

# Pacific Northwest National Laboratory

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## PRELIMINARY PCT DATA ON GLASS FORMULATIONS DEVELOPED FOR HANFORD SITE LOW-LEVEL WASTES

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Prepared for  
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under Contract DE-AC06-76RLO 1830

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Richland, Washington 99352

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## SUMMARY

Tank wastes stored at the Hanford Site are to be separated into high-level and low-level waste (LLW) fractions and vitrified for disposal (TPA 1994). The high content of  $\text{Na}_2\text{O}$  in the LLW, averaging about 80 wt% on an oxide basis, necessitates the development of durable high-sodium glasses. Pacific Northwest Laboratory (PNL) is providing glass formulations for the LLW vitrification program.

The most important considerations for acceptable LLW waste glass compositions are the following: (1) the capability to incorporate high sodium content from LLW; (2) satisfactory long-term durability; and (3) proper processability, such as desired viscosity at melting temperature.

### Introduction

The requirements for long-term durability and the link between short-term laboratory tests and long-term durability have not been established. To develop durable high-sodium glasses in a reasonably short time and to supply data needed for modeling the glass's long-term performance, several short-term test methods, such as 7-day PCT (Product Consistency Test) (Jantzen 1992), 28-day Materials Characterization Center MCC-1 test (MCC 1986), single-pass flow-through test (McGrail 1992), and vapor-hydration test (Bates 1982, Ebert 1993), have been used. A long-term static test (up to one year using PCT) (Ebert 1993) is also being performed for selected glasses.

This data report is provided in response to a request from the U.S. Department of Energy

and it includes only the PCT data available at the time of the publication. A comprehensive report summarizing the durability results from PCT, single-pass flow-through test, and vapor-hydration test, and viscosity data for glass formulations (included in this report) and glasses developed for the melter technology evaluation program (Wilson 1995) will be published soon.

The initial glass matrix under development consisted of 44 glasses at 20 wt% Na<sub>2</sub>O (except four of the glasses) in alkali-silicate systems as shown in Table 1. These alkali-silicate glasses contain: (L1 series) Al<sub>2</sub>O<sub>3</sub>; (L4 series) Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>; (L5) Al<sub>2</sub>O<sub>3</sub> and CaO; (L6 series) Al<sub>2</sub>O<sub>3</sub>, CaO and B<sub>2</sub>O<sub>3</sub>; (L7 series) Al<sub>2</sub>O<sub>3</sub>, CaO and B<sub>2</sub>O<sub>3</sub> at different sodium content; and (L8 series) Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, B<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>. Waste simulant used in these glass formulations is the nominal LLW simulant as shown in Table 2. The waste was added as solid reagent-grade chemicals.

## **Experimental**

The glasses were batched and melted at temperature ranges of 1200° to 1500°C. For each glass, the major glass components to be varied were batched separately as oxides and carbonates. The remaining components were batched together in constant proportions and treated as a single component, "Others." Each batch was then mixed in a grinding cell using a grinding machine for 5 min to achieve a homogeneous mixture.

A quantity of about 500 g of each glass was melted in a platinum crucible under a lid (to reduce volatilization) using an electrically heated resistance furnace. Furnace temperature was controlled by a controller/programmer and monitored by one S-type thermocouple on the controller and a second independent S-type thermocouple. These thermocouples were located in

the middle of the furnace hot zone. Variation in temperature readout from the two thermocouples was  $\pm 1.0^{\circ}\text{C}$  with respect to the preset melting temperatures. For better homogeneity, the glass was removed from the furnace after one hour of melting, cooled, and crushed in a tungsten-carbide disc mill and remelted under a lid for another hour. Molten glass was poured into bars and annealed for 2 h at  $520^{\circ}\text{C}$  for the MCC-1 test, glass solid characterization, and archives purposes. The remaining glass was poured onto a steel plate and air-quenched.

Samples (4-5 g) of selected glasses were sent for elemental analysis for comparison to the as-batched compositions. The compositions listed in Table 1 are nominal. The analyses of selected glasses show that the analyzed and nominal compositions are similar.

