CHEMICAL DURABILITY STUDIES ON GLASS COMPOSITIONS PERTAINING TO WASTE IMMOBILIZATION AT WEST VALLEY

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ABSTRACT

Leach tests have been initiated on several borosilicate glass compositions produced upon vitrification of simulated West Valley high-level wastes. The current reference composition exhibits low leach rates, similar to those of the current reference defense waste glass composition, in tests providing for both short and long contact times of the glass with water. Tests on experimental glasses which have significantly different compositions from that of the reference glass (in particular, a low B_2O_3 or Al_2O_3 content) indicate that such changes in composition can cause considerable increases in leach rates, especially at long contact times.

INTRODUCTION

The ongoing effort to develop a vitrification process and optimize the glass composition for immobilization of the West Valley commercial high-level (reprocessing) wastes[1] requires taking into consideration various, often conflicting, criteria. For instance, the addition of large amounts of alkali oxides cause a reduction in melt viscosity and permits melting at lower temperatures, but it usually has an adverse effect on the chemical durability of the glass. The purpose of the study described here was to characterize the chemical durability of the currently proposed central glass composition in a variety of tests which permit evaluation of long-term as well as short-term leach behavior. Secondly, preliminary comparative studies on the leach properties of this composition and two other glass compositions within the acceptable range for melting were carried out. Furthermore, the leach behavior of the West Valley glass composition was compared with that of a current reference glass composition developed for the immobilization of defense high level wastes. The latter composition is a result of an optimization program[2] which led to very significant improvements in long-term leach resistance.[3]

EXPERIMENTAL

Glass Compositions

Four glass compositions were employed in the present study. The studies concentrated on the current reference West Valley composition,[4] designated below as WVRG. Two experimental glass compositions included in the current study are also within the acceptable meltability range for West Valley wastes. One of them, Glass A (melted at West Valley) is a low-alumina composition. The other, Glass B (melted at The Catholic University of America) is mainly distinguished by a higher silica content and a lower boron content compared with WVRG. A nonradioactive simulation of the West Valley HLW streams was used in the preparation of all three glasses. The fourth glass composition was the Materials Characterization Center Defense Waste Reference Glass (DWRG),[5] based on the optimization studies of glass composition for defense wastes at the Savannah River Plant.[2] The compositions of the four glasses are listed in Table I. The composition of DWRG was determined by the Materials Characterization Center (I, based on Ref. 5, Appendix A) and by The Catholic University of America (II),[5,6] respectively.

The compositions of the other glasses are based on batch formulations.

Test Methods

Three types of leach tests were used in the present studies. These included a frequent-exchange, modified IAEA/ISO test[7,8] and a partial-exchange, pulsed-flow test[9,10] as well as an MCC-1 static test[11]. All tests were carried out with de-ionized water at 90°C. Both the frequent-exchange tests and the MCC-1 tests were carried out on rectangular block samples, each having a geometric surface area of 4×10^2 mm^2, cut with a 200-grit blade. The pulsed-flow test was carried out in each case on a quantity of -40+60 mesh powdered glass. The volume of leachant used in the frequent-exchange and MCC-1 tests was 40 mL, while in the case of the pulsed-flow test the leachant volume was 100 mL and a volume of 25 mL was periodically withdrawn for analysis and replaced by 25 mL of de-ionized water. Each test was carried out in triplicate.

The analytical methods used in leachate analysis, the use of blanks and the calculations of normalized leach rates were previously described[3,5,10].

RESULTS

Short-Contact-Time Tests

The modified IAEA/ISO test was carried out on Glass A and DWRG rectangular blocks. It consisted of complete leachate exchange every day for a week, followed by a weekly exchange for 22 weeks. By that time, the leachate concentrations (and the corresponding leach rates) were observed to approach constant levels. The resulting leach rates are summarized in Table II. They show that in the cases of both glasses dissolution is nearly congruent, except with respect to highly insoluble species (Fe, Mn). This agrees with the observation that the leachate concentrations of major matrix element with limited solubilities (Si, Al) reached in this rapid-exchange test are too low to approach saturation[5,6]. Generally, the leach rates observed for Glass A are higher by a factor of 1.5-2 than those measured for DWRG.

