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Retention of Halogens in Waste Glass

P Hrma

May 2010

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

In spite of their potential roles as melting rate accelerators and foam breakers, halogens are generally viewed as troublesome components for glass processing. Of five halogens, F, Cl, Br, I, and At, all but At may occur in nuclear waste. A nuclear waste feed may contain up to 10 g of F, 4 g of Cl, and ≤100 mg of Br and I per kg of glass. The main concern is halogen volatility, producing hazardous fumes and particulates, and the radioactive ^{129}I isotope of 1.7×10^7-year half life. Because F and Cl are soluble in oxide glasses and tend to precipitate on cooling, they can be retained in the waste glass in the form of dissolved constituents or as dispersed crystalline inclusions.

This report compiles known halogen-retention data in both high-level waste (HLW) and low-activity waste (LAW) glasses. Because of its radioactivity, the main focus is on I. Available data on F and Cl were compiled for comparison. Though Br is present in nuclear wastes, it is usually ignored; no data on Br retention were found.

Reporting on decontamination factors for halogens from HLW processing began in nineteen eighties, starting with the pilot-scale melter PSCM-22 (1986) and continued with several other melter tests, PSCM-23 (1990), LFCM-8 (1994), and SSHTM-3 (1994). The F retention was found relatively stable at 75±9%, whereas the Cl retention varied from 75% to 85%. Only in PSCM-22 test, retention values for I were determined based on chemical analysis of glass, resulting in a value of 8%, which was lower than the value from the off-gas analysis (23%).

Because halides are water soluble, they mostly partition to the LAW portion in waste pretreatment. Therefore, from nineteen nineties onwards crucible studies were performed and melter tests were evaluated with respect to the halogen retention in LAW glasses.

Li et al. (1995) melted borosilicate LAW glasses at temperature 1300°C to 1450°C. The excess of F above the solubility limit formed CaF_2 and NaF crystals and the excess Cl formed spherical NaCl inclusions (crystallized NaCl droplets). In 1996, Feng et al. found that LAW glasses heated for 2 h at 1130 to 1380°C with 4-9% CaO retained 100% of F, whereas glasses with ≤2% CaO retained only 85% and 77% F. The retention of Cl was 0.52±0.14%. Crichton et al. (1995) observed that F and Cl volatilized from the melt surface, but excess Cl separated into liquid NaCl inclusions that rose to the melt surface by buoyancy, where they made a segregated evaporating layer. Iodine created gaseous I_2 bubbles that rose to the melt surface, where they burst. In addition, iodine evaporates from the feed before it becomes glass.

According to by Whyatt et al., who compiled and evaluated various LAW vitrification tests in 1996, about~50% of Cl and 20% of I were retained in the glass processed by feeding slurry into a continuous Joule-heated melter. In 2002 and 2003, Matlack et al. and Lee André reported data on the retention of halogens in DuraMelter 100 containing 115−120 kg of glass, possessing the melt surface area of 0.108 m^2, and operating at the average melt temperature of 1150°C. Both glass offgas were analyzed. The F retention was consistently high (94%) and the Cl retention was ~60%, regardless the glass composition and the targeted halogen content. The targeted fraction of I was 0.1 mass% for all tests and the analyzed fractions of I in glass varied from <0.01 to 0.04 mass%, resulting in retention values of 23±10%. When the melter was idled for 2 months, the Cl concentration in glass dropped from 0.0022 to 0.0009. Also, the Cl retention decrease by ~1% for every 1-L/min increase in bubbling.

Generally, provided that the melter type and melting conditions are equal, the retention ratios of halogens linearly decrease with the halogen ionic radii and increase with the sodium halide melting temperatures, even though, as Crichton et al. observed, different mechanism of liberation from glass operates for different halogens.

Crucible studies are unreliable as predictors for the retention of halogens in continuous melters. Consistent data are obtainable during the normal mode of melter operation. These data vary little with glass composition within the LAW composition region and the anticipated halogen content. The retention ratios were 94% for F, 58% for Cl, and ~20% for I. If I losses that occur before the melter feed is converted to glass were preventable, higher concentrations of I would probably be retained in waste glass.

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1.0 Introduction

Of five halogens (F, Cl, Br, I, and At), only F was thoroughly explored in connection with commercial glass making. Some attention was also paid to Cl because NaCl is a fining agent. Volf (1984) only briefly mentions additions of bromides and iodides that can also function as fining agents. Additionally, halogens accelerate batch melting reactions.

Although additions of halides to nuclear waste feeds were briefly considered as melt-rate accelerators and foam breakers, halogens are generally viewed as troublesome components. Typical nuclear waste feeds contain up to 10 g of F and 4 g of Cl per kg of glass. The fractions of Br and I are even smaller, ≤100 mg per kg of glass. When halogens are present in nuclear wastes, the main concern is their volatility because halogen-containing fumes and particulates are hazardous. Moreover, ^{129}I is a radioactive isotope with a 1.7×10^7-year half life.

Commercial glass experience shows that F and Cl are soluble in oxide glasses to a limited extent. Because their solubility decreases as the melt temperature decreases, fluorides and chlorides tend to precipitate on cooling, producing opacity. Consequently, F and Cl can be retained in the waste glass in the form of a dissolved constituent or as a dispersed crystalline phase.

The response of halogens to waste glass processing is evaluated differently by materials scientists and by chemical engineers. Materials scientists are concerned with the glass product in terms of its chemical and phase composition, whereas chemical engineers are interested in the efficiency of melters and offgas equipment in removing halogens from liquid and gaseous streams into solid phases.

Materials scientists examine the effect of glass composition and the method of glass preparation on halogen retention with the aim to maximize the *i*-th halogen retention ratio, R_i, defined as

$$R_i = \frac{g_{ir}}{g_{i0}} \tag{1.1}$$

where g_{i0} is the *i*-th halogen nominal (or target) mass fraction in glass (the mass fraction if *i*-th halogen that would be present in glass if the total amount added with the feed were retained), and g_{ir} is the *i*-th halogen mass fraction in glass actually retained (as determined by chemical analysis of glass).

Since $g_{i0} \geq g_{ir}$, then $R_i \leq 1$. The difference between g_{i0} and g_{ir} is caused by losses to the atmosphere due to volatility. Values of $R_i \geq 1$ indicate an analytical error, either of the waste or of the glass; analytical errors are likely to occur in determining extremely minute concentrations, such as those of I in glass.