The PCT test (Jantzen 1992) was based on using deionized water in Teflon® containers at  $90^{\circ}\text{C}$ . Because they were new, the containers were baked at  $200^{\circ}\text{C}$  for one week to drive off fluorine and were washed thoroughly according to PCT procedure. The glass was ground in a tungsten-carbide grinding chamber and then sieved through 100- and 200-mesh stainless-steel sieves to obtain glass particle sizes between 75 and  $150\ \mu\text{m}$ . The large particles remaining on the top of the 100-mesh sieve were crushed repeatedly until all of the glass could pass through the sieve. The crushed glass was cleaned by washing in deionized water and ethanol using an ultrasonic cleaner. It was then dried and weighed; 4 g of glass were added to a 60 mL Teflon® container filled with 40 mL of deionized water. The ratio of the surface area of glass to solution volume was taken as 2000/m. The Teflon® container and its contents were placed in an oven, preheated to  $90^{\circ}\text{C}$ , for seven days. The

PCT test is performed in duplicate. Aliquots of the leachate were filtered through a 0.45  $\mu\text{m}$  filter after the test was terminated and were submitted for chemical elemental analysis.

Results are reported as normalized elemental mass releases according to:

$$NL_i = C_i / (f_i(S/V))$$

where  $NL_i$  is the normalized mass release of element  $i$  ( $\text{g}/\text{m}^2$ ),  $C_i$  is the analyzed concentration of element  $i$  in leachate ( $\text{g}/\text{m}^3$ ),  $f_i$  is mass fraction of element  $i$  in the glass (unitless), and  $S/V$  is the ratio of glass surface area to solution volume ( $1/\text{m}$ ), which is  $2000/\text{m}$  here. The data in Table 1 were calculated based on nominal glass compositions.

## ACKNOWLEDGMENTS

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## REFERENCES

Bates, J.K., L. J. Jardine, and M. J. Steindler. 1982. "The Hydration Process of Nuclear Waste Glasses: An Interim Report." Argonne National Laboratory Report ANL-82-11. Argonne, Illinois.

Ebert, W. L., J. K. Bates, and W. L. Bourcier. 1991. "The Hydration of Borosilicate Waste Glass in Liquid Water and Steam at 200°C." *Waste Management* 11: 205-221.

Ebert, W. L., J. K. Bates, C. R. Bradly, E. C. Buck, N. L. Dietz, and N. R. Brown. 1993. "Long-Term Alteration of Borosilicate Waste Glasses." *Ceram. Trans.* 39:333-40.

"Hanford Federal Facility Agreement and Consent Order." 1993, as amended. Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

Jantzen, C. M., N. E. Bibler, D. C. Beam, W. R. Ramsey, and B. J. Waters. 1992. *Nuclear Waste Glass Product Consistency Test (PCT), Ver. 5.0*, WSRC-TR-90-539, Rev. 2. Westinghouse Savannah River Company, Aiken, South Carolina.

Materials Characterization Center. 1986. *Nuclear Waste Materials Handbook*. DOE/TIC-11400, Revision Package No. 7. Richland, Washington.

McGrail, B. P. and K. M. Olson. 1992. "Evaluating Long-Term Performance of In-Situ Vitrified Waste Forms: Methodology and Results." PNL-8358, Pacific Northwest Laboratory, Richland, Washington.

Wilson, C. N., K. C. Burgard, E. T. Weber, and N. R. Brown. 1995. "Melter Technology Evaluation for Vitrification of Hanford Site Low-level Waste." WHC-SA-2857-FP, *American Ceramic Society 97th Annual Meeting Proceedings*. Cincinnati, Ohio.

