PNNL-12202

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

RECEIVED
JAN 25 2000
OSTI

Glass Formulation for Idaho National Engineering and Environmental Laboratory Zirconia Calcine High-Activity Waste

J. D. Vienna[a]
D. K. Peeler[b]
R. L. Plaisted[a]
T. J. Plaisted[a]
I. A. Reamer[b]
R. D. Tillotson[c]
J. V. Crum[a]
C. A. Musick[c]
T. L. James[b]

[a] Pacific Northwest National Laboratory, Richland, WA 99352
[b] Savannah River Technology Center, Aiken, SC 29808
[c] Lockheed Martin Idaho Technologies Company
Idaho Falls, ID 83415

December 1999

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161


This document was printed on recycled paper

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PNNL-12202

Glass Formulation For Idaho National Engineering and Environmental Laboratory Zirconia Calcine High-Activity Waste

J. D. Vienna[a]
D. K. Peeler[b]
R. L. Plaisted[a]
T. J. Plaisted[a]
I. A. Reamer[b]
R. D. Tillotson[c]
J. V. Crum[a]
C. A. Musick[c]
T. L. James[b]

[a] Pacific Northwest National Laboratory, Richland, WA 99352
[b] Savannah River Technology Center, Aiken, SC 29808
[c] Lockheed Martin Idaho Technologies Company, Idaho Falls, ID 83415

December 1999

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Testing was performed to identify a candidate glass to demonstrate the vitrification process with Idaho National Engineering and Environmental Laboratory (INEEL) high-activity waste (HAW). The specific HAW composition used in glass development was a best estimate of the product of separating the HAW fraction from zirconia calcine (called Zr-HAW). This waste stream contains roughly 93 mass% ZrO_2 on a dried, nonvolatile oxide basis. Therefore, the solubility of ZrO_2 in a low-temperature borosilicate glass was expected to dictate the loading of Zr-HAW. The following set of primary glass-property constraints was considered in formulating and selecting glasses:

1. A melter processing temperature (T_M) of 1150°C
2. Viscosity (η) between 2 and 10 Pas at T_M
3. A liquidus temperature (T_L) at least 100°C below T_M
4. Normalized boron, sodium, and lithium releases (r_B, r_{Na}, and r_{Li}) below 1 g/m^2 as measured with a 7-day product consistency test (PCT).

A series of 29 glasses was designed to meet the primary property constraints with systematically varying compositions. They were fabricated from oxide and carbonate precursors. The T_L, r_B, r_{Na}, and r_{Li} were measured for each of these 29 glasses. Table S.1 summarizes the composition and measured property values for these glasses. Although the η was not measured for all test glasses, visual observations of glass pouring by experienced technical staff suggested that all of the tested Zr-HAW glasses would meet the criteria $2 \leq \eta \leq$ Pa·s.

PCT results showed that several highly durable glasses were formed by mixing up to 16.2 mass% of Zr-HAW with a number of frit compositions. Of the 24 Zr-glasses (excluding the replicates) that were tested, only four (Zr-20, -22, -24, and -29) did not meet the stringent glass-performance restriction of 1 g/m^2 (although all glasses were well below the EA limit). The $T_L < 1050$°C constraint poses the largest technical challenge for glass formulation for optimized waste loading within this composition space. The T_L of Zr glasses ranged from 913°C for Zr-9 to 1336°C for Zr-15. Only 6 of the 29 Zr glasses met the restriction $T_L \leq 1050$°C—Zr-2, -4, -7, -9, -19 and -23—all of which passed the PCT criteria.

Based upon the initial glass-testing results, Zr-9 was chosen for further testing. Zr-19 has the highest Zr-HAW loading of the glasses that satisfy the T_L and PCT constraints; however, the T_L of Zr-19 was close to the 1050°C limit, and a higher temperature (1250°C) was required to make a homogeneous melt from this composition using standard laboratory procedures. Zr-9 had the lowest T_L of all glasses and an acceptable PCT release, with 15 mass% ZrO_2 (or 16.2 mass% loading). This glass was fabricated and tested at two laboratories to ensure reproducibility of results. The PCT and the T_L results from the refabricated Zr-9 glasses showed a high degree of reproducibility, even between laboratories.

Table S.1. Composition (in Mass Fraction Oxides) and Properties of Test Glasses

Glass ID	Al_2O_3	B_2O_3	Li_2O	Na_2O	ZrO_2	SiO_2	Others[a]	T_L (°C)	r_B (g/m^2)	r_{Na} (g/m^2)	r_{Li} (g/m^2)
Zr-1	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086	1064	0.239	0.241	0.338
Zr-2	0.0450	0.1000	0.0750	0.1116	0.1350	0.5256	0.0078	**964**	0.277	0.269	0.364
Zr-3	0.0450	0.1000	0.0750	0.1084	0.1650	0.4971	0.0095	1110	0.231	0.242	0.352
Zr-4	0.0300	0.1000	0.0750	0.1083	0.1500	0.5281	0.0086	**1038**	0.301	0.268	0.383
Zr-5	0.0600	0.1000	0.0750	0.1118	0.1500	0.4946	0.0086	1085	0.228	0.234	0.327
Zr-6	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086	1064	0.251	0.259	0.361
Zr-7	0.0450	0.0500	0.0750	0.1480	0.1500	0.5234	0.0086	**1005**	0.290	0.810	0.492
Zr-8	0.0450	0.1500	0.0750	0.0721	0.1500	0.4993	0.0086	1177	0.434	0.127	0.451
Zr-9	0.0450	0.1000	0.0600	0.1425	0.1500	0.4939	0.0086	**913**	0.293	0.383	0.295
Zr-10	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086	1064	0.247	0.240	0.336
Zr-11	0.0450	0.1000	0.0900	0.0776	0.1500	0.5288	0.0086	1140	0.237	0.127	0.356
Zr-12	0.0600	0.1500	0.0900	0.0398	0.1650	0.4858	0.0094	1250	0.220	0.020	0.310
Zr-13	0.0600	0.1500	0.0600	0.1046	0.1650	0.4509	0.0095	1189	0.420	0.205	0.485
Zr-14	0.0600	0.0500	0.0900	0.1157	0.1650	0.5098	0.0095	1314	nm	nm	nm
Zr-15	0.0600	0.0500	0.0600	0.1805	0.1650	0.4750	0.0095	1336	0.210	0.970	0.300
Zr-16	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086	1067	0.185	0.230	0.340
Zr-17	0.0300	0.1500	0.0900	0.0362	0.1650	0.5193	0.0095	1228	0.265	0.020	0.330
Zr-18	0.0300	0.1500	0.0600	0.1011	0.1650	0.4844	0.0095	1125	0.660	0.335	0.750
Zr-19	0.0300	0.0500	0.0900	0.1122	0.1650	0.5434	0.0094	**1034**	0.275	0.495	0.540
Zr-20	0.0300	0.0500	0.0600	0.1770	0.1650	0.5085	0.0095	1113	0.490	**1.175**	0.505
Zr-21	0.0600	0.1500	0.0900	0.0430	0.1350	0.5142	0.0078	1180	0.300	0.035	0.360
Zr-22	0.0600	0.1500	0.0600	0.1079	0.1350	0.4794	0.0077	1087	**1.030**	0.525	0.965
Zr-23	0.0600	0.0500	0.0900	0.1189	0.1350	0.5383	0.0078	**1003**	0.255	0.545	0.515
Zr-24	0.0600	0.0500	0.0600	0.1838	0.1350	0.5035	0.0077	1105	0.295	**1.160**	0.410
Zr-25	0.0300	0.1500	0.0900	0.0395	0.1350	0.5477	0.0078	1137	0.405	0.065	0.450
Zr-26	0.0300	0.1500	0.0600	0.1044	0.1350	0.5129	0.0077	1070	0.610	0.315	0.620
Zr-27	0.0300	0.0500	0.0900	0.1154	0.1350	0.5718	0.0078	1081	0.595	0.710	0.735
Zr-28	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086	1064	0.240	0.260	0.340
Zr-29	0.0300	0.0500	0.0600	0.1803	0.1350	0.5370	0.0077	1059	**3.890**	**3.085**	**2.715**

[a] Others is composed of 9.94 mass% CaO, 4.89 Cs_2O, 7.97 Gd_2O_3, 49.14 K_2O, 24.68 P_2O_5, 0.84 SrO, and 2.55 CeO_2.
nm- not measured

Additional testing was performed on Zr-9 to try to assess the glasses' processability. A gradient-temperature heat treatment of Zr-9 showed that crystallization began at roughly 915°C, and crystallinity continued to increase with decreasing temperature until 780°C, the lowest temperature tested. Glass heat treated at 780°C for 24 h showed less than 1 vol% crystallinity, which is not enough to significantly impede glass flow in the INEEL ¼-scale melter drain tube. No tests were made at lower temperatures. The Zr-9 glass η was measured as a function of temperature over the range from roughly 930°C to 1240°C. The 1150°C η was 6.05 Pa·s, well within the acceptable range of 2 to 10 Pa·s and very close to the design value of 6 Pa·s. A laboratory-scale melter (LSM) test was performed with Zr-9 glass. Results from the LSM test indicate that the glass η was acceptable, and there were no indications of problems related to glass redox or the corrosion of melter construction materials.

Based upon the results from crucible and LSM tests, we recommend that Zr-9 glass composition be used to demonstrate the vitrification of INEEL Zr-HAW. This glass, although not optimized, meets all processing and product-quality constraints while containing a reasonable loading of the Zr-HAW.

Glossary

Al-cal	alumina calcine
BL	blend (representing the "All-Blend" waste stream)
CVS	composition variation study
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	energy dispersive spectroscopy
η	viscosity
FY98	Fiscal Year 1998
HAW	high-activity waste
ICPP	Idaho Chemical Processing Plant
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
IX Res	ion-exchange resin
LAW	low-activity waste
LSM	laboratory-scale melter
MT	metric ton
NBS	National Bureau of Standards
OM	optical microscopy
Pas	Pascal seconds
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
r_B	normalized boron release (g/m^2)
r_{Li}	normalized lithium release (g/m^2)
r_{Na}	normalized sodium release (g/m^2)
SBW	sodium-bearing waste
SBW-sol	sodium-bearing waste and the undissolved solids from its dissolution
SEM	scanning electron microscopy
SRTC	Savannah River Technology Center
SVS	self-verifying sensor
TFA	Tanks Focus Area
T_A	lowest temperature at which a heat-treated glass sample does not contain any crystals
T_C	highest temperature at which a heat-treated glass sample contains crystals
T_g	glass-transition temperature
T_L	liquidus temperature

T_M	melter processing temperature
TTP	Technical Task Plan
UTF	uniform temperature furnace (method)
WAPS	Waste Acceptance Product Specification
WL	waste loading
WVNS	West Valley Nuclear Services
XRD	X-ray diffraction
Zr-HAW	HAW fraction of zirconia calcine
Zr-cal	zirconia calcine
Zr-sol	Zr-cal and the undissolved solids from its dissolution

Acknowledgments

The authors would like to acknowledge Michael Schweiger and Brad Scholes for laboratory assistance; Arlin Olson, Pavel Hrma, Bruce Staples, S. K Sundaram, and Carol Jantzen for insightful conversations; Donald Smith, Art Jurgensen, David Messimer, Mike Summer, Brenda Boyle, Lucinda Torres, and Jack Durden for sample analyses; William Holtzscheiter for management and guidance; and Wayne Cosby for preparation of this document and editorial assistance. This study was funded by the Department of Energy's (DOE's) Office of Science and Technology through the Tanks Focus Area. Pacific Northwest National Laboratory is operated for DOE by Battelle under Contract DE-AC06-76RLO 1830. Westinghouse Savannah River Company is operated for DOE under Contract DE-AC09-89SR 18035. Idaho National Engineering and Environmental Laboratory is operated for DOE by Lockheed Martin Idaho Technologies Company under Contract DE-AC07-94ID 13223.

Contents

Figures

Tables

1.0 Introduction

For about four decades, radioactive wastes have been collected and calcined from nuclear fuels reprocessing at the Idaho Nuclear Technology and Engineering Center (INTEC), formerly known as the Idaho Chemical Processing Plant (ICPP). During this time, secondary radioactive wastes have also been collected and stored as liquid from decontamination, laboratory activities, and fuel-storage activities. These wastes are known as sodium-bearing wastes (SBWs) (DOE 1995). The high-activity waste (HAW)[a] fractions are the result of dissolution and separation processes that separate the waste into high-activity and low-activity waste (LAW) streams. To meet regulatory milestones in 2012, Idaho National Engineering and Environmental Laboratory (INEEL) must start Title I design[b] for a facility designed to separate and treat the radioactive wastes in 2001 (Staples et al. 1999). To successfully design a waste-treatment facility that will meet INEEL regulatory milestones, new technologies must be developed or existing technologies evaluated. Vitrification is one of the technologies currently being evaluated to immobilize the HAW streams. Since these wastes are of unique composition, research and development is needed to formulate glass acceptable for immobilization.

The overall strategy of this Tanks Focus Area (TFA) Technical Task Plan (TTP)[c] is threefold: (1) identify glass-forming systems that optimize glass properties and loadings of specific INEEL HAW streams, (2) determine a glass-composition region (or regions) to cover glasses from each individual HAW stream or blending strategies with adequate processing and product-performance criteria, and (3) support INEEL with glass formulation and testing expertise to assist in flowsheet optimization and melter demonstrations. The fiscal year 1998 (FY98) glass-formulation activities were focused on defining candidate glass compositions to be processed in the INEEL ¼-scale melter and defining an extended test matrix encompassing all of the INEEL wastes as currently defined. Piepel et al. (1999) have documented the definition of the first phase of an extended test matrix and its objectives. Peeler et al. (1998) have documented the results of preliminary formulation work for an "All Blend" (BL) INEEL HAW composition. The status and data on INEEL ¼-scale melter demonstrations were reported by Musick et al. (1998). Sundaram et al. (1998) have discussed the impact of glass composition on the corrosion of commonly used melter construction materials. This report describes the status of the glass formulation work being performed at Pacific Northwest National Laboratory (PNNL) and Savannah River Technology Center (SRTC) to develop a glass composition to be used in a melter demonstration with a simulated HAW fraction of zirconia calcine (Zr-HAW).

---

[a] High-level waste is defined as (1) Irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and (3) solids into which such liquid wastes have been converted (10 CFR 60.2). High-level waste must be sent to a Federal Geologic Repository. High-activity waste is radioactive waste with greater than a certain limit of radioactivity as defined in 10 CFR 61.55. Most of the tank waste at INEEL is not HLW because it was generated from decontamination and laboratory activities. Most of the materials in the INEEL calcine bins are HLW.

[b] Title I design: a term used by the U.S. Department of Energy (DOE) to designate the final facility design. The input must include actual equipment size, utility requirements, etc.

[c] TFA TTPs PNNL-RL3-7-WT-31, SR1-6-WT-31, and ID7-7-WT-31.

The widely accepted approach to waste-glass formulation has been described by Piepel et al. (1997). Applying this strategy to INEEL via parallel studies is discussed elsewhere (Staples et al. 1999; Piepel et al. 1999). Here we discuss scoping studies for developing an acceptable glass for Zr-HAW. The work reported here is "scoping" in nature, and the glass compositions are not to be considered optimized. The objective of this report is to show that immobilization via vitrification is a viable option for specific INEEL HAW streams as identified by INEEL personnel. The primary output of this report is the recommendation of frit composition and waste loading (WL) for a scaled melter demonstration with Zr-HAW. The results of these tests will also provide important information to aid in selecting a pretreatment/separations strategy.