Chemical engineers view a glass melter as a reactor to which feed continuously enters and from which two streams exit, namely, molten glass and offgas. The efficiency of trapping a contaminant component in glass is measured in terms of the *i*-th component decontamination factor, D_{Fi}; defined as the ratio of the mass rate of flow of this component into the melter (N_{0i}) and its mass rate of flow in offgas exiting the melter (N_{gi}). Hence,

$$D_{Fi} = \frac{N_{0i}}{N_{gi}} \tag{1.2}$$

This definition makes sense only when a steady state is established, i.e., the streams are constant in magnitude and composition. Then $N_{0i} \geq N_{gi}$, and thus $D_{Fi} \geq 1$.

For a steady state, $N_{0i} = g_{i0}N_G$ and $N_{gi} = N_{0i} - g_{ir}N_G$, where N_G is the mass rate of flow of glass exiting the melter. Equation (1.2) can be expressed in the form

$$D_{Fi} = \frac{g_{i0}}{g_{i0} + g_{ir}} \tag{1.3}$$

Then, by Equation (1.1), we obtain

$$R_i = 1 - \frac{1}{D_{Fi}} \tag{1.4}$$

Equation (1.4) allows converting the D_{Fi} values, commonly reported in melter test protocols, to the retention ratios. In some reports, D_{Fi} values are determined from offgas data. The mass balance for an *i*-th contaminant can be written as

$$g_{i0} = g_{ir} + \sum_{j-1}^{K} g_{ij} + g_{ie} \tag{1.5}$$

where g_{ij} is the *i*-th component fraction trapped in *j*-th offgas equipment, g_{ie} is the *i*-th component fraction that escaped undetected (the fractions are all related to the amount of glass produced), and K is the number of offgas devices. Eliminating g_{ir} from Equations (1.1) and (1.5) leads to the expression

$$R_i = 1 - \sum_{1}^{K} \frac{g_{ij}}{g_{i0}} - \frac{g_{ie}}{g_{i0}} \tag{1.6}$$

If glass analysis is not performed (or only electropositive elements are determined and halogens are ignored), R_i can be obtained from Equation (1.6) provided that $g_{ie} << g_{i0}$. When the reported D_{Fi} values are determined from offgas data, it is important to check the overall mass balance of the contaminant to make certain that no unaccounted losses occurred, i.e., that indeed $g_{ie} << g_{i0}$.

The retention ratio of a component is different from its solubility limit. The solubility limit is defined as the fraction of component at a local equilibrium or with a gaseous atmosphere. However, the glassmaking process generally does not allow molten glass to reach equilibrium. While the portion of a component dissolved in the amorphous phase (or amorphous phases if phase separation occurs, e.g., in the presence of excess phosphates) may be undersaturated (i.e., below the solubility limit), a substantial portion may simultaneously exist in the form of inclusions (i.e., inhomogeneities). Therefore, the retention ratio is a dynamic quantity that depends on the glass-making conditions.

Glass-making conditions are determined by melter design and operation. A high surface-to-volume ratio and extensive convection promote volatilization. Convection in the melter can be driven by buoyancy or surface forces (natural convection) or by stirring or bubbling (forced convection). The surface-to-volume ratio is influenced by the degree of melt surface coverage by the cold cap (unreacted feed) and by the degree of process stability (the frequency and length of idling periods). The extensive free melt surface greatly influences losses to offgas. Inclusions tend to segregate from molten glass during idling periods. For example, chlorides segregated to the melt surface readily evaporate. The rate of volatilization is affected by the furnace atmosphere, whether dry or humid, moving or stagnant. The mode of feed preparation is also important because halides can evaporate even from the feed before it is converted to glass.

The main objective of this report is to compile the known data regarding the retention of halogens, mainly I, in both high-level waste (HLW) and low-activity waste (LAW) glasses. The main focus is on I because of its radioactivity. Available data on F and Cl were compiled for comparison. Though Br is present in nuclear wastes, it is usually ignored; no data on Br retention were found. The following sections summarize retention data for Hanford HLW and LAW glasses processed in both laboratory crucibles and in pilot-scale melters.

2.0 High-Level Waste Vitrification Studies

Reporting on decontamination factors for halogens, including I, began in the 1980s, starting with the pilot-scale melter PSCM-22 (Perez and Nakaoka 1986). The melter vitrified a simulated HLW. The loading fraction of waste in glass was 0.25, the melt volume in the melter was 270 L, the average melt temperature was 1150°C, and the melter operated for 384 h, producing 6.25 Mg of glass. Table 2.1 shows the retention values for F, Cl, and I. The g_{i0} values were calculated from the waste composition and the waste loading based on an unpublished report compiled by Nakaoka (see the Table 2.1 footnote). Perez and Nakaoka (1986) list D_{Fi} values for individual glass components. The R_i values were calculated using Equation (1.4), and the g_{ir} values were back-calculated using Equation (1.1).

Table 2.1. Retention Data for Halogens from a Pilot-Scale Melter Experiment (PSCM-22)

	g_{i0}	g_{ir}	D_{Fi}	R_i
F[(a)]	0.0475	0.0327	3.2	0.69
Cl[(a)(b)]	0.0250	0.0058	1.3	0.23
I	0.0025	0.0006	1.3	0.23

(a) g_{i0} values for the Reference Feed as reported in Nakaoka et al. (1985). Pilot-Scale Ceramic Melter Experiment, HWVP-86-V1124A, Pacific Northwest Laboratory, Richland, Washington.

(b) Cl was present in Fe_2O_3 as an $FeCl_3$ impurity.

Decontamination factors as recorded in various melter testing reports are summarized in Table 2.2. With the exception of PSCM-22, no I data were obtained for the melter experiments listed in Table 2.2. The R_i values were obtained from the reported D_{Fi} values using Equation (4). The D_{Fi} values themselves were estimated from offgas analyses assuming zero undetected amounts of halogens.

Table 2.2. Retention Ratios for Halogens Based on Offgas Data

	F	Cl	Report
LFCM-8	0.75	0.75	Perez et at. (1994a)
PSCM-22	0.69	0.23	Perez and Nakaoka (1986)
PSCM-23	0.89	0.85	Goles et al. (1990)
SSHTM-3(a)	0.67	0.80	Perez et at. (1994b)

(a) Melter designed for LAW vitrification.

As Table 2.2 shows, the F retention was relatively stable at 75±9%, whereas the Cl retention varied widely from 23% to 85%. However, the PDCM-22 test, in which only 23% Cl was retained in glass, is exceptional in two ways: Cl was not an intentional waste component, but an impurity in Fe_2O_3, and the simulated waste was made of hydroxides instead of nitrates. It is possible that a large portion of Cl was lost from the unmelted hydroxide feed, whereas the nitrate feeds would preserve halides as dissolved components in molten nitrates. Nitrates begin to melt at temperatures as low as 300°C and are decomposed by 750°C. It is likely that hydroxides are first converted to oxides that are later gradually incorporated into the alkali-borosilicate melt. This may occur at approximately 900°C, thus giving halogens ample opportunity to escape. Apart from the difference between PSCM-22 and -23 melter experiments in the feed makeup, the PSCM-23 test had higher process stability, resulting from a better cold-cap behavior, and hence provided a smaller free surface for volatilization.