**Table 1. Glass Composition and PCT Results of Glasses for Optimization Investigation**

Glass	Composition (mass fraction)										7-day PCT at 90°C					
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Others	Si	Al	B	Ca	Na	Final pH	
L0-0	0.763	0.2	0.2	0.01	0.022	0.022	0.022	0.022	0.022	Almost completely dissolved						
L1-6	0.718	0.2	0.2	0.06	0.022	0.022	0.022	0.022	0.022	Gel formed						
L1-9	0.688	0.2	0.2	0.09	0.022	0.022	0.022	0.022	0.022	0.68	0.65	5.99	12.72	12.72		
L1-12	0.658	0.2	0.2	0.12	0.022	0.022	0.022	0.022	0.022	0.70	0.66	6.18	12.75	12.75		
L1-15	0.628	0.2	0.2	0.15	0.022	0.022	0.022	0.022	0.022	0.40	0.39	2.65	12.33	12.33		
										0.40	0.39	2.64	12.35	12.35		
										0.21	0.22	0.86	11.63	11.63		
										0.21	0.22	0.86	11.63	11.63		
L4-69	0.628	0.06	0.2	0.09	0.022	0.022	0.022	0.022	0.022	0.22	0.11	0.47	0.53	10.88		
										0.22	0.11	0.47	0.53	10.88		
L4-612	0.598	0.06	0.2	0.12	0.022	0.022	0.022	0.022	0.022	0.13	0.13	0.15	0.27	10.71		
										0.13	0.13	0.16	0.27	10.70		
L4-615	0.568	0.06	0.2	0.15	0.022	0.022	0.022	0.022	0.022	0.13	0.13	0.15	0.24	10.62		
										0.13	0.13	0.14	0.23	10.61		
L4-96	0.628	0.09	0.2	0.06	0.022	0.022	0.022	0.022	0.022	0.78	0.01	2.95	2.28	10.60		
										0.79	0.01	3.00	2.30	10.64		
L4-99	0.598	0.09	0.2	0.09	0.022	0.022	0.022	0.022	0.022	0.21	0.06	0.78	0.60	10.43		
										0.21	0.06	0.77	0.59	10.59		
L4-912	0.568	0.09	0.2	0.12	0.022	0.022	0.022	0.022	0.022	0.13	0.13	0.28	0.30	10.52		
										0.13	0.13	0.28	0.30	10.54		
L4-915	0.538	0.09	0.2	0.15	0.022	0.022	0.022	0.022	0.022	0.12	0.12	0.20	0.22	10.41		
										0.12	0.12	0.20	0.23	10.26		
L4-129	0.568	0.12	0.2	0.09	0.022	0.022	0.022	0.022	0.022	0.24	0.04	1.61	1.10	10.36		
										0.25	0.03	1.69	1.16	10.41		
L4-1212	0.538	0.12	0.2	0.12	0.022	0.022	0.022	0.022	0.022	0.13	0.12	1.02	0.64	10.37		
										0.13	0.13	1.14	0.75	10.41		
L4-1215	0.508	0.12	0.2	0.15	0.022	0.022	0.022	0.022	0.022	0.11	0.11	0.60	0.39	10.11		
										0.12	0.12	0.68	0.43	10.04		
										0.12	0.12	0.66	0.41	10.08		

Table 1. Glass Composition and PCT Results of Glasses for Optimization Investigation (continued)

Glass	Composition (mass fraction)										7-day PCT at 90°C					Final pH			
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Others	Si	Al	B	Ca	Na	Normalized Release (g/m <sup>2</sup> )				
L5-69	0.628		0.2	0.06	0.09				0.022				0.01	1.87	0.34	0.31	0.01	1.87	12.18
L5-612	0.598		0.2	0.06	0.12				0.022				0.02	1.94	0.36	0.31	0.02	1.94	12.15
L5-615	0.568		0.2	0.06	0.15				0.022				0.05	1.00	0.15	0.14	0.05	1.00	11.95
L5-96	0.628		0.2	0.09	0.06				0.022				0.05	0.54	0.12	0.11	0.05	0.54	11.63
L5-99	0.598		0.2	0.09	0.09				0.022				0.01	2.18	0.50	0.33	0.01	2.18	12.22
L5-912	0.568		0.2	0.09	0.12				0.022				0.01	1.70	0.35	0.28	0.01	1.70	12.09
L5-915	0.538		0.2	0.09	0.15				0.022				0.02	0.93	0.32	0.27	0.02	0.93	12.24
L5-129	0.568		0.2	0.12	0.09				0.022				0.02	0.96	0.17	0.16	0.02	0.96	12.01
L5-1212	0.538		0.2	0.12	0.12				0.022				0.07	0.61	0.11	0.12	0.07	0.61	11.86
L5-1215	0.508		0.2	0.12	0.15				0.022				0.06	0.67	0.11	0.11	0.06	0.67	11.74
													0.01	1.34	0.29	0.23	0.01	1.34	12.17
													0.01	1.48	0.29	0.26	0.01	1.48	12.03
													0.01	1.39	0.29	0.23	0.01	1.39	12.07
													0.01	1.04	0.21	0.19	0.01	1.04	11.97
													0.02	1.06	0.21	0.19	0.02	1.06	11.97
													0.06	0.59	0.10	0.09	0.06	0.59	11.84
													0.06	0.61	0.10	0.09	0.06	0.61	11.75

Table 1. Glass Composition and PCT Results of Glasses for Optimization Investigation (continued)

