

Interlaboratory Study of the Reproducibility of the Single-Pass Flow-Through Test Method: Measuring the Dissolution Rate of LRM Glass at 70°C And Ph 10

prepared by
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**INTERLABORATORY STUDY OF THE REPRODUCIBILITY OF THE
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W.L. Ebert

Chemical Engineering Division

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ACRONYMS

ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
HLW	high-level radioactive waste
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectroscopy
ILS	interlaboratory study
LLNL	Lawrence Livermore National Laboratory
LRM	low-activity reference material (glass)
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
rsd	relative standard deviation
SEM	scanning electron microscope
SPFT	single-pass flow-through (test)

INTERLABORATORY STUDY OF THE REPRODUCIBILITY OF THE SINGLE-PASS FLOW-THROUGH TEST METHOD: MEASURING THE DISSOLUTION RATE OF LRM GLASS AT 70°C AND pH 10

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ABSTRACT

An international interlaboratory study (ILS) was conducted to evaluate the precision with which single-pass flow-through (SPFT) tests can be conducted by following a method to be standardized by the American Society for Testing and Materials – International. Tests for the ILS were conducted with the low-activity reference material (LRM) glass developed previously for use as a glass test standard. Tests were conducted at 70 ± 2 °C using a LiCl/LiOH solution as the leachant to impose an initial pH of about 10 (at 70 °C). Participants were provided with LRM glass that had been crushed and sieved to isolate the -100 +200 mesh size fraction, and then washed to remove fines. Participants were asked to conduct a series of tests using different solution flow rate-to-sample mass ratios to generate a range of steady-state Si concentrations. The glass dissolution rate under each test condition was calculated using the steady-state Si concentration and solution flow rate that were measured in the test. The glass surface area was estimated from the mass of glass used in the test and the Si content of LRM glass was known. A linear relationship between the rate and the steady-state Si concentration (at Si concentrations less than 10 mg/L) was used to estimate the forward dissolution rate, which is the rate in the absence of dissolved Si. Participants were asked to sample the effluent solution at least five times after reaction times of between 3 and 14 days to measure the Si concentration and flow rate, and to verify that steady-state was achieved. Results were provided by seven participants and the data sets provided by five participants were sufficient to determine the forward rates independently. The average of the forward rates is 1.44 g/(m²d). The combined results of all participants were used to determine the consensus forward rate, which is 1.64 g/(m²d), and the expanded uncertainty, which is ± 1.90 g/(m²d) at the 95% confidence level. (Note that the uncertainty in the specific surface area of the crushed glass has been excluded from the uncertainty in the measured rate.) The ILS data allowed for additional analyses of the glass dissolution behavior and rate. One participant conducted three series of tests with the -100 +200 mesh size fraction glass, which provided a measured intra-laboratory precision of 1.29 ± 0.39 g/(m²d), and one series of tests with -80 +100 mesh size fraction, which indicated that particle size did not affect the measured forward rate. Other participants conducted replicate tests using two different reactor designs, ran tests at several temperatures, and analyzed test solutions collected during the first 3 hours of reaction. These results indicate that the reactor design does not have a significant effect on the measured rates, the apparent activation energy is 72 kJ/mol near 70 °C, and the dissolution rate measured during the first 3 hours is about 2.5 times higher than that measured at longer times. The higher rate is attributed to the dissolution of glass at fracture surfaces (e.g., sharp points and edges) that were formed when the glass was crushed. The ILS results indicate that the draft ASTM SPFT test method provides adequate guidance for a first-time user to conduct the test. The method addresses the major uncertainties in determining the forward dissolution rate: temperature, pH, flow rate, and dissolved Si concentration, and the ILS provides insight regarding the practicality of control limits called for in the method. For example, steady-state Si concentrations and constant flow rates can be maintained within 10%. Temperatures should be controlled within 1 °C and the solution pH should be constant within 0.3 pH units so that the effects of these variables are within the uncertainty in the measured rate.

1. INTRODUCTION

This report presents the results of tests conducted as part of an international interlaboratory study (ILS) to evaluate the precision and bias from using a single-pass flow-through (SPFT) test method to measure the dissolution rate of a borosilicate glass. Scientists at laboratories in France, Germany, Japan, South Korea, and the United States participated in the ILS. Although some scientists had conducted SPFT tests previously, the majority of participants had not. The SPFT test method used in the ILS was developed for standardization by the American Society for Testing and Analysis (ASTM) – International, based on test methods developed at Lawrence Livermore National Laboratory (LLNL) (Weed and Jackson 1979; Bates et al. 1992) and Pacific Northwest National Laboratory (PNNL) (McGrail and Peeler 1995). In both of those methods, leachant solution is pumped through a reaction cell, and the effluent solution is collected for analysis. The apparatuses differ primarily in the design of the reaction cell: the test specimen, which is usually crushed material but may be a monolithic specimen, is held between two filters in the LLNL design, whereas the sample rests in the bottom of a solution bottle in the PNNL design. Recent SPFT tests run at Argonne National Laboratory (ANL) were conducted using an in-line reaction cell design, in which leachant solution flowed upwards through an unconfined charge of glass (Jeong et al. 2002). The design of the reaction cell containing the glass was not specified for the ILS because the dissolution rate must, of course, be independent of the apparatus design. That is, any impact of the cell design on the glass dissolution rate in the test should be manifested in the test results. For example, the reaction cell volume affects the steady-state solution concentration that is attained in tests with a particular amount of glass and at a particular volumetric solution flow rate. The ILS was conducted to measure the precision with which the dissolution rate of a borosilicate glass can be measured with the SPFT test method, including the use of various reaction cell designs by the different participants. The draft procedure provided to the participants is given in Appendix A.

In this report, the solution pumped into the reaction cell containing the glass is referred to as the leachant, and the solution recovered after reacting with the glass is referred to as the test solution. The term “leachant” is used in this report for convenience to distinguish the solution that has not yet contacted the glass from the solution that has contacted the glass. However, it is the dissolution rate of the glass matrix that is being measured, not a leaching rate. The solution entering the reaction cell is also referred to as the influent solution and the solution leaving the reaction cell is also referred to as the effluent or test solution.

Borosilicate glass dissolution occurs through hydrolysis reactions that break bonds in the silicate network (Grambow 1985; Bourcier 1991; McGrail et al. 1998). Reactions that result in the release of other glass components occur in parallel, but the release of silica represents degradation of the glass structure. The dissolution rates of borosilicate glasses are known to be influenced by temperature, pH, and the common ion effect, wherein the concentrations of key glass components in the solution affect the rates of reactions through which the glass dissolves. The solution concentration of silicon has the greatest effect, but since other components may also have an effect, the phenomenon is referred to generically as solution feedback. The SPFT test was designed to measure glass dissolution rate under conditions in which solution feedback effects are held constant by continuously replacing the solution contacting the glass with fresh solution. The composition of the leachant solution and the flow rate used in the test couple with the glass dissolution rate to establish a steady-state solution composition. By measuring (1) the concentrations of soluble glass components (particularly silicon) in the solution that is flushed from the reaction cell and (2) the solution flow rate, the glass dissolution rate can be calculated at the particular level of solution feedback established under the test conditions that are used. The rate cannot be measured in the total absence of feedback effects, because a minimum concentration of glass components is required for analytical measurements to determine the glass dissolution rate. That is, the analytical limit of quantitation establishes the minimum solution feedback effect that can be attained when measuring the dissolution rate. By measuring the rates at various levels of solution feedback, the rate in

the absence of feedback effects can be estimated by extrapolation to zero concentration. This approach and its accuracy are evaluated using the data sets presented in this report.

The rate expression commonly used to model borosilicate glass dissolution is given in Eq. 1:

$$rate = k_0 \cdot 10^{\eta pH} \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot \left(1 - \frac{Q}{K}\right) \quad (1)$$

where

- $rate$ = specific dissolution rate, g/(m²d)
- k_0 = intrinsic rate constant, g/(m²d)
- η = pH dependence, unitless
- E_a = activation energy, kJ/mol
- R = gas constant, kJ/(mol K)
- Q = ion activity product of the solution, M
- K = pseudo-equilibrium constant for the glass, M.

The term $\left(1 - \frac{Q}{K}\right)$ accounts for solution feedback, where Q/K gives the ratio of the solution concentration to that of an apparent saturation solution. Since glass is thermodynamically unstable, the solution can never become saturated and a true equilibrium constant does not exist. Instead, the conditions under which the dissolution rates are immeasurably low are modeled as saturation conditions, and the solution concentrations are represented by K . The SPFT test method can be used to provide a measure of the dissolution rates at different values of pH, temperature, and Q/K that are controlled during the test. In most cases, test conditions are selected to maintain dilute solutions in which $Q \ll K$. For the ILS, participants were asked to conduct tests under several conditions to generate a range of Q/K values at fixed pH and temperature to measure the rate at various values of Q/K .

The dissolution rate is determined experimentally from the amount of a soluble component i released into solution from a known exposed surface area over a known duration, where the mass fraction of component i in the glass is also known. The rate expression is

$$rate = \frac{m(i)}{S^\circ \cdot f(i) \cdot t} \quad (2)$$

where

- $m(i)$ = mass of element i released from glass, g
- S° = initial surface area of the crushed glass, m²
- $f(i)$ = mass fraction of element i in the original glass, unitless
- t = test duration, s.

The term $f(i)$ relates the mass of element i that is released to the mass of glass that has dissolved. Expressing the amount of the released component i as a concentration gives

$$rate = \frac{C(i) \cdot V}{S^\circ \cdot f(i) \cdot t} \quad (3)$$

where

- $C(i)$ = concentration of element i released from glass, g/m³
- V = volume of solution, m³.

Under flowing conditions and at steady state, the concentration of i due to glass dissolution is the measured steady-state concentration $C^{ss}(i)$ minus the concentration of i present in the leachant $C^o(i)$

$$C(i) = C^{ss}(i) - C^o(i) \quad (4)$$

and the term V/t is defined as the volumetric flow rate F . Substituting

$$rate = NR(i) = \frac{[C^{ss}(i) - C^o(i)] \bullet F}{S^o \bullet f(i)} \quad (5)$$

where

- $NR(i)$ = normalized dissolution rate, g/(m²d)
- $C^{ss}(i)$ = steady-state concentration of Si in effluent, mg/L
- $C^o(i)$ = concentration of element i in control test, mg/L
- F = leachant volumetric flow rate, m³/s
- S^o = initial surface area of the crushed glass, m²
- $f(i)$ = mass fraction of element i in the original glass.

The glass dissolution rates in the SPFT tests (at constant pH and temperature) are calculated using Eq. 5. The glass dissolution rate is referred to as the normalized dissolution rate, $NR(i)$, to emphasize that the rate is based on the release of element i and that it is normalized to the glass surface area used in the test. Note that the value of $NR(i)$ is in terms of grams glass, not grams element i . Note that Eq. 5 uses the initial surface area, which is estimated based on the mass of glass used in the test and the size fraction of the crushed glass and is highly uncertain. A commonly used method to take the change of surface area during the test into account is discussed in Section 4.3.5. The pH and temperature dependencies of the rates can be determined using Eq. 1 (or other dissolution rate model). Although rates were to be measured at one pH and one temperature value in the ILS, it was expected that slightly different temperatures would be attained in tests conducted by different participants. It was also expected that different final solution pH values would be measured by different participants, even though the leachant composition was specified. The pH and temperature dependencies for dissolution of low-activity reference material glass were estimated by using Eq. 1 to compare the rates measured by the different participants.

2. EXPERIMENTAL METHOD

The ILS was conducted following standard protocol (ASTM 1999) with a glass that was formulated and made previously for use as a standard material in acceptance tests of vitrified low-activity waste. The glass is referred to as low-activity reference material (LRM) glass. An earlier ILS was conducted with LRM glass to determine the precision with which the glass composition could be measured and the precision of product consistency tests (PCTs) at 40 and 90 °C (Ebert and Wolf 2000). Although it was formulated as a non-radioactive surrogate for potential low-activity waste glasses, the LRM glass is fairly representative of high-level radioactive waste (HLW) glasses. It is an alkali aluminoborosilicate glass with many minor components filling network-forming and network-modifying roles. The major difference is that the LRM glass has a higher soda content (about 20 mass % Na₂O in LRM glass, compared with about 10–17% total alkali metals in HLW glasses). The higher soda content does not affect the dissolution mechanism of the glass or the capacity of the test to measure its dissolution rate.

Crushed glass was prepared at ANL and provided to participants for use in the tests to remove variance due to sample preparation from the test precision measured in the ILS. The reaction temperature was specified to be 70 ± 2 °C. The pH was not specified directly; rather, the leachant was specified to be a 0.004 m LiCl + 0.003 m LiOH solution. This solution imposes a pH of about 10 at 70 °C, but it does not have significant buffering capacity. However, the SPFT test conditions that minimize buildup of dissolved glass components in the solution also minimize changes in the pH due to glass corrosion. Test conditions were selected based on discussions and input from participants (see Appendix B).

The SPFT tests were conducted with a measured mass of glass, which was used to estimate the initial glass surface area S^0 . The mass fractions of glass components $f(i)$ were known from previous analyses. The leachant composition $C^0(i)$, solution flow rates F , and steady-state concentrations $C^{ss}(i)$ were measured as part of the ILS. The surface area of the crushed glass remains the least accurately known parameter in glass corrosion studies. Since participants used crushed glass from the same source and the surface area was calculated in the same way for all results (see Section 2.3), the uncertainty in the accuracy of the surface area does not affect the measured test precision. The use of the initial surface area in Eq. 5 is based on the assumption that the decrease in the surface area as the glass dissolves during the test is negligible; this requires that the particle size be sufficiently large and the reaction time sufficiently short relative to the dissolution rate. The validity of this assumption can be evaluated when the rates are measured.

Participants were requested to conduct tests over a range of F/S values, which could be achieved by using various amounts of glass and/or a range of solution flow rates, and to measure the Si concentration in the eluent after between 3 and 14 days of reaction. They were asked to report the flow rate, pH, and Si concentration for each sampling to determine the dissolution rate. They were also asked to measure the Li concentration to confirm the composition and stability of the leachant over the test duration and corroborate the measured pH. Enough glass was provided to conduct replicate tests to measure the intra-laboratory precision, if desired.

The results of the tests described in this report are used to determine the interlaboratory precision of the SPFT test method, which will be included in the *Precision and Bias* sections of the ASTM standard. Lessons learned by participants during execution of the tests may result in revision of the test method.

2.1 LEACHANT SOLUTION

Solutions of 0.004 molal LiCl and 0.003 molal LiOH were used as the leachant. For example, approximately 20-L batches of solution were prepared by dissolving 4.83 g LiCl•H₂O (Alfa Aesar®) and 2.52 g LiOH•H₂O (Alfa Aesar®) in about 20 L of demineralized water for the tests conducted at ANL.

The solutions were made in a large Nalgene container. A line was drawn on the container when the first batch of solution was made to indicate the 20-kg fill height. The container was filled to this line for all subsequent batches. More than one batch of leachant solution was needed for each series of tests. The variability in the solution volume of different batches is estimated to be less than 0.1 L (0.5%). As mentioned above, new leachant solution was slowly pumped into the leachant reservoir during the test, such that consecutive batches were blended over time. Aliquots of leachant solution recovered from the control test over the course of each test series were analyzed for pH (at room temperature), Si, and Li to monitor its consistency. The solution is predicted to have a pH near 10.0 at 70 °C and about pH 11.5 at room temperature, and is expected to have a Li concentration near 48.6 mg /L. Variance in the Li content may indicate variance in the leachant pH. The density of the leachant solution was measured to be 0.999 ± 0.001 g/mL, which is approximated as 1.00 g/mL for all calculations in this report.

2.2 GLASS

About 1000 lb of LRM glass had been made previously by Ferro Corp. (Cleveland, Ohio) for use as a standard test material. Glass from this source was prepared at ANL for use in the ILS. The glass was crushed and sieved to isolate the -100 +200 mesh size fraction, then washed repeatedly with ethanol and demineralized water to remove fines. Small amounts of the prepared glass were examined with a scanning electron microscope (SEM) to verify that fines had been removed and to document the size and shape of the particles. Photomicrographs of the crushed glass are shown in Fig. 1. The composition of the LRM glass had been measured as part of a previous ILS (Ebert and Wolf 2000); the composition is given in Table 1 as the mean and standard deviation measured in that study (values of s_L are from Table 4 of that reference). The elemental mass fractions of B, Na, and Si in LRM glass are 0.02438, 0.1484, and 0.2533, respectively.

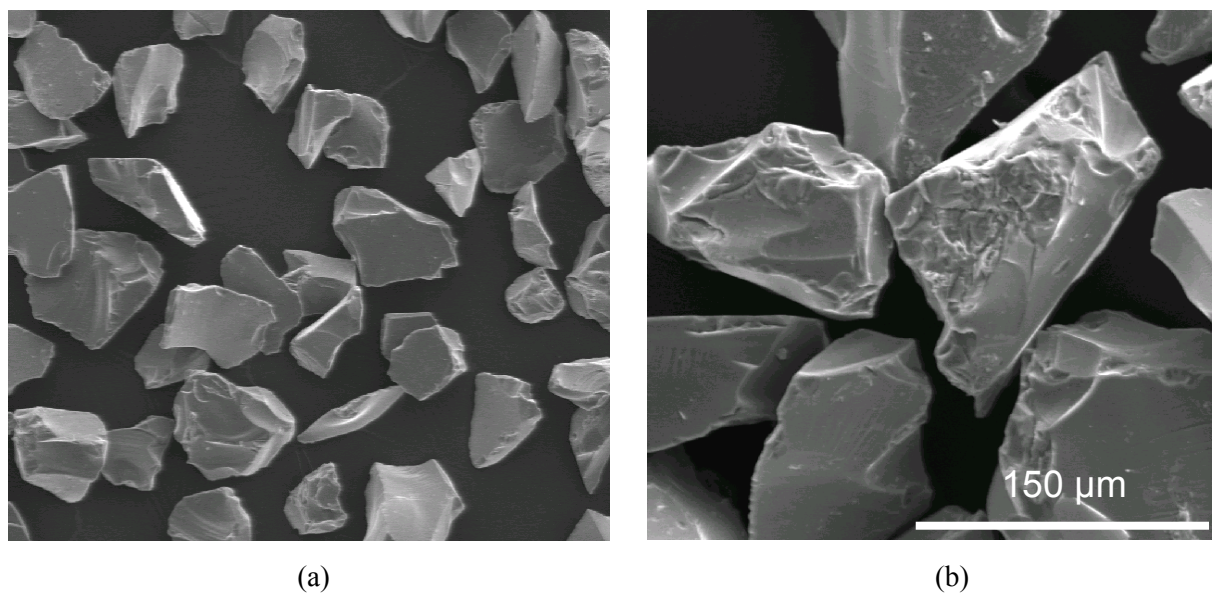


Figure 1. Crushed LRM glass in the -100 +200 mesh size fraction: (a) low magnification showing size distribution and (b) high magnification of individual particles.

Table 1. LRM Glass Composition, Oxide Mass % \pm Standard Deviation^a

Oxide	mass %	Oxide	mass %	Oxide	mass %
Al ₂ O ₃	9.51 \pm 0.34	K ₂ O	1.48 \pm 0.49	NiO	0.19 \pm 0.02
B ₂ O ₃	7.85 \pm 0.31	La ₂ O ₃	0.02 \pm nd ^b	P ₂ O ₅	0.54 \pm 0.07
CaO	0.54 \pm 0.09	Li ₂ O	0.11 \pm 0.03	PbO	0.10 \pm 0.02
CdO	0.16 \pm 0.02	MgO	0.10 \pm 0.01	SO ₃	0.30 \pm 0.06
Cr ₂ O ₃	0.19 \pm 0.02	MnO	0.08 \pm 0.01	SiO ₂	54.20 \pm 1.21
F	0.86 \pm 0.11	MoO ₃	0.10 \pm nd	TiO ₂	0.10 \pm 0.01
Fe ₂ O ₃	1.38 \pm 0.18	Na ₂ O	20.03 \pm 1.19	ZrO ₂	0.93 \pm 0.06

^a Sum of mean concentrations = 98.77%.^b Standard deviation not determined from ILS.

2.3 GLASS SURFACE AREA

Several methods have been used to calculate the specific surface area of crushed glass used in dissolution tests, including use of the arithmetic and geometric averages of the sieve sizes and by gas adsorption. In the present study, all tests were conducted with glass having the same size fraction and taken from the same source and the same specific surface area was used to calculate the rates from results of all participants. The method used to estimate the specific surface area does not affect the precision of the forward rate that is determined, although it does affect the accuracy of the rate.

For the ILS, the specific surface area of the –100 +200 mesh size fraction was estimated by assuming the particles of glass are spheres having a diameter of 112.5 μm , which is the arithmetic average of the 100 and 200 mesh sieve openings (75 and 150 μm , respectively). The sizes of the particles shown in Fig. 1 are consistent with the range of sieve openings, but the particles are not spherical. Some workers multiply the geometric area by a shape factor having a value between 1.5 and three to account for the irregular morphology. A shape factor was not used in the present analysis, although the rates calculated in this study can be easily adjusted if a more accurate surface area is determined. The density of a LRM prototype glass was measured to be $2.516 \pm 0.009 \text{ g/cm}^3$ (Wolf et al. 1998), and the density of the LRM glass used in the ILS is assumed to be the same. The specific surface area is calculated as

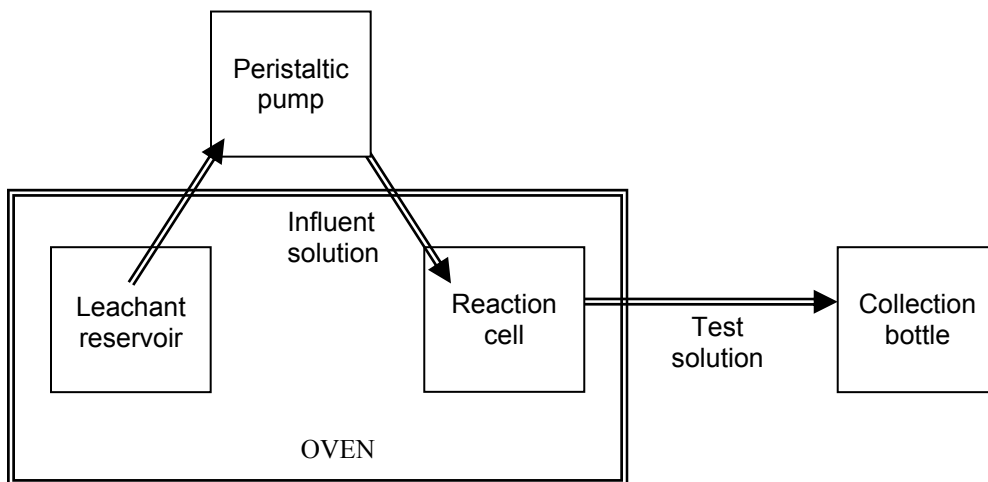
$$S_{sp}^{\circ} = \frac{6}{\rho \cdot d} \quad (6)$$

where S_{sp}° is the specific surface area of the unreacted glass, ρ is the density, and d is the diameter of the particle. The specific surface area of the –100 +200 mesh size fraction is calculated to be $0.021 \text{ m}^2/\text{g}$.

