°C, calcine particles were dispersed in a glass matrix. A considerable amount of calcine remained undissolved at 1000°C after one half hour.

A technique for measuring batch melting rate and foaming potential has been used to identify melting problems in waste glass batches. Sufficient batch to produce 25 g of waste glass was fed to a 2-3/16 in. dia by 3-5/8-in. high stainless steel can heated to 1050°C in a vertical resistance furnace. When reactions were complete and a quiet glass surface was present, additional batch charges were made until 100 g of glass was melted. Neither ICPP Zr-13 nor ICPP Zr-51 batches showed any indication of foaming. While both batches appeared to melt quickly, subsequent examination showed that unmelted calcine was present. Cross sections of both cans are shown in Figure 11. For ICPP Zr-13 batch, calcine particles tended to separate from the melt in a 3/8-in. layer on the glass surface. This separation could account for the ZrO_2 phase found during ICPP Zr-13 waste glass preparation. The ICPP Zr-51 batch container showed very little dissolution of calcine particles. The more viscous frit appeared to fuse calcine particles during the the melting trial rather than dissolve them. This incomplete melting was also observed in the gradient furnace run.

Neither situation has been noted for previously melted waste glass batches. While electric glass melting uses temperatures above 1050°C and some homogenization takes place, the impact of large, difficult-to-melt calcine particles on process operation must be evaluated in more detail.

FIGURE 11. Sections of Containers Following Melting Rate Trials (1050°C)

DEVITRIFICATION BEHAVIOR

The devitrification behavior of the two ICPP waste glass compositions, ICPP Zr-13 and ICPP Zr-51, was studied to determine the total crystallinity as a result of devitrification and to identify the crystalline phases present. For each sample approximately 7 g of ICPP Zr-13 or ICPP Zr-51 glass was remelted in an alumina crucible at 1050°C for 2 hr. At the end of each 2-hr melt, a pair of samples was either cooled at a controlled rate or cooled directly to one of the three selected annealing temperatures (800°C, 900°C, or 1000°C). In addition to these devitrification treatments, a sample of each glass composition was air-cooled directly from the melt temperature to yield a vitreous glass containing whatever insolubles were present at melt temperature.

After devitrification, the crucibles were sectioned from top to bottom and the glass from one of the crucible halves was crushed for analysis by powder x-ray diffraction, which identifies crystalline phases present. Standard curves of crystallinity as a function of integrated intensity of

the diffracted x-rays was used to determine the total crystallinity of each sample. This curve has been found to give good estimates of total crystallinity for several glass types.

The total crystallinity results for the controlled cooling study are given in Table 5; also included are the data for the air-cooled and as-received glasses. The high crystallinity in the as-received ICPP Zr-51 is due to an insoluble CaF_2 phase (discussed below). The controlled cooling rate results are plotted in Figure 12.

The results for the isothermal annealing study are listed in Tables 6 and 7. These results show that the total crystallinity reaches equilibrium very quickly at 800 and 900°C. At 1000°C the behavior with time is complex. The devitrification observed in ICPP Zr-13 at 1000°C after five days is the result of a glass/crucible interaction (discussed below). The devitrification behavior of ICPP Zr-51 at 1000°C is complicated by the initially high CaF_2 content, which eventually goes into solution. The results for the isothermally annealed samples are plotted in Figure 13. From these results, it is clear that at equilibrium both ICPP waste glasses are extensively crystalline from 800 to 1000°C. This temperature range is found in various locations in a melter during operation.

TABLE 5. Crystallinity Data for Controlled Cooling Rate Study of ICPP Waste Glasses

Cooling Rate (°C/min)	Total Crystallinity (wt%)	
	ICPP Zr-13	ICPP Zr-51
6.25	65	43
12.5	44	43
25	71	50
58.6	42	23
130	7	18
Air cool (1000°C)	3	12
As received	0	20

FIGURE 12. Total Crystallinity as a Function of Cooling Rate

Each of the ICPP waste glasses contains 18.5 wt% CaF_2 . In ICPP Zr-13, the CaF_2 is in solution in the glass; however, in ICPP Zr-51, the CaF_2 is found completely as a separate phase. The fractional crystallinity due to the CaF_2 content in ICPP Zr-51 was determined for the isothermally annealed samples and is illustrated in Figure 14. The results show that CaF_2 will go into solution after several hours at 1000°C. At 800 and 900°C, the CaF_2 content approaches an equilibrium value of approximately 9 to 10 wt%.