There are offgas data that may not provide precise retention values unless $g_{ie} << g_{i0}$, i.e., when some vaporized halogens, especially I, remain unaccounted for. To obtain values based on chemical analysis of glass, Goles (1989) performed pyrohydrolytic-ion chromatographic (PIC) analysis of glass products generated in PSCM-22 and -23 melter experiments. In the PIC method, a glass powder was hydrolyzed in a stream of Ar (0.5 L/min) and H_2O (1.5 mL/min) at 1200°C. The halogens were trapped in an aqueous scrubber, and their concentrations were determined with ion chromatography. Table 2.3 lists the results. The R_{Cl} values are in good agreement with those estimated from offgas analyses (Table 2.2). The R_F values are in excellent agreement only for PSCM-23.

Table 2.3. Retention Ratios for Halogens Based on Glass Analysis

	R_i		
	F	Cl	I
PSCM-22	0.27	0.19	0.08
PSCM-23	0.90	0.85	

3.0 Low-Activity Waste Vitrification Studies

Because halides are water soluble, most of the halides from the waste partition to the LAW portion. Consequently, greater attention was paid to retention of halides, especially I, in LAW glasses. Both crucible studies were performed, and melter tests were carefully evaluated with respect to their halogen retention efficiency.

3.1 Crucible studies

Feng et al. (1996) performed crucible studies of S, P, F, and Cl retention in six LAW glasses. Concentrations of halogens in glass were measured by X-ray fluorescence (XRF) analysis. All glasses had the same nominal mass fractions of halogens: $g_{\mathrm{F}0} = 0.0082$, $g_{\mathrm{Cl}0} = 0.0064$, and $g_{\mathrm{I}0} = 0.0013$. The analyzed fractions and retention ratios for F and Cl are summarized in Table 3.1; no analysis was performed for I.

Table 3.1. Retention of F and Cl in LDM Glasses

		F		Cl	
Glass ID	T_M °C	$g_{\mathrm{F}r}$	R_F	$g_{\mathrm{Cl}r}$	R_Cl
LDM-0912	1381	0.0082	1.00	0.0030	0.47
LDM-5412	1290	0.0099	1.21	0.0030	0.47
LDM-1	1310	0.0070	0.85	0.0034	0.53
LDM-2	1320	0.0089	1.09	0.0045	0.70
LDM-3	1410	0.0063	0.77	0.0019	0.30
LDM-4	1130	0.0113	1.38	0.0050	0.78

As Table 3.1 shows, all F was retained in four out of six glasses (values of $R_i \geq 1$ were caused by an analytical error). These four glasses contained 4 to 9% CaO. In glasses with a lower CaO content (2% LDM-1 and 0% in LDM-3), only 85% and 77% F was retained. The retention of Cl was nearly half or the nominal value ($R_\mathrm{Cl} = 0.49 \pm 0.18$).

In a similar study, Li (1995) added NaF and NaCl to Glass L6-5412 and measured both the mass loss due to volatilization and the maximum concentrations of F and Cl that remained dissolved in the glass without residual microscopic inclusions. For each melt, the batch mass was 130 g, and the melt surface-to-volume ratio was 0.2 mm^{-1}. The melting temperature varied from 1300°C to 1450°C, and the dwell time was 2 h.

The mass loss of glass spiked with F or Cl grew in proportion to the halogen fraction (g_{i0}). No attempt was made to determine the volatile species; they probably included halides and borates. Table 3.2 shows that the mass loss per halogen addition had a mild tendency to increase with increasing temperature.

Table 3.2 also shows the solubilities. At fractions above the solubility limit, the excess F formed CaF_2 and NaF crystals. The excess Cl formed spherical NaCl inclusions (crystallized NaCl droplets). Solubilities were also measured for Glass L4-9012 treated at 1350°C for 2 h. In this Ca-free glass, the dissolved fraction of F, 0.0132, was limited by NaF solubility and was higher than in Glass L6-5412 containing 4 mass% CaO; the Cl solubility, 0.0049, was slightly lower than in Glass L6-5412.

Table 3.2. Rates of Volatilization and Solubility Limits of F and Cl in Glass L6-5412, Data by Li (1995)

	Mass Loss Rate g glass/g X		Solubility Limit g X/g glass	
T_M (°C)	F	Cl	F	Cl
1300	0.7	1.6	0.0077	0.0056
1350	0.8	1.8	0.0092	0.0057
1400	0.8	2.0	0.0091	0.0052

X stands for halogen.

In-depth studies of F, Cl, and I solubilities and volatilization were performed by Crichton et al. (1995a and 1995b). They used the same Glass L6-5412 as Li (1995). Unlike Li, who used XRF, they measured halogen concentrations in glass with scanning electron microscopy (SEM) energy-dispersive spectroscopy (EDS) analysis. The temperature varied from 1100°C to1400°C and the dwell time was from 0.5 h to 2 h.

The mass loss of glasses spiked with F was a parabolic function of time (i.e., the mass loss increased linearly with $t^{1/2}$) regardless of F concentration in the glass. A similar behavior was observed when glass was spiked with ≤1.2 mass% Cl; at higher concentrations, the mass loss was initially a linear function of time, indicating evaporation of a segregated layer of molten NaCl on the glass melt surface. Almost all I was lost in 10 min at 1300°C. The volatilization of I was observed at temperatures as low as 900°C.

The maximum F addition that did not cause opalescence was 0.028 for glass melted at 1100°C; the analyzed content, in mass fraction, was 0.0279. This value is very much in excess of Li's result (0.0077 at 1300°C) shown in Table 3.2, especially considering that the solubility limit for F decreases rather than increases with decreasing temperature. Because the analytical methods were different in each study and the rates of quenching have not been quantified, it is difficult to assess which value is more correct.

The maximum Cl addition, in mass fraction, that did not cause opalescence was 0.008. The measured fraction was 0.0066, a value comparable with Li's data shown in Table 3.2. The difference in the added and retained Cl was attributed to volatilization.

The maximum I addition, in mass fraction, that did not cause gaseous I_2 to form bubbles was 0.0002. Interestingly, the SEM-EDS-measured fraction of I in glass with I bubbles was 0.0050 near the bubbles and 0.0082 in the bulk glass, indicating that 0.8 mass% I could dissolve in glass. However, this oversaturated concentration decayed, by evaporation, to 0.02 mass%.

