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The precision of product consistency tests conducted with a glass-bonded ceramic waste form

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Abstract

The product consistency test (PCT) that is used for qualification of borosilicate high-level radioactive waste (HLW) glasses for disposal can be used for the same purpose in the qualification of the glass-bonded sodalite ceramic waste form (CWF). The CWF was developed to immobilize radioactive salt wastes generated during the electrometallurgical treatment of spent sodium-bonded nuclear fuels. An interlaboratory study was conducted to measure the precision of PCTs conducted with the CWF for comparison with the precision of PCTs conducted with HLW glasses. The six independent sets of triplicate PCT results generated in the study were used to calculate the intralaboratory and interlaboratory consistency based on the concentrations of Al, B, Na, and Si in the test solutions. The results indicate that PCTs can be conducted as precisely with the CWF as with HLW glasses. For example, the values of the reproducibility standard deviation for Al, B, Na, and Si were 1.36, 0.347, 3.40, and 2.97 mg/l for PCT with CWF. These values are within the range of values measured for borosilicate glasses, including reference HLW glasses.

1. Introduction

Spent sodium-bonded nuclear fuel from the Experimental Breeder Reactor II will be treated using an electrometallurgical process developed at Argonne National Laboratory (ANL) to produce waste forms that are suitable for geologic disposal [1]. The waste form developed to immobilize radioactive salt wastes is referred to as the ceramic waste form (CWF). Work is in progress to support qualification of the CWF for disposal in a federal high-level waste repository. One of the requirements for qualification is to ensure that the production of waste forms is adequately controlled. The work described in this paper addresses the use of a standard test method to verify the consistency of the CWF.

The CWF is made by mixing waste salt with zeolite 4A to occlude the salt within the zeolite cage structure. The salt-loaded zeolite is then mixed with borosilicate glass (at a 3:1 mass ratio) and processed at about 900 °C. At temperatures above about 800 °C, the salt-loaded zeolite converts to the mineral sodalite. Salt that was occluded in the zeolite becomes incorporated into the sodalite structure, and the sodalite is encapsulated in the glass. The resulting waste form is composed of about 70% sodalite, 25% glass binder, and 5% consisting of halite and various oxide and silicate inclusions. The major radionuclides in the waste form are actinides and rare earth fission products, which are present as oxide inclusions in the binder glass; iodine, which is present in the sodalite and halite inclusions in the binder glass; and cesium, which is dissolved in the binder glass.

The requirements for qualification of the CWF for acceptance into the DOE waste disposal system are contained in the Waste Acceptance System Requirements Document (WASRD), which details the requirements for the waste form, waste package, process

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documents, etc. [2]. Borosilicate glass is identified as the standard high-level radioactive waste (HLW) form in the WASRD, and the CWF must be qualified as a non standard HLW form. While few specific details are provided in the WASRD for non-standard waste forms, it is likely that they must be shown to meet the same requirements as borosilicate glass waste forms. One of the requirements for glass waste forms is that the consistency of the products be determined. Requirement 4.2.3.1 H is:

1. "The producer shall demonstrate control of waste form production by comparing production samples or process control information, separately or in combination to the Environmental Assessment benchmark glass using the product consistency test (PCT) or equivalent".
2. "For acceptance, the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for concentrations in the glass, shall be less than those of the benchmark glass".

The solution concentrations of lithium, sodium, and boron are used because they are common components in HLW glasses, have high solubility limits, and are released faster than other glass components or radionuclides. The PCT has been standardized by the American Society for Testing and Materials (ASTM) as standard test method C1285. The PCT Method A is a crushed-glass durability test that 'can specifically be used to evaluate whether the durability and elemental release characteristics of waste glasses have been consistently controlled during production' [3]. Method A is used to monitor the consistency of HLW glasses. It is a seven-day test conducted at 90 °C with glass that has been crushed and sieved to isolate the −100 +200 mesh size fraction and washed to remove fines. Specific test conditions require using demineralized water and a stainless steel test vessel. The PCT Method B allows for the use of different test conditions to study glass dissolution behavior.

Several issues have been addressed in evaluating the possible use of the PCT to monitor the consistency of the CWF [4]. First, the CWF is a multiphase material, whereas the PCT addresses the evaluation of homogeneous and devitrified glasses. The PCT response resulting from the simultaneous dissolution of several phases is just as useful for monitoring product consistency as the response from the dissolution of a single phase, if the relative amounts of each phase is expected to be the same in all waste forms. This requires that the phase distribution in the crushed fraction be the same as that of the bulk CWF. The gross composition of the −100 +200 mesh size fraction of the CWF was shown to be the same as that of the bulk CWF.

Second, the CWF contains a small amount of halite as a soluble inclusion phase. The PCT procedure addresses the presence of soluble phases (in step 19.6.1 of [3]) by recommending that the potential for dissolution of soluble phases during the washing steps be taken into account by analyzing the wash solutions. Crushed CWF is washed first with absolute ethanol, to remove most of the fines, and then with demineralized water, to dissolve halite exposed at the surface of the crushed material. The ethanol wash solution is not analyzed, because halite is sparingly soluble in absolute ethanol and it is desired to quantify only the halite dissolved from the −100 +200 mesh fraction. The majority of Na and Cl present in the ethanol wash solution is assumed to be present in fines of halite, sodalite, and glass binder, and so does not provide a measure of the amount of halite in the CWF.

The wash water is analyzed for sodium and chloride ions. The water wash step is conducted at the same CWF mass/water volume ratio used in the PCT, namely, 1 g crushed solid/10 ml water. In this way, the amounts of Na and Cl dissolved in the water wash can be added directly to the amounts of Na and Cl released in the PCT, in determining the total amounts that were released. More importantly, the concentrations measured in the water wash provide a measure of the relative amount of halite in the waste form. This information can be used for process control. For clarity, we refer to the solution from the water wash as the 'water wash solution' and the solution generated during the seven-day PCT as the 'test solution'.

A third issue is whether the PCT response provides an indication that the process has been controlled. In the case of HLW glasses, the soluble components Li, Na, and B will be used to confirm that the composition of the glass is consistent with the target composition. In the case of the CWF, the releases of Na and Cl in the water wash and Al, B, Na, and Si in the PCT can be used to provide evidence that the relative amounts of halite, binder glass, and sodalite, respectively, have been controlled. Whereas the compositions of waste glasses will vary significantly between batches, the gross composition of the CWF is expected to remain fairly constant. This is because the same mass ratio of salt-loaded zeolite to binder glass will be used to make all CWFs, and these components comprise about 92% of the waste form. The balance is waste salt, which is primarily (Li, Na, K)Cl. Only very small changes in the composition of the CWF will occur due to changes in the amounts of radioactive waste in the salt, and these are not expected to measurably affect the PCT response.

The interlaboratory study (ILS) discussed in this paper was conducted to evaluate the precision with which the PCT could be conducted with the CWF. This must be known before the sensitivity of the PCT response to waste form composition can be determined. The ILS was conducted following the procedure in ASTM standard E691-99 [5]. All participants had extensive experience in conducting PCTs with borosilicate waste glasses, and the analytical laboratories were experienced in analyzing PCT test solutions. A laboratory-scale CWF product was made with a nonradioactive surrogate waste salt for use in testing. Sample lots provided to participants were taken from a CWF that had been crushed, sieved, and washed with absolute ethanol to remove fines at ANL. These sample preparation steps were done to maximize the homogeneity of the samples and to constrain the study to test execution and solution analysis by eliminating possible variations due to sample preparation. Participants were asked to perform one water wash of the provided lot and then conduct triplicate PCTs at 90 °C with the water-washed material. The factors that may contribute to variability in the test results include the operators for test execution and solution analysis, the analytical equipment used, calibration of the analytical equipment, and the laboratory environment.