TABLE 6. Crystallinity Data for Isothermal Annealing Study of ICPP Zr-13 Waste Glass

Temperature °C	Total Crystallinity (wt%)			
	2 hr	5 hr	24 hr	120 hr
800	9	40	47	36
900	1	37	27	33
1000	2	1	1	24

TABLE 7. Crystallinity Data for Isothermal Annealing Study of ICPP Zr-51 Waste Glass

Temperature °C	Total Crystallinity (wt%)			
	2 hr	5 hr	24 hr	120 hr
800	22	25	37	36
900	14	36	32	35
1000	13	16	1	5

FIGURE 13. Total Crystallinity as a Function of Temperature and Time

FIGURE 14. Crystalline CaF_2 Content as a Function of Time and Temperature

Four phases common to both glass compositions were identified in the devitrified ICPP waste glasses. The phases were ZrO_2 , CaF_2 , $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, and NaAlSiO_4 . As indicated above, CaF_2 was found as a partially insoluble phase in ICPP Zr-51. Although soluble in ICPP Zr-13, CaF_2 was observed as a minor devitrification product in the control-cooled samples and in the samples annealed at 800 and 900°C. However, CaF_2 was not found in ICPP Zr-13 annealed at 1000°C. For both glass compositions, ZrO_2 was found in measurable quantities in only a few samples. The main devitrification products were $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ and NaAlSiO_4 . The $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ phase is limited by the amount of available Zr, the

NaAlSiO₄ phase by the amount of available Al. If all the available ZrO₂ (6.8 wt%) was used to form Ca₃ZrSi₂O₉ and all the available Al₂O₃ (6.0 wt%) was used to form NaAlSiO₄, then the theoretical maximum total crystallinity could be determined. The theoretical crystallinity of each observed phase for conditions of maximum total crystallinity given in Table 8 is about 50 wt%. The results for two of the devitrified ICPP Zr-13 samples (cooled at 6.25°C/hr and 25°C/hr) exceed this limit. In both samples the NaAlSiO₄ phase was found in much higher concentrations than believed theoretically possible. The explanation for this was a significant interaction between the Idaho waste glasses and the Al₂O₃ crucibles. This interaction provided additional Al for formation of NaAlSiO₄.

Metallographic examination was conducted only on the samples which exhibited maximum total crystallinity (cooled at 25°C/hr). Optical micrographs of the microstructure of the two glass samples are shown in Figures 15 and 16. The microstructure of ICPP Zr-13 shown in Figure 15 is very porous and crystalline. Both Ca₃ZrSi₂O₉ and NaAlSiO₄ were found throughout the sample. The dendritic phase shown in Figure 16 is Ca₃ZrSi₂O₉; NaAlSiO₄ was found mainly along the glass/crucible interface. Scanning electron microscope (SEM) micrographs of the same two

TABLE 8. Theoretical Crystallinity Values of the Observed Phases for Maximum Total Crystallinity

Phase	Crystallinity (wt%)	
	ICPP Zr-13	ICPP Zr-51
ZrO ₂	0	0
CaF ₂	9.9	7.3
Ca ₃ ZrSi ₂ O ₉	23	23
NaAlSiO ₄	17	17
Total	49.9	47.3

200 μm

50 μm

50 μm

FIGURE 15. Photomicrograph of ICPP Zr-13 Glass Cooled at 25°C/hr

200 μm

50 μm

50 μm

FIGURE 16. Photomicrograph of ICPP Zr-51 Glass Cooled at 25°C/hr

samples are shown in Figure 17. Due to the greater depth of field of the SEM, the porous nature of the ICPP-13 is clearer in Figure 17. The lighter phase in the ICPP Zr-13 sample is $\text{Ca}_3\text{ZrSi}_2\text{O}_9$; the darker phase is NaAlSiO_4 . Little if any glassy matrix remains in the surface region. The near-surface glassy matrix may have been removed during the polishing process. Quantitative energy dispersive x-ray analysis of the two areas shown in Figure 17 indicates that the ICPP Zr-13 sample was depleted in Si and Ca and that both samples were enriched in Al. This supports both an attack of the glassy matrix during polishing and an increased Al content due to the glass/crucible interaction.