Crichton et al. (1995a and 1995b) observed a remarkable difference in the modes of transport of halogens from glass to the atmosphere. As mentioned above, F evaporates from the melt surface, whereas Cl, apart from direct volatilization, is separated into liquid NaCl inclusions that rise to the melt surface by buoyancy where they make a segregated evaporating layer. Finally, I creates I_2 bubbles that rise to the melt surface where they burst.

However, halides may evaporate even before the batch is converted to glass. This is least likely for fluorides; NaF melts at 996°C and thus, assuming that glass melt becomes connected at a temperature around 900°C, all F is likely to be incorporated into glass. NaCl is more likely to evaporate from the batch because NaCl melts at 801°C. Finally, NaI, melting at 660°C, is most likely to begin to vaporize before its incorporation in the glass melt.

The low retention of I in glass can be attributed to its evaporation from the unmelted batch and its low solubility in glass. Even though iodides may be preserved as minor components in the nitrate melt until the glass-forming melt becomes connected and the partial pressure of I_2 in gas bubbles may be high, a large portion of I is likely to escape from batch regardless of the processing method.

3.2 Melter Studies

Various technologies were tested to process glasses that incorporated simulated LAW in a series of pilot-scale experiments. Volatilities of feed components were measured and reported by Whyatt et al. (1996). To determine volatility losses more accurately, the authors corrected the measured g_{ir} values by multiplying them by a factor determined from the nominal-to-measured ratio of an abundant non-volatile component, such as SiO_2. Table 3.3 presents the results.

Table 3.3. Retention Ratios for LAW Glass Processed with Different Technologies

Melter	Feed	F	Cl	I
Low-temperature, Inconel electrodes	Slurry	0.47	0.52	0.18
High-temperature, Mo electrodes	Slurry	0.85	0.36	0.17
High-temperature, Mo electrodes	Pellets	0.99	0.93	0.90
Carbon-electrodes	Calcine	0.09	0.18	0.05
Plasma torch-fired cupola	Slurry	0.09	0.12	0.02
Gas-fired cyclone combustion	Slurry	0.08	0.13	0.06

Based on these data, one can estimate that about 20% of I is retained in the glass processed by feeding a slurry into a continuous Joule-heated melter. The data show that I retention is lower than Cl retention ($^1/_3$ to $^1/_2$ for slurry-fed Joule-heated melters). Note the remarkable high retentions of halides in the wetted pellet-fed high-temperature continuous electric melter (the melter was designed and operated by Envitco, Inc., a company based in Toledo, Ohio).

Matlack et al. (2002a-d, 2003a and 2003b) and André (2003) reported a wealth of data on the retention of halogens in glass for both laboratory crucibles and a pilot-scale melter. The melter (DuraMelter 100) contains 115 to 120 kg of glass, the melt surface area is 0.108 m^2, and the average melt temperature is 1150°C.

The results for halogen retention are summarized in Table 3.4 through Table 3.7 and Figure 3.1 through Figure 3.4. Retention ratios listed in Table 3.4 and Table 3.5 were determined from glass analyses, and those listed in Table 3.6 were obtained from offgas data.

Table 3.4. Retention Data for Cl and I, Crucible Test Results (g_i values are in mass%)

Report No.	Test	g_{Cl0}	g_{Clr}	R_{Cl}	g_{I0}	$g_{\mathrm{I}r}$	R_{I}
VSL-02R62N0-1	LAW A3-1	0.30	0.11	0.37	NA	NA	NA
	LAW A3-2	0.37	0.04	0.11	NA	NA	NA

Report No.	Test	g_{Cl0}	g_{Clr}	R_{Cl}	g_{I0}	$g_{\mathrm{I}r}$	R_{I}
	LAW A3-3	0.33	0.10	0.29	NA	NA	NA
VSL-02R62N0-2	LAW C1-1	0.07	0.04	0.61	NA	NA	NA
	LAW C1-2	0.09	0.02	0.27	NA	NA	NA
	LAW C1-3	0.09	0.02	0.18	NA	NA	NA
VSL-02R62N0-3	LAW A2(-15%)	0.11	0.05	0.45	0.10	0.01	0.10
	LAW A2(+15%)	0.14	0.06	0.43	0.10	0.01	0.10
	LAW A2	0.13	0.03	0.23	0.10	0.01	0.10
VSL-02R62N0-4	LAW A1(-15%)	0.49	0.21	0.43	0.10	0.02	0.20
	LAW A1(+15%)	0.62	0.13	0.21	0.10	0.01	0.10
VSL-02R62N0-6	LAW C1	0.14	0.04	0.29	0.10	<0.01	<0.10
	LAW A1	1.17	0.46	0.39	0.10	0.02	0.20
VSL-03R3410-1	LAW A2	0.42	0.06	0.14	0.10	0.01	0.10
	LAW B1	0.02	0.02	1.00	0.10	0.00	0.00
Average				0.36			0.11

NA: not analyzed

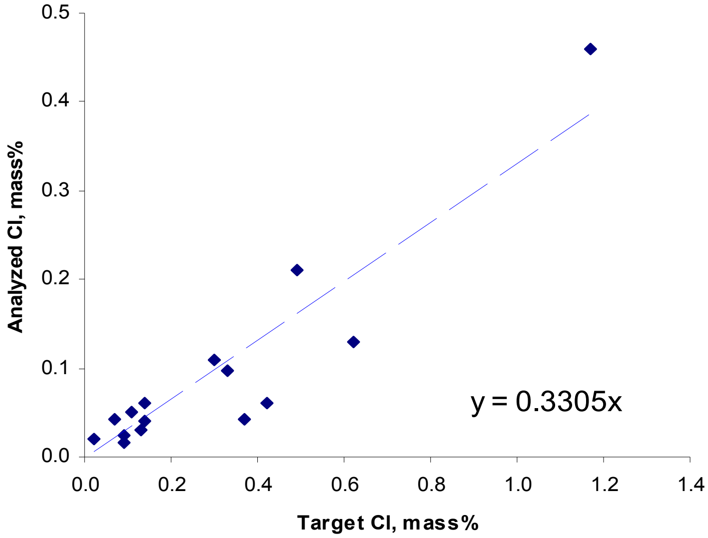


Figure 3.1. Chlorine Retention in Crucible Tests

As Table 3.4 and Figure 3.1 show, crucible melts retained 1/3 of Cl and 10–20% of I. These retention values were lower than those achieved in the melter. According to Table 3.5 and Figure 3.2, the Cl retention in the melter was ~60% and I retention was ~20%. The larger volatilization losses of halogens from laboratory crucible melts can be attributed to their high surface-to-volume ratios.