The database generated in the ILS is used to determine the precision that can be expected for execution of the PCT with the CWF. This information provides evidence that the PCT, along with process records, can be used to meet the WASRD requirement for demonstrating consistency of CWF products. The test results and statistical analyses for the ILS are presented in this paper.

Use of the PCT to monitor the consistency of a waste form requires identifying elements that are good indicators of chemical durability that remain in solution during the test. Generally, elements with high solubility limits that are released from the waste form structure by rapid reactions and are not sequestered in alteration phases that may form during the test are selected for this purpose. Alkali metals, boron, and silicon are commonly monitored for PCTs conducted with borosilicate waste glasses. In the case of the CWF, the PCT response is due to the dissolution of sodalite and borosilicate glass binder phases. Halite exposed at the surface is expected to dissolve completely during the water wash step and is not expected to contribute to the PCT test solution. Like waste glasses, the dissolution of the binder glass can be monitored by the concentrations of sodium, boron, and silicon. Dissolution of sodalite can be monitored by the concentrations of sodium, silicon, and chloride ion. Negligible amounts of sodalite or binder glass dissolve during the water wash step, so the measured concentrations of sodium and chloride ion are due to the dissolution of halite.

Whereas dissolution of both sodalite and binder glass contribute to the concentrations of sodium and silicon in the PCT step, only dissolution of binder glass contributes to the concentration of boron. All CWFs will be made using the same binder glass composition and the same mass ratio of binder glass and salt-loaded zeolite (which will result in the same mass ratio of binder glass and sodalite). Therefore, the compositions of all CWFs are expected to be very similar. The two primary consistency issues are to confirm that a CWF has an acceptable amount of halite and the correct mass ratio of binder glass and sodalite. Analysis of sodium or chloride ion in the water wash solution provides a measure of the amount of halite, and analysis of boron in the PCT solution provides a measure of the amount of binder glass in the CWF. Tracking the sodium and silicon concentrations in the PCT solution provides a measure of the total amount of sodalite and binder glass that has dissolved in the test. Because the compositions of sodalite and binder glass will be constant, their dissolution rates can be considered to be constant in all CWFs. Therefore, the consistency of the sodium and silicon concentrations in the PCT provides an indication that the relative amounts of sodalite and binder glass in the CWF are consistent. Although the pH of the PCT solution is not used for qualification of HLW glass and will not be used for qualification of the CWF, it is commonly tracked in PCTs conducted with waste glasses and is included in this ILS for completeness.

2. Experimental

A 500-g CWF product was prepared at ANL for use in the ILS. The CWF was crushed and sieved to isolate the −100 +200 mesh size fraction (i.e., the size fraction between 74 and 150 μm), then washed six times with absolute ethanol to remove fines. These steps were done at ANL to eliminate variation in the efficiencies of sieving and washing to remove fines from the study so that the precision of the two operations in the test procedure, i.e., the water wash and the seven-day PCT, was measured directly. The prepared material was divided into lots of about 5 g, which were provided to each participant for use in both the composition analysis and the PCT parts of the study. (Some participants requested and were provided more than one lot.) The participants were instructed to follow the PCT procedure for Method A at 90 °C as closely as possible, except that the tests with a standard reference glass that are called for in the PCT were not required. Key aspects of the test procedure are summarized below:

- The crushed CWF that was provided was to be washed once with a volume of water having a mass equal to 10 times the mass of the sample at room temperature. The wash solution was to be passed through a 0.45-μm pore-size filter to remove suspended material and then analyzed for Na or Cl.
- Triplicate PCTs were to be conducted at 90 °C with between 1 and 1.5 g of crushed CWF and a mass of demineralized water (ASTM Type I water) that was exactly 10 times the mass of the CWF used. This is

the mass ratio requirement in the PCT procedure for Method A.

- PCTs were to be conducted for seven days. The times of day a test vessel was placed in and removed from the oven were required to differ by no more than 3.4 h. This is the duration required in the PCT Method A procedure.
- Tests were to be conducted using unsensitized Type 304L stainless steel vessels, which are required by the PCT Method A procedure.
- Duplicate blank tests with demineralized water were to be conducted simultaneously with the tests with the CWF. The vessels used in the blank tests were to be cleaned in the same manner as the vessels used in the tests with the CWF. This is a requirement in the PCT Method A procedure.
- The oven temperature was to remain at 90 ± 2 °C throughout the test. This is the temperature stability requirement in the PCT Method A procedure.
- The total mass of the test vessel was not to change during the test by more than 5% of the mass of demineralized water that was initially added to the vessel. This is a requirement in the PCT Method A procedure.
- Solutions generated in the blank tests and the tests with CWF and were to be filtered through 0.45-μm pore-size filters, acidified with concentrated nitric acid, and then analyzed for B, Na, and Si. Estimated detection limits were to be reported. The PCT calls for analysis of elements that represent the maximum dissolution of the waste form.
- The analytical method for solution analysis was not specified.

3. Results

In the following discussion, the datasets provided by the ILS participants are designated by index letters A–H. In some cases, different scientists at the same participating laboratory provided more than one set of PCT results. Datasets were considered independent if different scientists conducted the test and different instruments were used for solution analysis. This decision was made to use the largest possible database to evaluate test precision. This decision was based on the assumption that the scientist performing the tests and the combination of the analyst and analytical method used to measure the solution concentrations are the major contributors to test precision, and that the laboratory environment has only a minor influence. Participant A conducted three sets of triplicate tests on separate days. These are referred to as A, D, and E for ease of reference; these data are not considered independent, and only data set A was used for the ILS statistical analysis. Participants A, B, and C are from the same laboratory. Because different scientists conducted the tests, and different analysts analyzed the test solutions using different instruments, datasets A, B, and C are considered independent. Participant F conducted nine replicate tests; the first set of test results was used for the ILS statistical analysis. The ILS statistical results are based on the six independent sets of results. The results of the three sets of triplicate tests conducted by Participant A and all nine triplicate tests conducted by Participant F are considered separately for further evaluation of test repeatability in Appendix A.

The measured solution concentrations were compared directly because the mass ratio of CWF/demineralized water in all of the tests was about 0.100 ± 0.001 for both the water wash and PCT steps. The 1% variation in the CWF-to-water mass ratio is assumed to be negligible relative to the analytical uncertainty. The PCT calls for subtracting the background concentration of an element from the concentration of that element in a test with glass. For all participants, only the concentrations of sodium and silicon in the blank tests were above the background detection limits. The sodium concentrations in the blank tests were significant with respect to the sodium concentrations in the PCT test solutions, and were used for background subtraction. The silicon concentrations in the blank tests were not significant with respect to the silicon concentrations reported in the PCT test solutions. (Participants F and G reported silicon concentrations to two significant figures, and the concentrations in the blanks were insignificant with respect to the reported values.)

The results for the analysis of the wash solution are given in Table 1. Blank tests were not conducted for the water wash step and participants were not asked to measure the Na and Cl concentrations in the demineralized water they used; those concentrations are certainly negligible relative to the high concentrations

Table 1
Results of wash solution analysis, in mg/l

Test no.	Cl	Na
A wash solution	273	180
B wash solution	235	171
C wash solution	243	168
D wash solution[a]	261	151
E wash solution[a]	266	178
F wash solution	242	153
G wash solution	Not reported	163
H wash solution	229	146
Mean ± std. dev.[b]	250 ± 17	164 ± 13
Mean ± std. dev.[c]	244 ± 17	164 ± 12

[a] Extra set of tests conducted by Participant A.