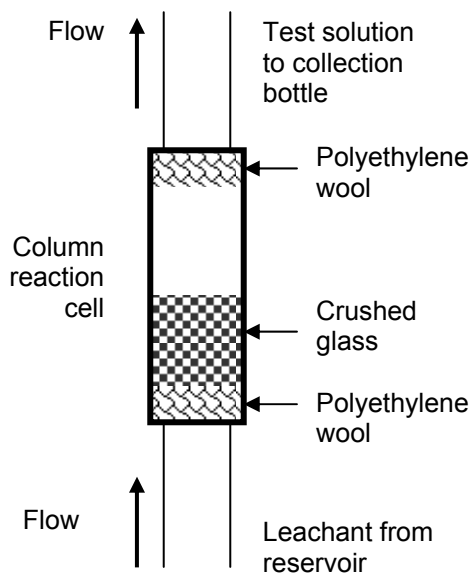
2.4 REACTOR DESIGN

The general apparatus design is shown in Fig. 2a and consists of a reservoir, a peristaltic pump that pulls leachant from the reservoir and pushes it through a reaction cell that contains the glass, and then out through an exit tube. Test solution exiting the reaction cell is either sampled for analysis or collected as waste. The leachant in the reservoir was purged with nitrogen by some participants to remove dissolved air. Other participants heated the leachant in the reservoir to exsolve dissolved air. The solution flow rate was controlled by the peristaltic pumping speed and the diameter of the tubing. Tests were conducted using one of two basic reactor configurations, referred to as column and jar designs. Schematic drawings

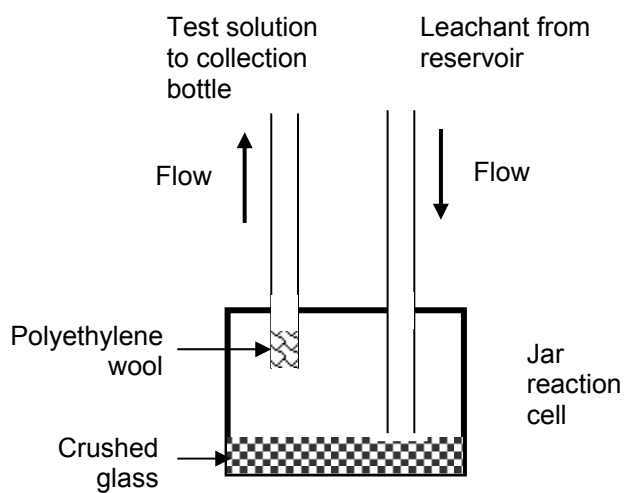
of the two cell types are shown in Figs. 2b and 2c. In the column-type reactor (Fig. 2b), the crushed glass is held in an in-line cell such that the solution is pumped up through the glass. A small amount of test solution may sit in the cell above the glass, or the cell may be completely filled with glass. The cell itself has a diameter similar to that of the tubing. In the jar-type reactor (Fig. 2c), glass sits at the bottom of a container that becomes filled with solution during the test. Incoming leachant displaces test solution from the jar and forces it out to the collection bottle. The leachant tube may project into the jar far enough that the leachant agitates the glass when it enters the cell. The test solution is mixed as a result of flow and diffusion. Plugs of polyethylene (or quartz) wool may be placed in the cell or exit tubing to prevent glass from being flushed out of the reactor (this was not a requirement in the draft procedure).



(a)



(b)



(c)

Fig. 2. Basic Designs of (a) Apparatus, (b) Column Reactor, and (c) Jar Reactor

3. RESULTS

Test results provided by each ILS participant are provided in the following sections. Participants are referred to as Participants A, B, C, D, E, F, and G to retain anonymity, which is standard practice in ILS. The results include the mass of glass used in the test; the pH (measured at room temperature), Si, and Li concentrations; and the solution flow rate, which was calculated from the measured mass of test solution that was collected and the collection time. Values of F/S were calculated for all test results from the flow rates reported by the participants and from the masses of glass used in a test using a specific surface area of $0.021 \text{ m}^2/\text{g}$. (No entries for F/S are shown for blank tests conducted without glass.) Entries given as “nr” indicate that values were not reported; pH and Li concentrations were not reported for all tests by all participants.

The Si concentrations that were measured in each sampling and the values of F/S are plotted to determine the steady-state values. The plotted concentrations have not been adjusted for background concentrations; the Si concentrations measured in the leachant solutions or blank tests are subtracted from the steady-state Si concentrations as part of the rate calculation. Dashed lines are drawn on most plots to show the mean values of F/S and Si concentrations for each test. The results of some samplings were excluded from the mean because the leachant flow was not stable or the result was a clear outlier. Due to the wide range of flow rates used by most participants, collection times for the samples of test solutions varied from a few minutes to several hours. Most participants did not report the time of day that solution collection started and stopped, and some participants reported the samplings in terms of consecutive collection numbers rather than test duration. Whereas this does not affect calculation of the steady-state flow rates (F/S) or Si concentrations, it does hinder calculation of temporal effects that may have occurred. The test duration at the time of sampling was estimated based on data that were provided by the participants.

3.1 RESULTS FROM PARTICIPANT A

Participant A conducted three test series: Series A-1 and A-2 both included tests at nine different F/S values and one blank test; Series A-3 included tests at 13 different F/S values and one blank test. In all tests, leachant was pumped vertically up through the glass sample in the reaction cell using a column-type reactor. A plug of polypropylene wool was placed at the top of each cell to prevent glass from being flushed out. Test solutions were sampled between 7 and 15 times (14 samplings for most tests) over the 10- to 14-day test durations. The test solutions were not filtered before analysis. Solutions were acidified with ultrapure nitric acid prior to analysis with inductively coupled plasma-mass spectrometry (ICP-MS).

The test results are compiled in Tables 2–4. The flow rates and Si concentrations measured in different tests are shown in Figs. 3–5 for series LRM-1, -2, and -3, respectively. The Si concentrations measured in the blank tests and tests with glass are given by the right ordinate, and the flow rates (for the blank tests) or F/S values (for tests with glass) are given by the left ordinate; both are plotted against the sample number. Note that the sample numbers are not linear with the reaction time; also, samples were collected daily for the first few days and twice daily for the remaining test duration. Dashed lines are drawn at the mean values of flow rate, F/S, and Si concentration.

Note that tests LRM-3-E, -F, -G, -H, and -I were terminated after seven samplings (10 days), and tests LRM-3-L, -M, -N, and -O were started using those reaction lines. Test LRM-3-J was terminated after nine samplings (12 days), and tests LRM-3-B, -C, and -D were terminated after 10 samplings (12 days).

Variations in the flow rates of the individual tests ranged from 0.44% relative standard deviation (rsd) in test LRM-1-H to 3.3% rsd in test LRM-3-J. Variations in the measured Si concentrations in each test were from 4.28% rsd in test LRM-3-E to 17.6% rsd in test LRM-3-O.

Table 2. Summary of Test Results for Participant A: Series LRM-1

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
LRM-1-A blank test						
LRM-1-A1	3	11.00	0.209	43.1	7.77E-10	–
LRM-1-A2	4	11.26	0.189	43.8	7.57E-10	–
LRM-1-A3	5	11.22	0.178	40.4	7.55E-10	–
LRM-1-A4	6	11.51	0.183	42.8	7.53E-10	–
LRM-1-A5	7	11.34	0.170	46.4	7.57E-10	–
LRM-1-A6	10	11.25	0.173	47.1	7.32E-10	–
LRM-1-A7	11	11.31	0.135	43.0	7.58E-10	–
LRM-1-A8	11.3	11.27	0.126	48.1	7.55E-10	–
LRM-1-A9	12	11.31	0.125	49.5	7.51E-10	–
LRM-1-A10	12.3	11.25	0.139	47.5	7.46E-10	–
LRM-1-A11	13	11.24	0.133	43.0	7.45E-10	–
LRM-1-A12	13.3	11.23	0.146	44.8	7.63E-10	–
LRM-1-A13	14	11.29	0.133	39.6	7.48E-10	–
LRM-1-A14	14.3	11.26	0.158	45.6	7.34E-10	–
LRM-1-B conducted with 0.20 g glass						
LRM-1-B1	3	10.97	8.44	35.5	7.83E-10	1.87E-07
LRM-1-B2	4	11.17	9.64	36.5	8.08E-10	1.92E-07
LRM-1-B3	5	11.16	9.17	36.4	7.84E-10	1.87E-07
LRM-1-B4	6	11.24	10.6	38.6	7.84E-10	1.87E-07
LRM-1-B5	7	11.28	10.0	36.8	7.88E-10	1.88E-07
LRM-1-B6	10	11.18	9.13	36.6	7.90E-10	1.88E-07
LRM-1-B7	11	11.25	9.29	37.6	7.82E-10	1.86E-07
LRM-1-B8	11.3	11.21	9.29	37.7	7.82E-10	1.86E-07
LRM-1-B9	12	11.19	10.2	40.1	7.89E-10	1.88E-07
LRM-1-B10	12.3	11.20	10.9	39.1	7.80E-10	1.86E-07
LRM-1-B11	13	11.18	9.14	33.8	7.86E-10	1.87E-07
LRM-1-B12	13.3	11.18	8.78	36.9	7.97E-10	1.90E-07
LRM-1-B13	14	11.22	8.25	34.9	7.84E-10	1.87E-07
LRM-1-B14	14.3	11.17	9.64	38.5	7.69E-10	1.83E-07
LRM-1-C conducted with 1.00 g glass						
LRM-1-C1	3	10.85	26.4	45.1	8.22E-10	3.91E-08
LRM-1-C2	4	11.04	25.7	43.4	8.37E-10	3.98E-08
LRM-1-C3	5	11.08	22.0	37.8	8.09E-10	3.85E-08
LRM-1-C4	6	11.11	23.9	39.5	8.13E-10	3.87E-08
LRM-1-C5	7	11.13	22.0	37.8	8.13E-10	3.87E-08
LRM-1-C6	10	11.05	25.0	42.0	7.91E-10	3.77E-08
LRM-1-C7	11	11.11	23.3	40.8	8.04E-10	3.83E-08
LRM-1-C8	11.3	11.04	24.0	38.7	8.14E-10	3.88E-08
LRM-1-C9	12	11.09	24.3	39.6	8.08E-10	3.85E-08
LRM-1-C10	12.3	10.97	26.7	43.0	8.23E-10	3.92E-08
LRM-1-C11	13	11.06	22.4	37.3	8.09E-10	3.85E-08
LRM-1-C12	13.3	11.13	26.8	43.5	8.07E-10	3.84E-08
LRM-1-C13	14	11.08	26.5	45.0	8.15E-10	3.88E-08
LRM-1-C14	14.3	11.03	26.1	43.7	7.85E-10	3.74E-08
LRM-1-D conducted with 0.50 g glass						
LRM-1-D1	3	10.95	19.1	45.5	8.23E-10	7.84E-08
LRM-1-D2	4	11.10	19.7	44.7	8.20E-10	7.81E-08
LRM-1-D3	5	11.16	19.1	44.1	8.23E-10	7.84E-08
LRM-1-D4	6	11.12	19.6	43.4	8.23E-10	7.84E-08
LRM-1-D5	7	11.22	20.8	45.0	8.26E-10	7.86E-08
LRM-1-D6	10	11.12	19.1	43.1	7.89E-10	7.52E-08

Table 2. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
LRM-1-D7	11	11.17	18.7	45.5	8.24E-10	7.85E-08
LRM-1-D8	11.3	11.12	19.2	42.8	8.24E-10	7.85E-08
LRM-1-D9	12	11.15	18.9	43.8	8.23E-10	7.83E-08
LRM-1-D10	12.3	11.10	18.9	44.7	8.21E-10	7.82E-08
LRM-1-D11	13	11.14	18.3	43.5	8.22E-10	7.83E-08
LRM-1-D12	13.3	11.12	17.4	41.0	8.19E-10	7.80E-08
LRM-1-D13	14	11.15	17.5	41.2	8.22E-10	7.83E-08
LRM-1-D14	14.3	11.08	18.4	41.5	8.11E-10	7.72E-08
LRM-1-E conducted with 1.00 g glass						
LRM-1-E1	3	11.07	13.9	45.2	3.64E-09	1.73E-07
LRM-1-E2	4	11.21	12.5	39.5	3.58E-09	1.70E-07
LRM-1-E3	5	11.26	13.7	40.7	3.60E-09	1.72E-07
LRM-1-E4	6	11.29	13.0	39.5	3.62E-09	1.73E-07
LRM-1-E5	7	11.27	12.9	39.4	3.60E-09	1.72E-07
LRM-1-E6	10	11.20	13.4	44.8	3.61E-09	1.72E-07
LRM-1-E7	11	11.17	11.5	39.3	3.60E-09	1.71E-07
LRM-1-E8	11.3	11.27	13.7	42.8	3.58E-09	1.71E-07
LRM-1-E9	12	11.20	13.4	43.0	3.62E-09	1.72E-07
LRM-1-E10	12.3	11.22	15.6	49.7	3.59E-09	1.71E-07
LRM-1-E11	13	11.20	13.0	42.0	3.62E-09	1.72E-07
LRM-1-E12	13.3	11.27	14.5	45.6	3.57E-09	1.70E-07
LRM-1-E13	14	11.22	14.2	44.9	3.59E-09	1.71E-07
LRM-1-E14	14.3	11.25	9.35	42.4	3.67E-09	1.75E-07
LRM-1-F conducted with 0.67 g glass						
LRM-1-F1	3	11.00	10.6	42.8	3.74E-09	2.66E-07
LRM-1-F2	4	11.28	9.99	40.6	3.72E-09	2.64E-07
LRM-1-F3	5	11.29	11.6	44.7	3.71E-09	2.64E-07
LRM-1-F4	6	11.30	10.4	39.7	3.71E-09	2.64E-07
LRM-1-F5	7	11.33	9.05	35.6	3.71E-09	2.64E-07
LRM-1-F6	10	11.21	7.72	32.5	3.71E-09	2.64E-07
LRM-1-F7	11	11.22	9.51	41.6	3.72E-09	2.65E-07
LRM-1-F8	11.3	11.29	9.61	39.1	3.70E-09	2.63E-07
LRM-1-F9	12	11.29	10.3	41.9	3.71E-09	2.63E-07
LRM-1-F10	12.3	11.26	9.36	38.1	3.71E-09	2.63E-07
LRM-1-F11	13	11.24	8.98	37.1	3.72E-09	2.65E-07
LRM-1-F12	13.3	11.24	10.1	42.6	3.68E-09	2.61E-07
LRM-1-F13	14	11.24	10.1	44.4	3.69E-09	2.62E-07
LRM-1-F14	14.3	11.25	15.7	52.2	3.58E-09	2.54E-07
LRM-1-G conducted with 1.00 g glass						
LRM-1-G1	3	11.09	9.27	51.4	6.59E-09	3.14E-07
LRM-1-G2	4	11.30	9.16	47.6	6.65E-09	3.17E-07
LRM-1-G3	5	11.31	7.95	41.7	6.56E-09	3.12E-07
LRM-1-G4	6	11.31	9.36	45.3	6.60E-09	3.14E-07
LRM-1-G5	7	11.32	11.8	57.9	6.60E-09	3.15E-07
LRM-1-G6	10	11.26	8.03	44.0	6.50E-09	3.10E-07
LRM-1-G7	11	11.25	7.72	43.2	6.59E-09	3.14E-07
LRM-1-G8	11.3	11.28	8.11	42.7	6.57E-09	3.13E-07
LRM-1-G9	12	11.30	9.07	46.6	6.56E-09	3.12E-07
LRM-1-G10	12.3	11.27	9.23	46.7	6.53E-09	3.11E-07
LRM-1-G11	13	11.25	8.65	44.3	6.56E-09	3.12E-07
LRM-1-G12	13.3	11.29	8.99	45.5	6.54E-09	3.11E-07
LRM-1-G13	14	11.26	9.34	47.8	6.56E-09	3.12E-07
LRM-1-G14	14.3	11.29	9.14	46.3	6.56E-09	3.12E-07

Table 2. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^a , m/s
LRM-1-H conducted with 0.33 g glass						
LRM-1-H1	3	10.96	6.10	45.7	3.65E-09	5.27E-07
LRM-1-H2	4	11.29	6.62	46.3	3.66E-09	5.28E-07
LRM-1-H3	5	11.28	6.10	43.2	3.64E-09	5.26E-07
LRM-1-H4	6	11.28	6.63	45.2	3.64E-09	5.26E-07
LRM-1-H5	7	11.36	6.42	42.3	3.65E-09	5.27E-07
LRM-1-H6	10	11.27	3.61	44.3	3.62E-09	5.22E-07
LRM-1-H7	11	11.21	5.65	45.6	3.65E-09	5.27E-07
LRM-1-H8	11.3	11.28	6.01	46.0	3.62E-09	5.22E-07
LRM-1-H9	12	11.28	6.07	46.3	3.64E-09	5.25E-07
LRM-1-H10	12.3	11.26	6.01	45.8	3.64E-09	5.25E-07
LRM-1-H11	13	11.26	5.86	44.0	3.64E-09	5.25E-07
LRM-1-H12	13.3	11.30	5.81	44.8	3.62E-09	5.22E-07
LRM-1-H13	14	11.26	4.18	47.4	3.64E-09	5.25E-07
LRM-1-H14	14.3	11.31	5.97	46.4	3.61E-09	5.21E-07
LRM-1-I conducted with 1.00 g glass						
LRM-1-I1	3	11.16	4.80	45.6	1.37E-08	6.52E-07
LRM-1-I2	4	11.33	4.87	42.8	1.38E-08	6.55E-07
LRM-1-I3	5	11.28	4.28	37.6	1.36E-08	6.50E-07
LRM-1-I4	6	11.31	4.25	36.6	1.37E-08	6.52E-07
LRM-1-I5	7	11.35	5.23	44.4	1.37E-08	6.50E-07
LRM-1-I6	10	11.28	4.17	43.1	1.34E-08	6.38E-07
LRM-1-I7	11	11.21	3.93	39.5	1.36E-08	6.45E-07
LRM-1-I8	11.3	11.33	4.14	40.4	1.36E-08	6.49E-07
LRM-1-I9	12	11.31	4.15	40.0	1.36E-08	6.49E-07
LRM-1-I10	12.3	11.31	4.96	45.6	1.36E-08	6.48E-07
LRM-1-I11	13	11.29	4.05	39.7	1.37E-08	6.50E-07
LRM-1-I12	13.3	11.31	4.64	43.3	1.34E-08	6.39E-07
LRM-1-I13	14	11.32	4.25	39.4	1.33E-08	6.34E-07
LRM-1-I14	14.3	11.32	4.86	44.9	1.32E-08	6.29E-07
LRM-1-J conducted with 0.20 g glass						
LRM-1-J1	3	11.06	4.16	44.9	3.64E-09	8.67E-07
LRM-1-J2	4	11.32	4.17	44.9	3.64E-09	8.67E-07
LRM-1-J3	5	11.32	4.15	43.8	3.64E-09	8.67E-07
LRM-1-J4	6	11.30	4.70	42.9	3.65E-09	8.69E-07
LRM-1-J5	7	11.34	4.36	46.2	3.64E-09	8.66E-07
LRM-1-J6	10	11.28	4.91	40.4	3.63E-09	8.65E-07
LRM-1-J7	11	11.23	3.24	40.5	3.64E-09	8.68E-07
LRM-1-J8	11.3	11.29	3.45	39.0	3.70E-09	8.81E-07
LRM-1-J9	12	11.31	3.98	46.1	3.66E-09	8.72E-07
LRM-1-J10	12.3	11.29	4.12	45.8	3.65E-09	8.68E-07
LRM-1-J11	13	11.28	3.78	42.5	3.62E-09	8.62E-07
LRM-1-J12	13.3	11.28	4.00	45.0	3.63E-09	8.64E-07
LRM-1-J13	14	11.29	5.69	43.8	3.62E-09	8.62E-07
LRM-1-J14	14.3	11.28	3.92	44.3	3.61E-09	8.60E-07

^aTest duration at time of sampling was estimated from data provided by Participant A.

Table 3. Summary of Test Results for Participant A: Series LRM-2

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
LRM-2-A test blank						
LRM-2-A1	3	11.04	0.219	45.9	7.38E-10	–
LRM-2-A2	4	11.06	0.213	43.2	7.30E-10	–
LRM-2-A3	5	11.03	0.192	38.5	7.76E-10	–
LRM-2-A4	6	11.18	0.192	41.0	7.53E-10	–
LRM-2-A5	7	11.20	0.175	36.9	7.74E-10	–
LRM-2-A6	10	11.29	0.175	37.0	7.08E-10	–
LRM-2-A7	11	11.39	0.170	41.9	7.99E-10	–
LRM-2-A8	11.3	11.35	0.188	43.5	7.61E-10	–
LRM-2-A9	12	11.35	0.189	49.4	7.91E-10	–
LRM-2-A10	12.3	11.34	0.184	48.1	7.81E-10	–
LRM-2-A11	13	11.38	0.163	42.3	7.85E-10	–
LRM-2-A12	13.3	11.37	0.166	42.0	8.05E-10	–
LRM-2-A13	14	11.38	0.164	38.7	7.85E-10	–
LRM-2-A14	14.3	11.37	0.185	41.2	7.70E-10	–
LRM-2-B conducted with 0.20 g glass						
LRM-2-B1	3	10.92	11.6	46.9	8.00E-10	1.90E-07
LRM-2-B2	4	10.94	11.6	47.9	7.87E-10	1.87E-07
LRM-2-B3	5	10.90	10.8	46.1	7.84E-10	1.87E-07
LRM-2-B4	6	11.08	12.3	46.5	7.84E-10	1.87E-07
LRM-2-B5	7	11.14	13.1	47.9	7.92E-10	1.89E-07
LRM-2-B6	10	11.24	13.1	47.4	7.82E-10	1.86E-07
LRM-2-B7	11	11.28	12.7	46.2	7.91E-10	1.88E-07
LRM-2-B8	11.3	11.28	13.6	47.9	7.81E-10	1.86E-07
LRM-2-B9	12	11.24	12.9	46.8	7.90E-10	1.88E-07
LRM-2-B10	12.3	11.23	13.0	46.9	7.88E-10	1.88E-07
LRM-2-B11	13	11.27	12.0	47.2	7.91E-10	1.88E-07
LRM-2-B12	13.3	11.29	12.5	47.4	8.13E-10	1.94E-07
LRM-2-B13	14	11.29	12.7	47.7	7.89E-10	1.88E-07
LRM-2-B14	14.3	11.28	13.7	49.6	8.02E-10	1.91E-07
LRM-2-C conducted with 1.00 g glass						
LRM-2-C1	3	10.81	25.8	44.5	8.52E-10	4.06E-08
LRM-2-C2	4	10.81	24.8	44.7	8.14E-10	3.88E-08
LRM-2-C3	5	10.80	19.5	35.1	7.81E-10	3.72E-08
LRM-2-C4	6	11.04	26.1	41.7	8.13E-10	3.87E-08
LRM-2-C5	7	11.04	26.3	41.2	8.19E-10	3.90E-08
LRM-2-C6	10	11.12	29.4	44.7	8.08E-10	3.85E-08
LRM-2-C7	11	11.15	24.7	36.6	8.14E-10	3.88E-08
LRM-2-C8	11.3	11.15	28.3	43.2	8.00E-10	3.81E-08
LRM-2-C9	12	11.12	29.3	44.9	8.07E-10	3.84E-08
LRM-2-C10	12.3	11.12	30.5	43.4	8.13E-10	3.87E-08
LRM-2-C11	13	11.13	16.7	40.0	8.06E-10	3.84E-08
LRM-2-C12	13.3	11.23	25.8	38.4	8.16E-10	3.88E-08
LRM-2-C13	14	11.18	26.2	39.9	8.23E-10	3.92E-08
LRM-2-C14	14.3	11.15	24.4	39.4	7.59E-10	3.62E-08
LRM-2-D conducted with 0.50 g glass						
LRM-2-D1	3	10.86	19.0	46.1	8.31E-10	7.91E-08
LRM-2-D2	4	10.86	19.0	45.8	8.37E-10	7.97E-08
LRM-2-D3	5	10.83	16.5	40.6	8.19E-10	7.80E-08
LRM-2-D4	6	11.00	17.2	37.8	8.32E-10	7.93E-08
LRM-2-D5	7	11.05	21.6	43.9	8.25E-10	7.85E-08
LRM-2-D6	10	11.16	19.3	39.2	8.27E-10	7.87E-08