FIGURE 17. SEM Micrographs of ICPP Zr-13 and ICPP Zr-51 Glasses Cooled at 25°C/hr

In summary, four devitrification products were found which were common to both glasses, CaF_2 , $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, NaAlSiO_4 , and a small amount of ZrO_2 . Both ICPP Zr-13 and ICPP Zr-51 glasses readily devitrified at 800 and 900°C and quickly reached equilibrium crystallinity values near 40 wt%. At 1000°C, devitrification was slow and due mainly to a glass/crucible interaction.

Temperatures as low as 900°C can be anticipated locally in waste vitrification equipment during idling conditions or in the event of a temporary power loss. Rapid devitrification could produce large quantities of crystalline material in vitrification equipment. As noted previously, this impacts flow (viscosity) and electrical properties (resistivity) of the molten glass, presenting possible operation problems. While an Al_2O_3 glass interaction accounted for some of the higher crystal levels in the Idaho glasses, values near 50 wt% are still projected if this effect is eliminated. This level of devitrification can be expected in canisters of either ICPP Zr-13 or ICPP ZR-51. Large canisters of molten glass are not expected to cool faster than 10 to 15°C/hr. Both Idaho glasses show considerable devitrification at rates below 50°C/hr. It is not known if devitrification affects waste glass chemical durability.

CORROSION

The resistance of melter and off-gas materials to attack by molten waste glass and vapors largely determines the useful operating life of vitrification equipment. The corrosion resistance of two refractories and three metals presently in PNL melters was observed from polished metallographic sections after exposure to molten glass and vapor. Test materials were suspended above and in molten glasses in covered alumina crucibles for 27 hr at 1200°C. Time at this temperature was limited due to the catastrophic failure of several crucibles. The materials examined and their application are listed in Table 9. Table 10 lists the corrosion behavior observations. These materials were examined for both molten

TABLE 9. Materials Examined for Corrosion Behavior

<u>Material</u>	<u>Description</u>	<u>Process Application</u>
Monofrax K-3	Chrome-alumina refractory	Glass contact refractory
Zirmul	Refractory thermal insulation	Backup to K-3
Inconel 601	High temperature nickel-chrome alloy	LFCM vapor space
Inconel 690	High temperature nickel-chrome alloy	Melter electrodes
304	Stainless steel	Melter box components, off-gas system, canisters

TABLE 10. Observations of Corrosion Behavior after 27 hr at 1200°C

<u>Material</u>	<u>Environment</u>	<u>ICPP Zr-51</u>	<u>ICPP Zr-13</u>
Monofrax K-3	Glass	Significant penetration, little dissolution	--
	Vapor	Slight chemical interaction	--
Zirmul	Glass	Little penetration, some reaction	--
	Vapor	No effect	--
Inconel 601	Glass	Intergranular attack starting	Intergranular and surface attack
	Vapor	Intergranular attack starting	Severe intergranular attack
Inconel 680	Glass	Severe surface dissolution	--
	Vapor	Intergranular attack	--

glass and vapor attack for ICPP Zr-51. Glass ICPP Zr-13 was only used for Inconel® 601. Photomicrographs of these samples are shown in Figures 18 through 23.

Both Monofrax® glass contact refractories and Zirmul® insulating refractories were relatively resistant to extensive attack by ICPP Zr-51 glass and vapor at 1200°C. Inconel 601, 690, and 304L stainless steel showed signs of intergranular attack by ICPP Zr-51 glass and vapor. ICPP Zr-13 was more aggressive than the ICPP Zr-51.