[b] Including D and E wash solution results.

[c] Excluding D and E wash solution results.

Table 2
PCT results

Test data	Test type	pH	Al (mg/l)	B (mg/l)	Na (mg/l)	Si (mg/l)
A1	PCT	8.97	25.3	2.09	31.4	33.6
A2	PCT	8.94	24.6	2.12	32.4	32.6
A3	PCT	8.97	24.5	2.16	31.4	33.7
AB1	Blank	Not reported	<0.1	<0.03	0.08	<0.03
AB2	Blank	Not reported	<0.1	<0.03	0.07	<0.03
B1	PCT	9.26	25.3	1.89	28.5	33.2
B2	PCT	9.21	25.7	1.76	27.8	32.3
B3	PCT	9.15	22.5	1.79	26.5	30.3
BB1	Blank	7.42	<0.1	<0.01	0.10	0.02
BB2	Blank	7.23	<0.1	<0.01	0.087	0.03
C1	PCT	8.94	24.2	1.89	34.0	32.8
C2	PCT	8.99	22.1	1.89	32.3	30.4
C3	PCT	8.84	23.2	2.19	31.7	32.9
CB1	Blank	5.09	<0.1	<0.001	0.19	<0.01
CB2	Blank	5.48	<0.1	<0.001	0.21	<0.01
D1[a]	PCT	9.06	23.1	2.72	37.2	33.2
D2[a]	PCT	9.07	24.9	2.48	33.0	35.5
D3[a]	PCT	8.97	24.7	2.37	35.4	33.7
DB1[a]	Blank	5.99	<0.1	<0.03	0.15	<0.3
DB1[a]	Blank	5.73	<0.1	<0.03	0.18	<0.3
E1[a]	PCT	8.86	22.5	2.38	31.2	31.5
E2[a]	PCT	8.86	21.8	2.55	31.3	32.1
E3[a]	PCT	8.74	22.1	2.47	31.6	32.9
EB1[a]	Blank	6.47	<0.1	<0.03	0.18	<0.3
EB2[a]	Blank	6.28	<0.1	<0.03	0.18	<0.3
F1	PCT	8.9	23	2.7	32	35
F2	PCT	9.0	24	2.6	31	35
F3	PCT	8.9	23	2.8	31	35
F4[b]	PCT	9.1	23	2.8	33	36
F5[b]	PCT	8.9	24	2.6	33	36
F6[b]	PCT	9.1	23	2.9	34	36
F7[b]	PCT	9.1	23	2.7	34	35
F8[b]	PCT	9.0	22	2.9	34	35
F9[b]	PCT	9.2	21	3.3	38	35
FB1	Blank	5.8	<0.07	<0.09	<0.2	<0.2
FB2	Blank	5.1	<0.07	<0.09	<0.2	0.49
G1	PCT	Not reported	12[c]	2.3	23	28
G2	PCT	Not reported	12[c]	2.3	23	28
G3	PCT	Not reported	11[c]	2.6	36	27
GB1	Blank	Not reported	Not reported	Not reported	0.76	0.29
GB2	Blank	Not reported	Not reported	Not reported	0.27	0.29
H1	PCT	9.02	25.8	2.51	30.5	35.2
H2	PCT	9.01	26.3	2.48	30.8	36.5
H3	PCT	9.02	25.3	2.49	30.3	35.4
HB1	Blank	6.92	<0.009	<0.07	0.40	<0.8
HB2	Blank	6.78	<0.009	<0.02	<0.1	<0.8

[a] Extra tests conducted by Participant A. Dataset excluded from interlaboratory statistics.

[b] Extra tests conducted by Participant F. Dataset excluded from interlaboratory statistics.

[c] Value excluded from analysis.

measured in the water wash step. Because participants were requested to make only a single measurement of the water wash solution, only the interlaboratory precision is evaluated. The pH results and the Al, B, Na, and Si concentrations measured in triplicate PCT and duplicate blank tests are summarized in Table 2. The values given for the PCT results have already been background-subtracted using the average of the blank values. Because all participants provided measured values, the consistency of the Al response in the PCT was also evaluated. The extra results provided by Participant A (as datasets D and E) and Participant F (as data F4 through F9) were not included in the calculations to evaluate the intralaboratory and interlaboratory test precisions.

4. Discussion of interlaboratory study with CWF

The results of the composition and PCT parts of the ILS were analyzed separately following the methods recommended in ASTM standard E691 [5] to assess repeatability and reproducibility. As defined in ASTM E691, Section 3.2.5, "repeatability concerns the variability between independent test results obtained within a single laboratory in the shortest practical period of time by a single operator with a specific set of test apparatus using test specimens taken at random from a single quantity of homogeneous material obtained or prepared for the ILS. Reproducibility deals with the variability between single test results obtained in different laboratories, each of which has applied the test method to test specimens taken at random from a single quantity of homogeneous material obtained or prepared for the ILS" [5]. In the formulae that are summarized below, a 'cell' refers to the result of a measurement made by a participant, x refers to the value that is being measured, x_p is a measured value, n is the number of replicate measurements made by a participant, and p is the number of participants that provided a measurement of that value.

- The cell average of values measured by a participant in replicate tests ($\bar{x}_p$) is

$$\bar{x}_p = \sum x_p/n. \tag{1}$$

- The cell standard deviation for a participant (s_p) is

$$s_p = \left[\left(\sum(x_p - \bar{x}_p)^2\right)/(n-1)\right]^{1/2}. \tag{2}$$

This is a measure of the intralaboratory variability.

- The consensus average of the measured value ($\bar{x}$) is

$$\bar{x} = \sum \bar{x}_p/p. \tag{3}$$

This is the average of the cell averages.

- The pooled intralaboratory standard deviation (s_r) is

$$s_r = \left[\sum s_p^2/p\right]^{1/2}. \tag{4}$$

This gives the estimated standard deviation for repeatability of measurements made within a laboratory.

- The standard deviation of the cell averages for replicate tests by the same participant from the consensus average ($s_{\bar{x}}$) is

$$s_{\bar{x}} = \left[\sum(\bar{x}_p - \bar{x})^2/(p-1)\right]^{1/2}. \tag{5}$$

- The interlaboratory estimate of precision (s_R) is

$$s_R = (s_{\bar{x}}^2 + s_r^2(n-1)/n)^{1/2}. \tag{6}$$

This is the reproducibility standard deviation.

Two other expressions were used to express the repeatability and reproducibility:

- The estimated 95% repeatability level, $I(r)$, is $I(r) = 2.83s_r$. On the basis of test error alone, the absolute value of the difference of two test results obtained in the same laboratory will exceed $I(r)$ only approximately 5% of the time.
- The estimated 95% reproducibility level, $I(R)$, is $I(R) = 2.83s_R$. On the basis of test error alone (including intra- and interlaboratory components), the absolute value of the difference between two test results obtained in different laboratories will exceed $I(R)$ only approximately 5% of the time.