2.0 Summary from Previous Status Report

2.1 Introduction

Preliminary glass-formulation efforts were made in support of the HAW vitrification program at INEEL (Peeler et al. 1998). These preliminary studies were of a scoping nature and not designed to optimize glass compositions. The goal of this study was to define a frit composition capable of incorporating a BL or average INEEL HAW composition with loadings in the range of 10 to 20 mass%. The resulting glass must meet processing and product quality-related criteria:

Processing

- Viscosity (η) at 1150°C is between 2 and 10 Pa·s ($2<\eta<10$ Pa·s)
- The liquidus temperature (T_L) is less than 1050°C ($T_L < 1050$°C)
- After a 24-h heat treatment at 850°C (HT_{850}), crystals can be redissolved in 4 h at 1050°C ($RD_{1050} < 4$ h)
- Corrosion of melter construction materials must be within an acceptable range.

Product Quality

- Normalized sodium release (r_{Na}) is below 1 g/m^2 by the product consistency test (PCT) (ASTM 1994) ($r_{Na} < 1$ g/m^2)
- Normalized boron release (r_B) is below 1 g/m^2 by the PCT ($r_B < 1$ g/m^2)
- Normalized lithium release (r_{Li}) is below 1 g/m^2 by the PCT ($r_{Li} < 1$ g/m^2)
- Homogeneous glass (i.e., absence of crystalline and amorphous phase separation upon initial fabrication).

Concurrent efforts are underway to develop acceptable glasses with zirconia-calcine waste and to optimize glass compositions for all waste streams as currently defined (Piepel et al. 1999; Staples et al. 1999).

The work reported here was performed as a joint research effort by a team composed of researchers at INEEL, PNNL, and SRTC. Details of the BL studies have been reported in a separate document (Peeler et al. 1998). These studies are summarized here to supply the appropriate background for assessing the process and product-quality properties and constraints in the following sections.

2.2 Previous Study

Table 2.1 lists composition estimates of the HAW fractions of separated wastes from alumina calcine (Al-cal) and the undissolved solids from its dissolution (Al-sol), Zr-cal and the undissolved solids from its dissolution (Zr-sol), SBW and its undissolved solids (SBW-sol), and ion-exchange resin (IX Res). The last column in Table 2.1 provides an overall estimate of weighted average compositions of all streams. The compositions, listed in Table 2.1, are high in zirconium, aluminum, potassium, and phosphorous. These compositions are estimates from

INEEL staff assuming full separations of the waste into high- and low- activity fractions. The databases for glass-property compositions and the predictive tools developed for Hanford (Hrma et al. 1994; Vienna et al. 1995; Crum et al. 1997; Mika et al. 1997; Feng et al. 1995), Savannah River (Jantzen et al. 1995) and West Valley (Piepel and Redgate 1997; Reimus et al. 1988; Chick et al. 1984; Bunnell 1988) are not adequate to calculate acceptable glass compositions for the high-zirconia, low-iron, INEEL HAW glasses.

Table 2.1. Preliminary INEEL HAW Stream Compositions in Mass% Oxides

Oxides	Al-Cal	Al-Sol	Zr-Cal	Zr-Sol	SBW	SBW-Sol	IX Res	All Blend
Al_2O_3	1.09	100.00	0.01	38.00	0.16	100.00	0.00	8.90
BaO	0.00	0.00	0.00	0.00	0.31	0.00	0.00	0.02
CaO	0.00	0.00	0.02	9.30	0.01	0.00	0.00	0.45
Cs_2O	15.46	0.00	0.28	0.00	0.45	0.00	0.00	0.50
CuO	0.00	0.00	0.00	0.00	0.00	0.00	31.98	0.36
Fe_2O_3	0.16	0.00	0.02	0.00	0.16	0.00	21.40	0.26
Gd_2O_3	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.36
K_2O	50.25	0.00	2.76	0.00	63.55	0.00	12.62	6.29
MoO_3	0.00	0.00	0.00	0.00	0.93	0.00	0.00	0.05
Na_2O	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	25.24	0.00	1.39	0.00	28.59	0.00	0.00	2.93
PbO	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.01
SiO_2	0.00	0.00	0.00	0.00	0.00	0.00	34.00	0.38
SrO	2.48	0.00	0.05	0.00	0.01	0.00	0.00	0.08
$TruO_2$	5.29	0.00	0.14	0.00	2.63	0.00	0.00	0.33
ZrO_2	0.00	0.00	94.89	52.70	2.96	0.00	0.00	79.09
mass of HAW (MT*)	2.97	0.001	146.82	8.48	8.90	12.93	2.03	182.13
mass% of INEEL's HAWs	1.6	0.0005	80.6	4.7	4.9	7.1	1.1	100.0

* Metric Ton

Five glasses were fabricated with 17.7 to 19 mass% of the BL waste. Using "BL" to signify an all-blend waste, these glass compositions were labeled BL-1 to -5. The compositions of BL-1 through BL-5 were consecutively altered to reduce the T_L until it was below 1050°C in BL-4 and BL-5. These consecutive formulations were required because adequate predictive tools for glass properties were not available. Both BL-4 and BL-5 were found to have unacceptable product-performance properties (i.e., the PCT normalized elemental releases were too high). So glasses BL-6 through BL-9 were formulated to maintain the high waste loading of BL-4 and BL-5 (19 mass%) while maintaining acceptable predicted PCT elemental releases and processing properties using preliminary glass-property models. Table 2.2 summarizes the frit compositions and observations of the test glasses BL-1 through BL-9.

Note: when compared to the constraints listed in Section 2.1, the measured properties of BL-6 through BL-9 are acceptable.

Glasses with BL waste loadings as high as 19 mass% have adequate processing and product-quality properties for demonstrating the vitrification concept in the INEEL ¼-scale melter. The properties of glasses BL-8 and BL-9 were superior to those required, suggesting that higher BL waste loadings are possible with proper optimization.

Table 2.2. Frit Compositions (mass% oxide), Waste Loadings (mass% BL), and Measured Properties of Resultant Glasses

	BL-1	BL-1Li[a]	BL-2	BL-3	BL-4	BL-5	BL-6	BL-7	BL-8	BL-9
Al_2O_3	3.0	2.9	0.0	0.0	0.0	0.0	0.0	0.0	2.9	0.0
B_2O_3	6.1	5.9	6.2	6.2	6.1	6.2	6.2	12.3	6.2	18.5
Li_2O	6.1	8.4	8.6	5.7	8.6	9.9	9.9	8.6	9.9	7.4
Na_2O	22.8	22.2	20.8	27.2	20.8	19.8	15.5	13.5	15.7	11.4
SiO_2	62.0	60.5	64.4	61.0	64.5	64.2	68.5	65.6	65.4	62.6
WL	17.7	17.3	19.0	19.0	18.3	19.0	19.0	19.0	19.0	19.0
T_L (°C)	1100-1150	1100-1150	1077	>1200	850-1050	850-1050	<1050	<1000	<1025	1025-1050
HT_{850} (vol%)					~50	~50			4	1
HT_{850} Phases			NZS[b]		NZS	NZS/LS			NZS	NZS
RD_{1050} (h)					~1.5	~1.5			~1	~1
r_B (g/m^2)					7.295	6.26			0.26	0.878
r_{Na} (g/m^2)					5.595	4.755			0.558	0.459
r_{Li} (g/m^2)					5.95	4.97			0.495	0.801
η_{1150} (Pa·s)	9.5								8.3	5.9

(a) BL-1Li glass is the BL-1 glass with a 2 mass% Li_2O addition.
(b) NZS – $Na_2ZrSi_2O_7$, LS – Li_2SiO_3

As previously mentioned, melter corrosion is also an issue for glass-formulation development. BL-8 and BL-9 were subsequently evaluated using Inconel 690, Monofrax K3, and Unicor I. Inconel 690 corroded in BL-8 more than in BL-9. The passivation of Inconel 690 by BL-8 depended on melt chemistry, suggesting promise for electrochemical protection of Inconel 690 in this melt. Molybdenum corroded in BL-8 and BL-9 to more or less the same extent, except in the case of electrochemical corrosion. Electrochemical corrosion of molybdenum in BL-8 was more than in BL-9. This was attributed to higher ionic activity in BL-8 (due to higher alkali content). Generally, molybdenum corroded about an order of magnitude less than Inconel 690 in these melts. Molybdenum was recommended as an alternative electrode material.

Monofrax K3 showed lower than acceptable corrosion in both baseline glasses as well as selected INEEL Composition Variation Study (CVS) glasses. Acceptability, here, was defined as being within the range of values measured for successful waste glass melter campaigns (see

Sundaram et al. 1998 for further discussion of acceptability). Unicor I was comparable to Monofrax K3. Unicor I was recommended as an alternative cost-effective refractory material. Zirchrom 30 showed severe corrosive attack due to its heterogeneity. Dense tin oxide showed excellent corrosion resistance in these melts. However, it was not recommended as the containment material due to its high electrical conductivity (greater than Monofrax K3 and E) at the processing-temperature range.

2.3 Recommendation

Based upon the scoping studies performed, it was decided that BL-8 and BL-9 glasses would be tested for corrosivity of melter construction materials. Since the results from these tests show that both glasses were acceptable, it was recommended (Peeler et al. 1998) that INEEL use BL-9 for a ¼-scale melter demonstration test in late FY98. BL-9 had the lowest T_L and therefore would likely be capable of handling slight composition variations in the melter without concern for crystallinity. The results of the ¼-scale melter demonstration with BL-9 are documented by Musick et al. (1998).

3.0 Experimental Approach

3.1 Property Restrictions

With the goal of developing an acceptable glass to demonstrate the vitrification process for INEEL Zr-HAW, we must first establish a definition of acceptable glass. Two types of glass-property limitations must be considered: (1) those product properties required for waste-form acceptance and (2) those processing properties required to ensure adequate melter processability. The product properties are dictated by the Waste Acceptance Product Specification (WAPS) (DOE 1995). The WAPS imposes limits on the performance of glass subjected to the PCT. The specific performance criterion required by the WAPS is that the release of boron, sodium, and lithium, normalized to glass composition, must be less than those of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) glass (Jantzen et. al. 1993). The r_B, r_{Na}, and r_{Li} for the DWPF-EA glass are 8.35 (g/m^2), 6.67 (g/m^2), and 4.78 (g/m^2), respectively (Jantzen et al. 1993). For plant operation, the r_B, r_{Na}, and r_{Li} must be maintained at the limit minus two standard deviations. Without information specific to the operation of a glass plant at INEEL, it is difficult to assess the safety margin that must be maintained in the release values. For the purposes of this study, we will take 1 g/m^2 as a conservative limit for r_B, r_{Na}, and r_{Li}. The WAPS also requires that the concentration, composition, and thermal stability of all phases present in the waste form be reported. Although this does not preclude the presence of secondary phases, in these preliminary tests, we will restrict the waste form to a single phase when air quenched. This will allow us to ignore the prediction of the concentration and composition of any secondary phases.

It is difficult to set limits on processing properties without knowing the specific processing technology to be used for HAW vitrification at INEEL. We will let the HAW vitrification experience at the DWPF and West Valley Nuclear Services (WVNS) be our guide. For these operating HAW vitrification plants, the nominal melter operating temperature is maintained at or close to 1150°C. The η at the operating temperature is maintained between 2 and 10 Pa·s. Finally, the T_L of glass in the melter is maintained at 100°C below the operating temperature. These three restrictions will be adopted for this study. An additional restriction generated because of the INEEL ¼-scale configuration for the melter pour spout will also be adopted in this study. Under idling or non-pouring conditions, the pour-spout tube, which will be filled with glass, is subjected to a temperature profile ranging from 1150°C at the melter interface to below the glass-transition temperature (T_g) at the cold end. Crystallization of glass will (most likely) occur somewhere in the temperature region between T_L and T_g. A continuous liquid (glass) phase must form before the melt can be poured. This may require dissolving most of the crystals formed in the drain tube during melter idling. Thus, there is a restriction that crystals formed after a 24-h HT between T_L and T_g must dissolve when heat treated at 1050°C for 4 h. See Peeler et al. (1998) for an example.

An additional processing-related concern is that glass corrodes melter materials during processing. The corrosion-related properties are described by Sundaram et al. (1998). Thorough study of these properties was out of the scope of this document, but preliminary tests were performed in a Laboratory Scale Melter (LSM) and are reported in Section 5.

3.2 Waste Composition

The Zr-HAW composition was estimated by INEEL personnel applying the best available information on calcine composition, pretreatment chemistry, and separations process. This composition is listed in Table 3.1 along with the composition estimates of other INEEL HAW streams. The compositions in Table 3.1 vary from those in Table 2.1 only in the combination of calcine and solids for each waste type. The Zr-HAW contains a high concentration of ZrO_2—92.58 mass%. No other waste components are in high enough concentrations to limit the WL in glass or to strongly influence the glass properties at moderate WL, based on previous glass-formulation experience. The Zr-HAW composition is similar to that of the BL waste, which is 85 mass% Zr-HAW. Thus, the logical starting point for this study is that previously reported by Peeler et al. (1998) and highlighted in Section 2.2.

Table 3.1. Waste Composition Estimates in Mass% Oxides

	Al-HAW	Zr-HAW	SBW-HAW	IX Res	BL
Al_2O_3	1.12	2.08	59.30	0.00	8.90
BaO	0.00	0.00	0.13	0.00	0.02
CaO	0.00	0.53	0.00	0.00	0.45
Cs_2O	15.46	0.26	0.18	0.00	0.50
CuO	0.00	0.00	0.00	31.98	0.36
Fe_2O_3	0.16	0.02	0.06	21.40	0.26
Gd_2O_3	0.00	0.42	0.00	0.00	0.36
K_2O	50.24	2.61	25.90	12.62	6.29
MoO_3	0.00	0.00	0.38	0.00	0.05
Na_2O	0.03	0.00	0.00	0.00	0.00
P_2O_5	25.23	1.31	11.65	0.00	2.93
PbO	0.00	0.00	0.10	0.00	0.01
SiO_2	0.00	0.00	0.00	34.00	0.38
SrO	2.47	0.04	0.01	0.00	0.08
$TruO_2$	5.29	0.14	1.07	0.00	0.33
ZrO_2	0.00	92.58	1.20	0.00	79.09
Mass (kg)	2,970	155,301	21,826	2,029	182,125
mass% of waste	2	85	12	1	100

3.3 Experimental Design

Starting with the glasses BL-8 and BL-9, which met the glass-property requirements, a series of glass compositions was developed for testing. The design was based upon an average composition of BL-8 and BL-9 glasses with various modifications. First, the Al_2O_3 content of the glass was increased to 4.5 mass% to accommodate a better r_B and r_{Na} response in the glass because of the more stringent specifications of this particular study. An increase in Al_2O_3 has a

very strong effect on r_B and r_{Na} until concentrations approaching 4.5 mass%, where the effect is seen to become significantly weaker (Vienna et al. 1995). Figure 3.1 illustrates the impact of changing the Al_2O_3 concentration on the r_{Na} values of two previously studied HAW glasses.

