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ABSTRACT

A series of tests have been performed to characterize the chemical stability of a DWPF borosilicate glass sample as part of the Waste Package Task of the NNWSI Project. This material was prepared at the Savannah River Laboratory for the purpose of testing the 165-frit matrix doped with a simulated non-radioactive waste. All tests were conducted at 90°C using deionized water and J-13 water (a tuffaceous formation groundwater). In the deionized water tests, both monoliths and crushed glass were tested at various ratios of surface area of the sample to volume of water in order to compare leach rates for different sample geometries or leaching times. Effects on the leach rates due to the presence of crushed tuff and stainless steel material were also investigated in the tests with J-13 water.

INTRODUCTION

Parametric testing is important because it helps to understand the behavior of a particular waste form under different experimental conditions. By optimizing these conditions, one can presumably design relatively short tests in order to establish the chemical stability of waste forms such as the DWPF borosilicate glass. The parameters investigated were leachant composition, ratios of waste form surface area to water volume (SA/V), effects of the presence of crushed tuff in some tests and of crushed tuff and stainless steel in others, and leaching times ranging from 1 to 182 days. All tests were conducted at 90°C and were of a static nature.

Four series of leaching tests were conducted. These were:

I. Glass monoliths and crushed glass with deionized water at SA/V ratios of 0.1, 0.3, 0.5, and 1.0 cm^{-1} for 1, 3, 7, 14, 28, and 56 days.
II. Glass monoliths with J-13 water at SA/V ratios of 0.3 and 0.5 cm^{-1} for 3, 7, 14, 28, and 56 days.
III. Glass monoliths with J-13 water and crushed tuff at SA/V ratios of 0.1 and 0.3 cm^{-1} for 7, 14, 28, 56, 91, and 182 days.
IV. Glass monoliths with J-13 water, crushed tuff, and stainless steel at SA/V ratios of 0.3 and 0.5 cm^{-1} for 3, 7, 14, 28, 56, and 91 days.

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EXPERIMENTAL

In order to perform the previously described parametric testing, the following materials were obtained: a borosilicate glass (DWPF) from the Savannah River Laboratory, crushed Topopah Spring tuff rock from an outcrop located at Fran Ridge (Nevada Test Site), J-13 groundwater from a well near the Yucca Mountain Site at the Nevada Test Site, and 304 L stainless steel coupons. Table I lists the nominal composition of the glass as supplied to LLNL by SRL and the average of the results of electron microprobe analyses performed at LLNL on five samples of the glass. For each sample, 10 spot analyses were performed and the data were averaged. The uncertainty estimates in Table I are based on the standard deviation of the average of the five sample averages. The SRL data giving the results of a partial analysis by x-ray fluorescence are also shown for comparison. The rock and water localities and composition are described by Knauss (1984)[1] and Oversby (1984)[2].

Table I
DWPF Glass (simulated waste) Composition

Component	Nominal[3] Wt%	LLNL Wt%	SRL[3] Wt%
SiO_2	53.47	54.9 ± 2.1	
Na_2O	11.40	9.74 ± 0.54	
Li_2O	5.04		
B_2O_3	7.20		
MgO	0.72	0.72 ± 0.04	0.65
ZrO_2	0.72	0.66 ± 0.07	0.58
Fe_2O_3	10.53	10.6 ± 0.7	10.2
MnO_2	2.35	2.72 ± 0.13	2.6
CaO	1.37	1.51 ± 0.32	1.2
NiO	1.06	0.84 ± 0.24	0.83
Al_2O_3	3.78	5.13 ± 0.18	
Zeolite	1.68		
CeO_2	0.42		
K_2O	0.14		
SrO	0.10		
RuO_2	0.036		
Cs_2O	0.0028		

[3]Data from Bibler, SRL, personal communication.

DWPF Glass Preparation

The glass sample was prepared by the Savannah River Laboratory under the direction of the Waste Solidification Technology Division (Bibler, 1983)[3]. The process was to slurry-feed a mixture of 165-frit and simulated waste to a small joule-heated melter. The final composition was 72 wt.% frit and 28 wt.% simulated waste. The glass was melted at 1150°C and poured into a 500 cc stainless steel beaker with a surface temperature of approximately 600°. The filling process took approximately four hours, which corresponds to a glass residence time in the melter of 10 hours. No annealing procedures were performed. Removal of the glass sample from the stainless steel can was only possible after cutting the can along three different lengths. During this procedure, the glass broke into several pieces which were later used to prepare the monoliths for the various tests.