TABLE I

Composition of Tested Glasses

	WVRG	Glass A	Glass B	DWRG I	DWRG II
SiO_2	45.2	44.7	50.4	50.4	51.6
Fe_2O_3	11.8	16.4	12.9	10.4	10.1
Na_2O	11.0	15.1	14.1	9.0	7.7
B_2O_3	10.0	8.6	7.0	6.6	7.3
K_2O	3.5	0.1	0.1	0.4	
Al_2O_3	3.3	0.7	2.1	6.7	5.5
Li_2O	3.1	3.7	3.2	4.9	4.1
ZrO_2	3.1	0.5	2.9	0.8	1.0
P_2O_5	2.5	3.3	2.9		0.2
MnO_2	1.7	0.7	1.5	2.2	3.4
MgO	1.3	1.6	0.5	0.9	0.8
TiO_2	1.0	0.6		0.1	0.1
NiO	0.7	0.5	1.0	1.9	2.1
CaO	0.6	0.1	0.7	2.0	1.9
Cr_2O_3	0.2	0.4	0.2		0.3
CeO_2	0.2	2.0	0.2		
SO_3	0.2		0.4		
Cs_2O	0.1			0.3	0.4
Nd_2O_3		1.0	0.1		
BaO			0.6		
La_2O_3			0.1		
U_3O_8				3.0	2.8
SrO				0.5	0.5

TABLE II

Results of Modified IAEA Test

De-ionized Water, 90°C, S/V=10m^{-1}, 7-day 100% Exchange

	Concentrations $g \cdot m^{-3}$		Normalized Leach Rates $g \cdot m^{-2} \cdot d^{-1}$	
	Glass A	DWRG	Glass A	DWRG
Si	12.9 ±0.4	7.6 ±1.3	0.87 ±0.03	0.51 ±0.09
B	1.92 ±0.15	0.81±0.15	1.18 ±0.03	0.49 ±0.09
P	0.58 ±0.05		0.58 ±0.05	
Li	1.04 ±0.06	0.84±0.16	0.86 ±0.05	0.62 ±0.12
Na	7.2 ±0.2	2.7 ±0.5	0.92 ±0.02	0.64 ±0.12
Al	0.24 ±0.01	0.99±0.21	0.99 ±0.04	0.46 ±0.10
Fe	0.01 ±0.02	0.01±0.03	0.002±0.002	0.002±0.004
Mn	0.002±0.001	0.02±0.02	0.004±0.002	0.01 ±0.01
pH	9.30	9.17		

MCC-1 Static Test

The results of 28-day MCC-1 tests are given in Table III. The glass samples included two batches of West Valley REference Glass, one (WVRG-I) melted at West Valley and the other (WVRG-II) at The Catholic University of America, as well as Defense Waste Reference Glass.

The results show that the differences between the leach test results on the two batches of WVRG are not significant. (An exception is the low result for Cs in the case of the WVRG-II sample, which may be due to volatilization loss in the course of melting). In general, the normalized elemental leach rates of WVRG are quite similar or slightly higher (by no more than 20%) than those of DWRG. As in the case of the frequent-exchange test (see above) the time of the test is too short and the surface-to-volume is too small to produce significant saturation effects, as reflected in the near-congruence of the dissolution. Only the highly insoluble species (Fe, Mn, Ti) stay undissolved or become re-precipitated or re-sorbed. The alkaline earths show limited leachability because of their limited solubility at high pH, especially in the case of Mg[5,6]. The dissolution rates based on overall weight loss agree well with the leach rates based on solution analysis.