Further composition modifications were in response to the composition of the waste stream being vitrified. The WL was to be set at an amount that would allow for a concentration of 15 mass% ZrO_2 in the final glass. This dictated a WL of 16.2 mass%, and all other component concentrations were therefore generated by the given waste-stream composition, as given in Table 3.1. The composition of this glass, designated Zr-1, is given in Table 3.2. Eight other glass compositions were generated by varying the concentrations of certain important components:

			mass%
Zr-2	WL	=	14.6
Zr-3	WL	=	17.8
Zr-4	$[Al_2O_3]$	=	3
Zr-5	$[Al_2O_3]$	=	6
Zr-7	$[B_2O_3]$	=	5
Zr-8	$[B_2O_3]$	=	15
Zr-9	$[Li_2O]$	=	6
Zr-11	$[Li_2O]$	=	9

In addition to these glasses, Zr-12 through Zr-29 were formulated to vary four components at a time (WL, Al_2O_3, B_2O_3, and Li_2O) to detect interactive effects. The concentrations of SiO_2 and Na_2O were also adjusted in all glasses to maintain a calculated η at 1150°C of 6 Pa·s. This would allow each to be a candidate for melter operation while gaining useful information about component effects on glass properties, i.e., for a "constant η" composition region. The final compositions of these scoping glasses are listed in Table 3.2. The second column of Table 3.2 lists the relative concentration for Al_2O_3, B_2O_3, Li_2O, and WL with three levels: low (l), medium (m), and high (h). Zr-1 glass composition was independently fabricated and tested five times (Zr-1, Zr-6, Zr-10, Zr-16, and Zr-28) throughout the study to assess uncertainties.

Table 3.2. Composition of Test Glasses in Mass Fraction Oxides

Glass ID	Al	B	Li	WL	Al_2O_3	B_2O_3	Li_2O	Na_2O	ZrO_2	SiO_2	Others[a]
Zr-1	m	m	m	m	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086
Zr-2	m	m	m	l	0.0450	0.1000	0.0750	0.1116	0.1350	0.5256	0.0078
Zr-3	m	m	m	h	0.0450	0.1000	0.0750	0.1084	0.1650	0.4971	0.0095
Zr-4	l	m	m	m	0.0300	0.1000	0.0750	0.1083	0.1500	0.5281	0.0086
Zr-5	h	m	m	m	0.0600	0.1000	0.0750	0.1118	0.1500	0.4946	0.0086
Zr-6	m	m	m	m	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086
Zr-7	m	l	m	m	0.0450	0.0500	0.0750	0.1480	0.1500	0.5234	0.0086
Zr-8	m	h	m	m	0.0450	0.1500	0.0750	0.0721	0.1500	0.4993	0.0086
Zr-9	m	m	l	m	0.0450	0.1000	0.0600	0.1425	0.1500	0.4939	0.0086
Zr-10	m	m	m	m	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086
Zr-11	m	m	h	m	0.0450	0.1000	0.0900	0.0776	0.1500	0.5288	0.0086
Zr-12	h	h	h	h	0.0600	0.1500	0.0900	0.0398	0.1650	0.4858	0.0094

Glass ID	Al	B	Li	WL	Al_2O_3	B_2O_3	Li_2O	Na_2O	ZrO_2	SiO_2	Others[a]
Zr-13	h	h	l	h	0.0600	0.1500	0.0600	0.1046	0.1650	0.4509	0.0095
Zr-14	h	l	h	h	0.0600	0.0500	0.0900	0.1157	0.1650	0.5098	0.0095
Zr-15	h	l	l	h	0.0600	0.0500	0.0600	0.1805	0.1650	0.4750	0.0095
Zr-16	m	m	m	m	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086
Zr-17	l	h	h	h	0.0300	0.1500	0.0900	0.0362	0.1650	0.5193	0.0095
Zr-18	l	h	l	h	0.0300	0.1500	0.0600	0.1011	0.1650	0.4844	0.0095
Zr-19	l	l	h	h	0.0300	0.0500	0.0900	0.1122	0.1650	0.5434	0.0094
Zr-20	l	l	l	h	0.0300	0.0500	0.0600	0.1770	0.1650	0.5085	0.0095
Zr-21	h	h	h	l	0.0600	0.1500	0.0900	0.0430	0.1350	0.5142	0.0078
Zr-22	h	h	l	l	0.0600	0.1500	0.0600	0.1079	0.1350	0.4794	0.0077
Zr-23	h	l	h	l	0.0600	0.0500	0.0900	0.1189	0.1350	0.5383	0.0078
Zr-24	h	l	l	l	0.0600	0.0500	0.0600	0.1838	0.1350	0.5035	0.0077
Zr-25	l	h	h	l	0.0300	0.1500	0.0900	0.0395	0.1350	0.5477	0.0078
Zr-26	l	h	l	l	0.0300	0.1500	0.0600	0.1044	0.1350	0.5129	0.0077
Zr-27	l	l	h	l	0.0300	0.0500	0.0900	0.1154	0.1350	0.5718	0.0078
Zr-28	m	m	m	m	0.0450	0.1000	0.0750	0.1100	0.1500	0.5114	0.0086
Zr-29	l	l	l	l	0.0300	0.0500	0.0600	0.1803	0.1350	0.5370	0.0077
BL-8					0.0169	0.1500	0.0600	0.0927	0.1503	0.5080	0.0221
BL-9					0.0400	0.0500	0.0800	0.1275	0.1503	0.5302	0.0220

[a] Others is composed of 9.94 mass% CaO, 4.89 Cs_2O, 7.97 Gd_2O_3, 49.14 K_2O, 24.68 P_2O_5, 0.84 SrO, and 2.55 CeO_2.

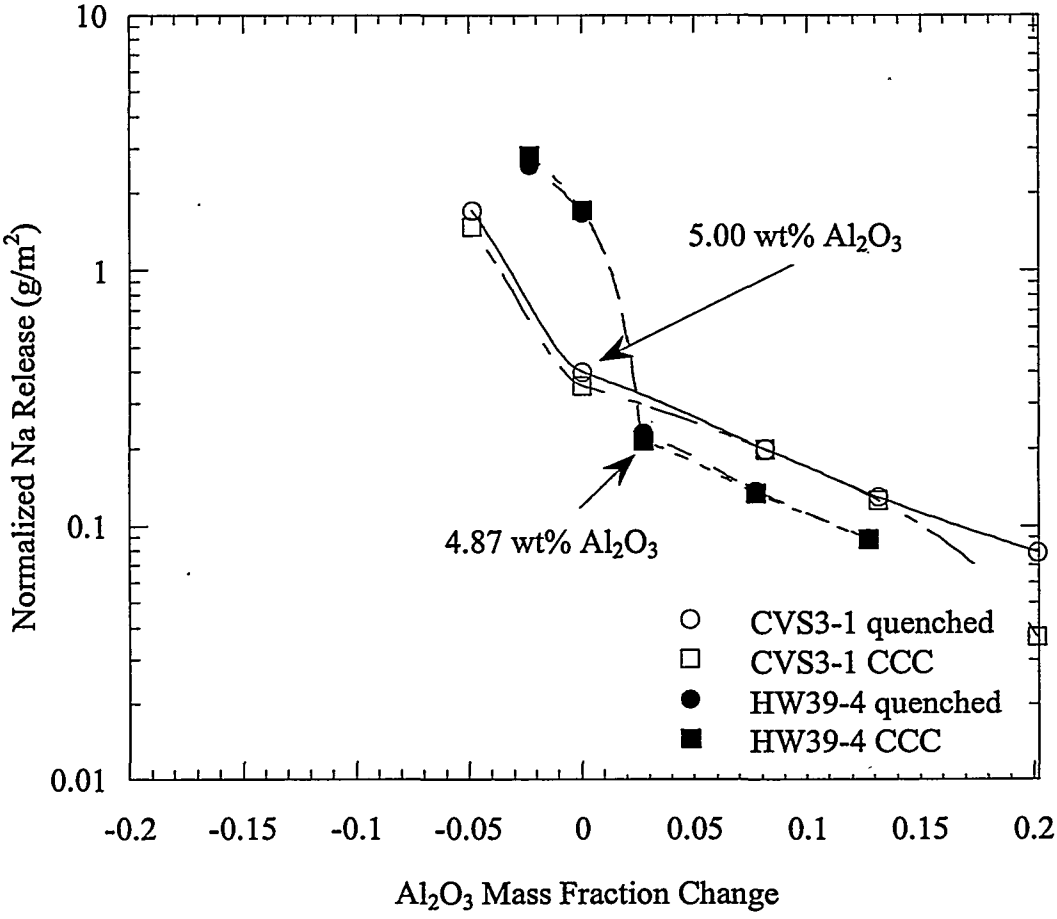


Figure 3.1. Effect of Al_2O_3 Concentration on r_{Na} of HAW Glasses (Vienna et al. 1995)

3.4 Preparation and Testing Procedures

Batches were prepared to make 250 g of glass with standard batching and melting procedures reported previously (Hrma et al. 1994). Reagent grade oxides, carbonates, sodium metaphosphate, and boric acid were used as the raw material sources. Materials were weighed to the nearest hundredth of a gram and thoroughly mixed in an agate disc mill. The well-mixed batch was placed into a Pt-10%Rh crucible and processed at 1150°C for 1 h, quenched, ground in a tungsten carbide mill to ensure homogeneity, and remelted for 1 h at 1150°C. In some glasses, undissolved material was detected after the first or second melt. If detected, the melting temperature of the second or third melt was raised until a homogenous glass was achieved. At the end of the final melt, the crucible was removed from the high-temperature furnace, and the glass was poured onto a stainless steel quench plate producing a glass patty. Glass remaining in the crucible was broken out (referred to throughout this report as "residual crucible glass") and archived with the pour patty for further evaluation or testing.

Visual observations of the pour patty and residual crucible glass were made and recorded in the appropriate laboratory notebook. Homogeneity is defined throughout this report by the absence of undissolved material, immiscible glass separation, or crystallization in the glass matrix (i.e., undissolved ZrO_2 is the likely candidate for these glasses) at the detection limit of the particular analytical instrument. Optical microscopy (OM), X-ray diffraction (XRD), and/or scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) were used to confirm visual observations. The residual crucible glass can contain undissolved material because of the settling potential resulting from density differences. Thus, both the pour patty and the residual crucible glass were examined to determine glass homogeneity.

The T_L was measured with the uniform-temperature method according to PNNL standard procedures.[d] The T_L measurement furnaces were validated with the Standard Reference Material (SRM) T_L glass – SRM-773 (NBS 1980). HT times no less than 22 h were used for glass samples in this study to ensure equilibrium was attained. Selected glass η's were measured with standard procedures reported by Hrma et al. (1994). A standard glass, SRM-711, was used to calibrate the viscometer before measurements (NBS 1964). The PCT-A (ASTM 1994) was performed on glasses in triplicate. Release values were normalized for concentration of elements in glass with as-batched glass compositions and for surface area of glass to volume of solution (i.e., to g/m^2) according to procedures described in Hrma et al. (1994). The composition of selected glasses was measured by fusion of the glass in KOH and in Na_2O_2, dissolution of the fused material in HNO_3, and ICP/AES of the solutions.

[d] *Standard Test Methods For Determining the Liquidus Temperature (T_L) of Waste Glasses and Simulated Waste Glasses*, GDL-LQT, Rev. 1., Pacific Northwest National Laboratory, Richland, WA (1999).

4.0 Results and Discussion

4.1 Initial Glass-Property Data

The following discussion describes the homogeneity, PCT, and T_L results from the tested glasses in addition to test variability assessed by the measurement of five replicate glasses.

4.1.1 General Observations

Evaluation of the as-fabricated glasses indicated that they were homogeneous with no undissolved materials in either the pour patties or residual crucible glass. Based on visual observations of the glasses while pouring and comparison with other high-level waste glasses processed at similar temperatures, the η of all glasses should be within the processing constraints of 2 to 10 Pa·s at 1150°C. However, glasses Zr-8, -12, -13, -14, -15, -17, -18, -19 and -21 were melted at temperatures above 1150°C because undissolved material was found after the first melt at 1150°C. These glasses are generally high in Al_2O_3 and/or ZrO_2 with low total alkali or B_2O_3 content. Formal high-temperature η measurements were not performed on all test glasses. However, η measurements are reported in section 4.2.2 for the selected glass.

4.1.2 Product Consistency Test

The r_B, r_{Na}, and r_{Li} values, with the exception of Zr-14, are reported in Table 4.1. Of the 27 glasses tested, 16 have release values more than one order of magnitude below those of the DWPF-EA glass. Glasses (Zr-13, -15, -18, -19, -20, -22, -23 and -24) with high levels of Al_2O_3 and/or ZrO_2 in conjunction with high levels of B_2O_3, Li_2O, or Na_2O had releases higher than one order of magnitude below those of the DWPF-EA glass. Likewise, glasses (Zr-7, -27 and -29) with high levels of Li_2O or Na_2O in conjunction with low levels of B_2O_3 or Al_2O_3, B_2O_3, and $_{ZrO2}$ had releases higher than one order of magnitude below those of the DWPF-EA glass. However, all but Zr-20, -22, -24, and -29 meet the 1 g/m^2 conservative constant being used for this study.

4.1.3 Liquidus Temperature

Table 4.2 lists the final melt temperature, T_{FM}, required to make a homogeneous glass, the T_L, the lowest temperature at which a heat-treated glass sample does not contain any crystals, T_A, the highest temperature at which a heat treated glass sample contains crystals, T_C, and the primary crystalline phase for each test glass. The T_{FM} should not be taken as the temperature required to melt these glass compositions on a large scale because of differences in feed chemistry, residence time, and heat/mass transport between the small Pt crucible and a melter. Instead, it is listed only for information on sample preparation.