The glass was black to olive-gray in color with well-developed concoidal patterns. We also noticed locally developed banding alternating from black to olive-gray and regions of frothy and vesicular mass at the top and center of the core. All surfaces were smooth and there was no evidence of crystalline phenocrysts. Representative samples from the above were analyzed by electron microprobe; the results of these analyses are shown in Table I and indicate that, despite its physical appearance suggesting a heterogeneous chemical composition, the glass material was very uniform based on the electron microprobe results.

Glass Sample Preparation

Glass samples were prepared as monoliths and particles according to MCC-1 and MCC-3 procedures (1983)[4]. A saw with diamond wheel was used to cut monoliths in the form of rectangular prisms with approximate dimensions of 1 x 2 cm lengths and 2-3 mm thick. Care was exercised not to use glass pieces that had been in contact with the stainless steel can. After cutting, the surface area of each monolith was measured with calipers, and then the glass was cleaned in an ultrasonic bath with deionized water and ethanol. Depending on the ratio of the specimen surface area to the leachant volume, samples with surface area of 200 to 600 mm^2 were used for the leaching.

The glass particles, 40-80 mesh size, were obtained by crushing pieces of glass, not suitable for monolith cutting, in a steel mortar and pestle. The crushed particles were sieved with the appropriate size screens and also cleaned in an ultrasonic bath with water and ethanol. The surface area of the particles was calculated from the average spherical size of each particle (298.5×10^{-6} m) using the following algorithm:

$$SA = \frac{6\, m_s}{\rho\, \bar{D}_p}$$

where

m_s = mass of sample, g
ρ = sample density, g/m^3
D_p = mean particle diameter, m

Rock Sample Preparation

The crushed tuff material was prepared by crushing small rock pieces with a small ceramic plate jaw crusher and then followed by further crushing with a plate grinder. The plates are made of high purity alumina. The rock powder from the plate grinder was sieved through 60 and 100 mesh screens on a mechanical sieve shaker. Finally, the rock powder was homogenized in a drum mixer for 24 hours before use in the leaching tests (Oversby, 1984)[2], and pretreated to remove the caliche. This procedure consisted of washing the crushed rock with deionized water, twice at room temperature by shaking, letting the tuff settle, and decanting the wash water, and once at 90°C by heating for 12 hours, letting it cool, and again decanting the wash water.

Stainless Steel Supports

In the fourth series of parametric testing, stainless steel supports were used to hold the glass monoliths. These stainless steel supports were made from 2.2 x 2.2 cm squares of 0.16 cm thick 304 L stainless steel coupons. The corners of the squares were bent downward to allow approximately 0.5 cm in space between the waste form and the crushed tuff resting at the bottom of the leaching container. Furthermore, the surface of the stainless steel support was perforated with nine holes 0.318 cm in diameter to allow a free path for water mixing around the waste form.

Leaching Procedures

Summarized below are the procedures used to conduct the four series of parametric testing of the DWPF borosilicate glass. The four tests were:

I. Glass with deionized water.
II. Glass with J-13 groundwater.
III. Glass with J-13 groundwater + tuff.
IV. Glass with J-13 groundwater + tuff + stainless steel.

In test I, monoliths were placed on teflon supports during the leaching period following procedures recommended by the MCC-1 leaching test (1983)[4]. In the case of the crushed glass experiments, the procedures were those recommended by the MCC-3 leaching test. In test II, only monoliths were used in the same manner as in test I. In test III, the crushed tuff was placed on the base of the leaching container and the glass monoliths rested on teflon supports above the tuff (there was no contact between glass and tuff). The ratio of J-13 water volume to tuff weight was 20 ml to 1 gram. In test IV, stainless steel supports were substituted for the teflon supports, but the glass-tuff configuration was the same as in test III. Appropriate blank samples (glass omitted) were run in each case in order to make background corrections.

The teflon containers used in tests I, II, and III were those recommended in the MCC-1 test (40 cm^3 capacity). The teflon containers used in test IV were 25 cm^3 in capacity, but were made of the same material as the 40 cm^3 capsules used in the first three tests. The reduction in size was necessary because of the size of stainless steel support.