Pulsed-Flow Tests

The pulsed-flow test described in References 9 and 10 was carried out on powdered samples of all the glasses listed in Table I. WVRG samples used included both glasses melted at West Valley (WVRG-II), cf. Table III. The test was carried out with a 25% exchange every week for 12 weeks, and the results were observed to approach constant values. The results of the pulsed-flow test are shown in Table IV. They show that under the test conditions selected here, i.e. a moderately long exchange time and a high surface-to-volume ratio, saturation of species such as Si and Al becomes a predominant effect. This causes preferential suppression of the leach rates of these elements as well as a large decrease in the leach rates of all glass components, including highly soluble species (boron, alkalis), as a result of the formation of alteration products on the surface of the glass[5,6]. The leach rates observed here are lower by more than an order of magnitude compared with those measured in the modified IAEA and MCC-1 tests (Tables II and III).

It can be concluded that this leach test, unlike the two tests described above, reflects the interaction between glass and water at long contact times, where saturation, rather than matrix corrosion, is the controlling mechanism. Under these conditions the relative leach rates of various glasses can be quite different than those observed at short contact times. For instance, at long contact times the dissolution rate of Glass A (based on the leach rates of the most leachable components) is larger by a factor of 6-10 than that of DWRG (cf. Table IV), while the corresponding factor under rapid-flow conditions is 1.5-2 (cf. Table II). Glass B is also much more leachable than DWRG and WVRG. In the case of Glass B the high leachate concentrations may be related to the high pH value, resulting from the low B_2O_3 content of the glass. The solubilities of silica and alumina rapidly rise with increasing pH in the moderately basic range[12]. The same interpretation has been proposed to account for the high leach rates of SRL TDS-131 glass, relative to those of DWRG, at long contact times[3]. The poor durability of Glass A compared with WVRG can be attributed to its low alumina content. (Glass A also has a very low zirconia concentration.) The presence of alumina, even at moderate levels, can cause a considerable decrease in silica solubility[12]. As a result, saturation effects limit the leaching process at much lower levels than in the absence of alumina. Finally, a remarkable resemblance between the leach behavior of WVRG and of DWRG, respectively, is observed at both short and long contact times. DWRG appears to be very slightly less leachable (by a factor of up to 1.2) than WVRG. The similarity between the two glass can be attributed to a combination of the two factors discussed above. DWRG is slightly more alkaline than WVRG, resulting in a higher leachate pH, but its alumina content is much higher. As a result, the observed saturation levels in the leachates obtained with these two glass are not significantly different.

In conclusion, the results of the present tests indicate that the currently proposed reference glass composition for West Valley high-level wastes has a high leach resistance, similar to that of the reference defense waste glass composition developed for the Savannah River Plant wastes. On the other hand, other experimental West Valley glass compositions have considerably lower leach resistance, especially upon prolonged contact with water. The high durability of the reference composition compared with that of the experimental glasses appears to be promoted by the high boron oxide and alumina content of the reference glass.

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TABLE III

Results of MCC-1 Leach Test

De-ionized Water, 90°C, S/V=10m^{-1}, 28 Days

	Concentrations g·m^{-3}			Normalized Leach Rates g·m^{-2}·d^{-1}		
	WVRG-I	WVRG-II	DWRG	WVRG-I	WVRG-II	DWRG
Si	30.1 ±0.9	30.0 ±0.1	26.4 ±1.8	0.46±0.01	0.46±0.01	0.45±0.03
B	6.7 ±0.2	5.9 ±0.2	2.8 ±0.1	0.69±0.02	0.62±0.06	0.51±0.01
P	1.7 ±0.1	1.6 ±0.1	0.08±0.01	0.50±0.04	0.47±0.03	0.39±0.05
Li	2.0 ±0.1	2.5 ±0.3	2.1 ±0.1	0.46±0.02	0.60±0.10	0.46±0.02
Na	15.1 ±0.9	15.3 ±1.7	8.8 ±0.6	0.59±0.04	0.60±0.10	0.62±0.04
K	6.0 ±0.2	6.6 ±0.1	0.05±0.01	0.67±0.02	0.74±0.01	0.62±0.10
Cs	0.07±0.01	0.19±0.01	0.51±0.08	0.23±0.03	0.62±0.03	0.50±0.08
Al	2.5 ±0.1	2.5 ±0.1	2.7 ±0.1	0.48±0.02	0.47±0.02	0.38±0.01
Ca	0.07±0.02	0.04±0.01	0.54±0.05	0.05±0.02	0.03±0.01	0.16±0.02
Mg	0.01±0.01	0.01±0.01	0.00±0.01	0.01±0.01	0.01±0.01	0.00±0.01
Fe	0.11±0.02	0.12±0.01	0.11±0.01	0.01±0.01	0.01±0.01	0.01±0.01
Mn	0.03±0.01	0.02±0.01	0.04±0.01	0.01±0.01	0.01±0.01	0.01±0.01
Ti	0.00±0.01	0.02±0.01	0.00±0.01	0.00±0.01	0.00±0.01	0.00±0.01
U			0.30±0.03			0.05±0.01
wt. loss				0.40±0.01	0.40±0.01	0.33±0.02
pH	9.37±0.01	9.37±0.03	9.41±0.09			