Table 4.1. Nomalized Release for 7-Day PCT

ID	r_B (g/m^2)	r_{Na} (g/m^2)	r_{Li} (g/m^2)
Zr-1	0.239	0.241	0.338
Zr-2	0.277	0.269	0.364
Zr-3	0.231	0.242	0.352
Zr-4	0.301	0.268	0.383
Zr-5	0.228	0.234	0.327
Zr-6	0.251	0.259	0.361
Zr-7	0.290	0.810	0.492
Zr-8	0.434	0.127	0.451
Zr-9	0.293	0.383	0.295
Zr-10	0.247	0.240	0.336
Zr-11	0.237	0.127	0.356
Zr-12	0.220	0.020	0.310
Zr-13	0.420	0.205	0.485
Zr-15	0.210	0.970	0.300
Zr-16	0.185	0.230	0.340
Zr-17	0.265	0.020	0.330
Zr-18	0.660	0.335	0.750
Zr-19	0.275	0.495	0.540
Zr-20	0.490	1.175	0.505
Zr-21	0.300	0.035	0.360
Zr-22	1.030	0.525	0.965
Zr-23	0.255	0.545	0.515
Zr-24	0.295	1.160	0.410
Zr-25	0.405	0.065	0.450
Zr-26	0.610	0.315	0.620
Zr-27	0.595	0.710	0.735
Zr-28	0.240	0.260	0.340
Zr-29	3.890	3.085	2.715
DWPF-EA[c]	8.880	nm	4.655
ARM-1	0.760	0.660	1.310
DWPF-EA[a]	8.348	6.673	4.783
BL-8[b]	0.260	0.558	0.495
BL-9[b]	0.878	0.459	0.801

[a] from Jantzen et al. 1993
[b] from Peeler et al. 1998
[c] from this study
nm – not measured

Table 4.2. Liquidus Temperature Results and Primary Crystalline Phases

ID	T_{FM} (°C)	T_A (°C)	T_C (°C)	T_L (°C)	Primary Phase[b]
Zr-1	1150	1063	1065	1064	ZS
Zr-2	1150	960	966	964	ZS
Zr-3	1150	1104	1111	1110	Z
Zr-4	1150	1032	1037	1038	Z
Zr-5	1150	1068	1074	1085	Z
Zr-6	1150	1063	1065	1064	ZS
Zr-7	1150	1002	1007	1005	PK
Zr-8	1200	1170	1177	1177	ZS
Zr-9	1150	904	915	913	PK
Zr-10	1150	1063	1065	1064	ZS
Zr-11	1150	1128	1141	1140	ZS
Zr-12	1400	1247	1253	1250	ZS
Zr-13	1350	1185	1192	1189	Z
Zr-14	1350	1310	1315	1314	Z
Zr-15	1350	1333	1337	1336	Z
Zr-16	1150	1070	1064	1067	ZS
Zr-17	1450	1224	1235	1228	Z
Zr-18	1350	1122	1129	1125	ZS
Zr-19	1250	1031	1035	1034	ZS
Zr-20	1150	1113	1120	1113	PK
Zr-21	1350	1177	1182	1180	ZS
Zr-22	1150	1081	1091	1087	PK
Zr-23	1150	999	1009	1003	ZS
Zr-24	1150	1100	1110	1105	PK
Zr-25	1150	1133	1141	1137	ZS
Zr-26	1150	1068	1074	1070	ZS
Zr-27	1150	1075	1085	1081	ZS
Zr-28	1150	1060	1066	1064	ZS
Zr-29	1150	1055	1063	1059	PK
BL-8[a]	1150	1025	-	<1025	-
BL-9[a]	1150	1050	1025	1025-1050	PK

[a] From Peeler et al. 1998, UTF (uniform temperature furnace method)
[b] Z = baddeleyite, ZS = zircon, and PK = parakeldyshite

The T_L of test glasses range from 913°C for Zr-9 to 1336°C for Zr-15. Six of the 29 Zr-glasses met the restriction $T_L \leq 1050$°C: Zr-2, -4, -7, -9, -19 and -23. Analysis of composition versus T_L suggests that the T_L increases in glasses with higher concentrations of Li_2O, ZrO_2, B_2O_3, and Al_2O_3. However, these effects are confounded by the effects of glass components on η at 1150°C as all glasses were designed with a calculated η of 6 Pa·s (see Vienna et al. 2000). As such, a decrease in Li_2O or B_2O_3 requires an increase in Na_2O to maintain η at 6 Pa·s. Since Na_2O, Li_2O, and B_2O_3 affect T_L and η in a similar manner (e.g., decrease both properties),

changes to Li_2O and B_2O_3 are counteracted by changes to Na_2O. Experience from earlier studies (Crum et al. 1997; Hrma et al. 1994) as well as the BL waste study (Peeler et al. 1998) suggested that Na_2O, Li_2O, and B_2O_3 decrease the T_L and Al_2O_3 and ZrO_2 increase the T_L of similar glasses crystallizing zirconium-containing phases.

The primary crystalline phase of glasses Zr-8, -9, -11, -12, -14, -18, -19, and -20 was identified with XRD. Appendix A presents XRD scans for selected glasses. The results showed the primary crystalline phase was zircon ($ZrSiO_4$) for glasses Zr-8, -11, -12, -18, and -19, parakeldyshite ($Na_2ZrSi_2O_7$) for Zr-9 and -20, and baddeleyite (ZrO_2) for Zr-14. Figure 4.1 shows an XRD scan of Zr-11 heat treated for 24 h at 1074°C (below the T_L). The majority of the glasses were not examined with XRD. To determine the primary crystalline phase for these glasses, the crystal morphology seen in the samples examined by XRD was compared with visual observations of other glasses seen under the optical microscope. Figure 4.2 (a through e) shows optical micrographs of crystals in glasses Zr-1, -7, -8, -9, and -11, respectively.

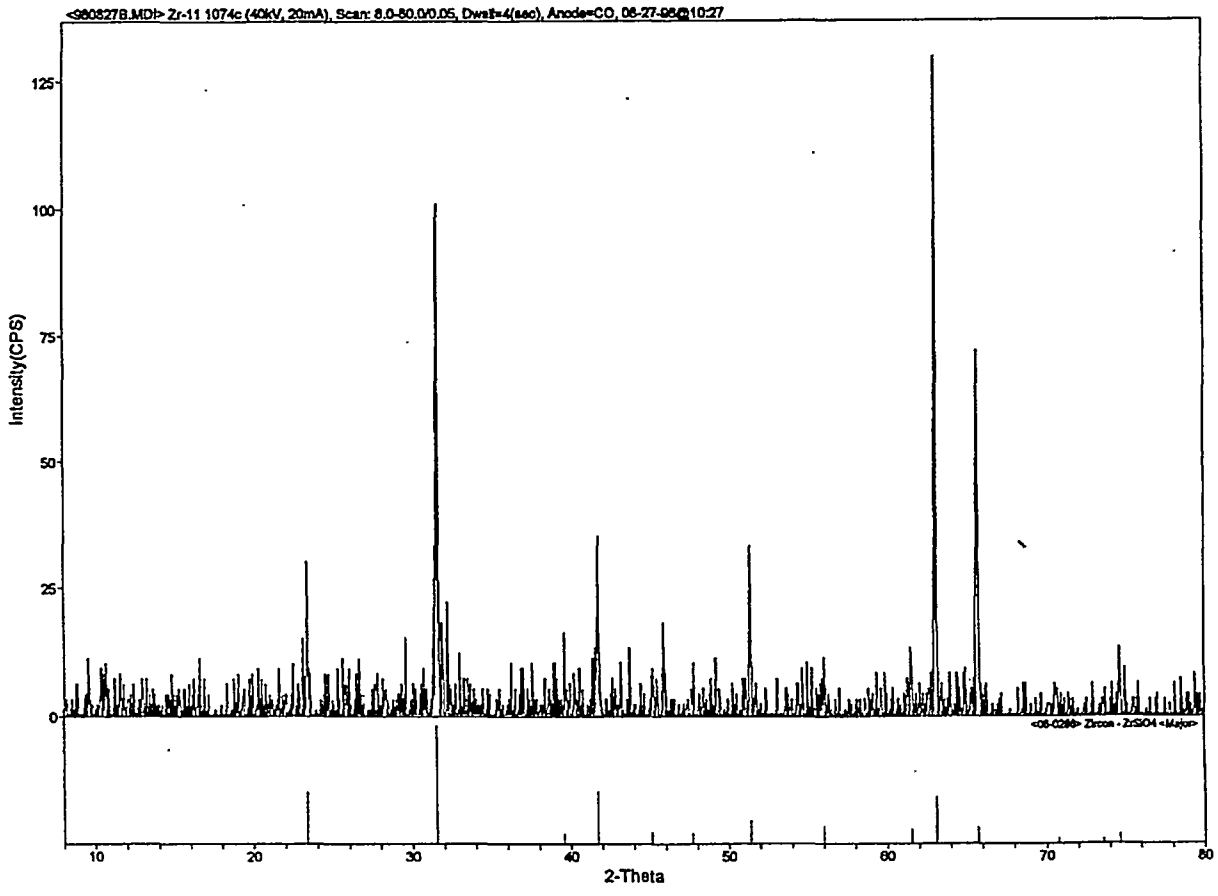
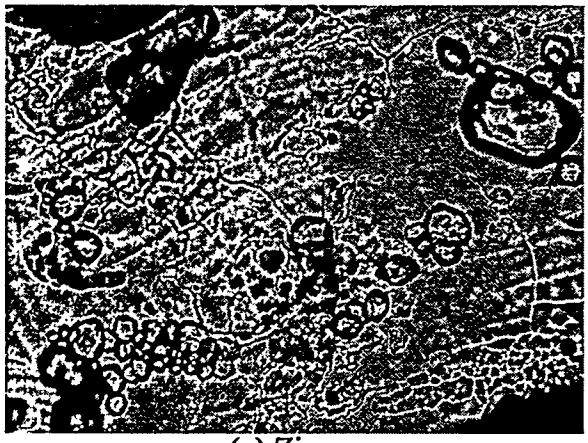
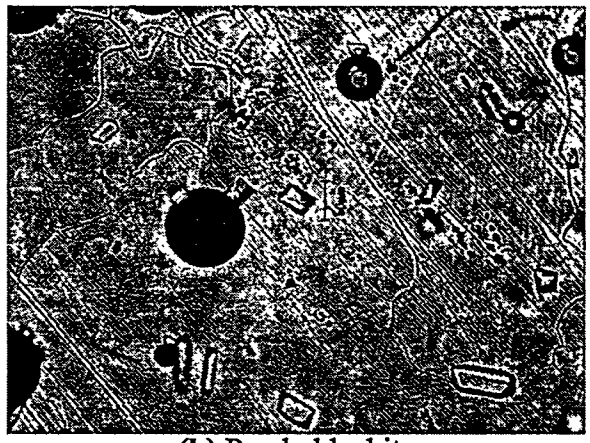


Figure 4.1. X-Ray Diffraction Trace Showing the Presence of Zircon in Zr-11 Heat Treated for 24 h at 1174°C



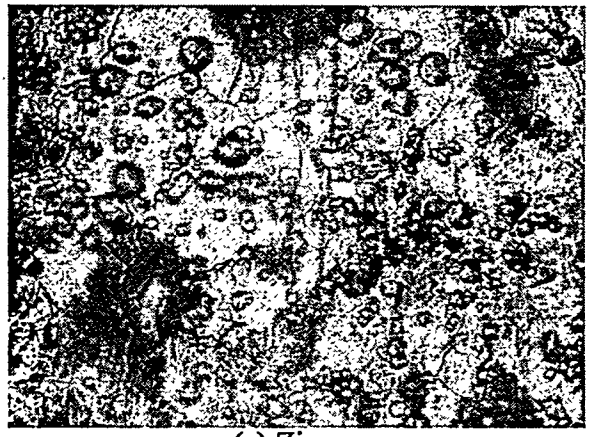
(a) Zircon



(b) Parakeldyshite

(c) Zircon

(d) Parakeldyshite



(e) Zircon

Figure 4.2. Transmitted Light Optical Micrographs of Crystals in Glasses (a) Zircon in Zr-1 1063°C, (b) Parakeldyshite in Zr-7 1005°C, (c) Zircon in Zr-8 1167°C, (d) Parakeldyshite in Zr-9 780°C, and (e) Zircon in Zr-11 1108°C

4.1.4 Replicate Glasses

The property results of the five replicate glasses, fabricated and tested as separate glasses with compositions blind to those performing the tests, (Zr-1, -6, -10, -16 and -28) are summarized in Table 4.3. The measured T_L for four of the five glasses was 1064°C while the T_L for the fifth glass (Zr-16) was 1067°C. PCT was measured for glasses Zr-1, -6, -10 and -16. The r_B for Zr-16 was quite low in comparison to the other three replicates measured. With the exception of the r_B, there is a high degree of reproducibility covering both glass fabrication and property measurement.

Table 4.3. Analysis of Replicate Glass-Property Values

Zr-1, -6, -10, -16, and –28	T_L (°C)	r_B (g/m^2)	r_{Na} (g/m^2)	r_{Li} (g/m^2)
mean value	1064.6	0.2305	0.2425	0.3438
standard deviation	1.2	0.031	0.012	0.012
percent variation[a]	0.28	28.6	12.0	7.3

(a) Range of property value divided by the mean value ×100.

4.2 Additional Testing on Selected Glass

The glass Zr-9 was selected for further testing because of its low T_L (913°C) and good PCT response (r_B=0.293 g/m^2) while maintaining high ZrO_2 loadings (15 mass%). The glass was fabricated at both laboratories (PNNL and SRTC) to ensure that the test results were reproducible. Further testing on this glass includes an investigation of the crystallization and redissolution behavior and replication of the PCT results. Corrosion of melter construction materials could not be tested during the time frame of this study. However, corrosion studies are planned for the near future and should be performed before melter testing.

4.2.1 Homogeneity

Visual observations indicated that all waste oxide components completely dissolved (i.e., no detection of undissolved ZrO_2 was observed) upon initial fabrication of Zr-9 at 1150°C. Visual observations were confirmed by optical microscopy, SEM, and XRD analysis. Figure 4.3 shows the XRD patterns obtained from the pour patty and residual crucible glass of Zr-9. The presence of an amorphous hump and absence of well-defined peaks indicate that the sample is homogeneous and contains no undissolved raw materials at the detection limit of the XRD unit (approximately 0.3 to 0.5 mass% based on the XRD run parameters). Figure 4.4 shows a SEM micrograph of the as-fabricated Zr-9 glass sample. The lack of any crystalline phases in this micrograph confirms the homogeneity of the sample. However, it should be noted that SEM is only a surface-sensitive technique, so the results are not conclusive.