Table 3. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
LRM-2-D7	11	11.17	19.8	39.7	8.25E-10	7.86E-08
LRM-2-D8	11.3	11.17	24.5	47.0	8.31E-10	7.91E-08
LRM-2-D9	12	11.14	22.1	42.9	8.25E-10	7.86E-08
LRM-2-D10	12.3	11.13	26.4	50.7	8.33E-10	7.94E-08
LRM-2-D11	13	11.12	20.2	40.6	8.24E-10	7.84E-08
LRM-2-D12	13.3	11.16	19.7	39.4	8.42E-10	8.02E-08
LRM-2-D13	14	11.22	22.5	44.4	8.07E-10	7.68E-08
LRM-2-D14	14.3	11.21	23.2	44.8	8.27E-10	7.87E-08
LRM-2-E conducted with 1.00 g glass						
LRM-2-E1	3	11.02	10.9	33.9	3.62E-09	1.72E-07
LRM-2-E2	4	11.02	13.0	41.6	3.63E-09	1.73E-07
LRM-2-E3	5	10.99	13.7	43.6	3.62E-09	1.72E-07
LRM-2-E4	6	11.13	13.4	39.6	3.62E-09	1.72E-07
LRM-2-E5	7	11.15	13.7	38.9	3.58E-09	1.70E-07
LRM-2-E6	10	11.29	13.9	36.3	3.62E-09	1.72E-07
LRM-2-E7	11	11.28	13.8	37.4	3.58E-09	1.71E-07
LRM-2-E8	11.3	11.33	13.9	35.1	3.60E-09	1.71E-07
LRM-2-E9	12	11.30	15.0	37.8	3.69E-09	1.76E-07
LRM-2-E10	12.3	11.35	15.7	39.4	3.59E-09	1.71E-07
LRM-2-E11	13	11.33	13.4	33.5	3.64E-09	1.73E-07
LRM-2-E12	13.3	11.38	16.9	41.3	3.60E-09	1.71E-07
LRM-2-E13	14	11.35	14.7	38.7	3.57E-09	1.70E-07
LRM-2-E14	14.3	11.35	14.8	37.5	3.57E-09	1.70E-07
LRM-2-F conducted with 0.67 g glass						
LRM-2-F1	3	11.00	10.4	43.0	3.77E-09	2.68E-07
LRM-2-F2	4	11.03	10.7	43.3	3.73E-09	2.65E-07
LRM-2-F3	5	11.05	11.5	45.2	3.72E-09	2.64E-07
LRM-2-F4	6	11.17	11.7	42.8	3.72E-09	2.65E-07
LRM-2-F5	7	11.20	11.6	42.0	3.74E-09	2.66E-07
LRM-2-F6	10	11.33	10.9	37.9	3.74E-09	2.66E-07
LRM-2-F7	11	11.30	11.3	39.0	3.68E-09	2.61E-07
LRM-2-F8	11.3	11.34	11.4	40.2	3.73E-09	2.65E-07
LRM-2-F9	12	11.32	10.2	38.0	3.72E-09	2.64E-07
LRM-2-F10	12.3	11.37	9.96	36.7	3.68E-09	2.62E-07
LRM-2-F11	13	11.38	11.0	41.5	3.72E-09	2.64E-07
LRM-2-F12	13.3	11.37	11.6	40.6	3.72E-09	2.65E-07
LRM-2-F13	14	11.35	12.2	42.3	3.74E-09	2.66E-07
LRM-2-F14	14.3	11.36	12.0	40.9	3.70E-09	2.63E-07
LRM-2-G conducted with 1.00 g glass						
LRM-2-G1	3	11.07	9.54	48.8	6.58E-09	3.13E-07
LRM-2-G2	4	11.06	9.08	46.9	6.55E-09	3.12E-07
LRM-2-G3	5	11.06	8.74	45.6	6.56E-09	3.13E-07
LRM-2-G4	6	11.20	8.84	43.2	6.62E-09	3.15E-07
LRM-2-G5	7	11.25	7.88	37.3	6.60E-09	3.14E-07
LRM-2-G6	10	11.35	8.51	38.1	6.52E-09	3.10E-07
LRM-2-G7	11	11.32	8.78	39.1	6.58E-09	3.13E-07
LRM-2-G8	11.3	11.35	10.4	42.8	6.54E-09	3.11E-07
LRM-2-G9	12	11.33	10.1	44.7	6.53E-09	3.11E-07
LRM-2-G10	12.3	11.38	11.2	46.6	6.55E-09	3.12E-07
LRM-2-G11	13	11.40	9.89	43.6	6.61E-09	3.15E-07
LRM-2-G12	13.3	11.39	9.84	42.5	6.55E-09	3.12E-07
LRM-2-G13	14	11.36	9.37	40.5	6.31E-09	3.01E-07
LRM-2-G14	14.3	11.34	9.66	40.7	6.57E-09	3.13E-07

Table 3. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^a , m/s
LRM-2-H conducted with 0.33 g glass						
LRM-2-H1	3	11.05	5.77	43.8	3.67E-09	5.29E-07
LRM-2-H2	4	11.06	4.90	37.4	3.66E-09	5.27E-07
LRM-2-H3	5	11.08	5.15	39.9	3.63E-09	5.23E-07
LRM-2-H4	6	11.18	4.94	36.0	3.66E-09	5.28E-07
LRM-2-H5	7	11.26	5.86	39.9	3.64E-09	5.25E-07
LRM-2-H6	10	11.37	5.50	38.5	3.67E-09	5.30E-07
LRM-2-H7	11	11.33	6.06	42.6	3.58E-09	5.17E-07
LRM-2-H8	11.3	11.36	7.09	45.2	3.52E-09	5.07E-07
LRM-2-H9	12	11.35	6.83	46.5	3.63E-09	5.24E-07
LRM-2-H10	12.3	11.40	7.73	50.2	3.64E-09	5.26E-07
LRM-2-H11	13	11.38	5.76	39.3	3.67E-09	5.29E-07
LRM-2-H12	13.3	11.39	5.84	37.1	3.64E-09	5.25E-07
LRM-2-H13	14	11.41	6.05	39.7	3.68E-09	5.31E-07
LRM-2-H14	14.3	11.40	6.90	45.0	3.63E-09	5.24E-07
LRM-2-I conducted with 1.00 g glass						
LRM-2-I1	3	11.08	7.08	47.8	1.37E-08	6.50E-07
LRM-2-I2	4	11.11	4.86	39.5	1.36E-08	6.49E-07
LRM-2-I3	5	11.09	4.46	39.3	1.35E-08	6.41E-07
LRM-2-I4	6	11.19	4.62	42.2	1.36E-08	6.47E-07
LRM-2-I5	7	11.26	5.07	45.3	1.37E-08	6.55E-07
LRM-2-I6	10	11.38	3.99	34.3	1.35E-08	6.41E-07
LRM-2-I7	11	11.35	4.61	38.0	1.34E-08	6.37E-07
LRM-2-I8	11.3	11.42	5.26	41.0	1.35E-08	6.43E-07
LRM-2-I9	12	11.36	5.83	47.0	1.35E-08	6.44E-07
LRM-2-I10	12.3	11.39	5.49	42.6	1.36E-08	6.46E-07
LRM-2-I11	13	11.39	4.87	40.5	1.36E-08	6.47E-07
LRM-2-I12	13.3	11.38	5.03	40.3	1.36E-08	6.48E-07
LRM-2-I13	14	11.39	5.23	43.6	1.36E-08	6.48E-07
LRM-2-I14	14.3	11.39	3.45	36.5	1.34E-08	6.38E-07
LRM-2-J conducted with 0.20 g glass						
LRM-2-J1	3	11.10	3.22	43.4	3.63E-09	8.64E-07
LRM-2-J2	4	11.12	3.37	44.4	3.62E-09	8.63E-07
LRM-2-J3	5	11.09	3.21	44.3	3.61E-09	8.59E-07
LRM-2-J4	6	11.21	2.95	41.3	3.66E-09	8.71E-07
LRM-2-J5	7	11.27	2.72	36.3	3.66E-09	8.71E-07
LRM-2-J6	10	11.36	3.06	37.7	3.65E-09	8.69E-07
LRM-2-J7	11	11.35	2.76	38.4	3.61E-09	8.60E-07
LRM-2-J8	11.3	11.38	3.15	42.4	3.63E-09	8.63E-07
LRM-2-J9	12	11.37	3.09	42.5	3.66E-09	8.71E-07
LRM-2-J10	12.3	11.40	3.23	38.6	3.65E-09	8.69E-07
LRM-2-J11	13	11.35	2.83	38.4	3.65E-09	8.69E-07
LRM-2-J12	13.3	11.41	3.23	40.5	3.61E-09	8.59E-07
LRM-2-J13	14	11.40	3.07	40.4	3.70E-09	8.81E-07
LRM-2-J14	14.3	11.40	3.21	44.2	3.61E-09	8.59E-07

^aTest duration at time of sampling was estimated from data provided by Participant A.

Table 4. Summary of Test Results for Participant A: Series LRM-3

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
LRM-3-A blank test						
LRM-3-A1	3	11.16	0.237	38.3	7.92E-10	–
LRM-3-A2	4	11.16	0.233	32.4	7.93E-10	–
LRM-3-A3	5	11.21	0.291	40.3	7.95E-10	–
LRM-3-A4	6	11.25	0.196	43.0	7.99E-10	–
LRM-3-A5	7	11.25	0.171	24.0	8.04E-10	–
LRM-3-A6	10	11.30	0.138	43.2	8.17E-10	–
LRM-3-A7	11	11.27	0.139	40.6	7.98E-10	–
LRM-3-A8	11.3	11.33	0.126	44.9	7.93E-10	–
LRM-3-A9	12	11.33	0.140	48.6	7.95E-10	–
LRM-3-A10	12.3	11.30	0.119	51.1	7.96E-10	–
LRM-3-A11	13	11.25	0.107	39.4	7.75E-10	–
LRM-3-A12	14	11.28	0.128	45.2	7.69E-10	–
LRM-3-B conducted with 0.20 g glass						
LRM-3-B1	3	11.04	11.0	44.0	8.05E-10	1.92E-07
LRM-3-B2	4	11.04	11.0	44.8	7.94E-10	1.89E-07
LRM-3-B3	5	11.09	11.8	45.8	8.05E-10	1.92E-07
LRM-3-B4	6	11.15	9.52	37.8	8.05E-10	1.92E-07
LRM-3-B5	7	11.16	10.5	41.4	8.01E-10	1.91E-07
LRM-3-B6	10	11.20	10.0	38.1	8.22E-10	1.96E-07
LRM-3-B7	11	11.21	11.4	44.2	7.99E-10	1.90E-07
LRM-3-B8	11.3	11.25	11.7	43.5	8.14E-10	1.94E-07
LRM-3-B9	12	11.25	12.6	46.8	7.94E-10	1.89E-07
LRM-3-B10	12.3	11.16	12.4	46.2	8.10E-10	1.93E-07
LRM-3-C conducted with 1.00 g glass						
LRM-3-C1	3	10.90	25.1	43.6	8.26E-10	3.94E-08
LRM-3-C2	4	11.22	27.9	41.6	8.15E-10	3.88E-08
LRM-3-C3	5	11.20	30.4	41.4	8.16E-10	3.89E-08
LRM-3-C4	6	11.17	29.3	42.8	8.46E-10	4.03E-08
LRM-3-C5	7	11.10	23.3	36.6	8.27E-10	3.94E-08
LRM-3-C6	10	11.12	25.4	39.7	8.22E-10	3.92E-08
LRM-3-C7	11	11.16	27.9	44.6	8.21E-10	3.91E-08
LRM-3-C8	11.3	11.15	25.3	40.0	8.26E-10	3.93E-08
LRM-3-C9	12	11.25	30.2	44.6	8.23E-10	3.92E-08
LRM-3-C10	12.3	11.23	32.7	46.7	8.17E-10	3.89E-08
LRM-3-D conducted with 0.50 g glass						
LRM-3-D1	3	10.97	17.9	40.0	8.25E-10	7.86E-08
LRM-3-D2	4	10.99	15.8	36.3	8.23E-10	7.84E-08
LRM-3-D3	5	11.03	17.3	37.5	8.12E-10	7.73E-08
LRM-3-D4	6	11.10	18.4	39.3	8.22E-10	7.83E-08
LRM-3-D5	7	11.10	18.8	40.3	8.26E-10	7.87E-08
LRM-3-D6	10	11.13	18.9	39.4	8.10E-10	7.71E-08
LRM-3-D7	11	11.20	15.2	33.3	8.27E-10	7.88E-08
LRM-3-D8	11.3	11.19	16.9	36.0	8.32E-10	7.92E-08
LRM-3-D9	12	11.18	20.8	42.8	8.20E-10	7.81E-08
LRM-3-D10	12.3	11.13	22.3	45.9	8.25E-10	7.86E-08
LRM-3-E conducted with 1.00 g glass						
LRM-3-E1	3	11.12	11.8	41.6	3.60E-09	1.72E-07
LRM-3-E2	4	11.15	12.2	41.2	3.58E-09	1.70E-07
LRM-3-E3	5	11.18	11.2	37.8	3.67E-09	1.75E-07
LRM-3-E4	6	11.23	11.7	39.4	3.59E-09	1.71E-07
LRM-3-E5	7	11.24	11.1	38.1	3.55E-09	1.69E-07
LRM-3-E6	8	11.21	11.6	39.0	3.61E-09	1.72E-07
LRM-3-E7	10	11.31	12.5	40.7	3.63E-09	1.73E-07

Table 4. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S°, m/s
LRM-3-F conducted with 0.67 g glass						
LRM-3-F1	3	11.15	8.79	40.0	3.76E-09	2.67E-07
LRM-3-F2	4	11.18	9.67	43.7	3.73E-09	2.65E-07
LRM-3-F3	5	11.24	10.1	43.9	3.74E-09	2.66E-07
LRM-3-F4	6	11.23	10.2	43.2	3.73E-09	2.65E-07
LRM-3-F5	7	11.26	9.73	42.8	3.74E-09	2.66E-07
LRM-3-F6	8	11.27	8.53	36.7	3.76E-09	2.67E-07
LRM-3-F7	10	11.32	9.43	40.5	3.70E-09	2.63E-07
LRM-3-G conducted with 1.00 g glass						
LRM-3-G1	3	11.17	7.65	41.4	6.72E-09	3.20E-07
LRM-3-G2	4	11.18	8.54	42.7	6.74E-09	3.21E-07
LRM-3-G3	5	11.23	7.67	37.2	6.72E-09	3.20E-07
LRM-3-G4	6	11.26	8.51	40.4	6.61E-09	3.15E-07
LRM-3-G5	7	11.28	7.53	36.5	6.74E-09	3.21E-07
LRM-3-G6	8	11.25	8.54	40.8	6.54E-09	3.11E-07
LRM-3-G7	10	11.37	8.60	41.2	6.51E-09	3.10E-07
LRM-3-H conducted with 0.33 g glass						
LRM-3-H1	3	11.16	5.31	44.5	3.70E-09	5.34E-07
LRM-3-H2	4	11.18	5.17	42.1	3.63E-09	5.24E-07
LRM-3-H3	5	11.24	5.08	40.5	3.67E-09	5.29E-07
LRM-3-H4	6	11.28	5.42	42.2	3.61E-09	5.21E-07
LRM-3-H5	7	11.26	4.62	39.0	3.67E-09	5.30E-07
LRM-3-H6	8	11.28	4.84	39.9	3.65E-09	5.27E-07
LRM-3-H7	10	11.35	5.12	42.9	3.59E-09	5.18E-07
LRM-3-I conducted with 1.00 g glass						
LRM-3-I1	3	11.22	5.42	42.5	1.39E-08	6.63E-07
LRM-3-I2	4	11.21	5.95	41.4	1.38E-08	6.59E-07
LRM-3-I3	5	11.26	6.13	43.0	1.37E-08	6.53E-07
LRM-3-I4	6	11.29	5.39	45.0	1.40E-08	6.65E-07
LRM-3-I5	7	11.28	5.26	45.5	1.43E-08	6.82E-07
LRM-3-I6	8	11.30	5.79	46.6	1.37E-08	6.52E-07
LRM-3-I7	10	11.38	6.13	46.0	1.38E-08	6.58E-07
LRM-3-J conducted with 0.20 g glass						
LRM-3-J1	3	11.21	4.27	43.1	3.73E-09	8.87E-07
LRM-3-J2	4	11.18	4.29	43.6	3.46E-09	8.25E-07
LRM-3-J3	5	11.26	4.24	45.7	3.60E-09	8.56E-07
LRM-3-J4	6	11.28	4.84	46.5	3.42E-09	8.13E-07
LRM-3-J5	7	11.25	4.66	46.3	3.45E-09	8.22E-07
LRM-3-J6	8	11.31	4.31	40.8	3.43E-09	8.17E-07
LRM-3-J7	10	11.36	4.39	43.5	3.41E-09	8.13E-07
LRM-3-J8	11	11.39	4.85	47.1	3.43E-09	8.16E-07
LRM-3-J9	12	11.36	4.69	49.6	3.36E-09	8.01E-07
LRM-3-K conducted with 2.50 g glass						
LRM-3-K1	3	10.84	38.5	43.1	7.15E-10	1.36E-08
LRM-3-K2	4	10.80	39.5	44.0	7.31E-10	1.39E-08
LRM-3-K3	5	10.90	39.7	45.1	7.13E-10	1.36E-08
LRM-3-K4	6	10.98	42.6	44.8	7.44E-10	1.42E-08
LRM-3-K5	7	10.96	39.2	42.7	6.94E-10	1.32E-08
LRM-3-K6	10	11.00	41.7	42.5	6.80E-10	1.30E-08
LRM-3-K7	11	11.03	41.4	42.6	7.11E-10	1.35E-08
LRM-3-K8	11.3	11.03	41.5	42.6	7.09E-10	1.35E-08
LRM-3-K9	12	11.05	41.4	43.9	7.16E-10	1.36E-08
LRM-3-K10	12.3	10.99	57.5	49.0	7.16E-10	1.36E-08
LRM-3-K11	13	10.98	44.0	47.0	7.23E-10	1.38E-08
LRM-3-K12	14	11.04	44	47.2	7.03E-10	1.34E-08

Table 4. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S°, m/s
LRM-3-L conducted with 0.50 g glass						
LRM-3-L1	0.7	11.42	3.42	45.6	1.44E-08	1.37E-06
LRM-3-L2	1	11.40	3.42	44.8	1.43E-08	1.36E-06
LRM-3-L3	1.7	11.40	4.02	52.4	1.42E-08	1.36E-06
LRM-3-L4	3	11.35	3.61	52.9	1.43E-08	1.36E-06
LRM-3-L5	4	11.36	3.68	51.7	1.40E-08	1.33E-06
LRM-3-L6	5	11.37	3.58	50.9	1.39E-08	1.32E-06
LRM-3-L7	6.7	11.35	3.20	51.1	1.39E-08	1.32E-06
LRM-3-L8	7	11.33	3.02	46.0	1.40E-08	1.33E-06
LRM-3-L9	7.7	11.35	2.94	51.0	1.38E-08	1.32E-06
LRM-3-L10	8	11.31	2.91	45.8	1.40E-08	1.33E-06
LRM-3-L11	8.7	11.29	2.79	47.7	1.38E-08	1.32E-06
LRM-3-L12	9	11.32	2.74	46.1	1.38E-08	1.32E-06
LRM-3-L13	9.7	11.30	2.97	50.6	1.36E-08	1.29E-06
LRM-3-L14	10	11.30	2.59	49.7	1.37E-08	1.31E-06
LRM-3-L15	10.7	11.30	3.03	50.8	1.37E-08	1.31E-06
LRM-3-M conducted with 0.37 g glass						
LRM-3-M1	0.7	11.42	2.75	40.0	1.47E-08	1.89E-06
LRM-3-M2	1	11.40	2.73	35.4	1.51E-08	1.95E-06
LRM-3-M3	1.7	11.39	2.65	39.0	1.38E-08	1.77E-06
LRM-3-M4	3	11.34	2.49	38.3	1.50E-08	1.93E-06
LRM-3-M5	4	11.37	2.48	38.3	1.44E-08	1.85E-06
LRM-3-M6	5	11.38	2.45	37.4	1.45E-08	1.86E-06
LRM-3-M7	6.7	11.37	2.15	39.8	1.44E-08	1.85E-06
LRM-3-M8	7	11.31	1.95	36.6	1.46E-08	1.88E-06
LRM-3-M9	7.7	11.33	2.06	35.5	1.45E-08	1.86E-06
LRM-3-M10	8	11.30	2.01	37.4	1.45E-08	1.86E-06
LRM-3-M11	8.7	11.27	2.03	37.8	1.43E-08	1.85E-06
LRM-3-M12	9	11.28	1.86	40.3	1.43E-08	1.84E-06
LRM-3-M13	9.7	11.34	2.01	37.5	1.43E-08	1.84E-06
LRM-3-M14	10	11.31	1.67	34.7	1.43E-08	1.84E-06
LRM-3-M15	10.7	11.28	1.56	35.3	1.36E-08	1.75E-06
LRM-3-N conducted with 0.25 g glass						
LRM-3-N1	0.7	11.41	1.68	42.2	1.41E-08	2.69E-06
LRM-3-N2	1	11.40	1.80	49.5	1.41E-08	2.69E-06
LRM-3-N3	1.7	11.39	1.79	45.2	1.40E-08	2.67E-06
LRM-3-N4	3	11.35	1.88	48.3	1.39E-08	2.65E-06
LRM-3-N5	4	11.38	1.83	52.0	1.36E-08	2.60E-06
LRM-3-N6	5	11.36	1.72	47.0	1.37E-08	2.61E-06
LRM-3-N7	6.7	11.40	1.72	49.9	1.37E-08	2.62E-06
LRM-3-N8	7	11.37	1.61	46.5	1.38E-08	2.62E-06
LRM-3-N9	7.7	11.33	1.57	48.5	1.37E-08	2.60E-06
LRM-3-N10	8	11.33	1.60	50.9	1.36E-08	2.58E-06
LRM-3-N11	8.7	11.27	1.43	50.5	1.36E-08	2.58E-06
LRM-3-N12	9	11.33	1.46	50.2	1.37E-08	2.60E-06
LRM-3-N13	9.7	11.34	1.48	48.1	1.36E-08	2.58E-06
LRM-3-N14	10	11.36	1.37	51.7	1.36E-08	2.60E-06
LRM-3-N15	10.7	11.33	1.69	52.7	1.42E-08	2.70E-06

Table 4. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^a , m/s
LRM-3-O conducted with 0.13 g glass						
LRM-3-O1	0.7	11.40	0.937	49.5	1.36E-08	4.99E-06
LRM-3-O2	1	11.40	0.816	38.0	1.39E-08	5.08E-06
LRM-3-O3	1.7	11.39	1.27	65.3	1.48E-08	5.44E-06
LRM-3-O4	3	11.34	0.889	50.8	1.39E-08	5.09E-06
LRM-3-O5	4	11.36	0.857	48.4	1.37E-08	5.03E-06
LRM-3-O6	5	11.37	0.846	49.1	1.35E-08	4.94E-06
LRM-3-O7	6.7	11.43	0.754	48.5	1.36E-08	4.99E-06
LRM-3-O8	7	11.37	0.801	49.5	1.38E-08	5.04E-06
LRM-3-O9	7.7	11.39	0.748	53.5	1.34E-08	4.92E-06
LRM-3-O10	8	11.38	0.770	52.6	1.36E-08	4.97E-06
LRM-3-O11	8.7	11.32	0.709	50.8	1.36E-08	4.98E-06
LRM-3-O12	9	11.37	0.718	53.7	1.36E-08	4.98E-06
LRM-3-O13	9.7	11.39	0.726	51.3	1.34E-08	4.92E-06
LRM-3-O14	10	11.33	0.730	50.5	1.37E-08	5.01E-06
LRM-3-O15	10.7	11.36	0.701	53.3	1.36E-08	4.97E-06

^aTest duration at time of sampling was estimated from data provided by Participant A.