These preliminary results indicate that Monofrax K-3 and Zirmul are good candidate refractory materials for a melter processing ICPP Zr-51 glass. Although an increase in metal attack with Idaho glasses was noted glass interface temperatures will be lower than 1200°C. Additional studies are ongoing to more specifically define material corrosion behavior.

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®Zirmul is a registered trademark of the Chas. Taylor Sons Company.

6.3X

50X

A. VAPOR CONTACT

6.3X

50X

B. GLASS CONTACT

FIGURE 18. Corrosion of Monofrax K3 in ICPP Zr-51 Waste Glass (1200°C, 27 hr)

6.3X

250X

A. VAPOR CONTACT

6.3X

250X

B. GLASS CONTACT

FIGURE 19. Corrosion of Zirmul in ICPP Zr-51 Waste Glass
(1200°C, 27 hr)

A. VAPOR CONTACT

12X

100X

B. GLASS CONTACT

12X

100X

FIGURE 20. Corrosion of Inconel 601 in ICPP Zr-51 Waste Glass
(1200°C, 27 hr)

12X

A. VAPOR CONTACT

100X

12X

B. GLASS CONTACT

100X

FIGURE 21. Corrosion of Inconel 601 in ICPP Zr-13 Waste Glass (1200°C, 27 hr)

A. VAPOR CONTACT 12X

100X

B. GLASS CONTACT 12X

100X

FIGURE 22. Corrosion of Inconel 690 in ICPP Zr-51 Waste Glass (1200°C, 27 hr)

12X

A. VAPOR CONTACT

100X

12X

B. GLASS CONTACT

100X

FIGURE 23. Corrosion of 304L Stainless Steel in ICPP Zr-51 Waste Glass (1200°C, 27 hr)

PROCESS COMPATIBILITY

The successful design and operation of a vitrification process depends on the properties of the feed constituents and resulting waste glass. Several important parameters for initial scoping of melter design were evaluated at PNL for the two Idaho candidate waste glasses, ICPP Zr-13 and ICPP Zr-51.

The rapid devitrification behavior of both ICPP Zr-13 and ICPP Zr-51 is a concern when either glass is processed in an electric melter. As long as process temperatures are maintained above 1050°C, viscosities and resistivities of both glasses are compatible with present electric glass melting processes. If temperatures fall below 1050°C, crystal contents will increase, approaching 50 wt% with time. Both viscosity and resistivity are affected by devitrification, as reported earlier. While backup systems can be designed to guard against lower temperatures, this situation introduces process control and operational uncertainties. Canisters of molten glass also generally cool at 10° to 15°C/hr. At these rates, both ICPP Zr-13 and ICPP Zr-51 would be substantially devitrified. While this is not directly a process operating concern, the impact on chemical durability must be examined. High temperature volatility is higher in ICPP Zr-13 and ICPP Zr-51 than in previously examined waste glasses. The identity, behavior, and effect on process components of these volatile species are not known. Preliminary corrosion work identified some vapor corrosion of metals by both Idaho glasses comparable to that for other processed waste glasses. Monofrax K-3 refractories will contain molten ICPP Zr-51 adequately.

The melting behavior of ICPP Zr calcine/frit mixtures is significantly different than that observed for other waste glass batches. Calcine particles tend to be large and require additional time at melting temperatures to become incorporated into a glass. While foaming is not a problem for either Idaho batch, segregation of calcine particles during

melting was noted. Higher melting temperatures and convection currents within an electric melter could increase melting rates and homogeneity; however, equipment trials are necessary to determine the impact on melter operation and product.

CONCLUSIONS AND RECOMMENDATIONS

Both Idaho waste glasses, ICPP Zr-13 and ICPP Zr-51, are acceptable candidates for electric glass melting in terms of viscosity and electrical resistivity. Significant processing and material questions exist; however, operating and design options are available. Final material selections and process design for an electric melting unit to process either ICPP Zr-13 or ICPP Zr-51 require additional work in three basic areas:

- volatility--species identification
- corrosion behavior of electrodes in glass and vapor at operating temperatures
- means of improving melting rates and glass homogeneity.

Devitrification is a process concern requiring additional melter operating control features. Reducing or eliminating this behavior would significantly improve the stability and control of any electric melting processes.

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