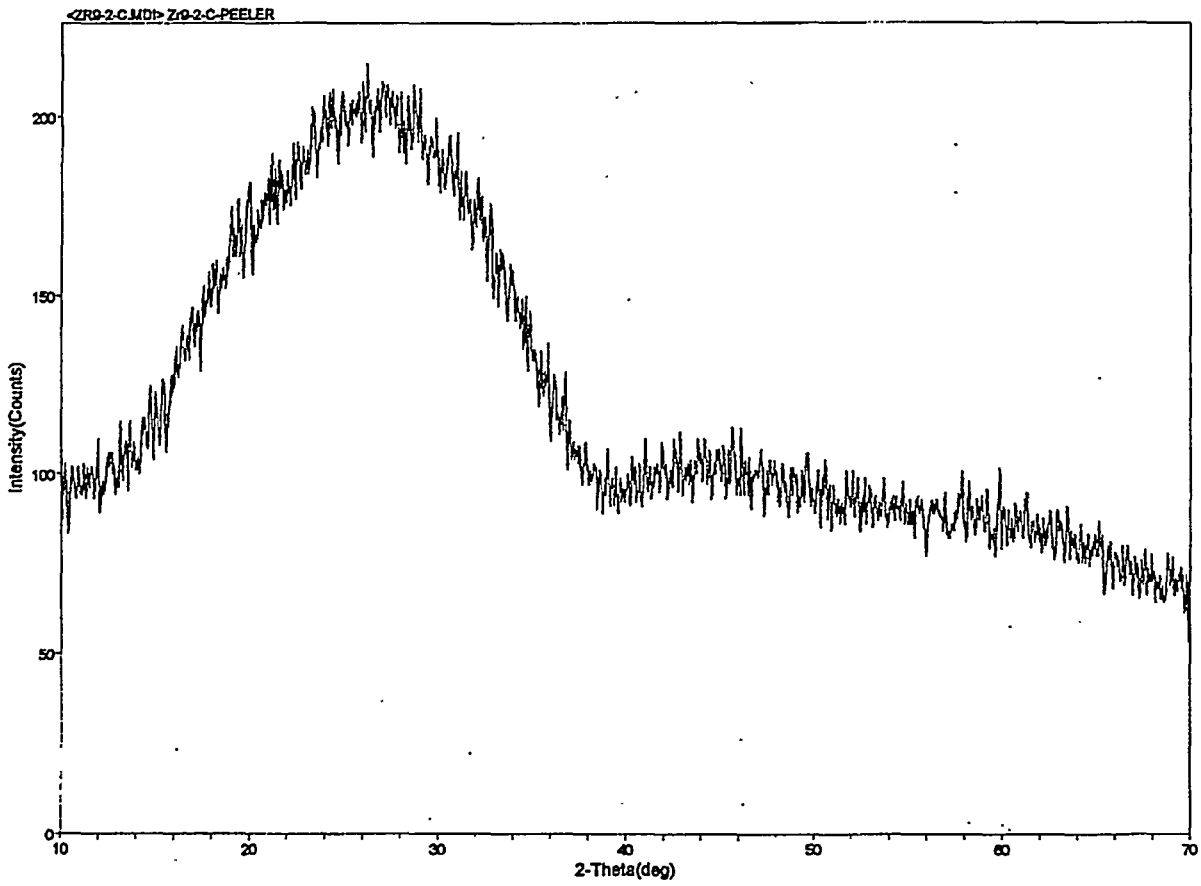


Figure 4.3. X-Ray Diffraction Scan of As-Fabricated Zr-9 glass

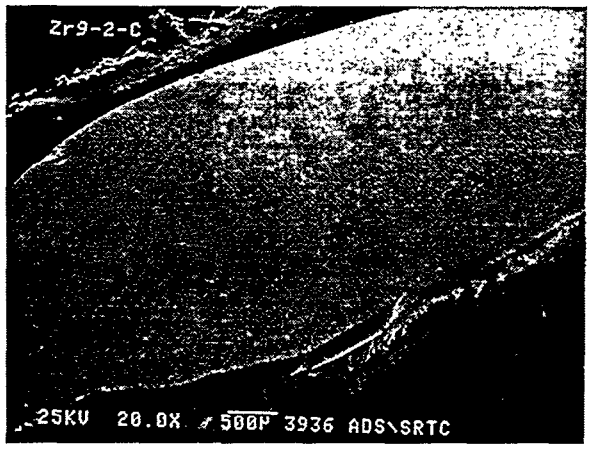


Figure 4.4. Scanning Electron Micrograph of As-Fabricated Zr-9 glass

4.2.2 Viscosity

The η of Zr-9 glass was measured as a function of temperature. The data were fitted to the two common η-temperature relationships:

$$\text{Fulcher } \ln\eta = A + \frac{B}{T - T_0} \tag{1}$$

$$\text{Arrhenius } \ln\eta = E + \frac{F}{T} \tag{2}$$

where A, B, T_0, E, and F are temperature-independent parameters, and T is the absolute temperature. The fitted values for these parameters were -6.416, 6982.8 K, 573 K, -13.307, and 21500 K for A, B, T_0, E, and F, respectively. Figure 4.5 shows the measured η data with the Arrhenius curve overlaid. The η at 1150°C is 6 Pa·s, which is within the 2 to 10 Pa·s constraint.

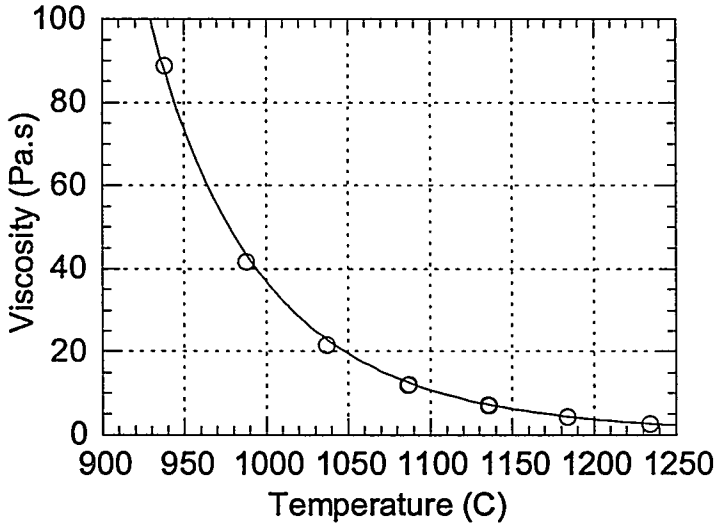


Figure 4.5. Viscosity of Zr-9 Glass as a Function of Temperature

4.2.3 Liquidus Temperature

A 24-h isothermal hold at 1050°C resulted in a homogeneous glass as shown in Figure 4.6 (XRD) and Figure 4.7 (SEM).[e] Therefore, the T_L constraint (T_L < 1050°C) was met for Zr-9. An additional T_L measurement of the refabricated Zr-9 glass with the gradient-temperature

[e] Although SEM analysis supports the XRD results of homogeneity, SEM is only a surface-sensitive technique, so the results are not conclusive.

method confirmed that the T_L of this glass is roughly 914°C, in good agreement with the 913°C value measured with the uniform-temperature method.

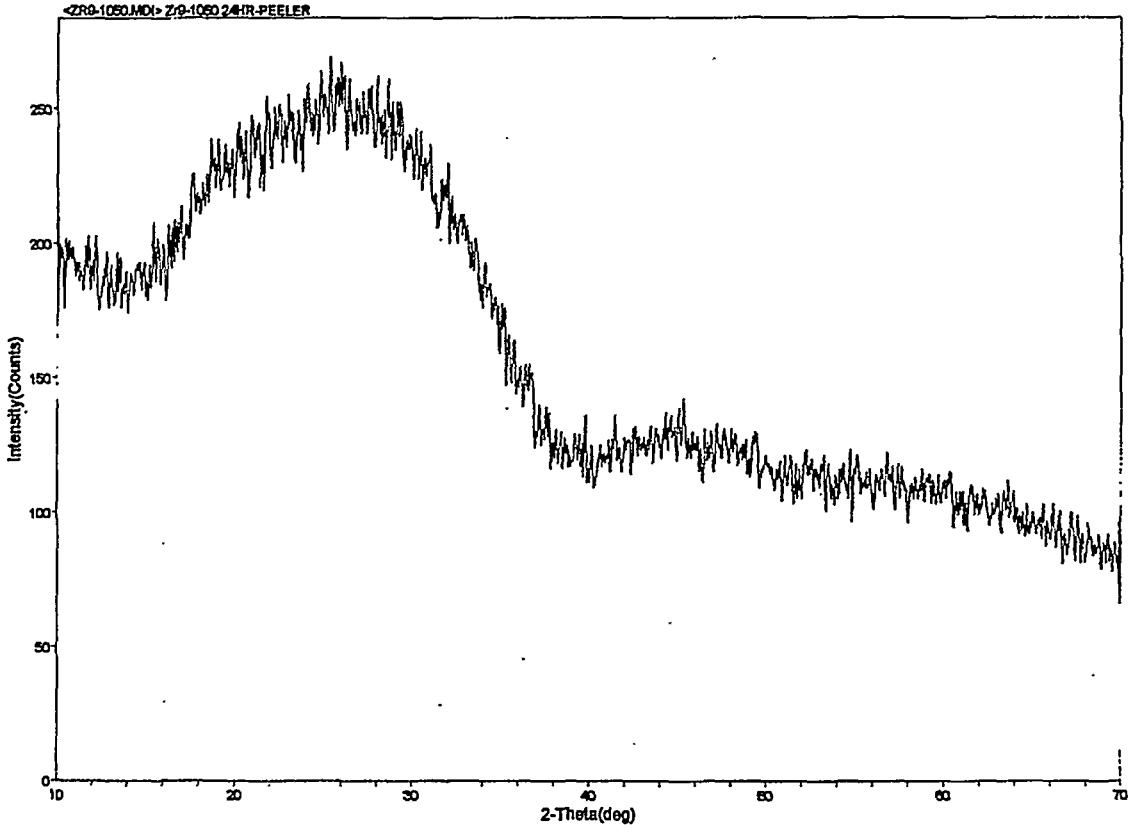


Figure 4.6. X-Ray Diffraction Trace of Zr-9 Glass Heat Treated at 1050°C for 24 h

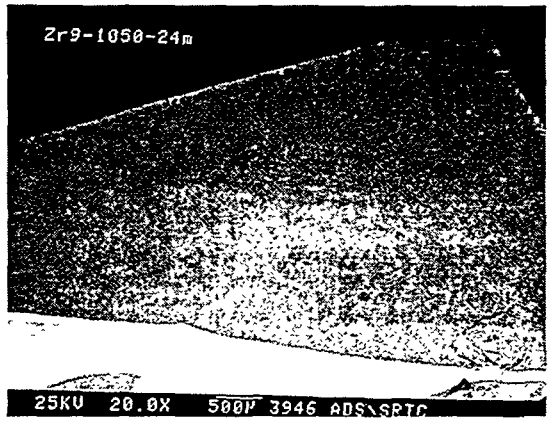


Figure 4.7. Scanning Electron Micrograph of Zr-9 Glass Heat Treated at 1050°C for 24 h

4.2.4 Product Consistency Test

The chemical durability of Zr-9, fabricated at both laboratories, was measured with the PCT. Table 4.4 summarizes the final solution pH and the normalized release of B, Na, and Li for Zr-9. The normalized releases for the EA glass are also provided for comparison. The normalized release values are all more than an order of magnitude below those from the DWPF-EA glass and meet the conservative criteria set for this study. The normalized release values are similar for the two duplicate glasses with percent variations in the range from 2 to 14%. The percent variations, which are the range of values divided by mean value times 100, include variation in glass fabrication from two sites and property measurement.

Table 4.4. Product Consistency Tests Results for Replicate Zr-9 Glasses

	Final pH	r_B (g/m^2)	r_{Na} (g/m^2)	r_{Li} (g/m^2)
Zr-9 (Lab #1)	10.75	0.293	0.383	0.295
Zr-9 (Lab #2)	10.74	0.255	0.365	0.290
Mean	10.75	0.274	0.374	0.293
Percent Variation	0.09	13.9	4.8	1.7
DWPF-EA[(a)]	11.85	8.348	6.673	4.783

[(a)] From Jantzen et al. (1993).

4.2.5 Redissolution Tests

Samples of the Zr-9 glass fabricated at the two sites (PNNL and SRTC) were heat treated to induce crystallization that may occur in the INEEL ¼-scale melter system in idle mode. One sample was heat treated for 24 h in a linear temperature gradient from 780°C to roughly 1000°C over 30 cm (7°C/cm). Examination of this sample showed that crystallization began at roughly 915°C (the T_L of Zr-9). As the temperature decreased from 915°C to 780°C, the crystalline fraction of the glass gradually increased. The highest crystallinity of the sample was found at 780°C where the crystallinity was estimated at slightly below 1 vol%. Figure 4.8 shows an optical micrograph of the gradient-temperature sample of Zr-9 heat treated at roughly 780°C. The redissolution of these crystals at 1050°C was not tested on this sample because the fraction of crystallinity was too low to significantly impede glass flow from the ¼-scale melter drain tube.

Three Zr-9 samples were isothermally heat treated at 850°C for 24 h in Pt-10% Rh crucibles to intentionally devitrify the samples.[f] By visual observation, all three samples were determined to be homogeneous, which is consistent with the gradient-temperature results. Each sample was found to be crystal free with XRD and SEM analyses. The lack of crystallinity at a temperature below T_L is likely due to insufficient time to crystallize the sample—the lower the temperature, the lower the rate of crystallization processes.

[f] Isothermal heat treatments at 850°C were initiated before the gradient-furnace determination of the maximum crystallization temperature of 780°C.

The lack of crystallinity at 850°C implied that there was no need to reheat these samples to verify any redissolution. These results suggest that if the melter is idled for 24 h, a minimal amount of devitrification will occur. However, complete devitrification kinetics for this specific glass is not known.

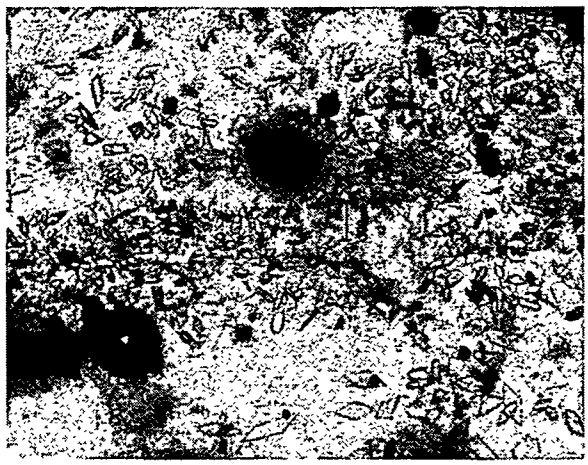


Figure 4.8. Optical Micrograph of Zr-9 Glass Heat Treated for 24 h at 780°C

5.0 Laboratory-Scale Melter Testing with Selected Glass Composition

This section describes the equipment and test procedure used for LSM testing with the selected glass composition (Zr-9); it also describes the test results for studies in corrosion, redox, η, and density.

5.1 Purpose and Scope

The purpose of this test was to collect qualitative processing data on the Zr-9 glass formulation before conducting pilot-scale melter operations. In addition, the properties of the glass fabricated from melter feed (rather than single-metal oxides and carbonates) should be tested to ensure consistency with crucible tests. The target compositions of the Zr-HAW, Zr-9 frit, and the Zr-9 glass (16.2 mass% Zr-HAW and 83.8 mass% Zr-9 frit) are reiterated in Table 5.1. The processing-related properties that were measured for the Zr-9 glass include corrosivity, redox, and η.

Table 5.1. Zr-HAW, Zr-9 Frit, 16.2 mass% Zr-HAW Glass Target Compositions

Oxide	Zr-HAW	Zr-9 Frit	Zr-9 Glass
Al_2O_3	2.08	4.97	4.50
B_2O_3	-	11.93	10.00
CaO	0.53	-	0.09
CeO	0.14	-	0.02
Cs_2O	0.26	-	0.04
Fe_2O_3	0.02	-	0.00
Gd_2O_3	0.42	-	0.07
K_2O	2.61	-	0.42
Li_2O_3	-	7.16	6.00
Na_2O	-	17.00	14.25
P_2O_5	1.31	-	0.21
SiO_2	-	58.94	49.39
SrO	0.04	-	0.01
ZrO_2	92.58	-	15.00
Loading			16.20%

5.2 Equipment Description

The LSM was fabricated with Monofrax K-3 fire-cast refractory and two Inconel 690 electrodes. The power supply for joule heating included a 120-volt Variac rheostat with a 0 to 140 volt AC/22 amp output. The current and voltage across the electrodes (through the melt) were monitored with two Fluke 87 digital multimeters. A modified (1200°C) Blue M furnace was used for initial heat up. A quartz fixture was added to facilitate raising and lowering the self-verifying sensor (SVS) temperature probe in and out of the melt while providing a non-conductive safety barrier for protecting the experimenter from electrical hazards. The melt

temperature was monitored with a SVS temperature probe located directly in the melt and a Type R thermocouple inside an alumina thermowell, which is also located in the melt. The furnace temperature was monitored with a Type K thermocouple located in the furnace cavity.