The repeatability of the water wash step was not evaluated in this ILS, although the three datasets provided by Participant A offer a measure of the repeatability at one laboratory. Instead, the pooled results were analyzed to determine the consensus mean and standard deviation. The consensus mean and standard deviation are 164 ± 13 mg/l for the analysis of sodium and 250 ± 17 mg/l for the analysis of chloride ion when the results for Participant D and E are included, and 164 ± 12 and 244 ± 17 mg/l when they are not. The results in datasets A, D, and E provided by Participant A have mean and standard deviations of 170 ± 16 mg/l for sodium and 268 ± 6 mg/l for chloride ion. The mean values for Participant A are slightly higher than the consensus average, but the intralaboratory precision (repeatability) for Participant A is similar to the interlaboratory precision (reproducibility) from the pooled results. The amounts of Na and Cl measured in the water wash solutions provide an indication of the relative amounts of halite, sodalite, and glass binder that have dissolved during the wash step. From the consensus mean concentration values, the mole ratio in solution is 7.13 ± 0.57 mol Na to 6.88 ± 0.48 mol Cl. If only halite (NaCl) dissolves in the water wash step, then the Na/Cl mole ratio will be 1.0. The ratio of the consensus concentrations is 1.04. The slightly greater release

Table 3
PCT results with the CWF

Dataset	pH	Al (mg/l)	B (mg/l)	Na (mg/l)	Si (mg/l)
A	8.96 ± 0.02	24.8 ± 0.4	2.12 ± 0.04	31.8 ± 0.6	33.3 ± 0.6
B	9.21 ± 0.06	24.5 ± 1.7	1.81 ± 0.07	27.6 ± 1.0	31.9 ± 1.5
C	8.92 ± 0.08	23.2 ± 1.1	1.99 ± 0.17	32.7 ± 1.2	32.0 ± 1.4
D[a]	9.03 ± 0.06	24.2 ± 1.0	2.52 ± 0.18	35.2 ± 2.1	34.1 ± 1.2
E[a]	8.82 ± 0.07	22.1 ± 0.4	2.47 ± 0.09	31.4 ± 0.2	32.2 ± 0.7
F[b]	8.93 ± 0.06	23.3 ± 0.6	2.70 ± 0.10	31.3 ± 0.6	35.0 ± 0.0
F[c]	9.02 ± 0.11	22.9 ± 0.9	2.81 ± 0.22	32.8 ± 1.3	35.3 ± 0.5
G	Not reported	12 ± 1[d]	2.4 ± 0.2	27.3 ± 7.5	27.7 ± 0.6
H	9.02 ± 0.01	25.8 ± 0.5	2.49 ± 0.02	30.5 ± 0.3	35.7 ± 0.7

[a] Extra tests conducted by Participant A.

[b] Mean and standard deviation for tests F1, F2, and F3.

[c] Mean and standard deviation for tests F1 through F9.

[d] Al result for Participant G excluded from statistics.

of Na may be due to the dissolution of a small amount of sodalite in the water wash step, although the difference is well within the analytical uncertainty.

The values of the mean ($\bar{x}_p$) and standard deviations (s_p) for the triplicate tests by each participant are summarized in Table 3. The Al values provided by Participant G were excluded from calculations of the test precision as outliers based on the Q-test. The results of extra tests conducted by Participant A (i.e., datasets D and E) and Participant F are included in Table 3 for completeness. They were excluded from calculation of the consistency statistics, and are compared with the expected intralaboratory and interlaboratory consistencies calculated based on the other data in Appendix A. (The mean values for datasets F and G are given to three significant figures although the results were reported to two significant figures. Calculations of the statistical values did not distinguish between the number of significant figures reported by different participants.) The datasets are compared graphically in Fig. 1, where the mean values and the standard deviations for each participant are plotted. In some cases, the standard deviation is less than the size of the symbol. The horizontal lines show the consensus average concentrations (excluding datasets D and E and tests F4 through F9). The plot shows that the Na and Si results for Participant G deviate most significantly from the consensus value. Whether or not these deviations are statistically significant is determined later. The Al value for Participant G was excluded from calculation of the mean and the other statistical parameters as an outlier.

The statistical parameter values calculated from the test results in Table 3 are summarized in Table 4. These values are used to evaluate the repeatability (the intralaboratory precision) and the reproducibility (the interlaboratory precision) for PCTs with the CWF. The results of extra tests conducted by Participant A (i.e., datasets D and E) and Participant F (i.e., tests F4 through F9) were excluded from these calculations. Those results are compared with the expected precisions that are calculated from the ILS in Appendix A.

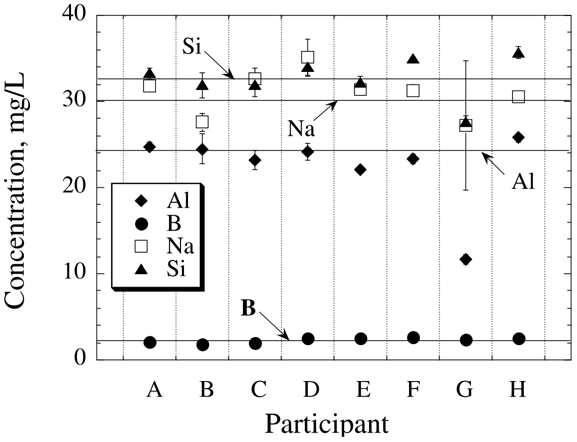

Fig. 1. Mean values of solution concentrations. Lines show consensus means (excluding values for Participants D and E) for: Al = 24.3, B = 2.25 mg/l, Na = 30.2 mg/l, and Si = 32.6 mg/l.

The intralaboratory consistency can be determined by using the k consistency statistic, which is defined as the standard deviation for a participant (s_p) divided by the repeatability standard deviation (s_r): $k = s_p/s_r$. The k consistency statistic provides a measure of how the variability within a particular laboratory compares with that of all laboratories combined. The k value is unitless. The k values for the measured concentrations of Al, B, Na, and Si are plotted in Fig. 2 for the six independent datasets. The critical k value for an ILS with six participants conducting triplicate tests is 1.98 (see Table 5 in Ref. [5]). The critical value is provided to determine if the variability in the results of a particular laboratory exceeds that expected due to random error. Examination

Table 4
Summary of precision statistics for PCTs with the CWF[a]

	$\bar{x}$	$s_{\bar{x}}$	s_r	s_R	$I(r)$	$I(R)$
pH	9.01	0.117	0.050	0.124	0.142	0.351
Al, mg/l	24.3	1.09	0.992	1.36	2.81	3.84
B, mg/l	2.25	0.334	0.113	0.347	0.320	0.982
Na, mg/l	30.2	2.23	3.15	3.40	8.91	9.62
Si, mg/l	32.6	2.86	0.949	2.97	2.69	8.40

[a] Symbols defined in text. Concentrations of Al, B, Na, and Si in mg/l. Datasets D and E and tests F4 through F9 excluded from statistics.

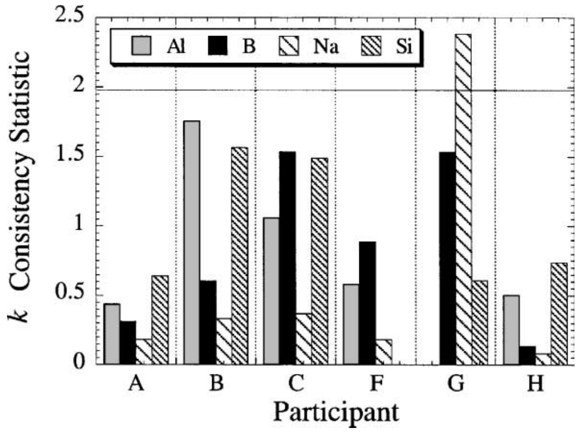

Fig. 2. Plot of k statistic values and critical value = 1.98 (for comparing intralaboratory consistency for six participants conducting triplicate tests) for PCTs with the CWF.

of Fig. 2 shows that the concentration of sodium measured by Participant G exceeds the critical k value. This means that the variation in the sodium results of Participant G is inconsistent with (higher than) that for the other participants. It also indicates intralaboratory imprecision, which may be related to the test procedure or the solution analysis. Laboratories with very small k consistency parameter values have a less sensitive measurement scale than the other laboratories. For example, Fig. 2 indicates that the silicon results from Participant F give a k value of zero. This probably reflects the fact that the results from Participant F were reported to two significant figures, whereas most of the other laboratories reported results to three significant figures.