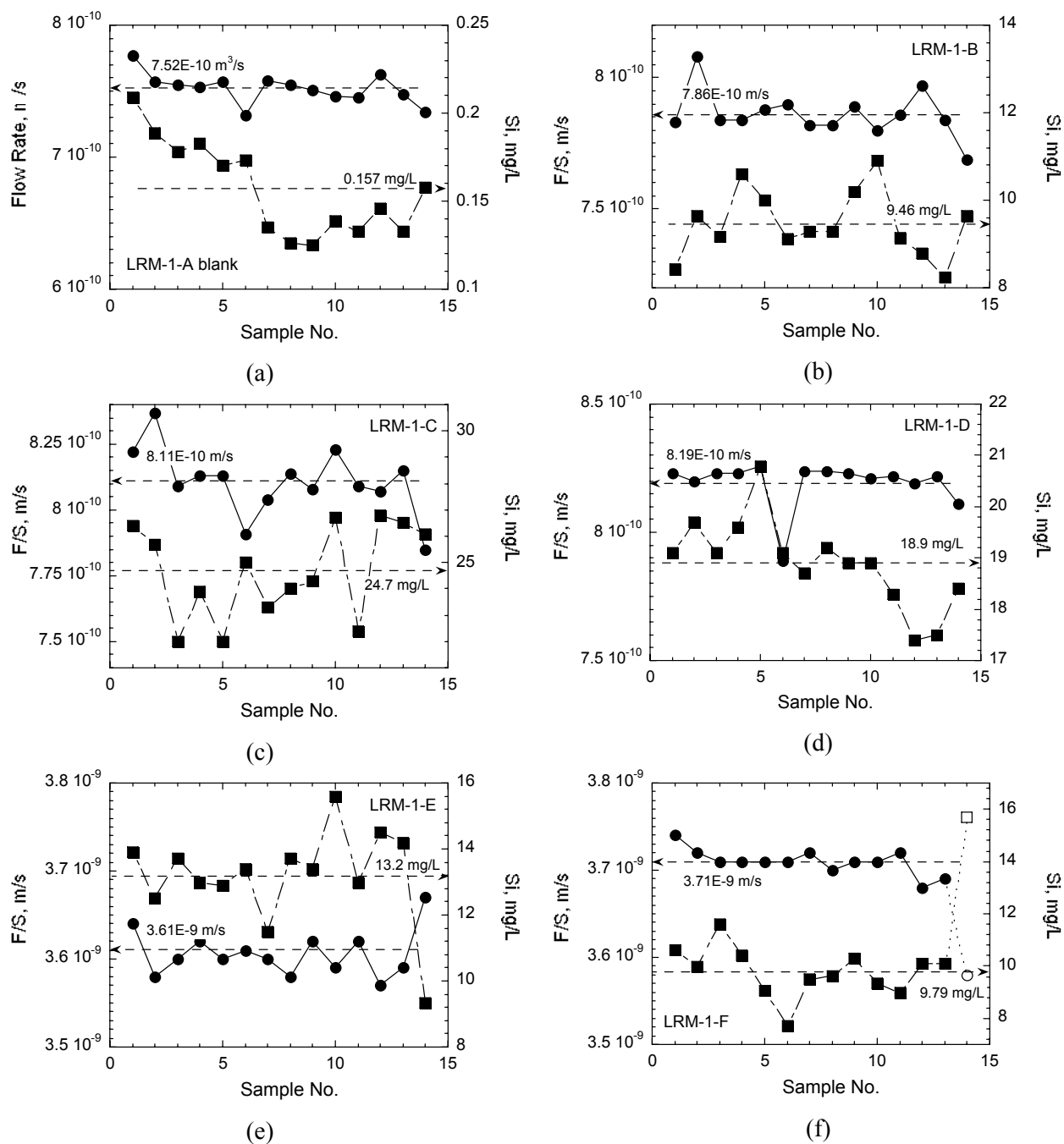
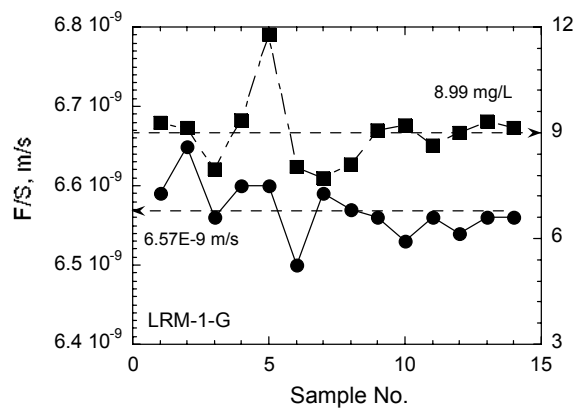
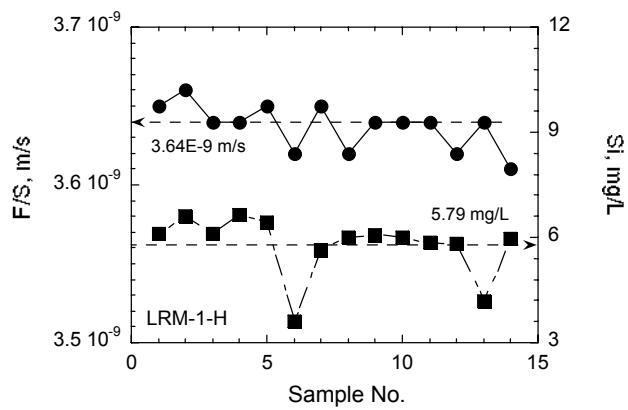


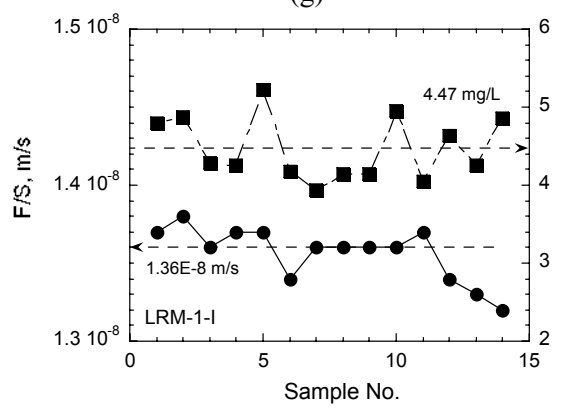
Fig. 3. Results from Participant A for Samples Taken in Tests (a) LRM-1-A, (b) LRM-1-B, (c) LRM-1-C, (d) LRM-1-D, (e) LRM-1-E, (f) LRM-1-F, (g) LRM-1-G, (h) LRM-1-H, (i) LRM-1-I, and (j) LRM-1-J: values of (●) flow rate (or F/S) and (■) Si concentrations. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)



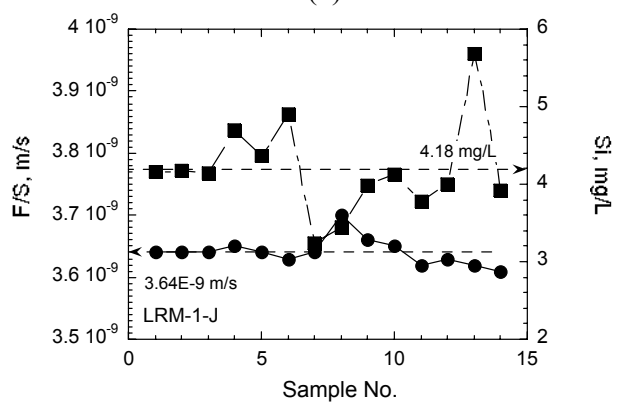
(g)



(h)



(i)



(j)

Fig. 3. (continued)

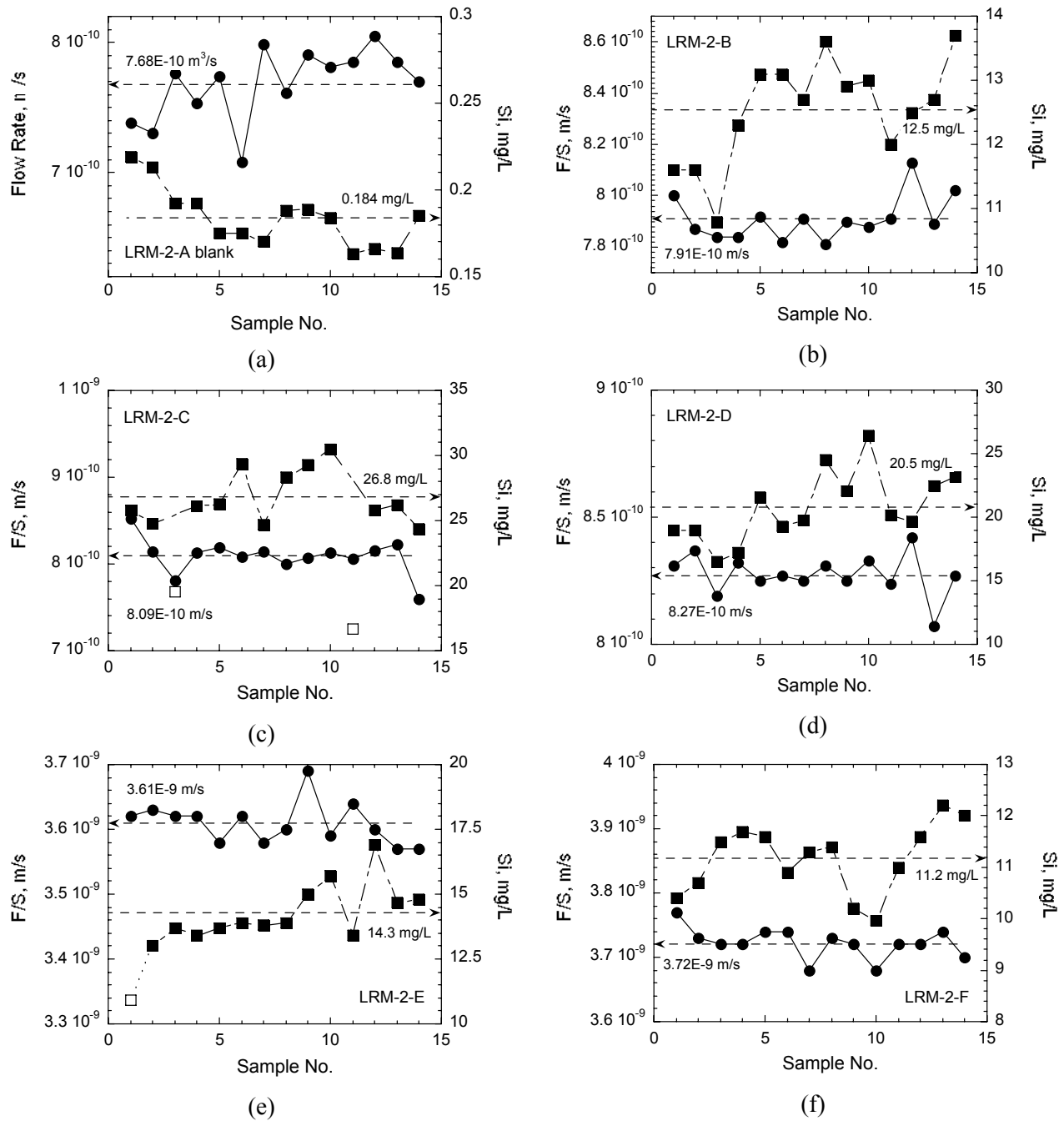
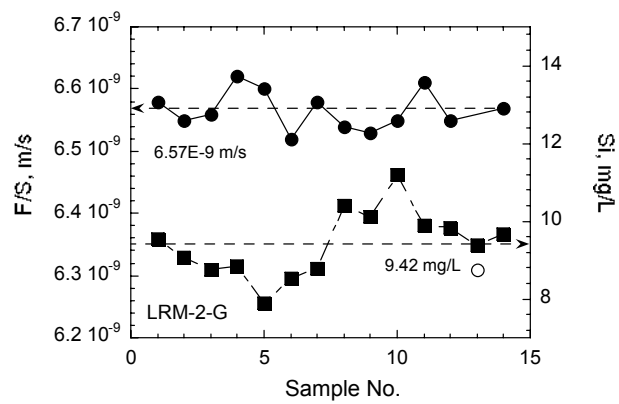
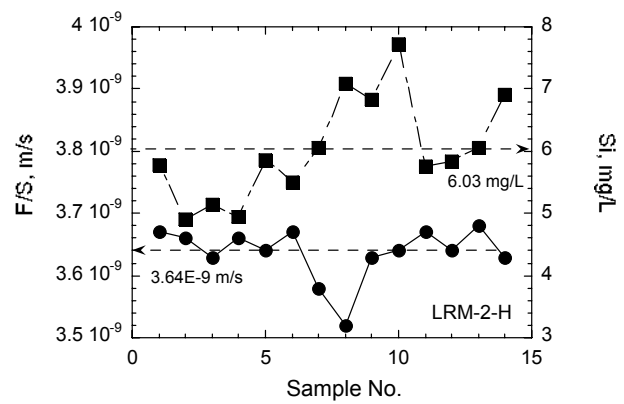


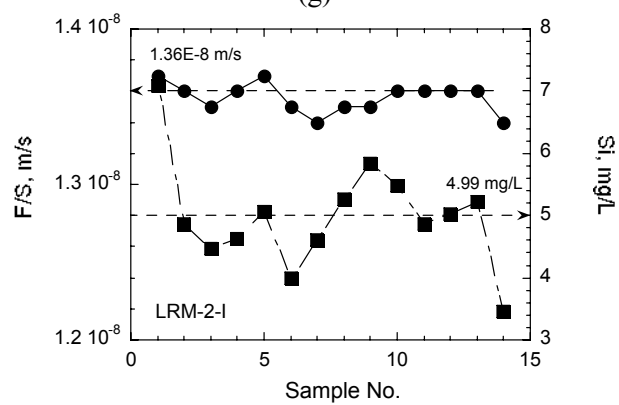
Fig. 4. Results from Participant A for Samples Taken in Tests (a) LRM-2-A, (b) LRM-2-B, (c) LRM-2-C, (d) LRM-2-D, (e) LRM-2-E, (f) LRM-2-F, (g) LRM-2-G, (h) LRM-2-H, (i) LRM-2-I, and (j) LRM-2-J: values of (●) flow rate (or F/S) and (■) Si concentrations. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)



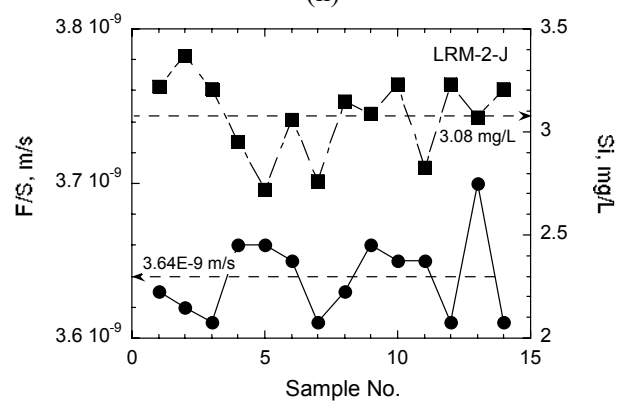
(g)



(h)



(i)



(j)

Fig. 4. (continued)

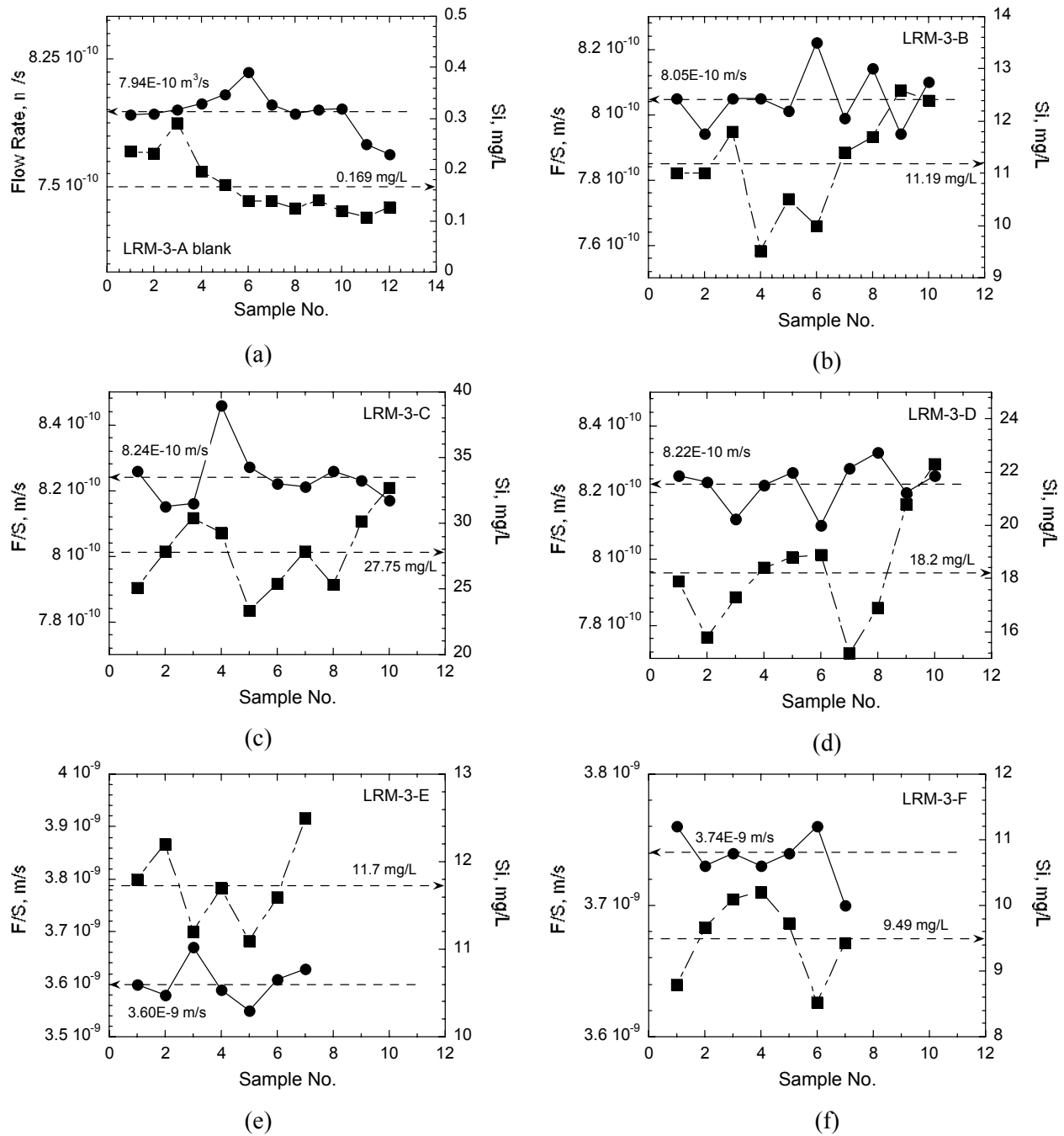
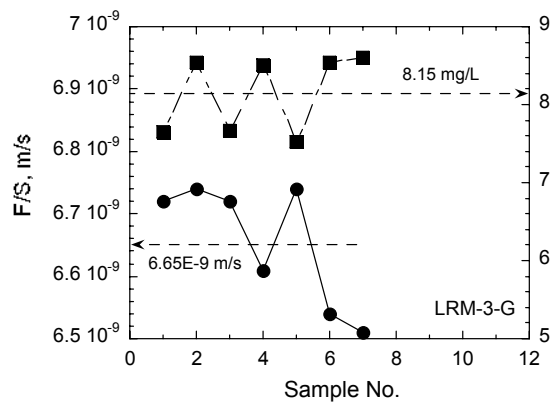
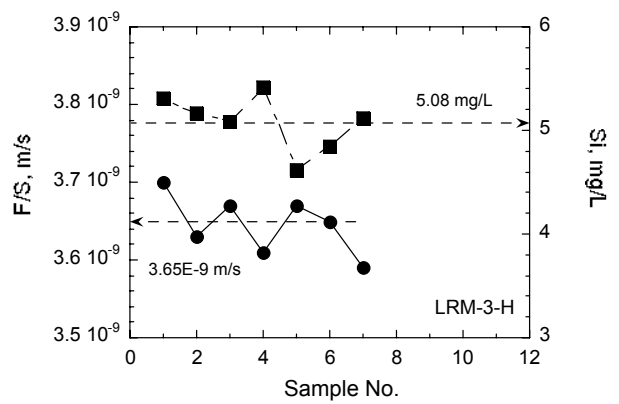


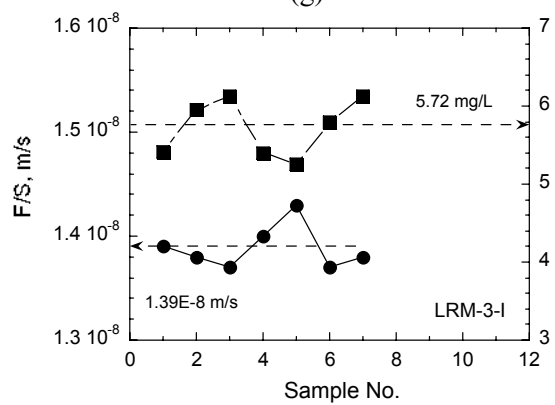
Fig. 5. Results from Participant A for Samples Taken in Tests (a) LRM-3-A, (b) LRM-3-B, (c) LRM-3-C, (d) LRM-3-D, (e) LRM-3-E, (f) LRM-3-F, (g) LRM-3-G, (h) LRM-3-H, (i) LRM-3-I, (j) LRM-3-J, (k) LRM-3-K, (l) LRM-3-L, (m) LRM-3-M, (n) LRM-3-N, and (o) LRM-3-O: values of (●) flow rate (or F/S) and (■) Si concentrations. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)



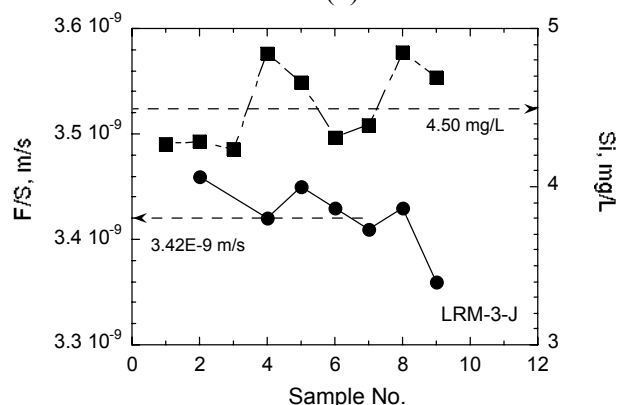
(g)



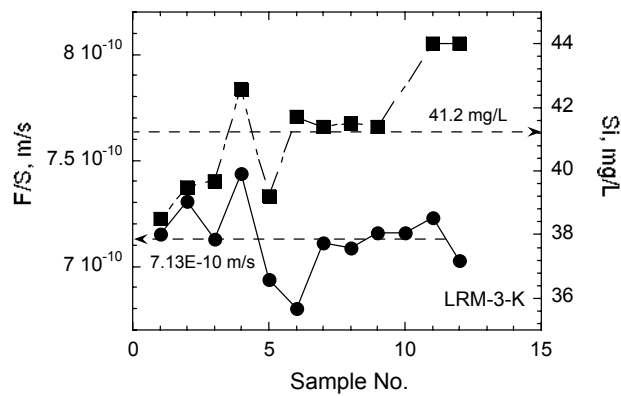
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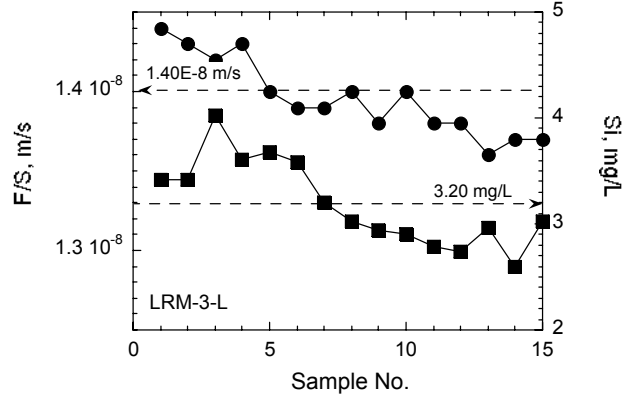
(i)