5.3 Test Procedure

The melter chamber was filled with oxides and carbonates in the ratios appropriate to form the Zr-9 glass. The SVS temperature probe and the in-melt Type R thermocouple were placed in the melt. The oven temperature was controlled to heat the melter at approximately 50°C/h. Temperature readings from the SVS probe, Type-R thermocouple, and the Type-K furnace-chamber thermocouple were recorded manually throughout the duration of the test. No foaming or phase separation were visually detected. Additional glass additives and simulated Zr-HAW were added as needed until the melt chamber was full. Joule heating was initiated at 717°C, and oven resistance heaters were turned off. Voltage and current readings were recorded at 1- to 5-min intervals. Current density was limited to 0.93 amps/cm^2 (6 amps/in^2). An initial "jump" in melt temperature from 717°C to 969°C occurred in the first 10 min of Joule heating. The melt temperature was increased at approximately 90°C/h to 1150°C and held for 5 h. After 5 h of 1150°C operation, Joule heating was terminated, and the SVS probe and Type-R thermocouple were removed. The melt was then poured onto a quench plate and collected for analysis.

5.4 Results

Suitable results were obtained in the corrosion, redox, η, density, and resistivity tests (see the following discussion for details).

5.4.1 Corrosion

Corrosion effects of Zr-9 vitrification on the Inconel 690 electrodes and the K3 refractory for the duration of this test were minimal. Melter electrodes were removed and quenched. Residual glass was removed manually and by soaking the electrodes in hydrofluoric acid for 15 minutes. Weight loss of each electrode was < 1%. Table 5.2 shows the initial and final weights of each electrode. Visual inspection of the electrodes through a microscope at 70× revealed that no excessive corrosion occurred. Electrodes are shown in Figure 5.1. The K3 refractory also appeared to have no significant corrosion. It must be recognized that the 5-h test is insufficient to draw conclusions on the corrosivity of this glass melt.

Table 5.2. Electrode Initial and Final Weights

Electrode	Initial Weight	Final Weight	% Change
4	75.4	74.8	0.8
5	75.0	74.3	0.9

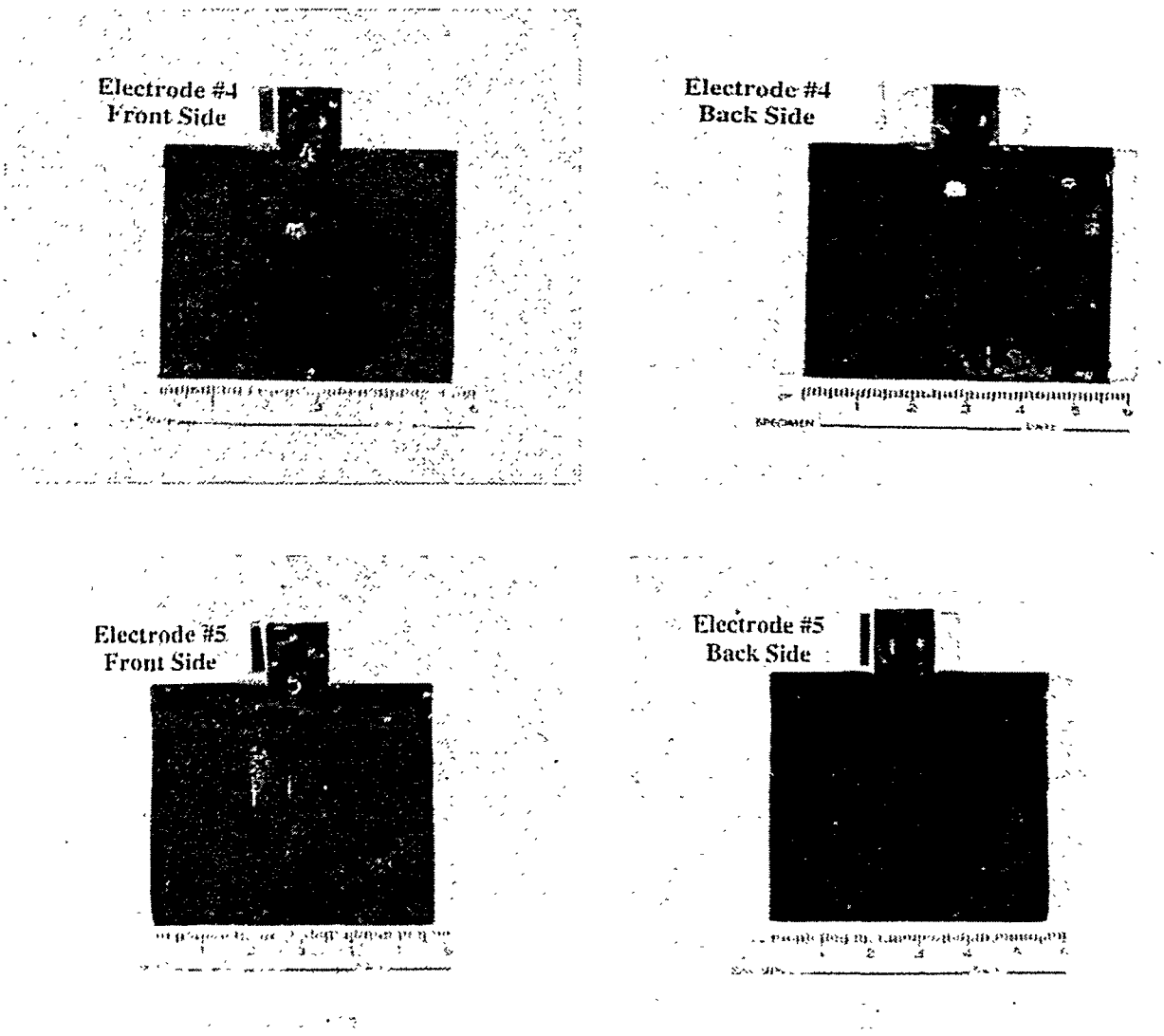


Figure 5.1. Electrodes #4 and #5 Front and Back

5.4.2 Redox

Redox conditions are considered to be suitable, based on the lack of foaming in the melt. Minimal corrosion of melt-contact refractories and electrodes may also indicate the suitability of melt redox conditions. No formal redox measurement was performed. In addition, no metallic particles were detected in the glass or on the bottom of the LSM.

5.4.3 Viscosity

The assumed operating temperature of an INTEC HAW glass melter is 1150°C with a preferred pouring η in the range of 2 to 10 Pas. Viscosity profiles of the Zr-9 LSM glass and the Zr-9 crucible glass, as shown in Figure 5.2, were measured as a function of temperature over the

range of 950°C to 1250°C. The η measurements given are based on the arithmetic mean of torque readings taken every 15 sec over a 5-min interval at a stable sample temperature. As seen from the data in Table 5.3, exact duplication of temperature points for torque readings could not be achieved when taken at duplicate set points. However, the data in Table 5.3 show that the η profiles of the crucible glass and the LSM glass are nearly the same with the pouring η well within the 2 to 10 Pa·s range at 1150°C.

Table 5.3. Viscosity Profiles for LSM and Crucible Fabricated Zr-9 Glasses

LSM Glass		Crucible Glass	
T(°C)	**η(Pas)**	**T(°C)**	**η(Pas)**
1158.3	6.9	1157.1	6.7
1107.1	12.1	1106.1	11.7
1056.7	22.4	1055.9	21.5
1106.9	12.1	1106.1	11.7
1156.3	7.0	1155.5	6.8
1205.3	4.4	1204.7	4.2
1254.2	2.8	1253.7	2.7
1156.4	7.3	1154.8	6.9
1006.8	46.2	1005.6	40.0
957.4	99.5	956.3	94.7

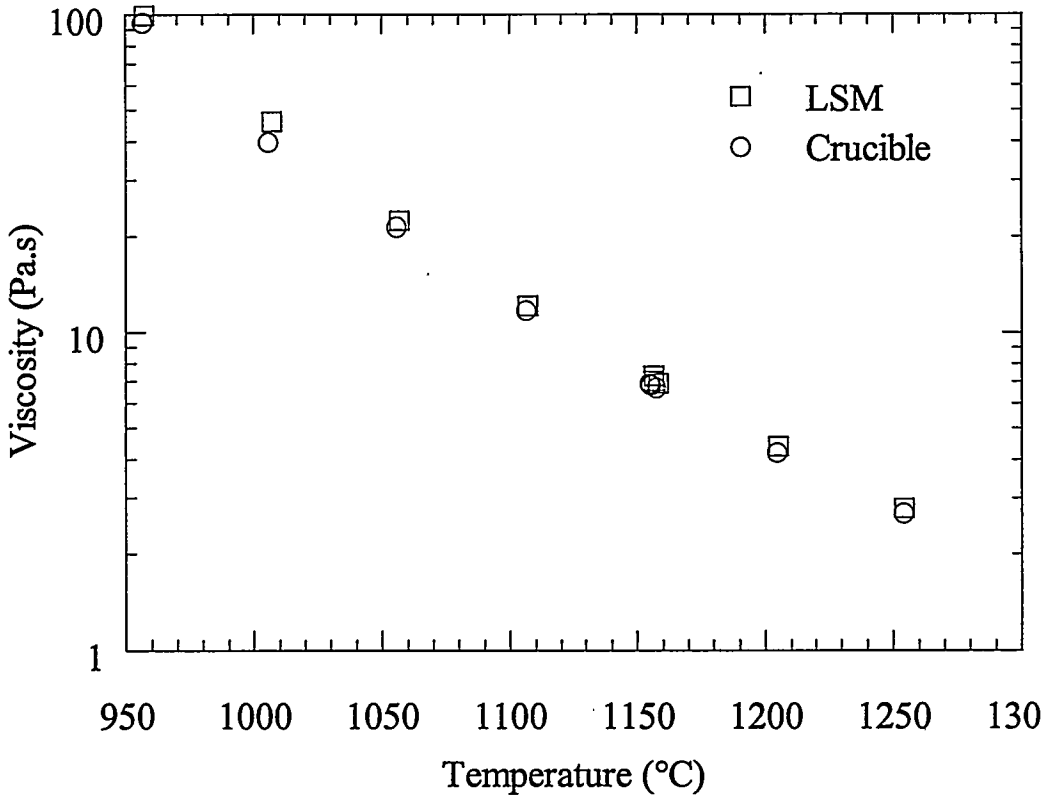


Figure 5.2. Viscosity of LSM and Crucible-Fabricated Zr-9 Glasses as Functions of Temperature

5.4.4 Density

Density measurements were performed on the Zr-9 glasses fabricated in the LSM and in the crucible with a gas-displacement pycnometer with multiple measurements, which were averaged. The LSM glass density was 2.6754 g/cm^3, compared to the 2.6713 g/cm^3 of the crucible glass. This comparison may indicate that there was little addition of chrome, nickel, and zirconium to the glass from the refractory or electrodes.

5.4.5 Resistivity

A resistivity curve for the Zr-9 glass was established for use in calculating the glass level in the pilot-scale melter (Figure 5.3). Current density was controlled to prevent excessive corrosion/erosion and melting of the electrodes. Glass resistivity was calculated from electrode voltage and current with the relationship

$$r = \frac{AV}{LI} \tag{3}$$

where r is resistivity, A is electrode area, V is voltage, L is length between electrodes, and I is current.

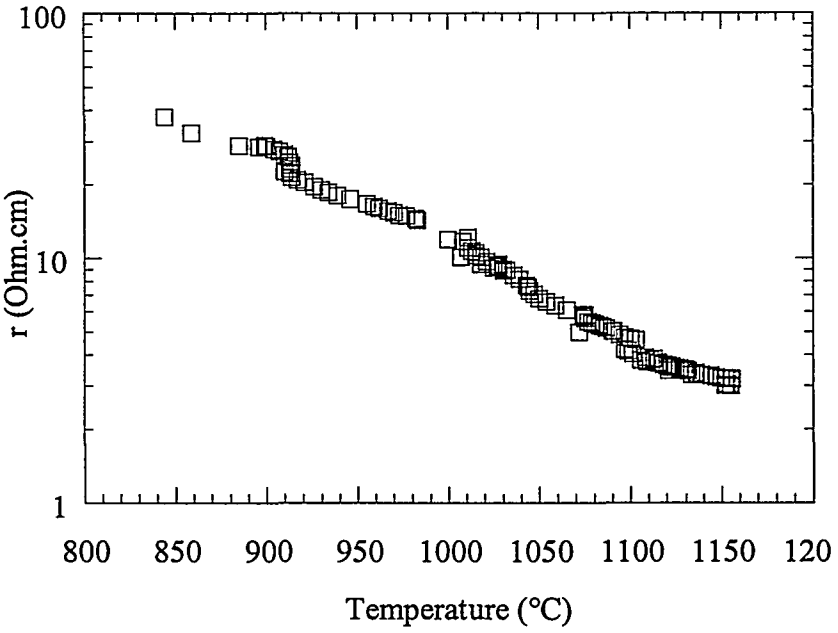


Figure 5.3. Glass Resistivity as a Function of Temperature

5.4.6 LSM Discussion

Data collected from the LSM run with Zr-9 glass will be used to conduct pilot-scale melter operations. Test results from the LSM indicate that the glass η was acceptable, and there were no indications of problems related to glass redox or corrosion of melter construction materials. It is recommended that testing in a pilot-scale melter be conducted to verify the processability of the Zr-9 glass.

6.0 Conclusions and Recommendations

A matrix of 29 candidate waste glasses with systematically varied compositions were fabricated and tested. Testing of 28 of the 29 Zr-glasses showed that several highly durable glasses were formed by mixing 16.2 mass% of Zr-HAW with a number of frit compositions based on BL-8 and BL-9. Of the 24 Zr-glasses (excluding the replicates) that were tested, only 4 did not meet the stringent glass-performance restriction of $r_i \leq 1$ g/m^2. Normalized release rates for the PCT will remain a limiting constraint on waste loading unless they are relaxed to 1.5 (g/m^2), which is still well below the EA glass limits.

The $T_L < 1050°C$ constraint poses the largest technical challenge for glass formulation (with maximum waste loading) within this composition space. The T_L of Zr glasses ranged from 914°C for Zr-9 to 1336°C for Zr-15. Only 6 of the 29 Zr glasses met the restriction $T_L \leq 1050°C$—Zr-2, -4, -7, -9, -19, and -23—all of which passed the conservative PCT normalized-release constraint. Based on this study, increasing the melter processing temperature (T_M) will provide the best opportunity for increasing waste loading in glass. If the T_M is increased by 100°C to 1250°C, 18 glasses in the study would satisfy the constraint, $T_L < 100°C$ below T_M, assuming all other processing constraints are met. However, increasing the T_M could lead to higher volatility rates (which may generate secondary waste streams) and a higher corrosion rate of the materials of melter construction. Therefore, these effects should be investigated before the T_M is increased.

Visual observations of glass pouring by experienced technical staff suggested that all of the tested Zr-HAW glasses would meet the criteria $2 \leq \eta \leq 10$ Pa·s. Based on preliminary property models and visual observations η does not appear to be a limiting constraint for this composition region. However, nine glasses (Zr-8, -12, -13, -14, -15, -17, -18, -19, and -21) were melted at temperatures above 1150°C because there was still undissolved material at 1150°C.