The interlaboratory consistency is determined by the h consistency statistic, which is the difference between the value measured by a participant ($\bar{x}_p$) and the consensus value ($\bar{x}$) divided by the standard deviation of the cell averages ($s_{\bar{x}}$): $h = (\bar{x}_p - \bar{x})/s_{\bar{x}}$. The h value can be used to evaluate the overall variability of the analyses among the participants and to compare the results of one participant against those of all the other participants. At the 0.5% significance level, the critical values of h for six participants is ±1.92 (see Table 5 in Ref. [5]). The h values calculated for the concentrations of Al, B, Na, and Si in the six independent datasets are plotted in Fig. 3. (The Al values for Participant G were excluded from the analysis.) Examination of the plot shows that the h values for all results are less than the critical value, including the Na and Si results from Participant G. Therefore, all test data are retained for calculation of the precision statistics for PCTs with the CWF, which are given in Table 4.

The expected values for product acceptance testing are given by the values of $I(r)$ for repeatability and $I(R)$ for reproducibility. At the 95% confidence level, two values measured at the same laboratory are expected to differ by less than $I(r)$ and two values measured at different laboratories are expected to differ by less than $I(R)$. The values of $I(r)$ and $I(R)$ should be taken into account when establishing process control limits to determine when the response of a PCT with a CWF exceeds the uncertainty due to testing and analysis. These values provide the minimum values that should be used for control limits; wider limits can be used to allow for acceptable variations in waste form composition. Additional tests are needed to determine the range of test

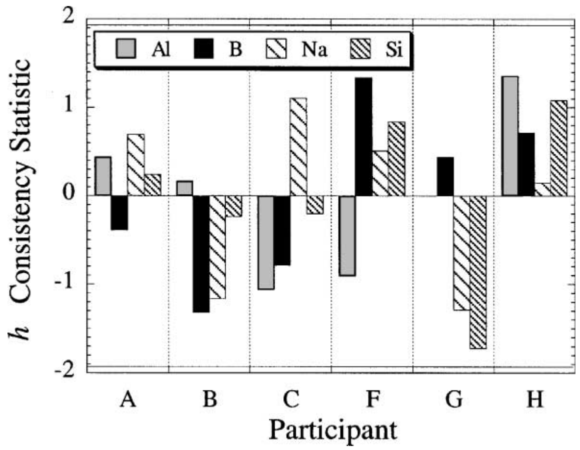

Fig. 3. Plot of h statistic values and critical value = ±1.92 (for comparing interlaboratory consistency for six participants) for PCTs with the CWF.

responses corresponding to the acceptable range of CWF compositions. Such tests will be conducted as part of the CWF process qualification process. The values of $I(r)$ and $I(R)$ measured in the present study will allow the variations in test response due to changes in the CWF compositions or processing conditions to be distinguished from the expected variations due to conducting the test.

5. Comparison with interlaboratory studies with borosilicate glasses

The test precision measured in this ILS conducted with CWF can be compared with the precision measured in other studies conducted with borosilicate glasses. An ILS was recently conducted with a borosilicate glass that was developed to be used as a low-activity reference material (referred to as LRM glass) for acceptance testing of Hanford low-activity waste glass [6]. The primary purpose of that study was to document consensus PCT responses and test precision. The organizers and many of the participants are the same in the ILS with LRM glass and the present ILS with the CWF. The ILS with LRM glass included conducting triplicate PCTs at 90 °C with analysis of Al, B, Na, and Si. Those results can be compared directly with the results of PCTs with CWF.

Another ILS was conducted with the National Institute of Science and Technology reference glass SRM-623, the Materials Characterization Center reference glass ARM-1, and two borosilicate glasses used to represent HLW glasses to be made at the Savannah River Site. These are referred to as SRL-G and SRL-P. The primary purpose of that study was to evaluate the effectiveness of the PCT to discriminate between glasses of different composition. The ILS test matrix included tests conducted during three different weeks and replicate solution analyses. Triplicate tests with SRL-G and single tests with the other glasses were conducted during the first week, and single tests with all four glasses were conducted during the second and third weeks. The ILS results were compiled and evaluated at Pacific Northwest National Laboratory (PNNL) [7]. The results of triplicate tests conducted during the first week with SRL-G glass, which we refer to as SRL-G (3 × 1), are best suited for comparison with the results of tests with the CWF. Note that, although the ILS conducted by PNNL had seven participants, the results from one participant (Lab 2) were determined to deviate significantly from the results of other participants using the k and h consistency values. We compare the statistic values from the ILS with the CWF with the results from the PNNL ILS excluding Lab 2.

We have calculated the statistics values using the data provided in Ref. [7] for the triplicate tests conducted with SRL-G during the first week, with the same spreadsheet being used to calculate the values for the ILS with the CWF. The same spreadsheet was also used for the ILS with LRM glass. The statistics values are summarized in Table 5. Note that the Al, B, Na, and Si concentrations attained in tests with LRM glass and SRL-G glass are all significantly higher than those attained in tests with the CWF, although this does not bear on the test precision. The values of s_r and s_R provide the best comparison of the test precision, as these represent the intralaboratory repeatability and interlaboratory reproducibility, respectively. The tests with the CWF had both the best intralaboratory repeatability (s_r) and interlaboratory reproducibility (s_R) for the measurement of B and Si. The precision for measuring the Na concentration was highest (the standard deviation was lowest) in the ILS with SRL-G glass.

Table 5 includes the precision of triplicate PCTs conducted with the CWF with single PCTs conducted with four glasses over three different seven-day intervals. (The tests conducted with SRL-G on three different weeks are referred to as SRL-G (1 × 3).) All values have been rounded to three significant figures. The standard deviations for the triplicate tests with the CWF are within the range of deviations in replicate tests with the glasses. The deviations in tests with the glasses include the added analytical uncertainty due to analyzing solutions on different days. That is, the day-to-day variation in the analytical measurement may reduce the test precision. This effect can be seen by comparing the two sets of results for SRL-G glass: the results for triplicate tests conducted simultaneously, SRL-G (3 × 1), have lower intralaboratory deviations than the results for single tests conducted three different weeks, SRL-G (1 × 3), whereas the interlaboratory deviations are about the same. This suggests there is an effect of when the tests are conducted and/or when the solutions are analyzed.

The ISL conducted by PNNL included analysis of a ‘standard solution’ containing Al, B, Na, and Si at concentrations similar to those in tests with the CWF. Those results provide insight into the contribution of the analytical uncertainty to the overall precision of the PCT. The repeatability of analyses of B in the standard solution is similar to the repeatability of the B concentration in the PCT for all glasses except ARM-1, which had a test precision about four times higher than the precision for B analysis. This indicates that the PCT precision is limited by the analytical precision in the case of boron. The repeatability of analyses of Na and Si in the standard solution is better than the repeatability of the Na and Si concentrations in the PCT for all materials except the CWF, which had a similar test precision. This indicates that the precision of conducting a PCT is not limited by the analytical precision in the cases of the sodium and silicon responses.