(j)

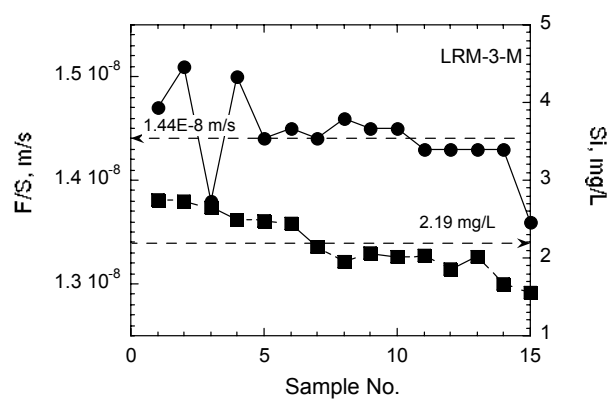


(k)

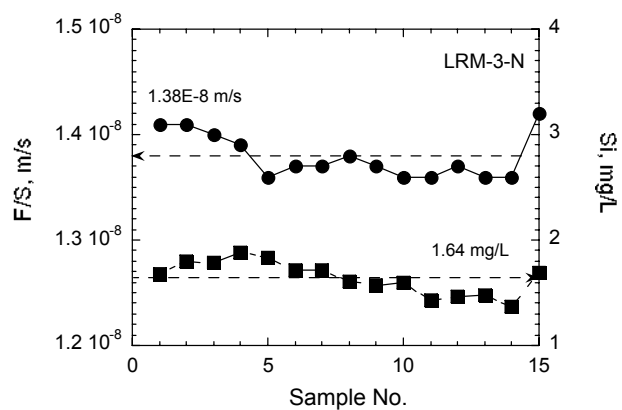


(l)

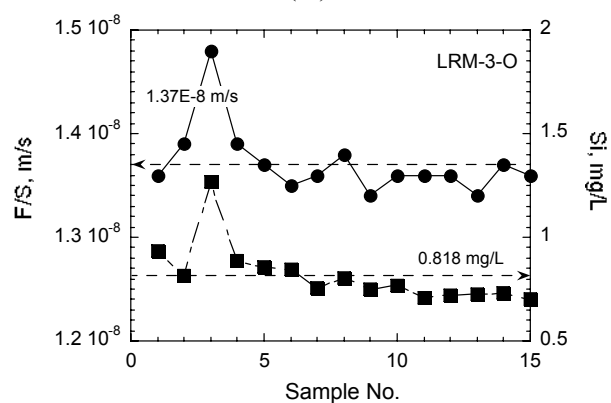
Fig. 5. (continued)



(m)



(n)



(o)

Fig. 5. (continued)

3.2 RESULTS FROM PARTICIPANT B

Participant B conducted two test series, with three tests and one blank test in each series. Tests were conducted using a 2-port jar cell design similar to that shown in Fig. 2c, and samples were collected within the oven. Test solutions were passed through 0.45- μm pore size filters and then acidified with ultrapure nitric acid prior to analysis. The Si concentrations were measured with inductively coupled plasma-optical emission spectroscopy (ICP-OES). The test results are compiled in Table 5 and plotted in Fig. 6. Variations in the flow rates of the individual tests ranged from 6.7% rsd in test L5 to 20.2% rsd in test L7. Variations in the measured Si concentrations in each test were smaller, from 1.3% rsd in test L4-2 to 7.3% rsd in test L5-2. The average concentration in the blank test in each series was used as the background concentration for the three tests in that series.

Table 5. Summary of Test Results for Participant B

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate ^a (m ³ /s)	F/S ^o , m/s
Test L4-1 blank test					
L4-1-1	3	10.98	0.05	3.83E-09	
L4-1-2	4	10.47	0.05	3.42E-09	
L4-1-3	8	10.75	0.05	3.11E-09	
L4-1-4	9	10.32	0.05	3.41E-09	
L4-1-5	10	10.31	0.05	3.43E-09	
L4-1-6	11	10.64	0.05	3.80E-09	
L4-1-7	14	9.94	0.05	3.27E-09	
Test L5-1 conducted with 0.999 g glass					
L5-1-1	3	10.99	6.71	3.66E-09	1.74E-07
L5-1-2	4	10.52	6.43	3.47E-09	1.65E-07
L5-1-3	8	10.87	6.52	3.76E-09	1.79E-07
L5-1-4	9	10.47	6.68	3.44E-09	1.64E-07
L5-1-5	10	10.29	6.68	3.09E-09	1.47E-07
L5-1-6	11	10.65	6.93	3.28E-09	1.56E-07
L5-1-7	14	10.01	6.65	3.49E-09	1.66E-07
Test L6-1 conducted with 1.003 g glass					
L6-1-1	3	10.96	6.58	3.72E-09	1.77E-07
L6-1-2	4	10.51	6.37	3.75E-09	1.79E-07
L6-1-3	8	10.89	6.40	3.05E-09	1.45E-07
L6-1-4	9	10.51	6.43	3.14E-09	1.49E-07
L6-1-5	10	10.34	6.43	3.92E-09	1.87E-07
L6-1-6	11	10.70	6.71	3.36E-09	1.60E-07
L6-1-7	14	10.09	5.88	3.91E-09	1.86E-07
Test L7-1 conducted with 0.999 g glass					
L7-1-1	3	11.01	7.71	3.40E-09	1.62E-07
L7-1-2	4	10.52	7.84	3.26E-09	1.55E-07
L7-1-3	8	10.92	7.25	3.03E-09	1.44E-07
L7-1-4	9	10.44	7.67	3.08E-09	1.47E-07
L7-1-5	10	10.37	7.61	3.31E-09	1.58E-07
L7-1-6	11	10.74	7.91	4.31E-09	2.05E-07
L7-1-7	14	10.20	6.79	3.52E-09	1.68E-07

Table 5. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S°, m/s
Test L4-2 conducted with 0.750 g glass					
L4-2-1	3	10.54	8.29	2.39E-09	1.52E-07
L4-2-2	4	10.69	8.01	2.18E-09	1.38E-07
L4-2-3	5	10.75	7.88	3.16E-09	2.01E-07
L4-2-4	6	10.58	10.5	3.32E-09	2.10E-07
L4-2-5	10	10.28	7.55	2.51E-09	1.59E-07
L4-2-6	11	10.13	7.04	2.68E-09	1.70E-07
L4-2-7	12	10.46	7.56	2.62E-09	1.66E-07
L4-2-8	13	10.38	7.65	1.72E-09	1.09E-07
L4-2-9	14	10.51	7.26	2.83E-09	1.79E-07
Test L5-2 conducted with 0.751 g glass					
L5-2-1	3	10.59	7.67	2.96E-09	1.88E-07
L5-2-2	4	10.69	8.25	2.48E-09	1.58E-07
L5-2-3	5	10.79	7.86	2.33E-09	1.47E-07
L5-2-4	6	10.64	7.69	2.95E-09	1.87E-07
L5-2-5	10	10.39	6.96	3.14E-09	1.99E-07
L5-2-6	11	10.23	6.64	2.87E-09	1.82E-07
L5-2-7	12	10.55	7.29	2.92E-09	1.85E-07
L5-2-8	13	10.42	7.01	3.11E-09	1.97E-07
L5-2-9	14	10.54	6.81	2.21E-09	1.40E-07
Test L6-2 conducted with 0.749 g glass					
L6-2-1	3	10.73	7.41	2.41E-09	1.53E-07
L6-2-2	4	10.72	7.04	3.25E-09	2.06E-07
L6-2-3	5	10.79	7.33	2.78E-09	1.77E-07
L6-2-4	6	10.75	7.89	3.03E-09	1.93E-07
L6-2-5	10	10.51	7.12	3.11E-09	1.97E-07
L6-2-6	11	10.31	6.73	3.14E-09	2.00E-07
L6-2-7	12	10.58	7.07	2.96E-09	1.88E-07
L6-2-8	13	10.47	6.89	1.93E-09	1.23E-07
L6-2-9	14	10.59	6.63	2.79E-09	1.77E-07
Test L5 blank test					
L8-2-1	3	10.79	0.747	2.90E-09	
L8-2-2	4	10.73	0.711	2.87E-09	
L8-2-3	5	10.75	0.665	2.75E-09	
L8-2-4	6	10.82	0.782	2.43E-09	
L8-2-5	10	10.61	0.655	2.71E-09	
L8-2-6	11	10.38	0.626	2.67E-09	
L8-2-7	12	10.63	0.660	2.57E-09	
L8-2-8	13	10.51	0.654	2.20E-09	
L8-2-9	14	10.63	0.514	2.65E-09	

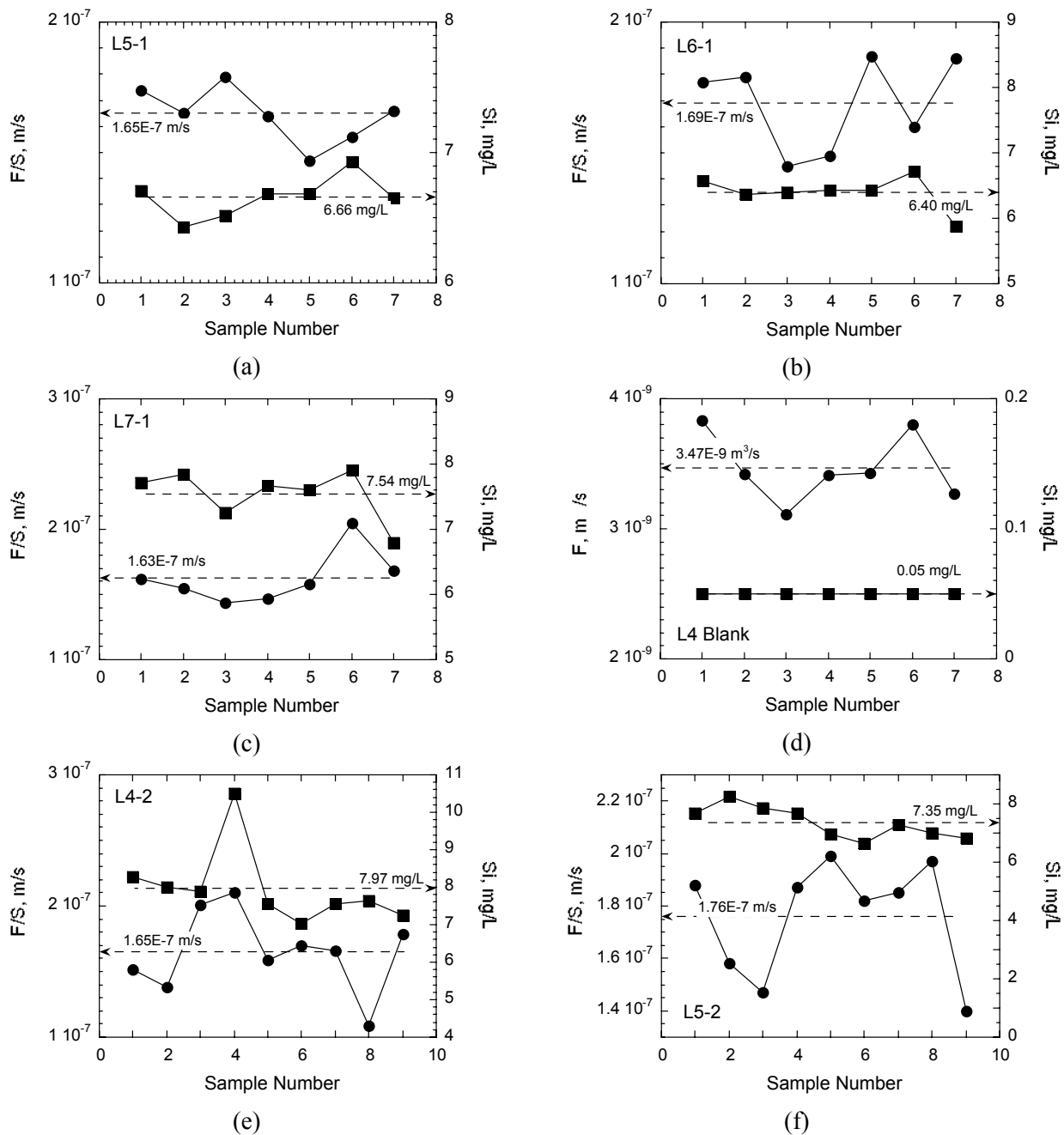


Fig. 6. Results from Participant B for Samples Taken in Tests (a) L5-1, (b) L6-1, (c) L7-1, (d) L4 blank test, (e) L4-2 (f) L5-2, (g) L6-2, and (h) L8 blank test: values of (●) flow rate (or F/S) and (■) Si concentrations. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)

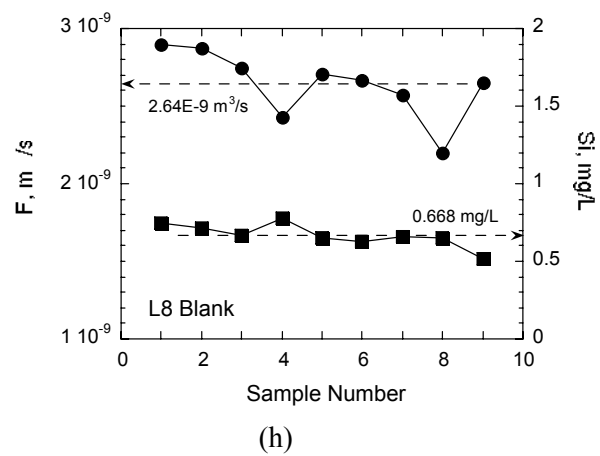
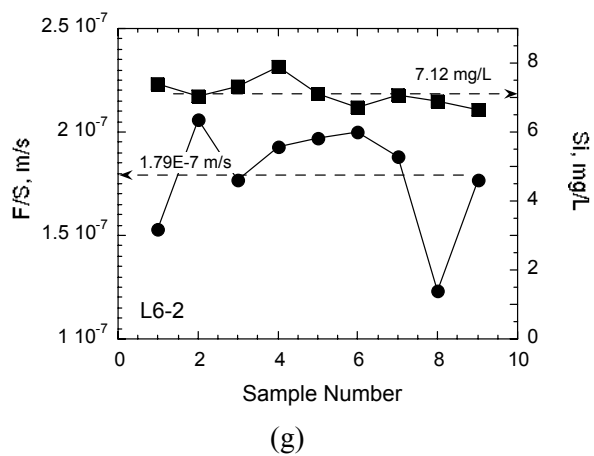


Fig. 6. (continued)

3.3 RESULTS FROM PARTICIPANT C

Participant C conducted three series of tests, each with three replicates and one blank test. Tests were conducted in a column-type reactor, with leachant solution pumped vertically up through a reaction cell containing the glass. Nitrogen gas was used to purge the leachant in the reservoir of CO₂ prior to the tests and intermittently during the tests, and to purge the test solutions when they were collected. Test solutions were acidified with 1 vol. % nitric acid prior to analysis with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The test results are compiled in Table 6. Test solutions were collected and analyzed after only three test durations; the collected solutions were purged with N₂. Samples 10-1, 10-2, and 10-3 were taken after 6, 8, and 12 days; samples 25-1, 25-2, and 25-3 were taken after 5, 8, and 13 days; and samples 60-1, 60-2, and 60-3 were taken after 3, 4, and 7 days. Results are plotted in Fig. 7. As seen in the plots, constant flow rates (reflected by F/S) or Si concentrations were not attained during most tests. The average values of the three samplings were used to calculate rates for comparison with other results.

Table 6. Summary of Test Results for Participant C

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S°, m/s
Test 10-1 conducted with 0.2094 g glass					
10-1-6	6	10.05	37	1.54E-10	3.51E-08
10-1-8	8	9.75	33	1.58E-10	3.58E-08
10-1-12	12	10.04	33	1.70E-10	3.86E-08
Test 10-2 conducted with 0.1967 g glass					
10-2-6	6	10.10	30	2.18E-10	5.28E-08
10-2-8	8	9.91	27	2.24E-10	5.42E-08
10-2-12	12	10.33	25	2.61E-10	6.31E-08
Test 10-3 conducted with 0.2082 g glass					
10-3-6	6	9.90	37	1.37E-10	3.13E-08
10-3-8	8	9.71	34	1.40E-10	3.21E-08
10-3-12	12	10.04	33	1.50E-10	3.44E-08
Test 10-BL blank test					
10-BL-6	6	10.03	<0.12	1.16E-10	
10-BL-8	8	9.77	<0.12	1.17E-10	
10-BL-12	12	10.10	<0.12	1.20E-10	
Test 25-1 conducted with 0.2022 g glass					
25-1-5	5	10.55	28	3.38E-10	7.96E-08
25-1-8	8	10.49	26	3.42E-10	8.07E-08
25-1-13	13	10.44	24	3.63E-10	8.56E-08
Test 25-2 conducted with 0.1947 g glass					
25-2-5	5	10.60	26	3.15E-10	7.70E-08
25-2-8	8	10.53	25	3.40E-10	8.31E-08
25-2-13	13	10.48	27	4.08E-10	9.97E-08
Test 25-3 conducted with 0.2019 g glass					
25-3-5	5	10.62	27	2.94E-10	6.94E-08
25-3-8	8	10.52	23	3.26E-10	7.70E-08
25-3-13	13	10.48	22	3.64E-10	8.58E-08
Test 25-BL blank test					
25-BL-5	5	10.72	<0.12	2.80E-10	
25-BL-8	8	10.63	<0.12	2.88E-10	
25-BL-13	13	10.55	<0.12	2.95E-10	
Test 60-1 conducted with 0.1987 g glass					
60-1-3	3	10.00	7.3	1.11E-09	2.66E-07
60-1-4	4	10.06	6.2	1.29E-09	3.09E-07
60-1-7	7	10.10	5.7	1.15E-09	2.75E-07

Table 6. (continued)

Test 60-2 conducted with 0.1966 g glass					
60-2-3	3	10.03	4.6	1.41E-09	3.41E-07
60-2-4	4	10.16	4.7	1.80E-09	4.36E-07
60-2-7	7	9.96	7.7	6.21E-10	1.50E-07
Test 60-3 conducted with 0.1997 g glass					
60-3-3	3	9.89	10.3	6.15E-10	1.47E-07
60-3-4	4	10.05	9.2	6.36E-10	1.52E-07
60-3-7	7	9.84	9.7	4.62E-10	1.10E-07
Test 60-BL blank test					
60-BL-3	3	9.81	4.7	7.09E-10	
60-BL-4	4	10.13	4.8	7.82E-10	
60-BL-7	7	10.06	4.3	9.03E-10	

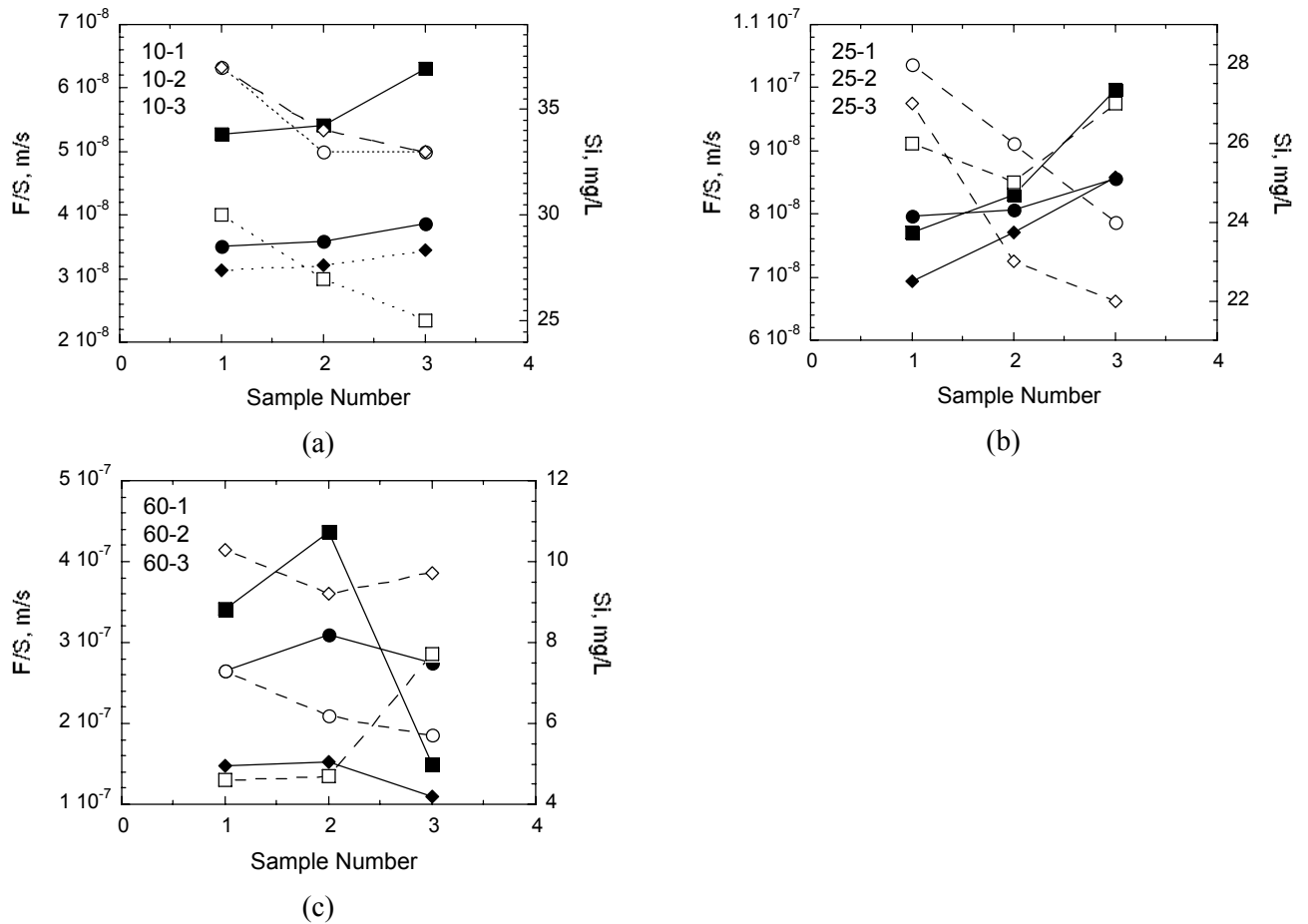


Fig. 7. Results from Participant C for Samples Taken in Tests (a) 10-1, 10-2, and 10-3; (b) 25-1, 25-2, and 25-3; and (c) 60-1, 60-2, and 60-3: F/S (m/s) for (●) X-1 tests, (■) X-2 tests, and (◆) X-3 tests, and measured Si concentration (mg/L) for (○) X-1 tests, (□) X-2 tests, and (◇) X-3 tests, where X = 10, 25, or 60.

3.4 RESULTS FROM PARTICIPANT D

Participant D reported the results of six series of replicate tests using a column reaction cell design. The test solutions were passed through 0.45- μ m pore size filters prior to analysis for B, Li, and Si with ICP-AES. The solutions were not acidified prior to analysis. The test results are compiled in Table 7 and plotted in Fig. 8. The result of one analysis of the leachant solution was reported for each test and is given in the rows for test “-B.” In all cases, the measured Si concentration was below the detection limit of 0.1 mg/L.