TABLE IV

Results of Pulsed Flow Leach Test

De-ionized Water, 90°C, S/V=291 m^{-1}, 7-day 25% Exchange

a. Concentrations, g·m^{-3}

	WVRG-I	WVRG-II	Glass A	Glass B	DWRG
Si	52 ±2	45 ±1	164 ±2	158 ±6	48 ±1
B	14.9 ±0.6	11.6 ±0.2	69 ±1	31 ±2	6.7 ±0.10
P	4.8 ±0.2	4.0 ±0.1	38 ±5	13.8 ±0.3	
Li	5.4 ±0.3	4.7 ±0.3	33 ±2	21 ±1	6.2 ±0.1
Na	36 ±2	26 ±1	184 ±5	131 ±3	15.2 ±0.3
K	8.8 ±0.3	8.3 ±0.1		0.83±0.06	
Cs	0.08±0.01	0.06±0.04			0.82±0.01
Al	2.9 ±0.1	3.1 ±0.1	0.24±0.01	1.5 ±0.2	3.9 ±0.1
Ca	0.00±0.01	0.00±0.02	0.00±0.01	0.13±0.03	0.29±0.05
Mg				0.00±0.01	0.00±0.01
Fe	0.14±0.03	0.16±0.02	0.34±0.01	0.33±0.05	0.37±0.01
Mn	0.01±0.01	0.02±0.01	0.04±0.06	0.04±0.01	0.04±0.01
Ti	0.00±0.01	0.01±0.01	0.01±0.01		0.01±0.01
U					1.02±0.06
pH	9.62±0.01	9.55±0.02	10.05±0.03	10.32±0.03	9.99±0.02

b. Normalized Leach Rates, g·m^{-2}·d^{-1}

	WVRG-I	WVRG-II	Glass A	Glass B	DWRG
Si	0.030±0.001	0.026±0.001	0.097±0.001	0.082±0.003	0.024±0.001
B	0.059±0.002	0.046±0.001	0.32 ±0.010	0.18 ±0.010	0.037±0.001
P	0.054±0.002	0.045±0.001	0.32 ±0.040	0.14 ±0.010	
Li	0.046±0.003	0.040±0.002	0.23 ±0.010	0.17 ±0.010	0.040±0.001
Na	0.054±0.003	0.039±0.001	0.20 ±0.010	0.15 ±0.010	0.032±0.001
K	0.037±0.001	0.035±0.001		0.20 ±0.010	
Cs	0.009±0.001	0.008±0.005			0.024±0.001
Al	0.020±0.001	0.022±0.001	0.009±0.001	0.016±0.002	0.016±0.001
Ca	0.000±0.001	0.000±0.001	0.000±0.001	0.003±0.001	0.003±0.001
Mg				0.000±0.001	0.000±0.001
Fe	0.000±0.001	0.000±0.001	0.000±0.001	0.000±0.001	0.001±0.001
Mn	0.000±0.001	0.000±0.001	0.001±0.002	0.001±0.002	0.000±0.001
Ti	0.000±0.001	0.000±0.001	0.000±0.001		0.002±0.001
U					0.005±0.001

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