Table 5
Summary of precision statistics for PCTs with the CWF and borosilicate glasses[a]

Material	p/n[b]	$\bar{x}$	$s_{\bar{x}}$	s_r	s_R	%rsd repeatability[c]	%rsd reproducibility[d]
Aluminium							
CWF[e]	6/3	24.3	1.09	0.992	1.36	4.08	5.60
LRM[f]	8/3	14.3	2.42	0.922	2.59	6.45	18.11
SRL-G (3 × 1)[g]	6/3	3.84	0.256	0.124	0.275	3.23	7.16
SRL-G (1 × 3)[h]	6/3	3.87	nr[i]	0.250	0.343	6.46	8.86
SRL-P[h]	6/3	3.51	nr	0.142	0.288	4.05	8.21
SRM 623[h]	6/3	3.34	nr	0.200	0.228	5.99	6.83
ARM-1[h]	6/3	4.65	nr	0.269	0.468	5.78	10.06
Standard solution[j]	6/3	4.09	nr	0.095	nr	2.32	nr
Boron							
CWF[e]	6/3	2.25	0.334	0.113	0.347	5.02	15.42
LRM[f]	8/3	26.7	2.48	0.647	2.54	2.42	9.51
SRL-G (3 × 1)[g]	6/3	14.7	0.523	0.287	0.573	1.95	3.90
SRL-G (1 × 3)[h]	6/3	14.4	nr	0.465	0.724	3.23	5.03
SRL-P[h]	6/3	25.3	nr	0.667	1.27	2.64	5.02
SRM 623[h]	6/3	7.05	nr	0.496	0.609	7.04	8.64
ARM-1[h]	6/3	27.5	nr	2.07	3.33	7.53	12.11
Standard solution[j]	6/3	19.6	nr	0.524	nr	2.67	nr
Sodium							
CWF[e]	6/3	30.2	2.23	3.15	3.40	10.4	11.26
LRM[f]	8/3	160	11.5	4.06	11.9	2.54	7.44
SRL-G (3 × 1)[g]	6/3	49.2	2.50	0.993	2.63	2.02	5.35
SRL-G (1 × 3)[h]	6/3	49.9	nr	1.51	2.49	3.03	4.99
SRL-P[h]	6/3	69.6	nr	3.47	3.90	4.99	5.60
SRM 623[h]	6/3	12.7	nr	0.87	0.961	6.85	7.57
ARM-1[h]	6/3	55.6	nr	4.16	5.08	7.48	9.14
Standard solution[j]	6/3	39.3	nr	0.557	nr	1.42	nr
Silicon							
CWF[e]	6/3	32.6	2.86	0.949	2.97	2.91	9.11
LRM[f]	8/3	82.0	4.36	1.25	4.48	1.52	5.46
SRL-G (3 × 1)[g]	6/3	110	4.30	1.09	4.39	0.99	3.99
SRL-G (1 × 3)[h]	6/3	112	nr	3.10	4.18	2.77	3.73
SRL-P[h]	6/3	110	nr	3.19	3.76	2.90	3.42
SRM 623[h]	6/3	46.1	nr	3.72	4.47	8.07	9.70
ARM-1[h]	6/3	80.2	nr	3.92	6.03	4.89	7.52
Standard solution[j]	6/3	40.8	nr	0.897	nr	2.20	nr

[a] Symbols defined in text. Concentrations of Al, B, Na, and Si in mg/l.

[b] p = number of participants or independent datasets; n = number of replicate tests.

[c] %rsd repeatability = $100s_r/\bar{x}$.

[d] %rsd reproducibility = $100s_R/\bar{x}$.

[e] Datasets D and E and tests F4 through F9 excluded from statistics.

[f] Results from [6].

[g] Results calculated from data in [7] for triplicate test conducted during week 1.

[h] Results calculated from data in [7] for single tests run during weeks 1, 2, and 3 (from s_R from Table C.2 and s_r from Table C.3).

[i] nr = not reported.

[j] Results calculated from data in [7] for replicate analysis of standard solution (from Table C.7 'without * values').

Consideration of the k statistics for the intralaboratory consistency and the h statistics for the interlaboratory consistency provides another indication that the PCT can be conducted with the CWF as consistently as with borosilicate glasses. The sodium response measured by one of the six participants exceeded the critical k statistic value in tests with the CWF, as can be seen in Fig. 2. The ILS with LRM glass [6] showed the values of one of eight participants to exceed the critical k statistic value for the boron and silicon responses (the critical k value for eight participants conducting triplicate tests is 2.06). In the ILS conducted by PNNL [7], values of three of the seven participants exceeded the critical k value for the boron, sodium, and/or silicon responses for PCT with one or more glass or analysis of the standard solution (the critical k value for seven participants conducting triplicate tests is 2.03). None of the participants exceeded the critical h statistic value in the ILS with the CWF, as can be seen in Fig. 3. The values of one of the eight participants in the ILS with LRM glass [6] and one of the seven participants in the ILS conducted by PNNL [7] exceeded the critical h value for the responses of Al, B, Na, and Si; those results have been excluded in the statistic values reported in Table 5 (the critical h value for seven participants is 2.05).

The percent relative standard deviations based on the repeatability ($\%\text{rsd} = 100s_r/\bar{x}$) and reproducibility ($\%\text{rsd} = 100s_R/\bar{x}$) are included in Table 5. Although the %rsd was used in Refs. [3,7] to evaluate and compare testing precision for the PCT conducted with borosilicate glasses, it is not called for in the ASTM standard for measuring the precision of a test method [5]. We have not used the %rsd for the present comparisons because comparison of the standard deviations s_r and s_R provide a direct comparison of the test precision. The absolute test response does not affect the precision of either test execution or solution analysis. Although high solution concentrations are often assumed to be analyzed more reliably than low solution concentrations, this is usually not the case because most test solutions must be diluted to within the quantifiable concentration window of the instrument. The values in Table 5 show how use of %rsd can belie the relative precisions of the PCT conducted with different materials. For example, the absolute standard deviation of the boron response in tests with the CWF are more than 2× lower than for SRL-G in terms of s_r and s_R, but the relative standard deviation is about 3× higher for tests with the CWF. This is because the mean boron response is about 6× higher for SRL-G than for the CWF.

6. Conclusions

An ILS was conducted to determine the precision with which a seven-day PCT at 90 °C can be conducted with the CWF and how this compares with the precision of PCTs conducted with borosilicate glass waste forms. Six independent datasets were generated by participants in four laboratories. The statistic values for the PCT with the CWF were within the range of values that have been determined in the PCT with borosilicate glass. The intralaboratory and interlaboratory consistencies were similar for the PCTs conducted with the CWF and with borosilicate glass. The results of this study indicate that, from the perspective of test repeatability and reproducibility, the PCT Method A is appropriate for monitoring the consistency of the CWF. The study also indicates that the intralaboratory consistency is best applied to tests that are conducted and analyzed as a group. The measured interlaboratory consistency $I(R)$ will likely provide a better measure of the expected long-term consistency of tests conducted in the same laboratory because it includes added uncertainty due to the use of different analytical instruments. Based on the results of datasets A, D, and E provided by Participant A (see Appendix A), this is similar to the day-to-day analytical uncertainties of a particular instrument.