Table 3.5. Retention Data for Cl and I, DuraMelter 100 Test Results (all g_i values are in mass%)

Report No.	Test	g_{Cl0}	g_{Clr}	R_{Cl}	g_{I0}	$g_{\mathrm{I}r}$	R_{I}
VSL-02R62N0-1(a)	LAW A3-1	0.30	0.21	0.69	NA	NA	NA
	LAW A3-2	0.37	0.24	0.65	NA	NA	NA
	LAW A3-3(b)	0.33	0.21	0.63	NA	NA	NA
VSL-02R62N0-2(c)	LAW C1-1	0.07	0.04	0.63	NA	NA	NA

Report No.	Test	g_{Cl0}	$g_{\mathrm{Cl}r}$	R_{Cl}	g_{I0}	$g_{\mathrm{I}r}$	R_{I}
	LAW C1-2	0.09	0.06	0.67	NA	NA	NA
	LAW C1-3	0.09	0.06	0.70	NA	NA	NA
VSL-02R62N0-3(d)	LAW A2(-15%)	0.11	0.07	0.64	0.10	0.02	0.20
	LAW A2(+15%)	0.14	0.07	0.50	0.10	0.02	0.20
	LAW A2	0.13	0.07	0.54	0.10	0.01	0.10
VSL-02R62N0-4(e)	LAW A1(-15%)	0.49	0.28	0.57	0.10	0.04	0.40
	LAW A1(+15%)	0.62	0.34	0.55	0.10	0.02	0.20
VSL-02R62N0-6(f)	LAW C1	0.14	0.09	0.64	0.10	<0.01	<0.10
	LAW A1	1.17	0.67	0.57	0.10	0.03	0.30
VSL-03R3410-1(g)	LAW A2	0.42	0.24	0.57	0.10	0.03	0.30
	LAW B1	0.02	0.02	1.00	0.10	0.01	0.10
Average				0.64			0.23
St. Deviation				0.12			0.10

(a)Cl concentration decreased during idling and increased during subsequent continuous processing; halides escaped in the form of gas.

(b)XRF average for tests 3B and 3C.

(c)By FTIR analysis, Cl and F escaped in the form of HF and HCl; I in the form of gas.

(d)Cl and F escaped in the form of particulates, I in the form of gas.

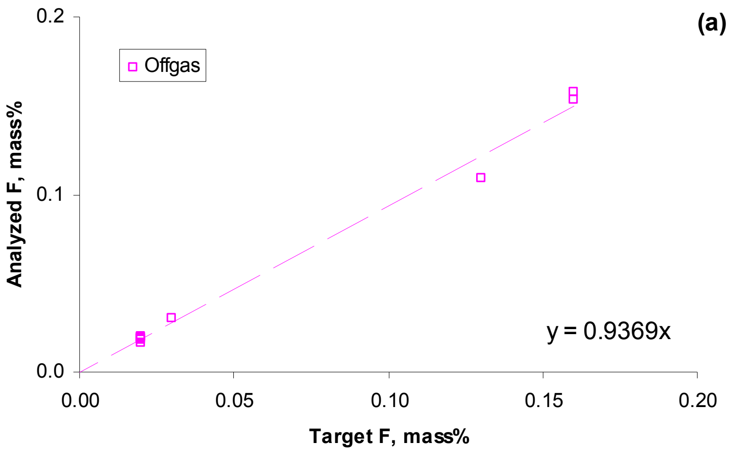
(e)Most Cl and I escaped in the form of particulates.

(f)Bubbling affects Cl retention; see Table 3.7. Cl was trapped as particulate emission; I was exclusively gaseous.

(g)30-h idling period caused a dip in Cl concentration (from 0.25 to 0.16%); I retention increases with alkali content; Cl was nearly equally divided between gas and particulate emissions, and I was almost exclusively gaseous.

NA: not analyzed

Figure 3.2 compares glass analysis data with offgas data. Only offgas-based data are available for F (Figure 3.2a). Their scatter is low, and the F retention is consistently high (94%), regardless of glass composition and the targeted F content.



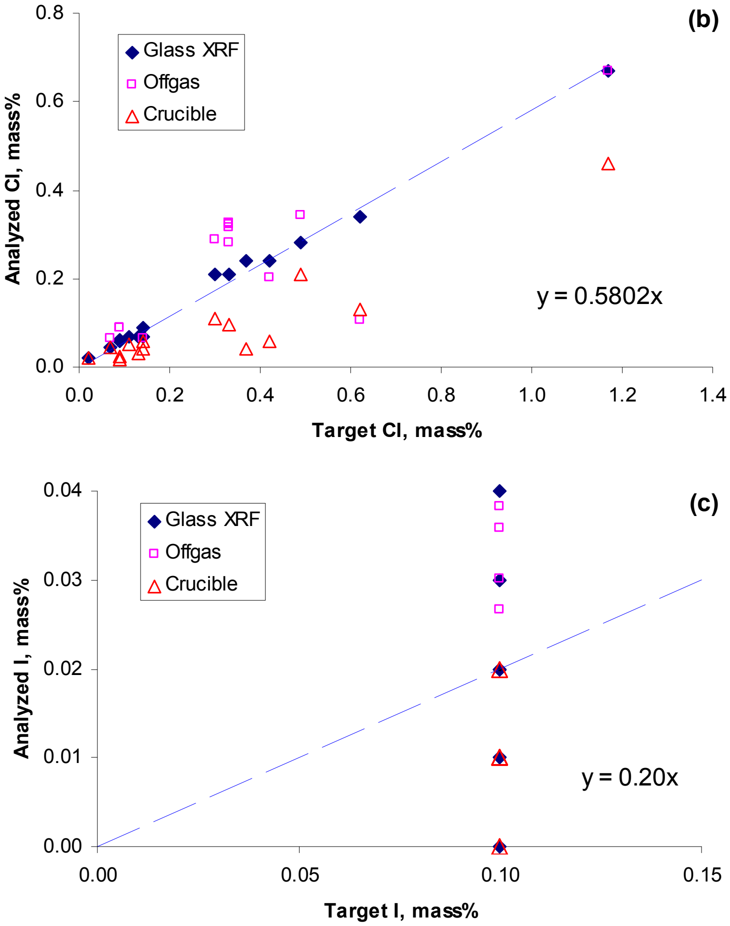


Figure 3.2. Retention of Halogens in DuraMelter 100 Tests

The plot of $g_{\mathrm{Cl}r}$ versus $g_{\mathrm{Cl}0}$ values (Figure 3.2b) shows little scatter for glass analysis-based data. The trendline through these data indicates that 58% of Cl was retained in glass regardless of composition variation (for example, Na_2O content varied from 6 mass% to 21 mass%) and regardless of the targeted Cl content. The scatter of offgas-based data is large, but the data points are well distributed around the trendline representing the glass analysis-based results. The crucible Cl retention data, apart from having low values, are also widely scattered. The average retention ratio for Cl is 64%, based on glass analysis (Table 3.5), and 79%, based on offgas analysis (Table 3.6).