Table 7. Summary of Test Results for Participant D

Sample Number	Reaction Time, ^a d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test LRM-A conducted with 0.1 g glass						
LRM-A-B	3	11.37	< 0.1	46.5	1.71E-09	
LRM-A-1	4	11.32	3.7	46.6	1.71E-09	8.17E-07
LRM-A-2	5	11.27	4.2	47.2	1.71E-09	8.16E-07
LRM-A-3	6	11.30	4.5	46.6	1.71E-09	8.16E-07
LRM-A-4	7	11.28	4.1	46.8	1.71E-09	8.15E-07
LRM-A-5	10	11.28	4.0	47.6	1.71E-09	8.16E-07
LRM-A-6	12	11.30	3.7	47.7	1.71E-09	8.16E-07
LRM-A-7	13	11.22	3.6	48.6	1.71E-09	8.16E-07
Test LRM-A' conducted with 0.1 g glass						
LRM-A'-B	3	11.41	< 0.1	47.1	1.73E-09	
LRM-A'-1	4	11.29	5.9	47.5	1.73E-09	8.23E-07
LRM-A'-2	5	11.27	5.8	47.2	1.73E-09	8.22E-07
LRM-A'-3	6	11.34	5.8	46.9	1.73E-09	8.23E-07
LRM-A'-4	7	11.27	5.8	46.5	1.73E-09	8.23E-07
LRM-A'-5	10	11.29	5.6	47.8	1.73E-09	8.22E-07
LRM-A'-6	12	11.29	5.3	48.1	1.73E-09	8.22E-07
LRM-A'-7	13	11.20	5.1	49.1	1.73E-09	8.22E-07
Test LRM-A2 conducted with 0.1 g glass						
LRM-A2-B	3	11.12	<0.1	49.9	7.52E-10	
LRM-A2-1	4	11.54	7.0	49.9	8.58E-10	4.09E-07
LRM-A2-2	5	11.75	5.2	50.5	1.53E-09	7.27E-07
LRM-A2-3	6	11.81	4.9	50.6	1.61E-09	7.65E-07
LRM-A2-4	7	11.80	5.4	49.7	1.61E-09	7.66E-07
LRM-A2-5	10	11.49	5.0	36.4	1.35E-09	6.45E-07
LRM-A2-6	11	11.54	3.5	36.6	1.64E-09	7.83E-07
LRM-A2-7	12	11.53	3.5	37.1	1.65E-09	7.86E-07
LRM-A2-8	14	11.49	3.6	38.5	1.64E-09	7.83E-07
Test LRM-B2 conducted with 0.1 g glass						
LRM-B2'-B	leachant	11.77	<0.1	49.6	4.82E-09	
LRM-B2'-1	1	11.78	2.7	48.1	4.81E-09	2.29E-06
LRM-B2'-2	2	11.78	2.5	47.8	4.81E-09	2.29E-06
LRM-B2'-3	3	11.76	3.9	50.3	3.09E-09	1.47E-06
LRM-B2'-4	4	11.84	2.3	48.2	4.80E-09	2.28E-06
LRM-B2'-5	4	11.76	2.4	49.8	4.47E-09	2.13E-06
LRM-B2'-6	8	11.85	1.9	49.1	4.17E-09	1.99E-06
LRM-B2'-7	8	11.91	1.7	50.2	4.81E-09	2.29E-06
LRM-B2'-8	9	11.92	1.8	48.7	3.88E-09	1.85E-06
LRM-B2'-9	9	11.94	1.5	49.4	4.82E-09	2.30E-06

Table 7. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test LRM-B3 conducted with 0.1 g glass						
LRM-B3-B	leachant	11.91	<0.1	49.6	4.69E-09	
LRM-B3-1	1	11.89	2.3	50.1	4.62E-09	2.20E-06
LRM-B3-2	2	11.88	2.4	50.5	4.66E-09	2.22E-06
LRM-B3-3	3	11.92	2.4	50.3	4.78E-09	2.28E-06
LRM-B3-4	4	11.92	2.3	49.2	4.81E-09	2.29E-06
LRM-B3-5	7	11.75	1.8	36.6	4.82E-09	2.30E-06
LRM-B3-6	8	11.71	1.8	36.8	4.81E-09	2.29E-06
LRM-B3-7	9	11.70	1.9	36.8	4.82E-09	2.29E-06
LRM-B3-8	11	11.62	1.8	39.2	4.82E-09	2.30E-06
Test LRM-B4 conducted with 0.1 g glass						
LRM-B4-B	leachant	11.85	<0.1	48.8	4.48E-09	
LRM-B4-1	1	11.87	1.8	48.1	4.71E-09	2.24E-06
LRM-B4-2	2	11.91	2.0	48.8	4.80E-09	2.28E-06
LRM-B4-3	3	11.85	2.1	49.2	4.70E-09	2.24E-06
LRM-B4-4	4	11.89	2.2	49.9	4.72E-09	2.25E-06
LRM-B4-5	7	11.84	2.2	51.2	4.82E-09	2.29E-06
LRM-B4-6	8	11.88	2.1	51.7	4.81E-09	2.29E-06
LRM-B4-7	9	11.87	2.0	51.5	4.81E-09	2.29E-06
LRM-B4-8	11	11.85	1.8	53.9	4.81E-09	2.29E-06
LRM-C-7	14	11.84	6.8	0.66	1.37E-09	6.51E-07
Test LRM-D conducted with 0.1 g glass						
LRM-D-B	leachant	11.31	<0.1	47.0	9.75E-10	
LRM-D-1	4	11.28	5.5	47.3	9.82E-10	4.68E-07
LRM-D-2	5	11.31	6.0	47.9	9.83E-10	4.68E-07
LRM-D-3	6	11.34	6.0	48.4	9.72E-10	4.63E-07
LRM-D-4	7	11.32	6.0	48.7	9.86E-10	4.70E-07
LRM-D-5	10	11.25	5.8	49.5	9.94E-10	4.73E-07
LRM-D-6	11	11.29	5.4	51.1	9.92E-10	4.72E-07
LRM-D-7	12	11.33	5.3	51.1	9.93E-10	4.73E-07
LRM-D-8	14	11.39	5.6	52.0	9.99E-10	4.76E-07
Test LRM-D' conducted with 0.1 g glass						
LRM-D'-B	leachant	11.13	<0.1	48.0	8.60E-10	
LRM-D'-1	4	11.31	5.5	47.3	9.58E-10	4.56E-07
LRM-D'-2	5	11.32	5.5	47.8	9.93E-10	4.73E-07
LRM-D'-3	6	11.30	5.6	48.5	9.35E-10	4.45E-07
LRM-D'-4	7	11.32	5.3	48.7	9.84E-10	4.69E-07
LRM-D'-5	10	11.21	5.5	49.5	9.35E-10	4.45E-07
LRM-D'-6	11	11.18	6.1	51.0	8.59E-10	4.09E-07
LRM-D'-7	12	11.23	6.1	51.4	9.03E-10	4.30E-07
LRM-D'-8	14	11.39	6.0	52.0	9.63E-10	4.59E-07
Test LRM-E conducted with 0.1 g glass						
LRM-E-B	leachant	11.92	<0.1	47.5	7.82E-09	
LRM-E-1	1	12.00	1.6	47.6	7.82E-09	3.72E-06
LRM-E-2	1	11.88	1.5	48.0	7.84E-09	3.73E-06
LRM-E-3	2	11.88	1.5	48.7	7.80E-09	3.72E-06
LRM-E-4	3	11.94	1.6	49.7	7.80E-09	3.72E-06
LRM-E-5	4	11.92	1.6	50.7	7.82E-09	3.72E-06
LRM-E-6	6	11.94	1.5	53.3	7.84E-09	3.73E-06
LRM-E-7	8	11.99	1.5	57.3	7.82E-09	3.72E-06
LRM-E-8	10	11.97	1.6	66.1	7.81E-09	3.72E-06

Table 7. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test LRM-E' conducted with 0.1 g glass						
LRM-E'-B	leachant	11.91	<0.1	47.3	7.66E-09	
LRM-E'-1	1	12.00	1.4	47.8	7.73E-09	3.68E-06
LRM-E'-2	1	11.87	1.4	47.8	7.78E-09	3.70E-06
LRM-E'-3	2	11.85	1.4	48.3	7.77E-09	3.70E-06
LRM-E'-4	3	11.94	1.4	49.4	7.77E-09	3.70E-06
LRM-E'-5	4	11.91	1.4	50.7	7.79E-09	3.71E-06
LRM-E'-6	6	11.96	1.3	53.5	7.81E-09	3.72E-06
LRM-E'-7	8	11.97	1.2	57.3	7.78E-09	3.70E-06
Test LRM-E2 conducted with 0.1 g glass						
LRM-E2-B	leachant	11.89	<0.1	48.9	7.60E-09	
LRM-E2-1	1	11.87	1.8	48.1	7.59E-09	3.62E-06
LRM-E2-2	2	11.93	1.6	48.7	7.78E-09	3.71E-06
LRM-E2-3	3	11.90	1.5	49.1	7.77E-09	3.70E-06
LRM-E2-4	4	11.92	1.5	50.2	7.79E-09	3.71E-06
LRM-E2-5	7	11.90	1.5	51.2	7.78E-09	3.70E-06
LRM-E2-6	8	11.90	1.5	51.7	7.78E-09	3.71E-06
LRM-E2-7	9	11.89	1.3	51.3	7.77E-09	3.70E-06
LRM-E2-8	11	11.90	1.1	53.8	7.79E-09	3.71E-06
Test LRM-G conducted with 0.1 g glass						
LRM-G-B	leachant	11.89	<0.1	44.4	1.39E-08	
LRM-G-1	0.1	11.87	0.80	44.6	1.39E-08	6.62E-06
LRM-G-2	1.1	11.83	1.00	45.3	1.39E-08	6.61E-06
LRM-G-3	2	11.86	1.00	46.0	1.38E-08	6.59E-06
LRM-G-4	3	11.80	1.80	45.1	6.94E-09	3.30E-06
LRM-G-5	4	11.84	0.96	44.8	1.36E-08	6.47E-06
LRM-G-6	7	11.91	0.85	45.3	1.37E-08	6.54E-06
LRM-G-7	9	11.88	0.49	45.1	1.37E-08	6.50E-06
LRM-G-8	11	11.82	0.27	45.4	1.38E-08	6.57E-06
Test LRM-G' conducted with 0.1 g glass						
LRM-G'-B	leachant	11.86	<0.1	44.7	1.40E-08	
LRM-G'-1	0.1	11.86	0.81	44.7	1.40E-08	6.67E-06
LRM-G'-2	1.1	11.83	1.00	45.6	1.40E-08	6.65E-06
LRM-G'-3	2	11.88	0.96	45.7	1.39E-08	6.64E-06
LRM-G'-4	3	11.81	0.91	45.3	1.40E-08	6.65E-06
LRM-G'-5	4	11.86	0.90	44.9	1.40E-08	6.65E-06
LRM-G'-6	7	11.91	0.82	45.4	1.39E-08	6.63E-06
LRM-G'-7	9	11.85	0.73	44.4	1.38E-08	6.57E-06
LRM-G'-8	11	11.81	0.66	45.6	1.36E-08	6.47E-06
Test LRM-G4 conducted with 0.1 g glass						
LRM-G4-B	leachant		<0.1	51.2	3.87E-09	
LRM-G4-1	3	11.60	1.00	51.5	9.57E-09	4.56E-06
LRM-G4-2	4	11.64	0.70	51.6	1.38E-08	6.59E-06
LRM-G4-3	7	11.63	0.72	51.5	1.32E-08	6.27E-06
LRM-G4-4	8	11.62	0.70	51.1	1.36E-08	6.49E-06
LRM-G4-5	10	11.65	0.87	50.6	1.36E-08	6.48E-06
LRM-G4-6	11	11.62	0.79	50.1	1.37E-08	6.54E-06
LRM-G4-7	14	11.65	0.74	50.5	1.30E-08	6.19E-06
LRM-G4-8	15	11.60	0.70	50.7	1.30E-08	6.21E-06
LRM-G4-9	16	11.70	0.65	49.9	1.34E-08	6.36E-06
LRM-G4-10	17	11.69	0.66	51.1	1.26E-08	6.01E-06
LRM-G4-11	18	11.67	0.63	51.0	1.29E-08	6.15E-06

Table 7. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Li, mg/L	Flow rate (m ³ /s)	F/S ^a , m/s
Test LRM-H3 conducted with 0.1 g glass						
LRM-H3-B	leachant	11.30	<0.1	48.5	1.65E-08	
LRM-H3-1	0.1	11.32	0.75	48.9	1.66E-08	7.89E-06
LRM-H3-2	1.2	11.32	0.88	49.4	1.67E-08	7.96E-06
LRM-H3-3	2	11.40	0.87	50.8	1.67E-08	7.97E-06
LRM-H3-4	3	11.34	0.86	50.0	1.68E-08	7.98E-06
LRM-H3-5	4	11.37	0.69	51.0	1.67E-08	7.97E-06
LRM-H3-6	7	11.31	0.53	49.8	1.67E-08	7.95E-06
LRM-H3-7	9	11.29	0.49	50.3	1.67E-08	7.93E-06
LRM-H3-8	11	11.34	0.45	52.2	1.64E-08	7.80E-06
Test LRM-H3' conducted with 0.1 g glass						
LRM-H3'-B	leachant	11.28	<0.1	48.9	1.59E-08	
LRM-H3'-1	0.1	11.30	0.71	48.3	1.65E-08	7.88E-06
LRM-H3'-2	1.2	11.32	0.85	49.3	1.65E-08	7.86E-06
LRM-H3'-3	2	11.40	0.84	50.8	1.65E-08	7.87E-06
LRM-H3'-4	3	11.34	0.87	49.8	1.66E-08	7.91E-06
LRM-H3'-5	4	11.35	0.83	51.6	1.67E-08	7.96E-06
LRM-H3'-6	7	11.30	0.78	50.1	1.55E-08	7.36E-06
LRM-H3'-7	9	11.27	0.42	50.2	1.70E-08	8.08E-06
LRM-H3'-8	11	11.32	0.38	52.0	1.68E-08	7.99E-06
Test LRM-H5 conducted with 0.1 g glass						
LRM-H5-B	leachant	11.50	<0.1	48.0	1.25E-08	
LRM-H5-1	3	11.39	0.92	48.5	1.60E-08	7.61E-06
LRM-H5-2	4	11.37	0.88	49.1	1.63E-08	7.77E-06
LRM-H5-3	7	11.51	0.90	50.5	1.62E-08	7.70E-06
LRM-H5-4	8	11.51	0.89	50.3	1.61E-08	7.68E-06
LRM-H5-5	10	11.60	0.85	49.8	1.57E-08	7.49E-06
LRM-H5-6	11	11.60	0.88	50.0	1.59E-08	7.59E-06
LRM-H5-7	14	11.66	0.79	51.0	1.61E-08	7.67E-06
LRM-H5-8	15	11.62	0.69	50.4	1.63E-08	7.75E-06
LRM-H5-9	16	11.71	0.69	52.1	1.62E-08	7.72E-06
LRM-H5-10	17	11.69	0.65	52.7	1.63E-08	7.74E-06
LRM-H5-11	18	11.69	0.82	53.2	1.23E-08	5.85E-06

^aReaction time through end of sample collection.

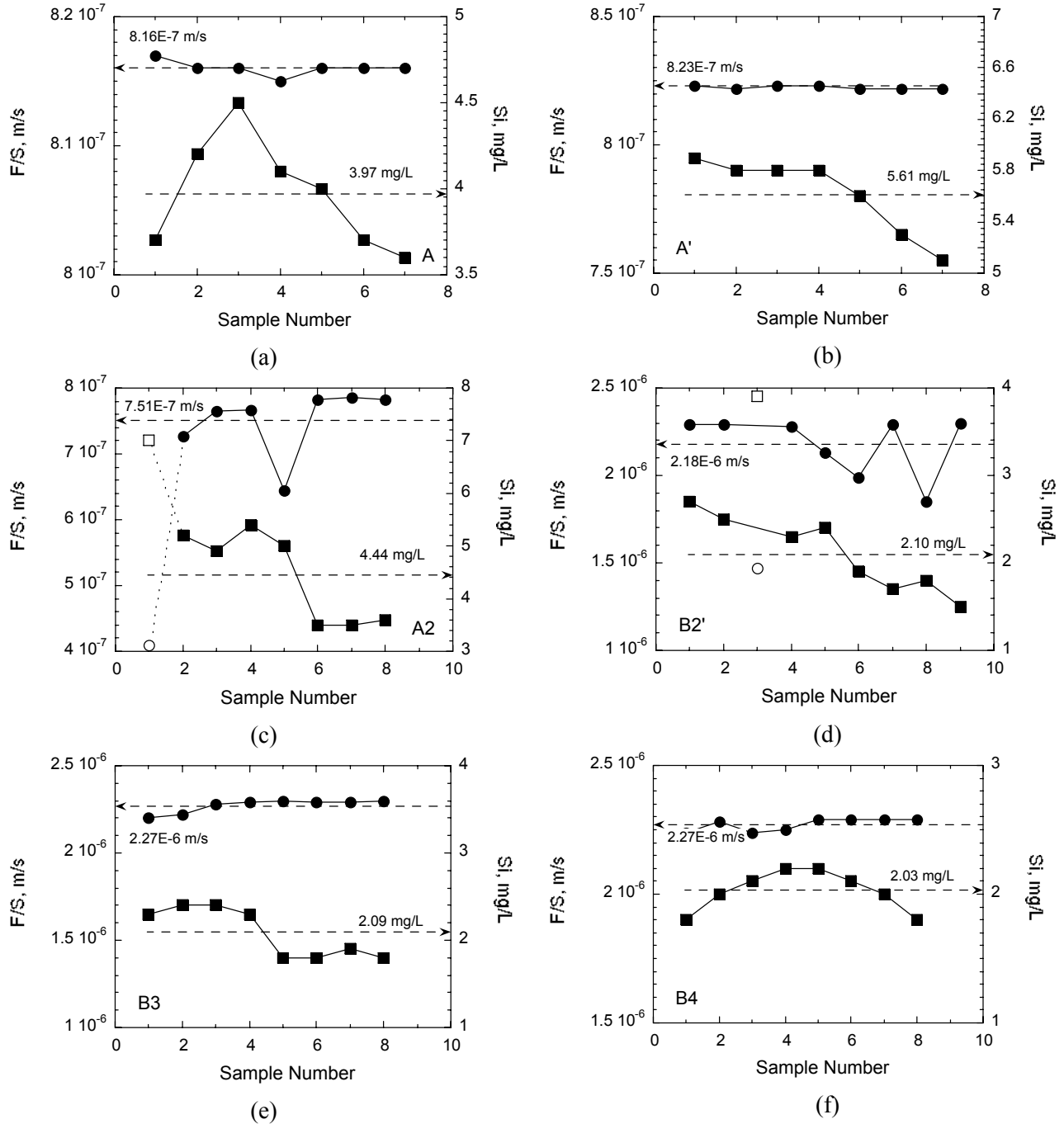
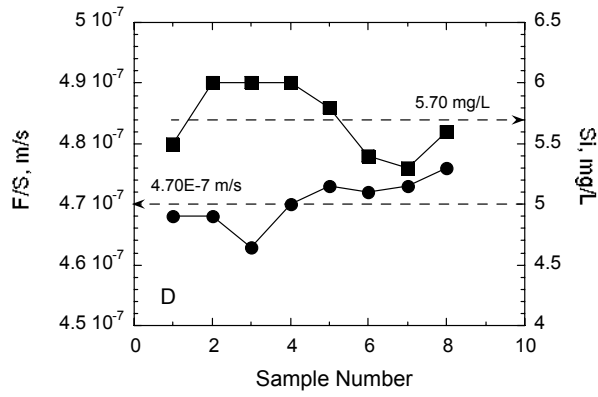
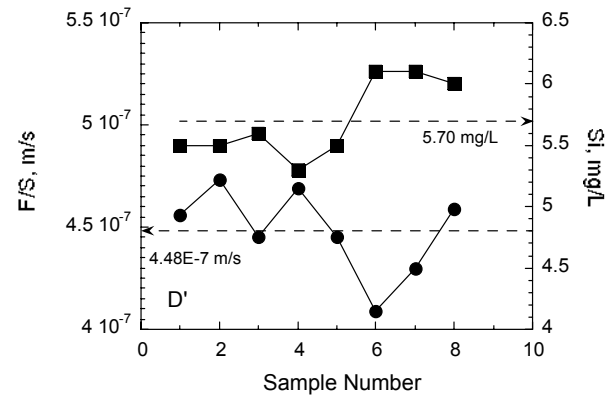


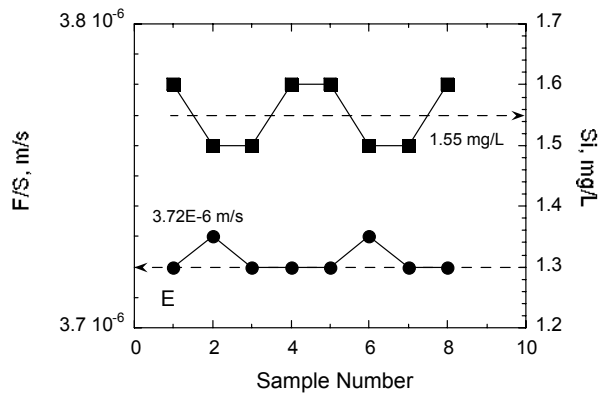
Fig. 8. Results from Participant D for Samples Taken in (a) Test A, (b) Test A', (c) Test A2, (d), Test B2', (e) Test B3, (f) Test B4, (g) Test D, (h) Test D', (i) Test E, (j) Test E', (k) Test E2, (l) Test G, (m) Test G', (n) Test G4, (o) Test H3, (p) Test H3', and (q) Test H5: values of (●) F/S and (■) Si concentration. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)



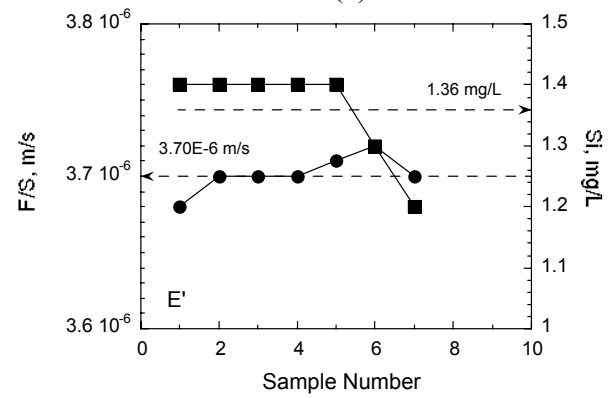
(g)



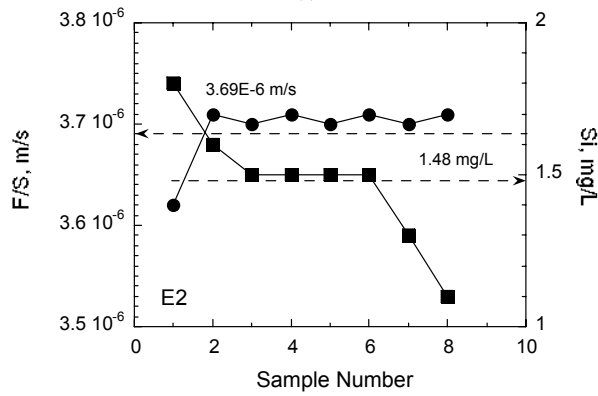
(h)



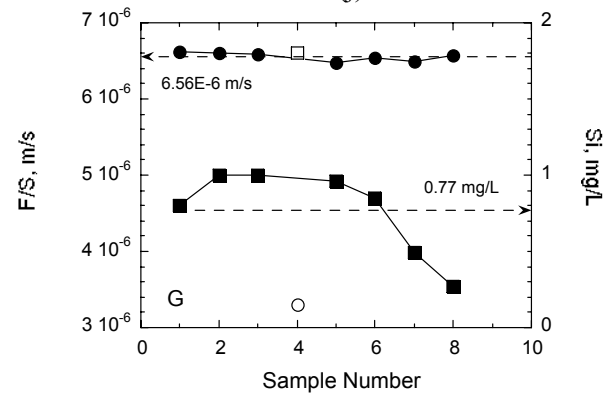
(i)