Acknowledgements

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Appendix A

The extra results provided by Participants A (datasets D and E) and F (tests F4 through F9) can be compared with the expected test precision from the ILS. From Table 4, the expected intralaboratory consistencies $I(r)$ are 2.81, 0.320, 8.91, and 2.69 mg/l and the expected interlaboratory consistencies $I(R)$ are 3.84, 0.982, 9.62, and 8.40 mg/l for measuring Al, B, Na, and Si concentrations, respectively. That is, the absolute differences of the concentrations measured within a set of replicate tests are expected to agree within the value of $I(r)$, and differences between different sets of replicate tests are expected to agree within the value of $I(R)$. Tests for which the concentrations differ by more than the value of $I(r)$ or $I(R)$ should be considered suspect. The absolute values of the differences between the Al, B, Na, and Si concentrations measured in replicate tests conducted by Participant A (datasets A, D, and E) and by Participant F (test data F1 through F9) are tabulated in Tables 6 and 7. (Calculations of $I(r)$ and $I(R)$ did not include datasets D and E or tests F4 through F9.) Differences in test results within a dataset that are greater than $I(r)$ are shown in bold font. The difference between the boron results in tests D1 and D3 conducted by Participant A exceeds the expected intralaboratory consistency of 0.32 mg/l. Likewise, the differences between the boron result for test F9 and other tests in dataset F exceed 0.32 mg/l. This indicates that test F9 and either test D1 or D3 are suspect.

Table 6 also shows the comparisons between datasets A, D, and E provided by participant A. Differences are

Table 6
Consistency of nine replicate tests conducted by Participant A, in mg/l

	Test number								
	A1	A2	A3	D1	D2	D3	E1	E2	E3
I(*r*) *Al* = *2.81*; *I*(*R*) *Al* = *3.84*									
25.3	0.0	0.7	0.8	2.2	0.4	0.6	2.8	3.5	3.2
24.6	0.7	0.0	0.1	1.5	0.3	0.1	2.1	2.8	2.5
24.5	0.8	0.1	0.0	1.4	0.4	0.2	2.0	2.7	2.4
23.1	2.2	1.5	1.4	0.0	1.8	1.6	0.6	1.3	1.0
24.9	0.4	0.3	0.4	1.8	0.0	0.2	2.4	3.1	2.8
24.7	0.6	0.1	0.2	1.6	0.2	0.0	2.2	2.9	2.6
22.5	2.8	2.1	2.0	0.6	2.4	2.2	0.0	0.7	0.4
21.8	3.5	2.8	2.7	1.3	3.1	2.9	0.7	0.0	0.3
22.1	3.2	2.5	2.4	1.0	2.8	2.6	0.4	0.3	0.0
I(*r*) *B* = *0.320*; *I*(*R*) *B* = *0.982*									
2.09	0.00	0.03	0.07	0.63	0.39	0.28	0.29	0.46	0.38
2.12	0.03	0.00	0.04	0.60	0.36	0.25	0.26	0.43	0.35
2.16	0.07	0.04	0.00	0.56	0.32	0.21	0.22	0.39	0.31
2.72	0.63	0.60	0.56	0.00	0.24	**0.35**	0.34	0.17	0.25
2.48	0.39	0.36	0.32	0.24	0.00	0.11	0.10	0.07	0.01
2.37	0.28	0.25	0.21	**0.35**	0.11	0.00	0.01	0.18	0.10
2.38	0.29	0.26	0.22	0.34	0.10	0.01	0.00	0.17	0.09
2.55	0.46	0.43	0.39	0.17	0.07	0.18	0.17	0.00	0.08
2.47	0.38	0.35	0.31	0.25	0.01	0.10	0.09	0.08	0.00
I(*r*) *Na* = *8.91*; *I*(*R*) *Na* = *9.62*									
31.4	0.0	1.0	0.0	5.8	1.6	4.0	0.2	0.1	0.2
32.4	1.0	0.0	1.0	4.8	0.6	3.0	1.2	1.1	0.8
31.4	0.0	1.0	0.0	5.8	1.6	4.0	0.2	0.1	0.2
37.2	5.8	4.8	5.8	0.0	4.2	1.8	6.0	5.9	5.6
33.0	1.6	0.6	1.6	4.2	0.0	2.4	1.8	1.7	1.4
35.4	4.0	3.0	4.0	1.8	2.4	0.0	4.2	4.1	3.8
31.2	0.2	1.2	0.2	6.0	1.8	4.2	0.0	0.1	0.4
31.3	0.1	1.1	0.1	5.9	1.7	4.1	0.1	0.0	0.3
31.6	0.2	0.8	0.2	5.6	1.4	3.8	0.4	0.3	0.0
I(*r*) *Si* = *2.69*; *I*(*R*) *Si* = *8.40*									
33.6	0.0	1.0	0.1	0.4	1.9	0.1	2.1	1.5	0.7
32.6	1.0	0.0	1.1	0.6	2.9	1.1	1.1	0.5	0.3
33.7	0.1	1.1	0.0	0.5	1.8	0.0	2.2	1.6	0.8
33.2	0.4	0.6	0.5	0.0	2.3	0.5	1.7	1.1	0.3
35.5	1.9	2.9	1.8	2.3	0.0	1.8	4.0	3.4	2.6
33.7	0.1	1.1	0.0	0.5	1.8	0.0	2.2	1.6	0.8
31.5	2.1	1.1	2.2	1.7	4.0	2.2	0.0	0.6	1.4
32.1	1.5	0.5	1.6	1.1	3.4	1.6	0.6	0.0	0.8
32.9	0.7	0.3	0.8	0.3	2.6	0.8	1.4	0.8	0.0

The responses in the nine replicate tests for each element are given in the left-hand column. For each element, the values give the absolute differences between the responses in the replicate tests.

all less than the values of $I(R)$ for Al, B, Na, and Si. However, many of the differences between the boron and silicon results in the three datasets provided by Participant A exceed the value of $I(r)$; these are shown in bold font. We attribute the poorer consistency of the combined dataset compared to the individual datasets A, D, and E (with respect to $I(r)$) to added analytical uncertainty for solutions that are analyzed on different days, as discussed in the text. The observation that the consistency of the combined datasets A, D, and E were within the values of $I(R)$ for Al, B, Na, and Si indicates that the interlaboratory consistency better represents the expected intralaboratory consistency for test solutions analyzed on different days. Note that the results of test D1 differ from the other tests more than the results of test D3, which suggests that D1 is the suspect test. Table 8 shows differences between the results in dataset F with the results from Participant A in datasets A, D, and E.