At the conclusion of each leaching period, the solutions were cooled and the pH was measured within a few hours. In the tests involving glass particles and crushed tuff, the solutions were passed through a 45 μm filter before measuring the pH. The solutions were then acidified by adding concentrated ultrex nitric acid in amounts equal to 1% of the original volume. After acidification, all solutions were heated for 12 hours at 90°C. At the end of this period, the solutions were cooled and aliquots were removed for ICP elemental analysis. ICP data were obtained for Li, B, Na, Mg, Al, Si, K, Ca, Mn, Fe, Ni, Sr, and Zr.

RESULTS AND DISCUSSION

The four series of tests performed on the DWPF glass generated an enormous amount of data, of which only the Li, B, Na, and Si results will be discussed in this paper. The results for the remaining species will not be addressed because the concentrations as measured by ICP were too close to the limit of detection of the instrument.

Normalized elemental leach rates were calculated using the elemental concentrations in the leachates. The algorithm to calculate leach rate can be expressed as:

$$\text{Leach rate} = \frac{(C_x)(V)}{(f_x)(SA)(t)}$$

where:

C_x = concentration of element x in leach solution, g/cm^3
V = volume of leach solution, cm^3
f_x = mass fraction of element x in the unleached specimen
SA = specimen surface area, m^2
t = leaching time, d

The leach rates for Test I are shown in Tables II and III, and a comparison of the Li data for samples run at SA/V ratios of 0.3 and 0.5 cm^{-1} is shown in Figure 1. Agreement between the two forms of glass, monolithic and crushed, is very good at all time-intervals and is typical of the B, Na, and Si data. The leach rate data for Li, B, and Na suggest congruent dissolution of the glass, but the Si results are low by as much as 30% compared to the Li, B, and Na, thus suggesting that the leaching mechanism is affected by precipitation of insoluble phases or saturation of some elements such as Si.

The Li data shown in Table III were also plotted in Figure 2. This graph shows that, based on Li release rates, the DWPF glass obeys the scaling law (SA/V)(time). This conclusion is also true if the B, Na, and Si data in Table III were also plotted in a similar manner.

Table II
Test I
DWPF Glass (Monoliths) - Deionized Water
Normalized Elemental Leach Rate ($g/m^2.d$)

Leach Time	SA/V	Li	B	Na	Si
1	0.1	0.96	0.87	0.91	0.94
3	0.1	1.60	1.49	1.66	1.48
7	0.1	1.08	1.02	1.13	0.94
14	0.1	0.80	0.75	0.84	0.66
28	0.1	0.52	0.50	0.55	0.42
56	0.1	0.32	0.30	0.33	0.26
1	0.3	1.64	1.48	1.69	1.47
3	0.3	1.23	1.06	1.28	1.06
7	0.3	0.78	0.72	0.82	0.61
14	0.3	0.55	0.45	0.50	0.37
28	0.3	0.27	0.25	0.28	0.20
56	0.3	0.17	0.15	0.17	0.12
1	0.5	1.55	1.47	1.60	1.39
3	0.5	0.95	0.81	0.98	0.78
7	0.5	0.56	0.54	0.59	0.44
14	0.5	0.33	0.32	0.35	0.26
28	0.5	0.18	0.18	0.19	0.14

Table III
Test I
DWPF Glass (Crushed) Deionized Water
Normalized Elemental Leach Rate (g/m^2.d)

Leach Time	SA/V	Li	B	Na	Si
3	0.3	1.13	1.14	1.18	0.93
7	0.3	0.83	0.83	0.85	0.65
14	0.3	0.48	0.48	0.49	0.37
28	0.3	0.32	0.31	0.34	0.24
56	0.3	0.17	0.17	0.17	0.13
3	0.5	0.92	0.92	0.95	0.73
7	0.5	0.58	0.58	0.60	0.45
14	0.5	0.37	0.37	0.38	0.28
28	0.5	0.21	0.21	0.22	0.16
56	0.5	0.12	0.12	0.12	0.087
1	1.0	1.19	1.17	1.26	0.93
3	1.0	0.67	0.66	0.70	0.51
7	1.0	0.40	0.38	0.41	0.30
14	1.0	0.23	0.23	0.24	0.17
28	1.0	0.14	0.14	0.15	0.10