(j)



(k)



(l)

Fig. 8. (continued)

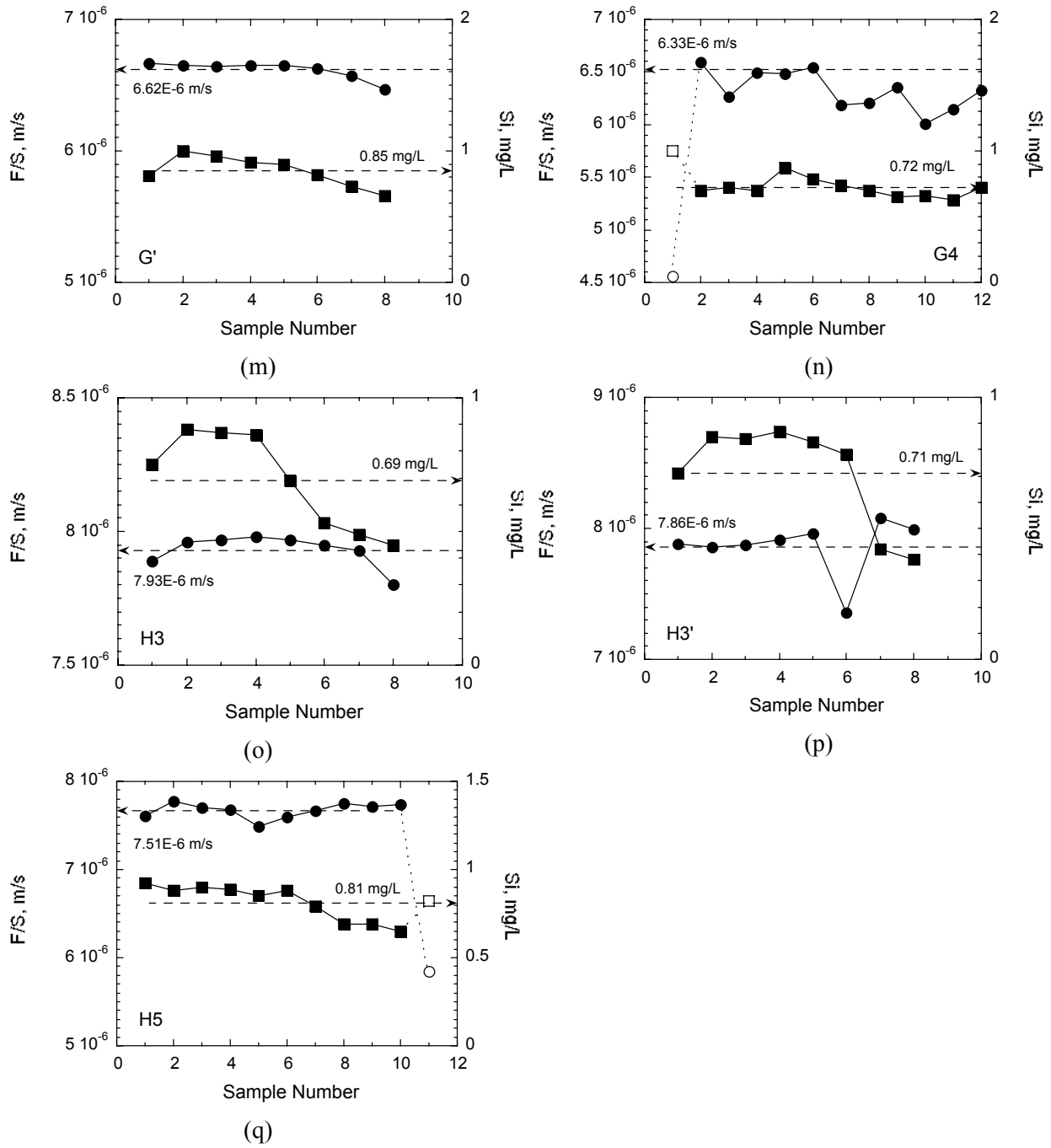


Fig. 8. (continued)

3.5 RESULTS FROM PARTICIPANT E

Participant E conducted eight tests, referred to as LRM-I through LRM-IX (results were not reported for a test LRM-VII). The reaction cell design and analytical method used to measure the Si contents were not reported. The results are summarized in Table 8 and plotted in Fig. 9. During most collections, two samples were taken in sequence. For the first sample (designated “a”), 0.1 mL of nitric acid was added to the collection bottle prior to collecting the solution. For the second sample (designated “b”), the solution was acidified with the same amount of nitric acid after it was collected. For clarity, the results for the “b” samples are offset to the right of the “a” samples in the plots. Because there was no obvious effect on the measured concentration of when the samples were acidified (within the scatter of other samplings), the steady state values for each test were calculated using both samples collected at each interval. Samples taken during the first three days after the test was started were excluded from the means to exclude the effects of any remaining fines and the dissolution of high energy fracture surfaces (sharp points and edges) that were generated by crushing the glass. Figure 10 shows a photomicrograph of a glass grain reacted 14 days that is partially covered with an Fe-bearing phase that appears to have settled as sediment (Participant E referred to it an Fe corrosion layer). Participant E noted that geochemical calculations indicate that some test solutions may be supersaturated with respect to several iron-oxide phases. The sediment may mask some of the glass surface and bias the rate measured in the test to a lower value.

Table 8. Summary of Test Results for Participant E

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test LRM I conducted with 0.50063 g glass					
1a	0.98	11.75	nr	8.25E-09	7.86E-07
1b	1.01	11.75	4.789	8.34E-09	7.93E-07
1c	1.03	11.75	4.436	9.21E-09	8.76E-07
1d	1.03	11.75	nr	8.02E-09	7.63E-07
2a	1.79	11.80	4.087	8.77E-09	8.34E-07
2b	1.81	11.80	nr	8.44E-09	8.03E-07
2c	1.82	11.78	nr	8.79E-09	8.36E-07
2d	1.88	11.78	3.829	8.67E-09	8.25E-07
3a	2.77	11.84	3.513	9.00E-09	8.57E-07
3b	2.79	11.81	3.484	8.47E-09	8.06E-07
3c	2.82	11.81	nr	8.93E-09	8.50E-07
3d	2.83	11.80	nr	8.78E-09	8.36E-07
4a	4	11.72	3.774	8.71E-09	8.29E-07
5a	5	11.67	4.198	8.52E-09	8.11E-07
6a	6	11.82	3.732	9.64E-09	9.17E-07
6b	6	11.82	3.498	9.34E-09	8.89E-07
7a	7	11.79	3.346	8.48E-09	8.07E-07
7b	7	11.79	3.206	8.99E-09	8.56E-07
8a	8	11.79	3.341	8.97E-09	8.53E-07
8b	8	11.78	3.319	8.84E-09	8.42E-07
9a	9	11.54	3.438	8.56E-09	8.15E-07
9b	9	11.54	3.352	9.00E-09	8.56E-07
10a	10	11.55	3.441	9.32E-09	8.87E-07
10b	10	11.54	3.335	8.97E-09	8.54E-07
11a	11	11.44	3.443	6.91E-09	6.58E-07
12a	12	11.45	3.135	7.13E-09	6.78E-07
13a	13	11.56	3.033	9.19E-09	8.74E-07
13b	13	11.57	3.038	9.48E-09	9.02E-07
14a	14	11.57	2.756	8.98E-09	8.55E-07
14b	14	11.56	2.800	8.97E-09	8.53E-07

Table 8. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test LRM II conducted with 0.50076 g glass					
1a	1.02	11.50	7.657	1.05E-08	1.00E-06
1b	1.06	11.51	7.502	4.83E-09	4.59E-07
2a	5	11.55	7.152	4.63E-09	4.40E-07
2b	5	11.54	6.940	4.77E-09	4.54E-07
3a	6	11.56	6.558	6.12E-09	5.82E-07
3b	6	11.54	6.889	4.60E-09	4.38E-07
4a	7	11.59	7.793	4.66E-09	4.44E-07
4b	7	11.57	7.714	4.88E-09	4.64E-07
5a	8	11.57	7.207	4.65E-09	4.43E-07
5b	8	11.57	7.085	4.76E-09	4.53E-07
6a	9	11.57	6.815	4.72E-09	4.50E-07
6b	9	11.57	6.823	4.73E-09	4.50E-07
7a	10	11.55	7.102	4.31E-09	4.10E-07
8a	11	11.55	7.102	4.64E-09	4.42E-07
9a	12	11.58	6.348	4.71E-09	4.48E-07
9b	12	11.57	6.431	4.80E-09	4.57E-07
10a	13	11.58	6.115	4.75E-09	4.52E-07
10b	13	11.57	5.940	4.70E-09	4.48E-07
11a	14	11.59	6.023	4.73E-09	4.50E-07
11b	14	11.57	5.919	4.81E-09	4.57E-07
12a	15	11.57	6.384	5.73E-09	5.45E-07
12b	15	11.55	6.153	4.78E-09	4.55E-07
Test LRM III conducted with 0.50060 g glass					
1a	0.95	11.53	3.28	1.05E-08	1.00E-06
1b	0.98	11.50	3.32	1.07E-08	1.02E-06
2a	5	11.61	3.57	8.08E-09	7.69E-07
2b	5	11.58	3.58	8.39E-09	7.98E-07
3a	6	11.59	4.37	8.08E-09	7.69E-07
3b	6	11.56	4.30	8.17E-09	7.78E-07
4a	7	11.57	3.82	8.22E-09	7.82E-07
4b	7	11.56	3.78	8.27E-09	7.87E-07
5a	8	11.56	3.69	8.32E-09	7.92E-07
5b	8	11.57	3.57	8.39E-09	7.98E-07
6a	9	11.59	3.37	8.18E-09	7.78E-07
6b	9	11.57	3.38	8.52E-09	8.11E-07
7a	10	11.57	4.87	8.72E-09	8.30E-07
8a	11	11.57	4.31	8.05E-09	7.66E-07
9a	12	11.56	4.16	8.12E-09	7.73E-07
9b	12	11.55	4.15	7.86E-09	7.48E-07
10a	13	11.59	4.67	8.46E-09	8.05E-07
10b	13	11.59	4.71	8.18E-09	7.79E-07
11a	14	11.61	4.04	8.32E-09	7.92E-07
11b	14	11.59	4.00	8.39E-09	7.98E-07
12a	15	11.60	3.61	8.28E-09	7.88E-07
12b	15	11.57	3.63	8.33E-09	7.92E-07
Test LRM IV conducted with 0.50036 g glass					
1a	1.02	11.40	11.630	4.75E-09	4.52E-07
1b	1.19	11.45	9.783	4.04E-09	3.85E-07
2a	2.02	11.47	6.180	5.05E-09	4.80E-07
2b	2.06	11.46	6.165	4.91E-09	4.67E-07
3a	3.02	11.48	6.323	4.66E-09	4.43E-07
3b	3.10	11.47	6.293	4.71E-09	4.48E-07

Table 8. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
4a	4	11.47	7.323	5.65E-09	5.38E-07
4b	4	11.47	7.166	4.56E-09	4.34E-07
5a	5	11.45	7.005	4.07E-09	3.87E-07
6a	6	11.44	6.617	4.62E-09	4.40E-07
7a	7	11.46	6.351	4.96E-09	4.72E-07
7b	7	11.47	6.217	4.71E-09	4.48E-07
8a	8	11.54	6.256	4.69E-09	4.46E-07
8b	8	11.52	6.225	4.69E-09	4.47E-07
9a	9	11.52	6.513	4.61E-09	4.39E-07
9b	9	11.51	6.471	4.71E-09	4.48E-07
10a	10	11.52	6.037	4.71E-09	4.49E-07
10b	10	11.53	5.874	4.64E-09	4.42E-07
11a	11	11.46	5.910	4.73E-09	4.50E-07
11b	11	11.45	5.996	4.62E-09	4.40E-07
12a	12	11.50	4.495	4.59E-09	4.37E-07
13a	13	11.50	4.571	4.66E-09	4.44E-07
14a	14	11.54	4.659	4.66E-09	4.43E-07
14b	14	11.33	4.434	4.65E-09	4.43E-07
Test LRM V conducted with 0.50039 g glass					
1a	0.77	11.47	6.52	1.04E-08	9.85E-07
1b	0.79	11.47	6.22	1.02E-08	9.71E-07
2a	1.78	11.44	8.51	1.06E-08	1.01E-06
2b	1.80	11.43	8.50	1.04E-08	9.88E-07
3a	2.83	11.46	7.97	1.04E-08	9.86E-07
3b	2.86	11.42	7.85	9.77E-09	9.30E-07
4a	4	11.45	7.11	9.52E-09	9.06E-07
4b	4	11.41	7.25	9.75E-09	9.28E-07
5a	5	11.50	12.37	9.69E-09	9.22E-07
6a	6	11.47	11.87	9.43E-09	8.97E-07
7a	7	11.47	10.21	1.00E-08	9.56E-07
7b	7	11.47	10.42	1.00E-08	9.52E-07
8a	8	11.57	8.48	9.89E-09	9.41E-07
8b	8	11.54	8.34	9.93E-09	9.45E-07
9a	9	11.52	7.46	9.82E-09	9.35E-07
9b	9	11.52	8.40	9.87E-09	9.40E-07
10a	10	11.56	8.41	1.01E-08	9.64E-07
10b	10	11.55	8.44	9.78E-09	9.30E-07
11a	11	11.51	7.20	1.01E-08	9.59E-07
11b	11	11.50	7.10	1.00E-08	9.54E-07
12a	12	11.50	6.74	1.01E-08	9.66E-07
13a	13	11.50	6.28	1.01E-08	9.63E-07
14a	14	11.51	6.14	1.03E-08	9.76E-07
14b	14	11.52	6.12	9.71E-09	9.24E-07
Test LRM VI conducted with 0.49979 g glass					
1a	0.85	11.45	3.72	9.00E-09	8.57E-07
1b	0.88	11.45	3.64	1.05E-08	1.00E-06
2a	1.83	11.50	1.63	1.08E-08	1.03E-06
2b	1.86	11.50	2.16	1.05E-08	1.00E-06
3a	2.73	11.47	4.78	1.04E-08	9.87E-07
3b	2.75	11.47	4.67	1.04E-08	9.91E-07
4a	4	11.47	4.74	1.02E-08	9.72E-07
5a	4	11.49	5.05	1.05E-08	1.00E-06
6a	6	11.50	4.15	1.03E-08	9.83E-07
6b	6	11.50	4.46	1.03E-08	9.80E-07

Table 8. (continued)

Sample Number	Reaction Time, d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
7a	7	11.49	4.99	1.02E-08	9.75E-07
7b	7	11.49	4.79	1.04E-08	9.94E-07
8a	8	11.51	4.57	1.02E-08	9.67E-07
8b	8	11.49	4.70	1.01E-08	9.57E-07
9a	9	11.50	4.59	1.06E-08	1.01E-06
9b	9	11.50	5.00	1.06E-08	1.01E-06
10a	10	11.50	4.57	1.05E-08	9.95E-07
10b	10	11.52	4.69	1.00E-08	9.56E-07
12a	12	11.47	5.06	1.10E-08	1.05E-06
13a	13	11.50	5.39	1.04E-08	9.94E-07
13b	13	11.49	5.28	9.78E-09	9.31E-07
14a	14	11.49	4.91	1.03E-08	9.82E-07
14b	14	11.48	4.81	9.84E-09	9.37E-07
Test LRM VIII conducted with 0.49981 g glass					
1a	3.10	11.64	16.38	1.01E-09	9.61E-08
2a	4	11.47	14.44	1.02E-09	9.74E-08
3a	7	11.55	15.49	1.04E-09	9.87E-08
4a	8	nr	15.24	9.17E-10	8.73E-08
5a	9	11.68	8.64	1.20E-09	1.14E-07
6a	10	nr	13.10	1.03E-09	9.83E-08
7a	11	11.60	14.09	1.04E-09	9.93E-08
8a	14	nr	9.73	1.10E-09	1.04E-07
9a	15	11.69	nr	9.41E-10	8.95E-08
10a	16	11.69	12.32	1.04E-09	9.86E-08
11a	17	11.73	13.43	1.02E-09	9.75E-08
Test LRM IX conducted with 0.49982 g glass					
1a	3.04	11.62	15.84	1.12E-09	1.07E-07
2a	4	11.59	17.99	1.12E-09	1.06E-07
3a	7	11.62	18.10	1.08E-09	1.03E-07
4a	8	nr	15.62	6.78E-10	6.46E-08
5a	9	11.65	11.72	1.23E-09	1.17E-07
6a	10	nr	16.34	1.09E-09	1.03E-07
7a	11	11.61	15.96	1.32E-09	1.26E-07
8a	14	nr	12.10	1.12E-09	1.06E-07
9a	15	11.64	12.38	1.08E-09	1.03E-07
10a	16	11.66	13.32	1.08E-09	1.03E-07
11a	17	11.62	14.92	1.09E-09	1.04E-07

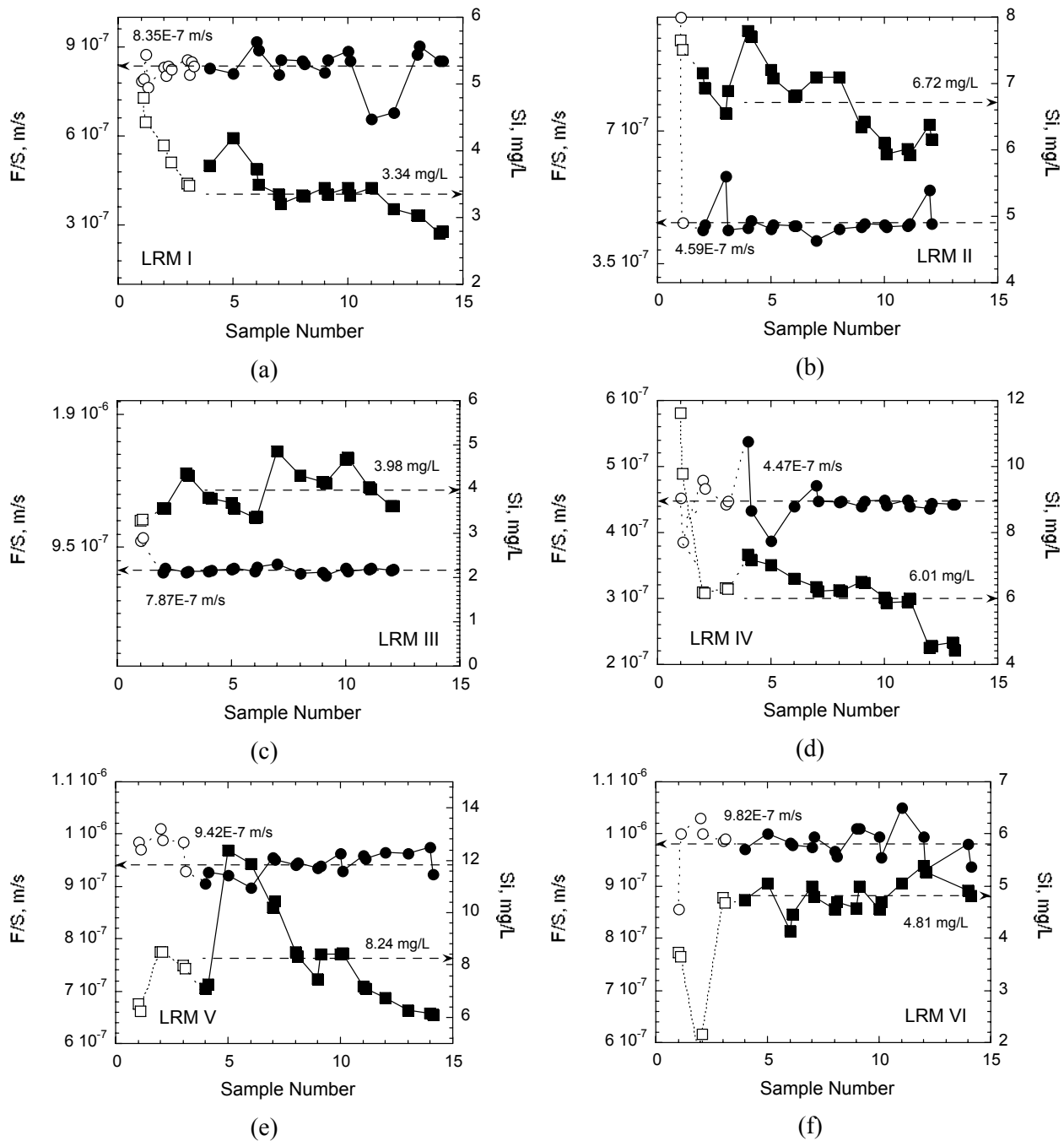
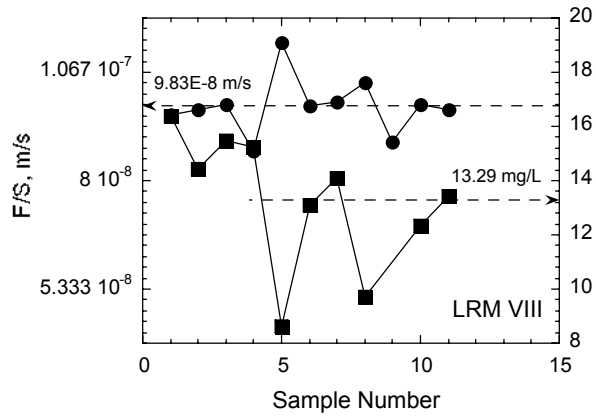
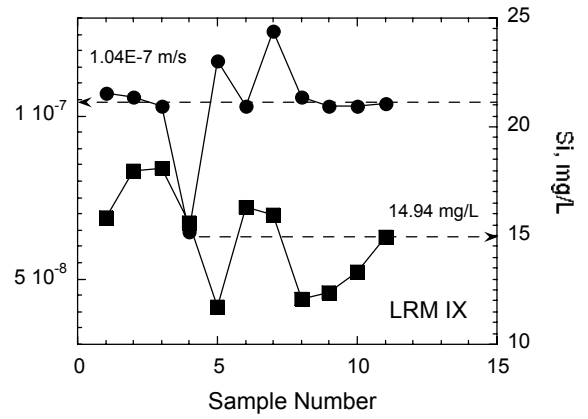


Fig. 9. Results from Participant E for Samples Taken in Tests (a) LRM I, (b) LRM II, (c) LRM III, (d) LRM IV, (e) LRM V, (f) LRM VI, (g) LRM VIII, and (h) LRM IX: values of (●) F/S and (■) Si concentration. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)

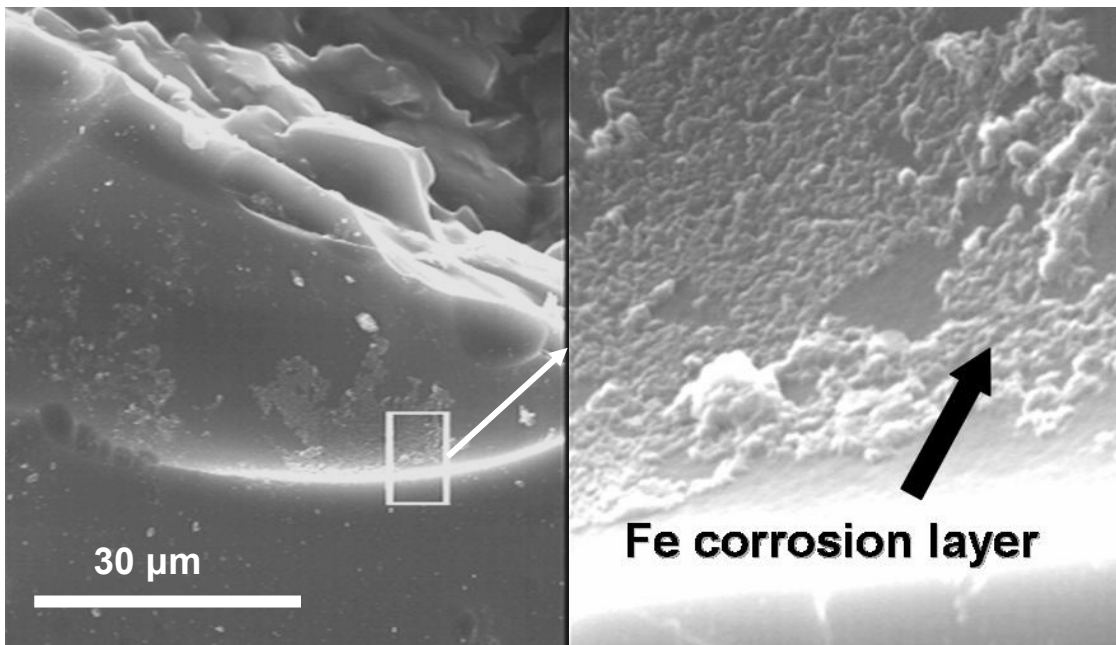


(g)



(h)

Fig. 9. (continued)



(a)

(b)

Fig. 10. SEM Images of Corroded LRM Glass from Test Showing Fe-bearing Deposits at (a) low magnification and (b) 10X higher magnification.