Table 7
Consistency of nine replicate tests conducted by Participant F, in mg/l

	Test no.								
	F1	F2	F3	F4	F5	F6	F7	F8	F9
$I(r)$ Al = 2.81									
23	0	1	0	0	1	0	0	1	2
24	1	0	1	1	0	1	1	2	**3**
23	0	1	0	0	1	0	0	1	2
23	0	1	0	0	1	0	0	1	2
24	1	0	1	1	0	1	1	2	**3**
23	0	1	0	0	1	0	0	1	2
23	0	1	0	0	1	0	0	1	2
22	1	2	1	1	2	1	1	0	1
21	2	**3**	2	2	**3**	2	2	1	0
$I(r)$ B = 0.320									
2.7	0.0	0.1	0.1	0.1	0.1	0.2	0.0	0.2	**0.6**
2.6	0.1	0.0	0.2	0.2	0.0	0.3	0.1	0.3	**0.7**
2.8	0.1	0.2	0.0	0.0	0.2	0.1	0.1	0.1	**0.5**
2.8	0.1	0.2	0.0	0.0	0.2	0.1	0.1	0.1	**0.5**
2.6	0.1	0.0	0.2	0.2	0.0	0.3	0.1	0.3	**0.7**
2.9	0.2	0.3	0.1	0.1	0.3	0.0	0.2	0.0	**0.4**
2.7	0.0	0.1	0.1	0.1	0.1	0.2	0.0	0.2	**0.6**
2.9	0.2	0.3	0.1	0.1	0.3	0.0	0.2	0.0	**0.4**
3.3	**0.6**	**0.7**	**0.5**	**0.5**	**0.7**	**0.4**	**0.6**	**0.4**	0.0
$I(r)$ Na = 8.91									
32	0	1	1	1	1	2	2	2	6
31	1	0	0	2	2	3	3	3	7
31	1	0	0	2	2	3	3	3	7
33	1	2	2	0	0	1	1	1	5
33	1	2	2	0	0	1	1	1	5
34	2	3	3	1	1	0	0	0	4
34	2	3	3	1	1	0	0	0	4
34	2	3	3	1	1	0	0	0	4
38	6	7	7	5	5	4	4	4	0
$I(r)$ Si = 2.69									
35	0	0	0	1	1	1	0	0	0
35	0	0	0	1	1	1	0	0	0
35	0	0	0	1	1	1	0	0	0
36	1	1	1	0	0	0	1	1	1
36	1	1	1	0	0	0	1	1	1
36	1	1	1	0	0	0	1	1	1
35	0	0	0	1	1	1	0	0	0
35	0	0	0	1	1	1	0	0	0
35	0	0	0	1	1	1	0	0	0

The responses in the nine replicate tests for each element are given in the left-hand column. For each element, the values give the absolute differences between the responses in the replicate tests.

The boron result of test F9 is significantly different (difference > 0.982) than the results of tests A1, A2, and A3. The differences between the results are otherwise within the expected interlaboratory consistency $I(R)$ values. The boron result for test F9 was also flagged as suspect based on the intralaboratory consistency. The intralaboratory consistency of the boron response measured in this study is quite low, relative to the other elemental responses. Viewed from the perspective of process control, using the intralaboratory consistency $I(r)$ of the boron response to detect variant test responses gave one or two false positives in dataset D (test D1, test D3, or both) and one false positive in dataset F (test F9). Using the intralaboratory consistency of the aluminum response gave one false positive in dataset F (test F9). The intralaboratory consistencies for sodium and silicon gave

Table 8
Consistency of nine replicate tests conducted by Participants A and F, in mg/l

		Test no.								
		A1	A2	A3	D1	D2	D3	E1	E2	E3
		25.3	24.6	24.5	23.1	24.9	24.7	22.5	21.8	22.1
$I(R)\ Al = 3.84$										
F1	23	2.3	1.6	1.5	0.1	1.9	1.7	0.5	1.2	0.9
F2	24	1.3	0.6	0.5	0.9	0.9	0.7	1.5	2.2	1.9
F3	23	2.3	1.6	1.5	0.1	1.9	1.7	0.5	1.2	0.9
F4	23	2.3	1.6	1.5	0.1	1.9	1.7	0.5	1.2	0.9
F5	24	1.3	0.6	0.5	0.9	0.9	0.7	1.5	2.2	1.9
F6	23	2.3	1.6	1.5	0.1	1.9	1.7	0.5	1.2	0.9
F7	23	2.3	1.6	1.5	0.1	1.9	1.7	0.5	1.2	0.9
F8	22	3.3	2.6	2.5	1.1	2.9	2.7	0.5	0.2	0.1
F9	21	4.3	3.6	3.5	2.1	3.9	3.7	1.5	0.8	1.1
$I(R)\ B = 0.982$										
		2.09	2.12	2.16	2.72	2.48	2.37	2.38	2.55	2.47
F1	2.7	0.61	0.58	0.54	0.02	0.22	0.33	0.32	0.15	0.23
F2	2.6	0.51	0.48	0.44	0.12	0.12	0.23	0.22	0.05	0.13
F3	2.8	0.71	0.68	0.64	0.08	0.32	0.43	0.42	0.25	0.33
F4	2.8	0.71	0.68	0.64	0.08	0.32	0.43	0.42	0.25	0.33
F5	2.6	0.51	0.48	0.44	0.12	0.12	0.23	0.22	0.05	0.13
F6	2.9	0.81	0.78	0.74	0.18	0.42	0.53	0.52	0.35	0.43
F7	2.7	0.61	0.58	0.54	0.02	0.22	0.33	0.32	0.15	0.23
F8	2.9	0.81	0.78	0.74	0.18	0.42	0.53	0.52	0.35	0.43
F9	3.3	**1.21**	**1.18**	**1.14**	0.58	0.82	0.93	0.92	0.75	0.83
$I(R)\ Na = 9.62$										
		31.4	32.4	31.4	37.2	33.0	35.4	31.2	31.3	31.6
F1	32	0.6	0.4	0.6	5.2	1.0	3.4	0.8	0.7	0.4
F2	31	0.4	1.4	0.4	6.2	2.0	4.4	0.2	0.3	0.6
F3	31	0.4	1.4	0.4	6.2	2.0	4.4	0.2	0.3	0.6
F4	33	1.6	0.6	1.6	4.2	0.0	2.4	1.8	1.7	1.4
F5	33	1.6	0.6	1.6	4.2	0.0	2.4	1.8	1.7	1.4
F6	34	2.6	1.6	2.6	3.2	1.0	1.4	2.8	2.7	2.4
F7	34	2.6	1.6	2.6	3.2	1.0	1.4	2.8	2.7	2.4
F8	34	2.6	1.6	2.6	3.2	1.0	1.4	2.8	2.7	2.4
F9	38	6.6	5.6	6.6	0.8	5.0	2.6	6.8	6.7	6.4
$I(R)\ Si = 8.40$										
		33.6	32.6	33.7	33.2	35.5	33.7	31.5	32.1	32.9
F1	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1
F2	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1
F3	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1
F4	36	2.4	3.4	2.3	2.8	0.5	2.3	4.5	3.9	3.1
F5	36	2.4	3.4	2.3	2.8	0.5	2.3	4.5	3.9	3.1
F6	36	2.4	3.4	2.3	2.8	0.5	2.3	4.5	3.9	3.1
F7	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1
F8	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1
F9	35	1.4	2.4	1.3	1.8	0.5	1.3	3.5	2.9	2.1

no false positives within these datasets. Use of the interlaboratory consistency $I(R)$ gave no false positives for the Al, B, Na, or Si responses between datasets A, D, and E, and one false positive between datasets A, D, E, and F (the boron response in test F9).

References

[1] Record of Decision for the Treatment and Management of Sodium-Bonded Spent Nuclear Fuel. Fed. Regist. 65 (182) (2000) 56565.

[2] Waste Acceptance System Requirements Document (WASRD), Rev. 3, DOE/RW-0351. U.S. Department of Energy, Office of Civilian Radioactive Waste Management report E00000000-00811-1708-00001, April 1999.

[3] Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT) Standard C1285-98. Annual Book of ASTM Standards Vol. 12.01, American Society for Testing and Materials, West Conshohocken, PA.

[4] M.A. Lewis, M.L. Stanley, W.L. Ebert, Development of a Method for Monitoring the Consistency of Glass-Bonded Sodalite Waste Forms, Argonne National Laboratory Report, ANL-00/12, May 2000.

[5] Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method Standard E 691-99. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 14.02, West Conshohocken, PA.

[6] W.L. Ebert, S.F. Wolf, J. Nucl. Mater. 282 (2000) 112.

[7] G.F. Piepel, T.E. Jones, D.L. Eggett, G.B. Mellinger, Product Consistency Test Round Robin Conducted by the Materials Characterization Center-Summary Report, Pacific Northwest National Laboratory Report PNL-6967, 1989.