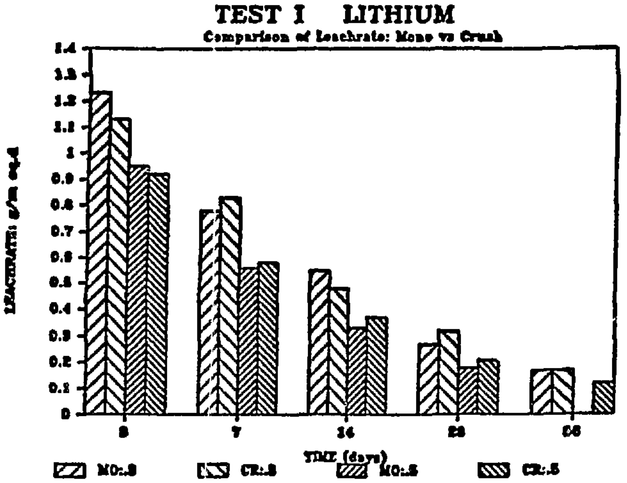

FIGURE 1

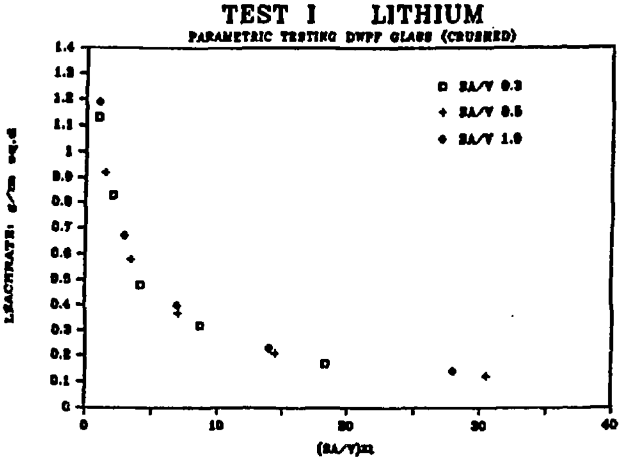

FIGURE 2

As stated previously, Tests II, III, and IV were different from Test I in that J-13 water was the leachant. Furthermore, Tests III and IV were complicated by using crushed tuff in Test III, and crushed tuff and stainless steel in Test IV. J-13 is a tuffaceous formation groundwater which contains 0.04, 0.14, 27, and 42 ppm of Li, B, Si, and Na, respectively. In examining the ICP data from tests II, III, and IV, we decided that the B, Si, and Na data were not suitable for calculation of leach rates because, in most instances, the data for the real samples and for the blank samples were of the same magnitude. In a few cases, the blanks were slightly higher than the samples, but this artifact may be attributable to statistical variations in the measurements. Consequently, only the Li data appear to be useful.

We have tabulated in Table IV the calculated leach rates for Li for all tests at SA/V ratios of 0.3 and 0.5 cm^{-1}. The data columns are ordered according to the complexity of the test to show differences in the values from test to test. First, it appears that glass behavior is very much leachant-type dependent, since the leach rates in deionized water are about one order of magnitude higher than in J-13 water. Secondly, it is not clear that the additions of tuff in Test II and tuff and stainless steel in Test IV have any effect on the Li leach rates; these appear to be about the same as in Test II with the exception of the day-3 samples. The data for the day-28 and the day-91 samples are shown with an uncertainty which represents the standard deviation of the average of two separate samples.

Table IV
Normalized Elemental Leach Rate ($g/m^2 \cdot d$)
Lithium

Leach Time	SA/V = 0.3 cm^{-1}				SA/V = 0.5 cm^{-1}			
	I	II	III	IV	I	II	III	IV
3d	1.23	0.0076	ND	0.035	0.95	0.15	-	0.067
7d	0.78	0.043	0.047	0.043	0.56	0.045	-	0.045
14d	0.55	0.032	0.041	0.038	0.33	0.022	-	0.042
28d	0.27	0.023 ±14%	0.020 ±5%	0.023	0.18	0.018 ±70%	-	0.026 ±10%
56d	0.17	0.023	Lost	0.011	-	0.018	-	0.015
91d	-	-	0.012 ±7%	0.010 ±3%	-	0.018	-	0.010 ±8%
182d	-	-	0.0079	-	-	-	-	-

ND = Nondetectable
I = Glass + DI water
II = Glass + J-13 water
III = Glass + J-13 water + tuff
IV = Glass + J-13 water + tuff + stainless steel

References

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[2] Oversby, V. M. (1984), Reaction of the Topopah Spring Tuff with J-13 Well Water at 90°C and 150°C, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53552.

[3] Bibler, N. E. (1983), Letter communication, June 6, 1983.

[4] Nuclear Waste Materials Handbook Test Methods, DOE/TIC-11400 (1983).