The target fraction ($g_{\mathrm{I}0}$) of I was 0.1 mass% for all tests. As Figure 3.2c shows, I retention data are widely scattered. The trendline in Figure 3.2c indicates 20% retention for glass analysis; the average value (Table 3.5) is 23%. The wide scatter of the results is caused by the very low $g_{\mathrm{I}r}$ values (<0.01–0.04 mass% of I in glass). Offgas data indicate an apparent higher I retention (49%), but these high values are misleading because a fraction of I escaped detection (the I mass balance did not come up to 100%).

Table 3.6. Retention Ratios Based on DuraMelter 100 Test Offgas Data

	Test	F	Cl	I
VSL-02R62N0-1	LAW A3-1	0.84	0.96	0.44
	LAW A3-2	1.00	NA	0.41
	LAW A3-3A	0.91	0.98	0.23
	LAW A3-3B	0.98	0.99	0.82
	LAW A3-3C	0.94	0.96	0.41
	LAW A3-3D	0.98	0.98	0.85
VSL-02R62N0-2	LAW C1-1	0.84	0.91	0.23
	LAW C1-2	0.98	1.00	0.60
	LAW C1-3	0.96	1.00	0.38
VSL-02R62N0-4	LAW A1(-15%)	NA	0.70	0.84
	LAW A1(+15%)	NA	0.17	0.38
VSL-02R62N0-6	LAW C1	NA	0.46	0.30
	LAW A1	NA	0.57	0.27
VSL-03R3410-1	LAW A2	NA	0.48	0.36
	LAW B1	NA	0.00	0.00
TRP-PLT-062(a)	LAW A1	0.96	0.85	0.84
Average		0.94	0.79	0.49
St. deviation		0.06	0.27	0.24

(a) Gaseous species were HF, HCl, HJ, F_2 (traces), Cl_2 (traces), and I_2 (most).

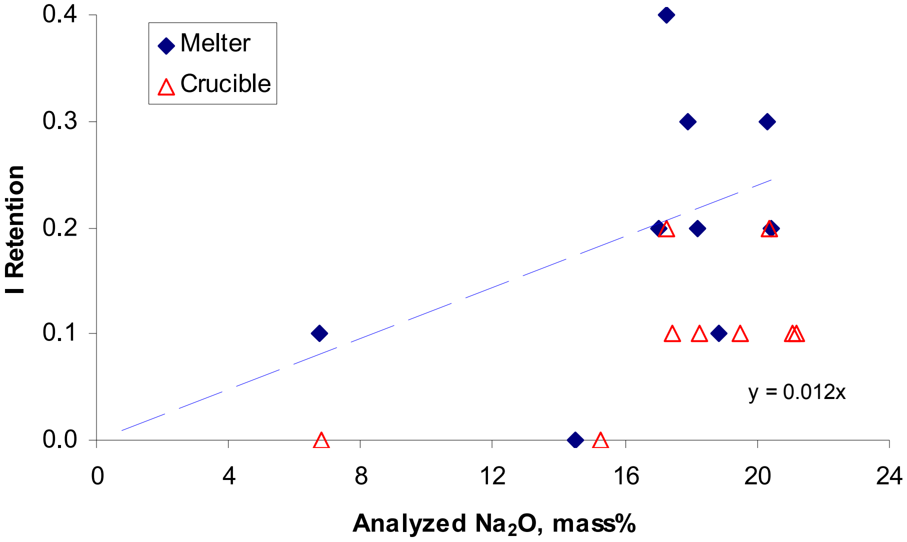


Figure 3.3. Iodine Retention Versus Na_2O Content in Glass

Other variables that affect the retention of halogens are glass composition, temperature, time, and bubbling. The retention of I can also be affected by glass redox because, as Crichton et al. (1995a and 1995b) observed, I is released in the form of I_2 vapors.

As Figure 3.2 indicates, glass composition did not affect F and Cl retention, at least within the LAW composition region. Regarding I, Matlack et al. (2002a-d, 2003a and 2003b) claim that I retention increases with increasing content of alkalis in the glass. This conclusion is based on one data point measured for a glass containing 6 mass% Na_2O. As Figure 3.3 shows, evidence for such a conclusion is weak.

Because the glass processing temperature was ~1150°C, nearly constant for all tests, its effect on halogen retention was not observed. However, the impact of time was evidenced in sharp decreases in Cl concentration in glass after the melter was idled; for example, 2-month idling resulted in a decrease of Cl mass fraction from 0.0022 to 0.0009, indicating that tiny NaCl inclusions had enough time to ascend to the melt surface where they evaporated.

In a test with varying rates of bubbling, the Cl retention showed a tendency to decrease as the bubbling rate increased (Table 3.7). The trendline in Figure 3.4 shows that the Cl retention decreased by approximately 1% when the rate of bubbling increased by 1 L/min.

Table 3.7. Effect of Rate of Bubbling on Cl Retention for LAW A1 Sub-Envelope

Bubbling L/min	g_{ir}	*R*
1.9	0.94	0.80
9.0	0.67	0.57
16.0	0.76	0.65

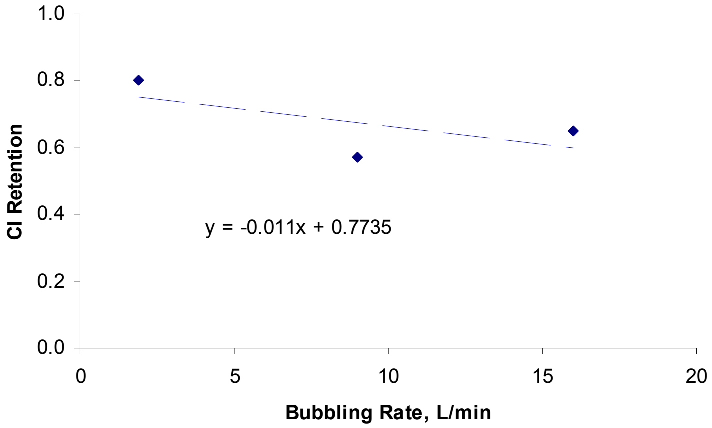


Figure 3.4. Chlorine Retention Versus Bubbling Rate

The oxidation of I^- to I_2 can proceed as the a reaction with Fe(III) as follows:

$$2NaI + Fe_2O_3 = I_2 + 2FeO + Na_2O$$

According to this reaction, reduced glass promotes I retention. Unfortunately, there are not enough data to support this hypothesis. In tests reported by Matlack et al. (2002a-d, 2003a and 2003b), glasses were either oxidized (Fe(II)/Fe < 0.008, where 0.008 is the detection limit for the colorimetric method used) or, in a series of tests where Fe(II)/Fe was increased up to 0.645, I concentration was not measured (Matlack et al. 2002a). The only exception is test LAW A1(-15%) reported in Matlack et al. (2002d) where Fe(II)/Fe = 0.06. As Table 3.5 shows, the I retention for this reduced glass was the highest based on glass analysis data (0.4); according to Table 3.6, the offgas-based retention value was also one of the highest (0.84).