Based upon the initial glass-testing results, Zr-9 was chosen for further testing. Zr-19 has the highest Zr-HAW of the glasses that satisfy the T_L and PCT constraints; however, the T_L of Zr-19 was close to the 1050°C limit, and a higher temperature (1250°C) was required to make a homogeneous melt from this composition using standard laboratory procedures. Zr-9 had the lowest T_L of all glasses and acceptable PCT release, with 15 mass% ZrO_2. This glass was fabricated and tested at two laboratories to ensure reproducibility of results. The PCT and the T_L results from the refabricated Zr-9 glasses showed a high degree of reproducibility, even between laboratories.

Additional testing was performed on Zr-9 to try to assess the glasses' processability. Gradient-temperature HT of Zr-9 showed that crystallization began at roughly 915°C, and crystallinity continued to increase with decreasing temperature until 780°C, the lowest temperature tested. Glass heat-treated at 780°C for 24 h showed less than 1 vol% crystallinity, which is not enough to significantly impede glass flow in the INEEL ¼-scale melter drain tube. No tests were made at lower temperatures. The Zr-9 glass η was measured as a function of temperature over the range from roughly 930°C to 1240°C. The 1150°C η was 6.05 Pa·s, well within the acceptable range of 2 to 10 Pa·s and very close to the design value of 6 Pa·s.

An LSM test was performed with Zr-9 glass. Results from the LSM test indicate that the glass η was acceptable, and there were no indications of problems related to glass redox or corrosion of melter construction materials.

Based upon the results from crucible and LSM tests, we recommend that Zr-9 glass composition be used to demonstrate the vitrification of INEEL Zr-HAW in a scaled melter test. This glass, although not optimized, meets the primary processing and product-quality constraints while containing a reasonable loading of the Zr-HAW.

7.0 References

American Society for Testing and Materials (ASTM). 1994. *Standard Test Method for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT),* ASTM-C-1285-94 (1994).

Bunnell, L. R. 1988. *Laboratory Work in Support of West Valley Glass Development,* PNL-6539, Pacific Northwest Laboratory, Richland, Washington.

Chick, L. A., W. M. Bowen, R. O. Lokken, J. W. Wald, L. R. Bunnell, and D. M. Strachan. 1984. *West Valley High-Level Nuclear Waste Glass Development: A Statistically Designed Mixture Study,* PNL-4992, Pacific Northwest Laboratory, Richland, Washington.

Crum, J. V., M. J. Schweiger, P. Hrma, and J. D. Vienna. 1997. "Liquidus Temperature Model for High-Zirconia Hanford High-Level Waste Glasses," *Scientific Basis for Nuclear Waste Management XX,* Materials Research Society, pp 79-86.

DOE (see U.S. Department of Energy)

Feng, X., P. Hrma, J. H. Westsik, Jr., M. J. Schweiger, H. Li, J. D. Vienna, G. F. Piepel, D. K. Peeler, S. E. Palmer, B. P. McGrail, D. E. Smith, D. S. Kim, Y. Peng, A. J. Bakel, and W. L. Ebert. 1995. *Glass Optimization for Vitrification of Hanford Site Low-Level Tank Waste,* PNNL-10918, Pacific Northwest Laboratory, Richland, Washington.

Hrma, P., G. F. Piepel, M. J. Schweiger, D. E. Smith, D. S. Kim, P. E. Redgate, J. D. Vienna, C. A. LoPresti, D. B. Simpson, D. K. Peeler, and M. H. Langowski. 1994. *Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C,* PNL-10359, Vol. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

Jantzen, C. M., N. E. Bibler, D. C. Beam, C. L. Crawford, and M. A. Pickett. 1993. *Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material,* WSRC-TR-92-346, Rev. 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Jantzen, C. M., J. B. Pickett, K. G. Brown, T. B. Edwards, and D. C. Beam. 1995. *Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using A Thermodynamic Hydration Energy Reaction Model (THERMO) (U),* WSRC-TR-93-672, Rev. 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Mika, M., M. J. Schweiger, P. Hrma, and J. D. Vienna. 1997. "Liquidus Temperature of Spinel Precipitating High-Level Waste Glasses," *Scientific Basis for Nuclear Waste Management XX,* Materials Research Society, pp 71-78.

Musick, C. A., B. A. Staples, J. D. Vienna, D. K. Peeler, B. C. Norby, R. J. Kirkham, and P. A. Tullock. 1998. *FY-98 Pilot Scale Melter Tests Using Surrogate High-Activity Waste – All Blend - Glass Formulation,* INEEL/EXT-98-00991, Lockheed Martin Idaho Technologies Co, Idaho Falls, Idaho.

National Bureau of Standards (NBS). 1980. *Certificate, Standard Reference Material 773, Soda-Lime-Silica Glass for Gradient-Furnace Liquidus Temperature,* Washington, D.C.

National Bureau of Standards (NBS). 1964. *Certificate of Viscosity Values, Standard Sample No. 711, Lead-Silica Glass*, Washington, D.C.

Peeler D. K., I. A. Reamer, J. D. Vienna, and J. V. Crum. 1998. *Technical Status Report, Preliminary Glass Formulation Report for INEEL HAW*, WSRC-TR-98-00132, Rev. 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Piepel, G. F. and P. E. Redgate. 1997. "Mixture Experiment Techniques for Reducing the Number of Components Applied for Modeling Waste Glass Sodium Release," *J. Am. Ceram. Soc.*, Vol. 80, pp. 3038-44.

Piepel, G. F., P. Hrma, and J. D. Vienna. 1997. "Glass Chemistry Development Strategy for Hanford High-Level Waste (HLW)," *Science and Technology for Disposal of Radioactive Tank Wastes*, Plenum Publishing, New York.

Piepel, G. F., J. D. Vienna, and P. Hrma. 1999. *Phase I Experimental Design for the INEEL HLW Glass Composition Variation Study,* PNNL-SA-29594, Rev. 2, Pacific Northwest National Laboratory, Richland, Washington.

Reimus, M. A. H., G. F. Piepel, G. B. Mellinger, and L. R. Bunnell. 1988. *West Valley Glass Product Qualification Durability Studies, FY 1987-1988: Effects of Composition, Redox State, Thermal History, and Groundwater,* PNL-6723, Pacific Northwest Laboratory, Richland, Washington.

Staples, B. A., D. K. Peeler, J. D. Vienna, B. A. Scholes, and C. A. Musick. 1999. *The Preparation and Characterization of INTEC HAW Phase 1 Composition Variation Study Glasses*, INEEL/EXT-98-00970, Rev. 1, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

Sundaram, S. K., J. D. Vienna, G. F. Piepel, R. Plaisted, B. M. Jorgensen, J. V. Crum, D. K. Peeler, I. A. Reamer, and T. James. 1998. *INEEL HLW Corrosion and Preliminary Glass Formulation for INEEL Zirconia HAW – Final Report*, PNNL-SA-12012, Pacific Northwest National Laboratory, Richland, Washington.

U.S. Department of Energy (DOE). 1995. *The INEEL Spent Nuclear and Environmental Restoration and Waste Management Programs Environmental Impact Statement*, DOE\EIS-0202-F, April 1995, U.S. Department of Energy, Washington, D.C.

Vienna, J. D., P. Hrma, M. J. Schweiger, M. H. Langowski, P. E. Redgate, D. S. Kim, et al. 1995. *Effect of Composition and Temperature on the Properties of High-Level Waste Glasses Melting Above 1200°C*, PNNL-10987, Pacific Northwest Laboratory, Richland, Washington.

Vienna, J. D., D. K. Peeler, T. J. Plaisted, R. L. Plaisted, I. A. Reamer, and J. V. Crum. 2000. "Glass Formulation for Idaho National Engineering and Environmental Laboratory Zirconia High-Activity Waste," *Ceramic Transactions 107*, American Ceramic Society, Westerville, Ohio.

Appendix A:
X-Ray Diffraction Analysis

Appendix A:
X-Ray Diffraction Analysis

Figures A.1 through A.8 show XRD traces of selected glasses heat treated below T_L.