Glass	Composition (mass fraction)										7-day PCT at 90°C						Final pH
	SiO2	B2O3	Na2O	CaO	Al2O3	MgO	Fe2O3	ZrO2	Others	Si	Al	B	Ca	Na	Normalized Release (g/m2)		
L6-546	0.628	0.05	0.20	0.04	0.06				0.022	0.22	0.18	0.23	0.04	0.91	11.89		
L6-549	0.598	0.05	0.20	0.04	0.09				0.022	0.22	0.19	0.24	0.04	0.97	11.91		
L6-5412	0.568	0.05	0.20	0.04	0.12				0.022	0.16	0.14	0.17	0.03	0.58	11.64		
L6-5415	0.538	0.05	0.20	0.04	0.15				0.022	0.16	0.15	0.17	0.03	0.61	11.66		
L6-3312	0.598	0.03	0.20	0.03	0.12				0.022	0.12	0.11	0.13	0.02	0.39	11.39		
L6-6612	0.538	0.06	0.20	0.06	0.12				0.022	0.12	0.12	0.13	0.02	0.40	11.41		
L6-669	0.568	0.06	0.20	0.06	0.09				0.022	0.10	0.10	0.11	0.02	0.31	11.22		
L7-15	0.612	0.05	0.15	0.04	0.12				0.017	0.10	0.10	0.11	0.02	0.30	11.26		
L7-25	0.524	0.05	0.25	0.04	0.12				0.028	0.15	0.15	0.16	0.02	0.56	11.63		
L7-30	0.480	0.04	0.30	0.03	0.11				0.033	0.16	0.15	0.17	0.02	0.59	11.64		
L7-35	0.436	0.04	0.35	0.03	0.11				0.039	0.11	0.10	0.12	0.04	0.39	11.47		
										0.10	0.10	0.11	0.04	0.37	11.46		
										0.13	0.12	0.14	0.05	0.49	11.36		
										0.13	0.12	0.14	0.05	0.49	11.37		
										0.06	0.06	0.07	0.03	0.15	10.39		
										0.06	0.06	0.07	0.03	0.15	10.41		
										0.37	0.34	0.38	0.02	1.50	12.22		
										0.37	0.35	0.40	0.02	1.51	12.22		
										0.97	0.97	1.28	0.01	6.38	12.88		
										0.94	0.91	1.10	0.01	5.66	12.90		
										13.60	0.10	36.10	0.00	29.10	13.38		
										19.60	0.30	52.50	0.00	41.90	13.33		

Table 1. Glass Composition and PCT Results of Glasses for Optimization Investigation (continued)

Glass	Composition (mass fraction)										7-day PCT at 90°C					
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Others	Si	Al	B	Ca	Na	Final pH	
L8-1	0.568	0.06	0.20	0.09	0.09	0.06	0.022	0.06	0.022	0.12	0.12	0.17	0.34	0.34	11.01	
L8-2	0.568	0.20	0.06	0.09	0.09	0.06	0.022	0.06	0.022	0.12	0.13	0.17	0.35	0.35	10.99	
L8-3	0.568	0.06	0.20	0.06	0.09	0.09	0.022	0.06	0.022	0.19	0.14	0.00	0.95	0.95	11.86	
L8-4	0.568	0.03	0.20	0.03	0.09	0.09	0.022	0.06	0.022	0.18	0.19	0.00	1.11	1.11	11.87	
L8-5	0.568	0.06	0.20	0.06	0.09	0.09	0.022	0.06	0.022	0.16	0.14	0.24	0.69	0.69	11.57	
L8-6	0.568	0.06	0.20	0.06	0.09	0.09	0.022	0.06	0.022	0.15	0.12	0.24	0.65	0.65	11.59	
										0.44	0.00	1.28	1.00	1.00	10.70	
										0.43	0.00	1.30	1.03	1.03	10.71	
										0.21	0.22	0.01	1.17	1.17	11.93	
										0.22	0.20	0.01	1.15	1.15	11.94	
										0.19	0.17	0.24	0.62	0.62	11.46	

**Table 2.** Composition of Nominal Low-Level Waste Simulant Used in Glass Formulation

<b>Component</b>	<b>Nominal (wt%)</b>
SiO <sub>2</sub>	0.03
B <sub>2</sub> O <sub>3</sub>	0.00
Na <sub>2</sub> O	84.42
CaO	0.01
Al <sub>2</sub> O <sub>3</sub>	6.19
Others	9.35
<b>Total</b>	<b>100.00</b>
<b>"Others" Component</b>	<b>(wt%)</b>
Bi <sub>2</sub> O <sub>3</sub>	0.06
Cr <sub>2</sub> O <sub>3</sub>	0.15
Fe <sub>2</sub> O <sub>3</sub>	0.02
K <sub>2</sub> O	1.38
MnO	0.03
Nd <sub>2</sub> O <sub>3</sub>	0.05
ZrO <sub>2</sub>	0.02
P <sub>2</sub> O <sub>5</sub>	5.01
SO <sub>3</sub>	1.35
Cl	0.39
F	0.90
<b>Subtotal</b>	<b>9.35</b>

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