The retention ratios indicated by the slopes of the trendlines in Figure 3.2 represent normal conditions of melter operation and are based on a large number of data. Therefore, they should be considered representative for the behavior of halides in DuraMelter 100. These characteristic retention ratios are summarized in Table 3.8. They were plotted against halogen ionic radii and sodium halide melting temperatures in Figure 3.5. The relatively good linear correlation allowed estimating a retention ratio for Br by interpolation. Its value, shown in Table 3.8, indicates that 42% Br can be retained in glass processed in DuraMelter 100.

Table 3.8. DuraMelter 100 Retention Rates, Ionic Radii (r), and NaX Melting Temperatures (T_m)

	R_i	r, nm	T_m, °C
F	0.9396	0.133	996
Cl	0.5802	0.181	801
Br	*0.4209*	0.220	660
I	0.2000	0.196	747

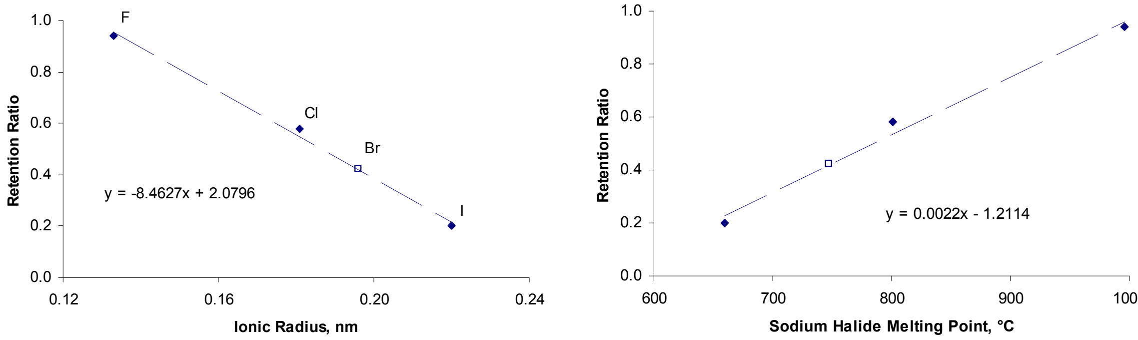


Figure 3.5. Halogen Retention Ration Versus Ionic Radius and Sodium Halide Melting Point

The correlation between R_i and the ionic radius can be fortuitous. First, as Crichton et al. (1995a and 1995b) observed, the mechanism of liberation from glass is different for the three halogens (F, Cl, and I) for which data are available. Second, data for F are based on offgas measurements, whereas data for Cl and I are based on glass analysis. These data may not be comparable because offgas data plus glass analysis data rarely recover 100% of halogens. Finally, I data are subjected to an extremely high scatter. The I retention values based on glass analysis vary between 0.1 and 0.4 (0.23±0.10 on average; see Table 3.5), and the values based on offgas measurements vary between 0 and 0.85 (0.49±0.24 on average;

see Table 3.6). The offgas data for I are shown in Figure 3.6 where the value measured for the reduced glass (with Fe(II)/Fe = 0.06) is represented by a large full square.

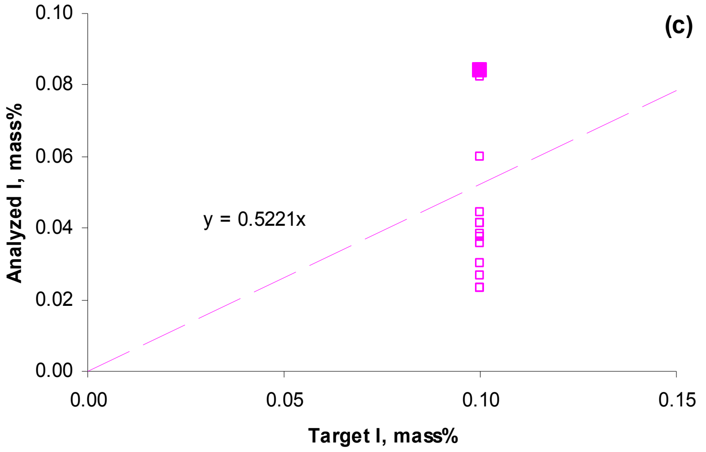


Figure 3.6. Retention of I in DuraMelter 100 Tests, Offgas Data

Provided that the correlation between halogen retention and ionic radius (or a similar property, such as alkali halide melting point) is real, we can expect that this correlation would strongly depend on the vitrification technology used. As Figure 3.7 shows, Envitko achieved a very low decrease of retention with increasing ionic radius.

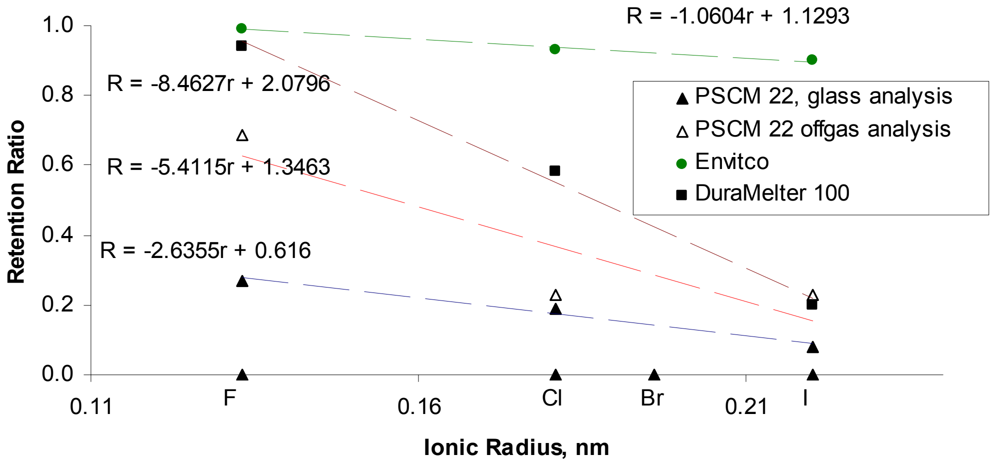


Figure 3.7. Halogen Retention Ration Versus Ionic Radius for Various Melter Technologies and Two Evaluation Methodologies

4.0 Conclusion

Neither crucible studies nor the early melter experiments appear representative for the retention of halogens in waste glasses expected during the normal mode of operation of a continuous electric melter. Fortunately, tests conducted with DuraMelter 100 present consistent data showing that the halogen retention ratio based on glass analyses varied little with glass composition within the LAW composition region. This ratio was independent of the halogen content in the waste feed, at least up to 0.2 mass% F and 1.5 mass% Cl (these mass% values are based on the glass produced). Only feeds with a single value of 0.1 mass% I were processed. The retention ratios, as based on XRF glass analysis, were 94% for F, 58% for Cl, and ~20% for I (42% was an estimated retention for Br).