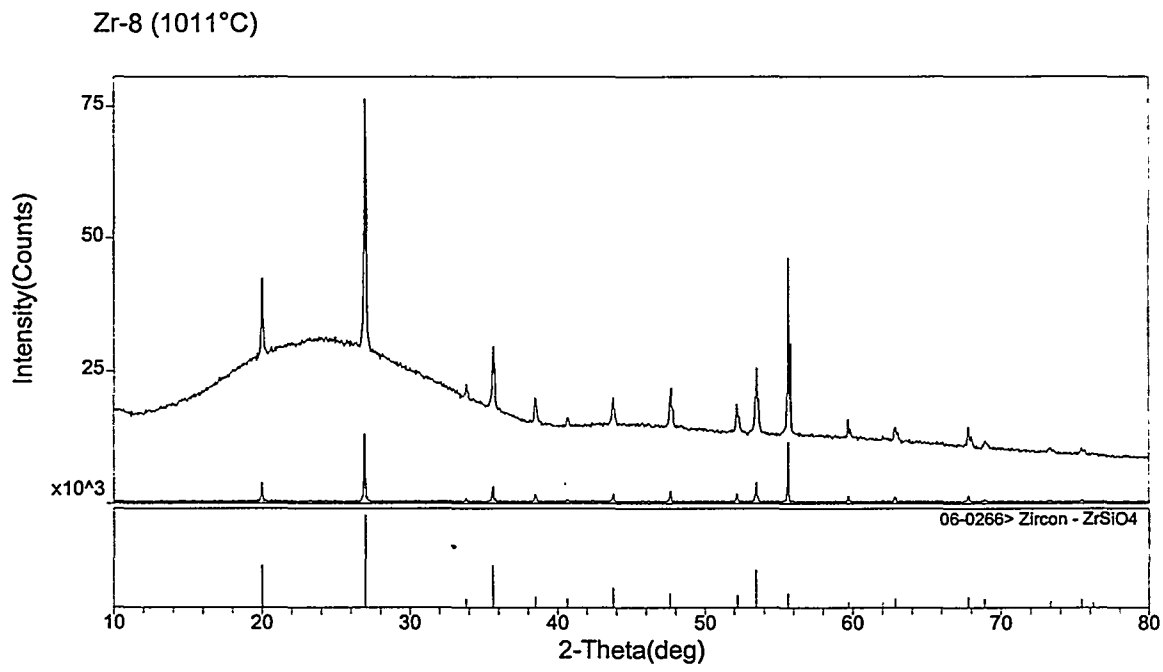


Figure A.1. XRD Trace of Zr-8 Glass Heat Treated at 1011°C for 24 h

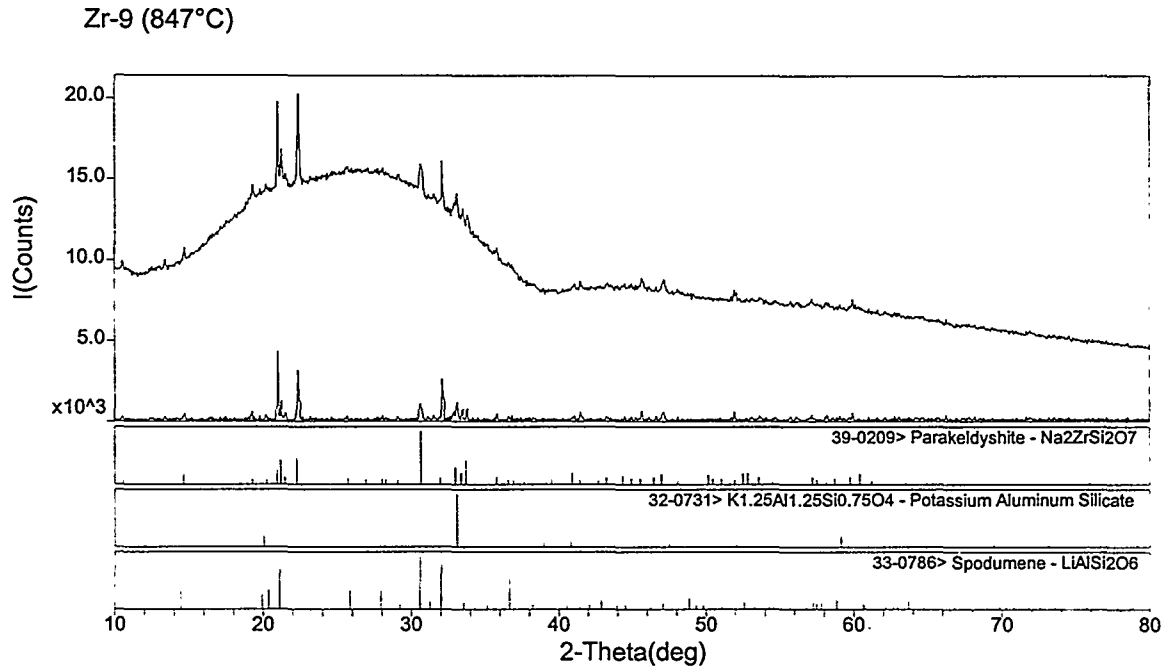


Figure A.2. XRD Trace of Zr-9 Glass Heat Treated at 847°C for 24 h

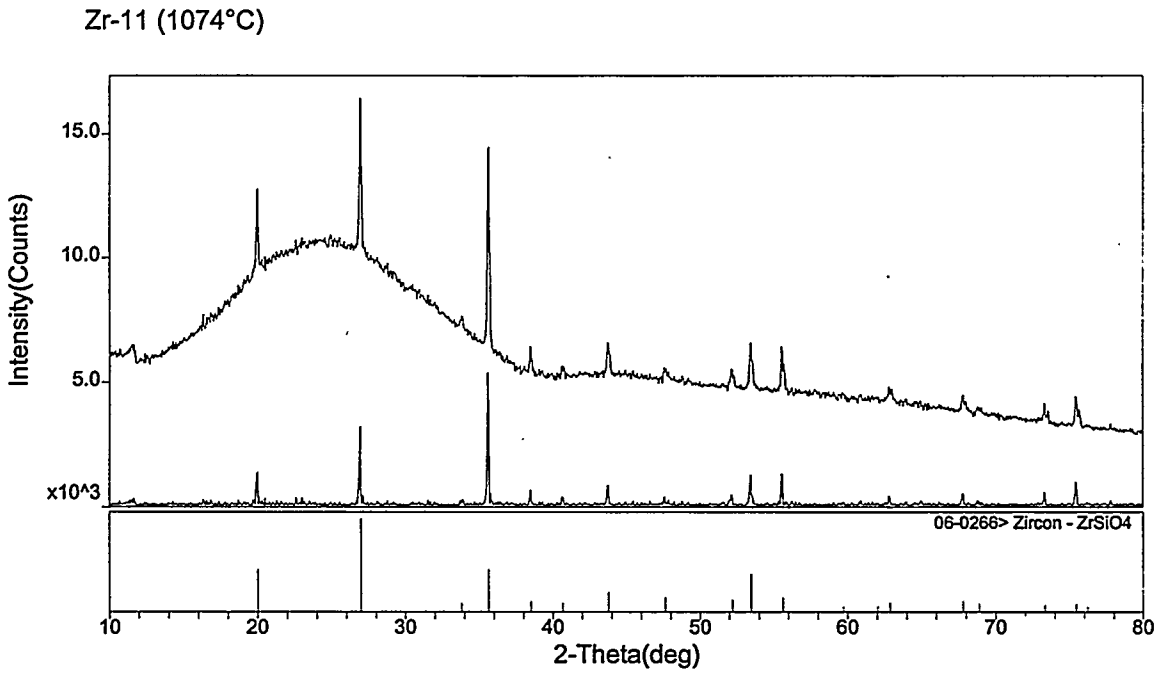


Figure A.3. XRD Trace of Zr-11 Glass Heat Treated at 1074°C for 24 h

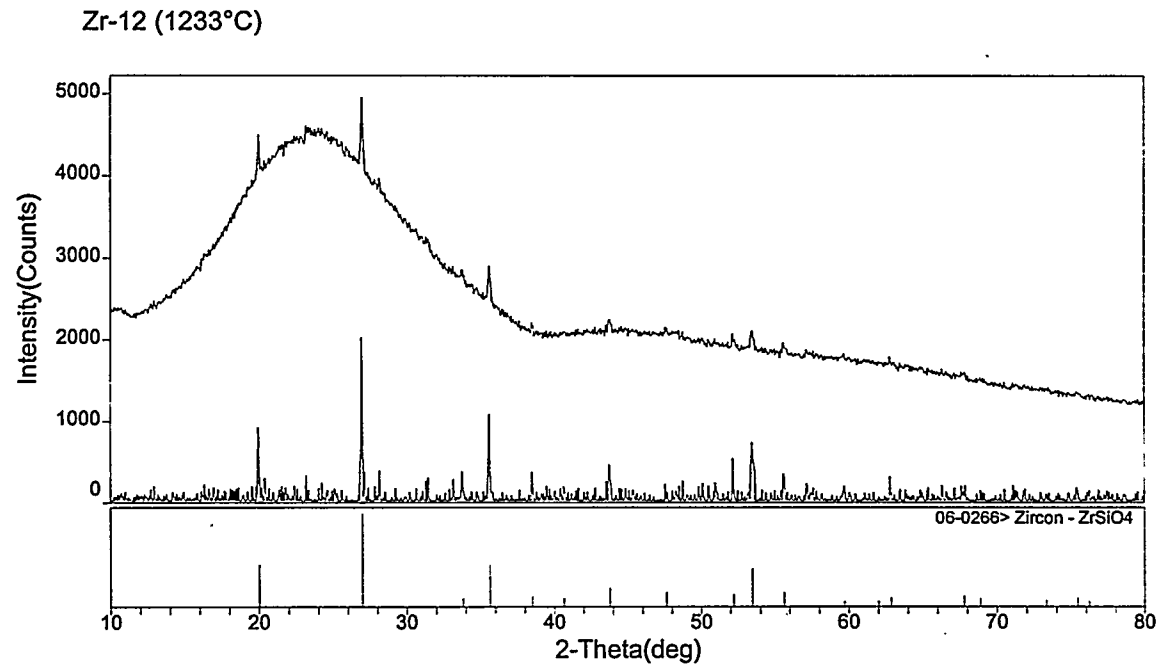


Figure A.4. XRD Trace of Zr-12 Glass Heat Treated at 1233°C for 24 h

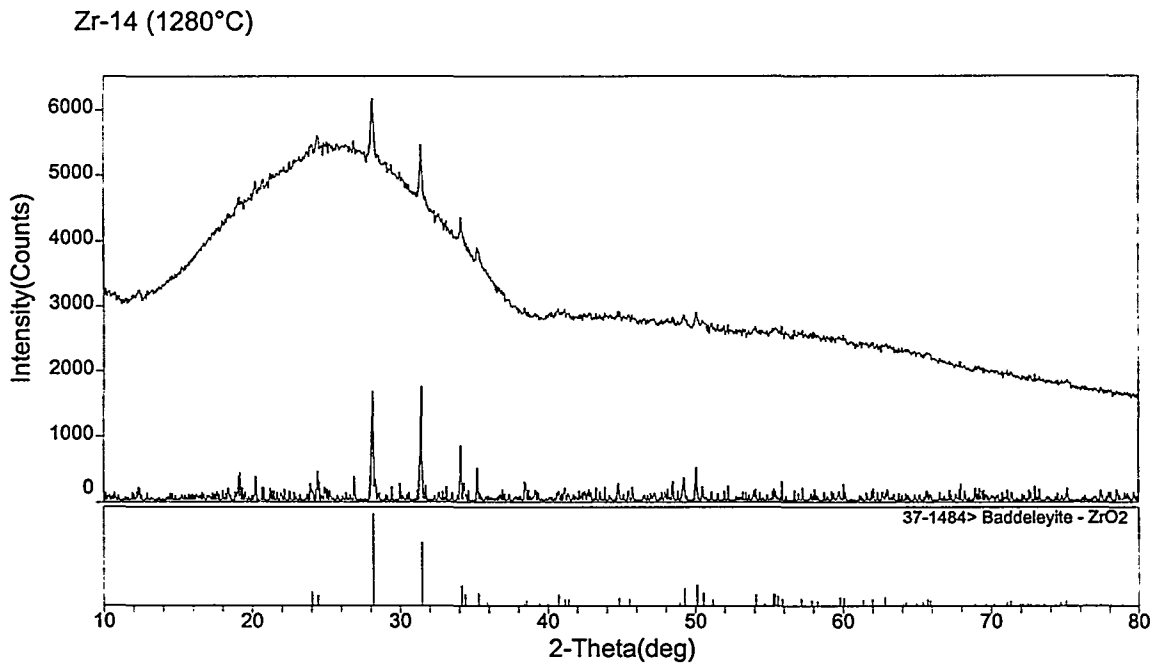


Figure A.5. XRD Trace of Zr-14 Glass Heat Treated at 1280°C for 24 h

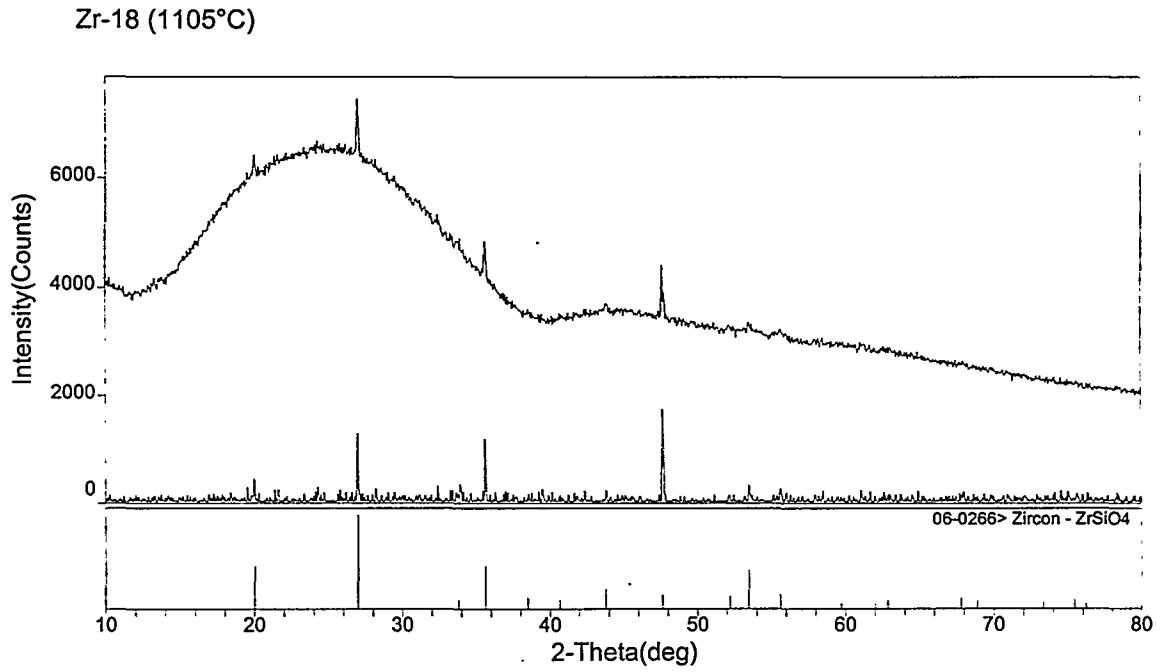


Figure A.6. XRD Trace of Zr-18 Glass Heat Treated at 1105°C for 24 h

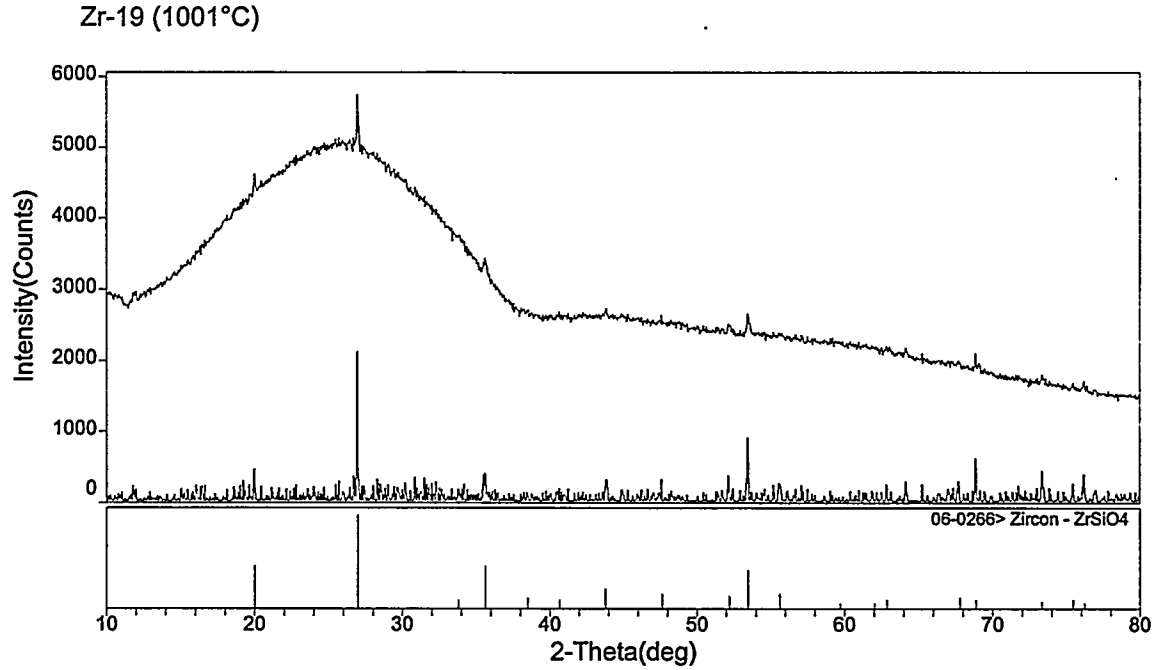


Figure A.7. XRD Trace of Zr-19 Glass Heat Treated at 1001°C for 24 h

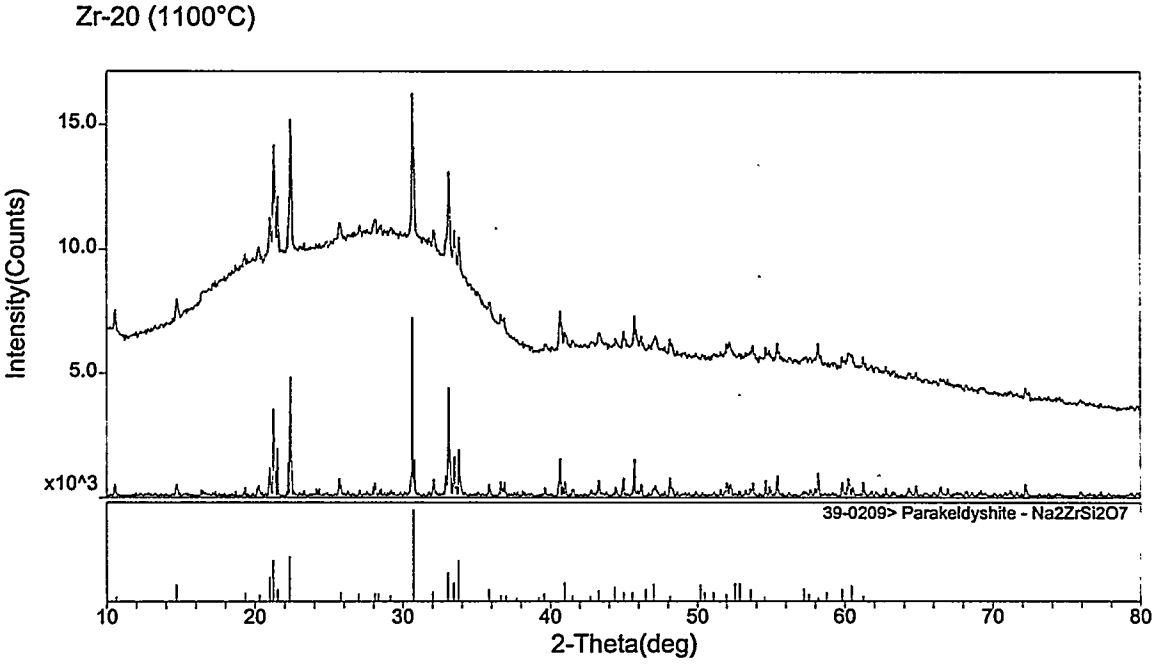


Figure A.8. XRD Trace of Zr-20 Glass Heat Treated at 1100°C for 24 h

Distribution

No. of Copies

OFFSITE

2 U.S. DOE / Office of Scientific and Technical Information

1 DOE Idaho Operations Office
750 DOE Place, MSIN: 1145
Idaho Falls, ID 83402
Attn: Kieth Lockie

13 Idaho National Engineering and Environmental Laboratory
P. O. Box 1625
Idaho Falls, ID 83415

Attn:		
	J. D. Herzog	MS 3710
	C. A. Musick (5)	MS 5218
	A. L. Olson	MS 5218
	W. B. Palmer	MS 3211
	J. Rindfleisch	MS 5218
	B. A. Scholes	MS 5218
	B. A. Staples	MS 5218
	R. D. Tillotson	MS 5218
	J. H. Valentine	MS 3211

14 Westinghouse Savannah River Co.
SRTC, Bldg 773-A
Aiken, South Carolina 29808

Attn:		
	D. A. Crowley	773-43A
	T. B. Edwards	773-41A
	J. R. Harbour	774-43A
	E. W. Holtzscheiter	773-A
	C. M. Jantzen	773-A
	J. C. Marra	773-43A
	S. L. Marra	704-T
	D. K. Peeler (5)	773-43A
	I. A. Reamer	773-A
	R. H. Spires	773-A

No. of Copies

ONSITE

2 DOE Richland Operations Office
P. O. Box 550, MS: K8-50
Richland, Washington 99352

Attn:		
	T. P. Pietrok	K8-50
	D. A. Brown	K8-50

2 PHMC, Hanford

Attn:		
	J. O. Honeyman	R2-58
	S. L. Lambert	R3-75

34 Pacific Northwest National Laboratory

W. F. Bonner	K9-14
J. L. Buelt	K9-09
J. V. Crum	K6-24
P. Hrma	K6-24
H. Li	K6-24
E. V. Morrey	P7-28
J. M. Perez	A0-21
L. M. Peurrung	K6-24
G. F. Piepel	K5-12
D. E. Smith	K6-24
M. J. Schweiger	K6-24
J. D. Vienna (10)	K6-24
B. J. Williams (TFA) (8)	K9-69
Technical Report Files (5)	P8-55