The retention of I is subjected to a large uncertainty and may be underestimated because:

- A very high I retention value obtained in the wetted pellet-fed high-temperature continuous electric melter (0.9) indicates that I retention can be substantially increased.
- The offgas data suggest that the actual I retention could be 50% or higher (provided that XRF analysis underestimated I concentration in glass).
- The I retention value of 20%, though consistent with historical data, is subjected to a large error (±10%) that can be decreased when more accurate analytical methods are applied and a better inventory of I is achieved for the melter system.

The retention ratio appeared to decrease linearly with the halogen ionic radius. The slope of this plot was different for different vitrification technologies. A very low slope was achieved by the Envitco system where 90 mass% of I was retained in glass. Crucible studies also indicate that high I retention is realistic because most of the I losses seem to occur before the melter feed is converted to glass. If these losses were prevented and molten salt segregation was avoided, a higher amount of I would be retained in waste glass.

5.0 References

André, L. 2003. RPP-WTP Pilot Melter Envelope A Melter Emissions Test Results Report, TRR-PLT-062, Duratek, Inc., Columbia, MD.

Crichton, S.N., T.J. Barbieri, and M. Tomozawa. 1995a. "Solubility Limits for Troublesome Components in a Simulated Low Level Waste Glass," Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries (Ed. V. Jain and R. Palmer), Ceramic Transactions, Vol. 61, p. 283-290.

Crichton, S.N., T.J. Barbieri, and M. Tomozawa. 1995b. "Volatilization Rates of Troublesome Components from a Simulated Low Level Nuclear Waste Glass," Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries (Ed. V. Jain and R. Palmer), Ceramic Transactions, Vol. 61, p. 291-298.

Feng, X., M.J. Schweiger, H. Li, and M. Gong. 1996. Retention of Sulfur, Phosphorus, Chlorine, and Fluorine in Hanford Phase II Vendor LLW Glasses," Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum '96, p. 555-562, American Nuclear Society, La Gland Park, Illinois.

Goles, R.W. 1989. Determination of Halogen Content in Glass for Assessment of Melter Decontamination Factors, HWVP-89-IVJ0020500D, Pacific Northwest Laboratory, Richland, Washington.

Goles, R.W., R.K. Nakaoka, J.M. Perez, G.J. Sevigny, S.O. Bates, M.R. Elmore, D.E. Larson, K.D. Wiemers, M.E. Peterson, C.M. Andersen, W.C. Buchmiller, and C.M. Ruecker. 1990. Hanford Waste Vitrification Program Pilot Scale Ceramic Melter Test 23, PNL-7142 UC-721, Pacific Northwest Laboratory, Richland, Washington.

Li, H. 1995. Data Package of Minor Component Study for Low-Level Nuclear Waste Glass, PVTD C95-02.01B, Pacific Northwest Laboratory, Richland, Washington.

Matlack, K.S., W. Gong, and I.L. Pegg. 2002a. Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope A3 Feed in Support of the LAW Pilot Melter, VSL-01R62N0-1, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Matlack, K.S., W. Gong, and I.L. Pegg. 2002b. Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope C1 Feed (LAWC22 Glass) in Support of the LAW Pilot Melter, VSL-02R62N0-2, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Matlack, K.S., W. Gong, and I.L. Pegg. 2002c. Compositional Variation Tests on DuraMelter 100 with LAW Sub-Envelope A2 Feed (LAWA88 Glass) in Support of the LAW Pilot Melter, VSL-02R62N0-3, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Matlack, K.S., W. Gong, and I.L. Pegg. 2002d. Compositional Variation Tests on DuraMelter 100 with Sub-Envelope A1 Feed (LAWA44 Glass) in Support of the LAW Pilot Melter, VSL-02R62N0-4, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Matlack, K.S., W. Gong, and I.L. Pegg. 2003a. DuraMelter 100 Sub-Envelope Changeover Testing Using LAW Sub-Envelopes A1 and C1 Feeds in Support of the LAW Pilot Melter, VSL-02R62N0-6, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Matlack, K.S., W. Gong, and I.L. Pegg. 2003b. DuraMelter 100 Sub-Envelope Changeover Testing Using LAW Sub-Envelope A2 and B1 Feeds in Support of the LAW Pilot Melter, VSL-03R3410-1, Vitreous State Laboratory, The Catholic University of America, Washington DC.

Perez Jr., J.M. and R.W. Nakaoka. 1986. "Vitrification Testing of Simulated High-Level Radioactive Waste from Hanford," Waste Management 1986 (Ed. By R.G. Post) Proceedings of the Symposium in Waste Management at Tucson, AZ, Vol. 2, pp. 495-505.

Perez J.M., Whitney L.D., Buchmiller W.C., Daume J.T., and Whyatt G.A. 1994a. HWVP Pilot-Scale Vitrification System Campaign - LFCM-8 Summary Report. PNNL-11096. PHTD-93-04.15DK963. Pacific Northwest Laboratory, Richland, Washington.

Perez, J.M., P.J. Shafer, and W.C. Buchmiller. 1994b. Test Results of Vitrifying TWRS DSSF Low-Level Waste Simulant; Small-Scale, High-Temperature Melter Test 3 (SSHTM-3), PVTD-C95-03.01A, Pacific Northwest Laboratory, Richland, Washington.

Volf, M.B. 1984. Chemical Approach to Glass, Elsevier, Amsterdam.

Whyatt, W.A., J.W. Shade, and G.E. Steegen. 1996. „Volatility and Entrainment of Feed Components and Product Glass Characteristics During Pilot-Scale Vitrification of Simulated Hanford Site Low-Level Waste," Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum '96, p. 555-584-593, American Nuclear Society, La Gland Park, Illinois.

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