3.6 RESULTS FROM PARTICIPANT F

Participant F reported results for tests conducted with two different apparatus designs. Tests F31-1, F31-2, and F31-3 were conducted in a column design having upward solution flow at high solution flow rates. Test F31-4 was conducted using a jar reactor design that included a mechanical stirrer. The crushed glass was enclosed in a gold bag (63 mesh) and the flow rate was changed several times during the 10-day test duration. None of the tests were conducted following the procedure prescribed for the ILS with regard to when samples were collected, and none demonstrated that steady-state Si concentrations were achieved. Tests F31-1 and F31-2 were sampled during the first 5 hours and 4 hours, respectively, and Test F31-3 was sampled during the first three days. In all tests, solutions were collected for alternately short and long collection times to determine what the participant referred to as the instantaneous and integrated rates. The consistency of these samples provides some insight into whether steady state was achieved. The pH of the leachant solution was reported to be 11.03 at 25 °C and 9.99 at 70 °C, although neither the pH values nor the Li concentrations were reported for individual samplings. Test F31-1 includes a study of the effect of flow rate for samplings between 5 hours and about 3 days. The results of additional tests to measure the effect of temperature in Test F31-2 were also reported; these are discussed in Section 4.3.2.

The results of Tests F31-1, F31-2, and F31-3 conducted in the column reactor are summarized in Table 9 and plotted in Figs. 11 and 12. (The results of Test F31-2, conducted at different temperatures beyond 242 minutes, are presented in Section 4.3.3.) The results of Test F31-4 conducted in the stirred jar reactor are summarized in Table 10 and plotted in Fig. 13. Mean values of F/S and the Si concentration are shown by dashed lines on the plots; the results shown by open symbols were excluded from the mean. Participant F indicated that the results of tests in the stirred reactor did not represent the glass dissolution rate because the gold bag impeded mixing of the test solution, which would bias the rates measured in the tests low. The results were analyzed for comparison with results from other participants using a similar apparatus design but without a bag.

Table 9. Summary of Test Results for Participant F, Column Reactor

Sample Number ^a	Reaction Time, minutes	Si, mg/L	Flow rate mL/minute	Flow rate, m ³ /s	F/S ^{o, b} m/s
Test F31-1 conducted in a column reactor with 0.1575 g crushed glass					
F31-1-1	15	0.75	2.11	3.52E-08	1.12E-05
F31-1-2	17	0.95	1.94	3.24E-08	1.03E-05
F31-1-3	30	1.07	1.94	3.23E-08	1.02E-05
F31-1-4	32.5	1.11	2.00	3.33E-08	1.06E-05
F31-1-5	60	1.20	1.93	3.22E-08	1.02E-05
F31-1-6	62.5	1.22	2.02	3.36E-08	1.07E-05
F31-1-7	90	1.23	1.92	3.19E-08	1.01E-05
F31-1-8	92.5	1.19	1.94	3.24E-08	1.03E-05
F31-1-9	120	1.25	1.88	3.14E-08	9.96E-06
F31-1-10	122.5	1.32	1.66	2.76E-08	8.76E-06
F31-1-11	180	1.21	1.83	3.05E-08	9.69E-06
F31-1-12	182.5	1.14	1.94	3.23E-08	1.03E-05
F31-1-13	270	1.16	1.92	3.19E-08	1.01E-05
F31-1-14	272.5	1.17	1.87	3.12E-08	9.91E-06
F31-1-15	300	1.17	1.89	3.15E-08	9.99E-06
F31-1-16	302.5	1.15	1.89	3.15E-08	1.00E-05

Table 9. (continued)

Sample Number ^a	Reaction Time, minutes	Si, mg/L	Flow rate mL/minute	Flow rate, m ³ /s	F/S ^{o, b} m/s
Tests F31-1 with different flow rates ^c					
F31-1-17	306	1.15	1.89	3.15E-08	1.00E-05
F31-1-18	320	0.77	2.92	4.87E-08	1.54E-05
F31-1-19	335	0.68	3.61	6.02E-08	1.91E-05
F31-1-20	345	0.521	4.56	7.61E-08	2.41E-05
F31-1-21	355	0.441	5.48	9.13E-08	2.90E-05
F31-1-22	365	0.374	6.39	1.07E-07	3.38E-05
F31-1-23	375	0.328	6.89	1.15E-07	3.64E-05
F31-1-24	381	0.279	7.71	1.28E-07	4.08E-05
F31-1-25	387	0.250	8.47	1.41E-07	4.48E-05
F31-1-26	394	0.247	7.71	1.28E-07	4.08E-05
F31-1-27	420	1.04	1.97	3.28E-08	1.04E-05
F31-1-28	435	1.369	1.45	2.41E-08	7.65E-06
F31-1-29	460	1.826	0.991	1.65E-08	5.24E-06
F31-1-30	481	2.871	0.595	9.91E-09	3.15E-06
F31-1-31	510	3.665	0.405	6.75E-09	2.14E-06
F31-1-32	540	7.898	0.113	1.88E-09	5.98E-07
F31-1-33	1440	8.034	0.0419	6.99E-10	2.22E-07
Test F31-2 conducted in a column reactor with 0.0975 g crushed glass					
F31-2-1	15	0.14	4.81	8.02E-08	4.11E-05
F31-2-2	17	0.18	5.49	9.15E-08	4.69E-05
F31-2-3	30	0.31	3.97	6.61E-08	3.39E-05
F31-2-3	32	0.42	3.08	5.14E-08	2.64E-05
F31-2-4	60	0.43	3.22	5.36E-08	2.75E-05
F31-2-5	62	0.40	3.31	5.51E-08	2.83E-05
F31-2-6	150	0.43	3.35	5.58E-08	2.86E-05
F31-2-7	152	0.43	3.46	5.77E-08	2.96E-05
F31-2-8	180	0.45	3.41	5.69E-08	2.92E-05
F31-2-9	181.5	0.43	3.31	5.52E-08	2.83E-05
F31-2-10	215	0.44	3.24	5.39E-08	2.77E-05
F31-2-11	216.5	0.44	3.26	5.43E-08	2.78E-05
F31-2-12	240	0.43	3.26	5.44E-08	2.79E-05
F31-2-13	241.5	0.42	3.46	5.77E-08	2.96E-05
Test F31-3 conducted in a column reactor with 0.1125 g crushed glass					
F31-3-1	15	0.23	1.97	3.29E-08	1.46E-05
F31-3-2	17	0.43	1.97	3.29E-08	1.46E-05
F31-3-3	30	0.46	2.30	3.83E-08	1.70E-05
F31-3-4	32	0.48	2.51	4.18E-08	1.86E-05
F31-3-5	60	0.57	2.42	4.03E-08	1.79E-05
F31-3-6	62	0.59	2.47	4.12E-08	1.83E-05
F31-3-7	90	0.62	2.41	4.02E-08	1.79E-05
F31-3-8	92	0.62	2.40	4.00E-08	1.78E-05
F31-3-9	120	0.54	2.83	4.72E-08	2.10E-05
F31-3-10	122	0.56	2.84	4.73E-08	2.10E-05
F31-3-11	240	0.60	2.56	4.26E-08	1.89E-05
F31-3-12	242	0.60	2.42	4.03E-08	1.79E-05
F31-3-13	300	0.59	2.57	4.28E-08	1.90E-05
F31-3-14	302	0.58	2.62	4.37E-08	1.94E-05
F31-3-15	360	0.51	2.93	4.88E-08	2.17E-05
F31-3-16	361.5	0.45	3.25	5.42E-08	2.41E-05

Table 9. (continued)

Sample Number ^a	Reaction Time, minutes	Si, mg/L	Flow rate mL/minute	Flow rate, m ³ /s	F/S ^o , m/s
F31-3-17	480	0.46	3.20	5.34E-08	2.37E-05
F31-3-18	481.5	0.43	3.31	5.51E-08	2.45E-05
F31-3-19	1387	0.43	3.07	5.12E-08	2.28E-05
F31-3-20	1388.5	0.40	3.44	5.74E-08	2.55E-05
F31-3-21	1560	0.41	3.21	5.36E-08	2.38E-05
F31-3-22	1561.5	0.39	3.30	5.50E-08	2.45E-05
F31-3-23	1740	0.41	3.21	5.35E-08	2.38E-05
F31-3-24	1741.5	0.39	3.32	5.54E-08	2.46E-05
F31-3-25	1920	0.39	3.51	5.85E-08	2.60E-05
F31-3-26	1921.5	0.38	3.22	5.37E-08	2.39E-05
F31-3-27	2847	0.38	3.24	5.40E-08	2.40E-05
F31-3-28	2848.5	0.38	3.12	5.21E-08	2.31E-05
F31-3-29	3000	0.37	3.21	5.35E-08	2.38E-05
F31-3-30	3001.5	0.36	3.23	5.38E-08	2.39E-05
F31-3-31	3180	0.36	3.22	5.36E-08	2.38E-05
F31-3-32	3181.5	0.37	3.17	5.28E-08	2.35E-05
F31-3-33	3360	0.37	3.21	5.35E-08	2.38E-05
F31-3-34	3361.5	0.36	3.17	5.28E-08	2.35E-05
F31-3-35	4264	0.36	3.25	5.41E-08	2.40E-05
F31-3-36	4265.5	0.34	3.41	5.68E-08	2.52E-05
F31-3-37	4450	0.36	3.29	5.48E-08	2.44E-05
F31-3-38	4451.5	0.35	3.21	5.35E-08	2.38E-05

Table 10. Summary of Test Results for Participant F, Stirred Reactor

Sample Number ^a	Reaction Time, minutes	Si, mg/L	Flow rate mL/minute	Flow rate, m ³ /s	F/S ^o , ^b m/s
Test F31-4 conducted in a stirred reactor with 0.1183 g crushed glass					
F31-4-1	15	0.1	3.251	5.42E-08	2.29E-05
F31-4-2	16.5	0.1	3.263	5.44E-08	2.30E-05
F31-4-3	30	0.1	3.281	5.47E-08	2.31E-05
F31-4-4	33	0.1	3.309	5.52E-08	2.33E-05
F31-4-5	60	0.187	3.300	5.5E-08	2.32E-05
F31-4-6	63	0.233	3.302	5.5E-08	2.33E-05
F31-4-7	90	0.244	3.260	5.43E-08	2.30E-05
F31-4-8	93	0.262	3.313	5.52E-08	2.33E-05
F31-4-9	120	0.277	3.234	5.39E-08	2.28E-05
F31-4-10	123	0.273	3.367	5.61E-08	2.37E-05
F31-4-11	150	0.274	3.278	5.46E-08	2.31E-05
F31-4-12	153	0.263	3.322	5.54E-08	2.34E-05
F31-4-13	270	0.276	3.231	5.39E-08	2.28E-05
F31-4-14	273	0.249	3.413	5.69E-08	2.40E-05
F31-4-15	330	0.236	3.250	5.42E-08	2.29E-05
F31-4-16	333	0.224	3.341	5.57E-08	2.35E-05
F31-4-17	360	0.308	1.882	3.14E-08	1.33E-05
F31-4-18	365	0.350	1.966	3.28E-08	1.38E-05
F31-4-19	390	0.357	1.880	3.13E-08	1.32E-05
F31-4-20	395	0.362	1.958	3.26E-08	1.38E-05
F31-4-21	421	0.364	1.900	3.17E-08	1.34E-05
F31-4-22	426	0.351	1.950	3.25E-08	1.37E-05
F31-4-23	448	0.357	1.900	3.17E-08	1.34E-05
F31-4-24	453	0.334	1.980	3.3E-08	1.39E-05
F31-4-25	523	0.636	1.02	1.71E-08	7.21E-06
F31-4-26	573	0.950	0.69	1.15E-08	4.84E-06
F31-4-27	1445	4.75	0.031	5.24E-10	2.21E-07
F31-4-28	2270	10.6	0.020	3.41E-10	1.44E-07
F31-4-29	2850	9.84	0.034	5.67E-10	2.40E-07
F31-4-30	3332	8.15	0.038	6.41E-10	2.71E-07
F31-4-31	4060	7.55	0.043	7.11E-10	3.00E-07
F31-4-32	4830	7.2	0.027	4.54E-10	1.92E-07
F31-4-33	9015	7.53	0.033	5.5E-10	2.33E-07
F31-4-34	10448	7.5	0.031	5.17E-10	2.19E-07
F31-4-35	11490	4.74	0.082	1.36E-09	5.75E-07
F31-4-36	12008	3.9	0.109	1.81E-09	7.66E-07
F31-4-37	12913	4.24	0.095	1.58E-09	6.66E-07
F31-4-38	13516	4.27	0.093	1.55E-09	6.56E-07
F31-4-39	14340	4.32	0.097	1.61E-09	6.82E-07

^aSample numbers assigned for this report.^bValues calculated using data provided by Participant F.^cTotal reaction time estimated from reported starting times of sample collections.

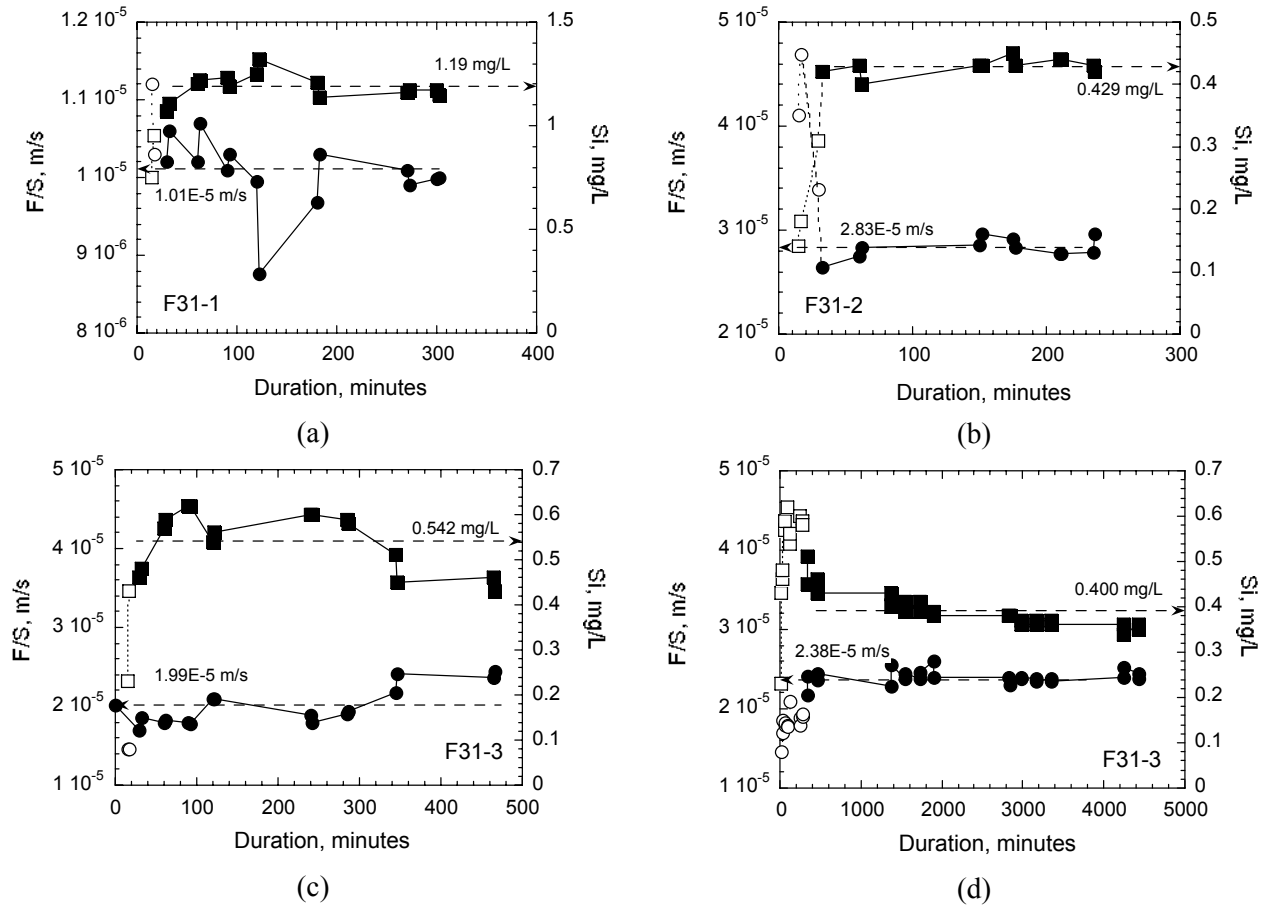


Fig. 11. Results from Participant F for Samples Taken in Tests (a) F31-1, (b) F31-2, and (c) F31-3 during first 500 minutes, and (d) F31-3 through 4,450 minutes: values of (●) F/S and (■) Si concentration. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)

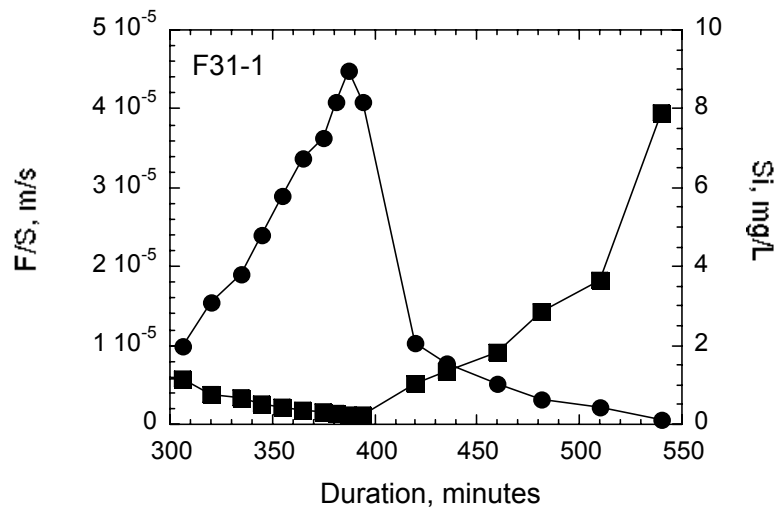


Fig. 12. Results for Continuation of Test F31-1 at Different Flow Rates: values of (●) F/S and (■) Si concentrations.

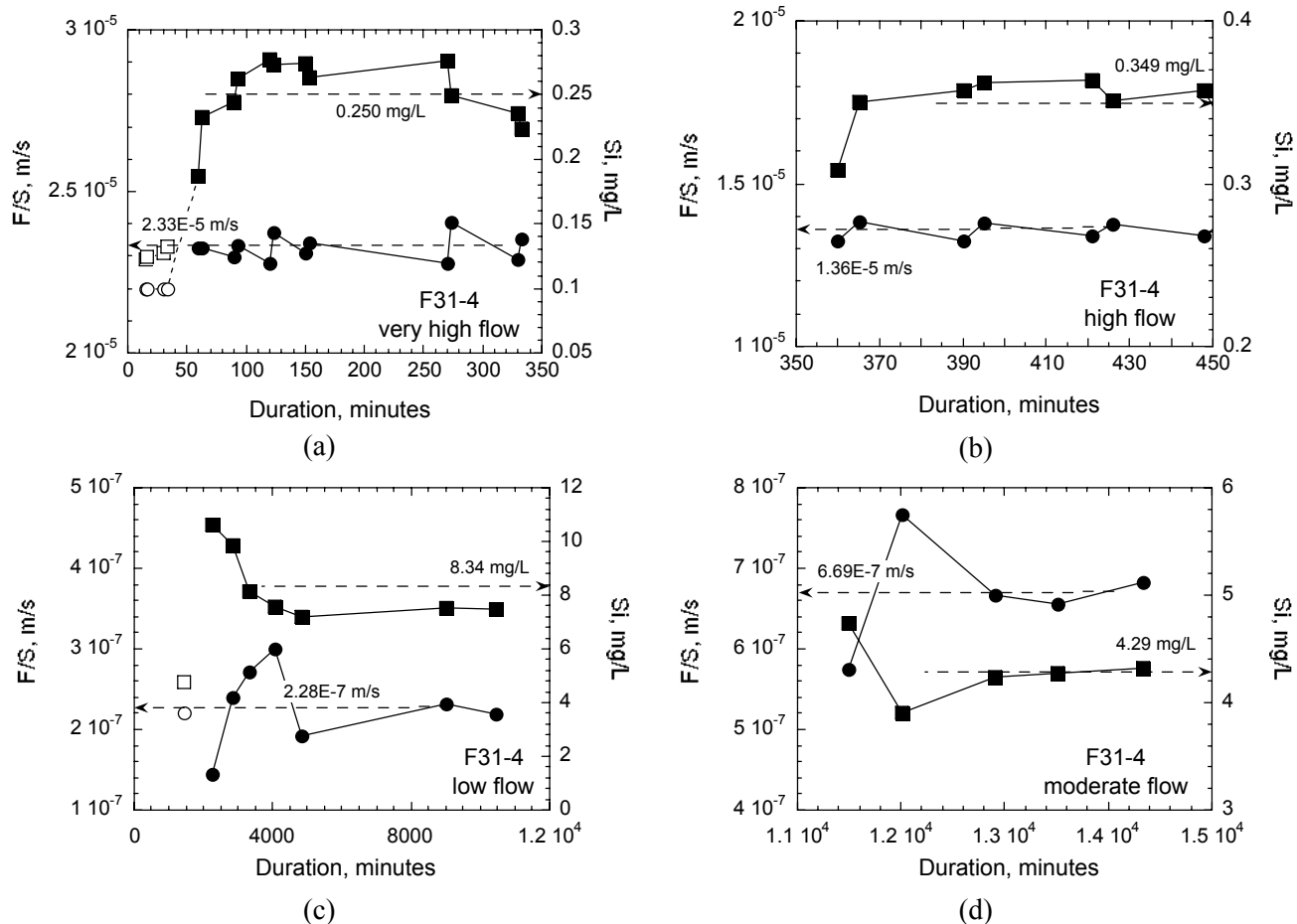


Fig. 13. Results from Participant F for Samples Taken at Different Pumping Rates in Test F31-4 in a Stirred Reactor: (a) very high initial flows during initial 30 to 333 minutes, (b) high flows between 333 and 448 minutes, (c) low flows between about 1445 and 10448 minutes, and (d) moderate flows between about 10448 and 14340 minutes: values of (●) F/S and (■) Si concentration. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)

3.7 RESULTS FROM PARTICIPANT G

Nine test series (referred to as “Test No.”) were conducted by Participant G, with parallel tests at different flow rates (referred to as “runs”). Tests were conducted using a column reactor design similar to that shown in Fig. 2b. The leachant and test solutions were purged with argon to avoid pH drift due to the uptake of CO₂ from the air. The solutions were not filtered prior to analysis with ICP-AES. The results are summarized in Table 11 and plotted in Fig. 14. The first sample collected in most runs was excluded from the average used to calculate the steady state values because the flow rate was not reported or the flow rate had not yet stabilized.

Table 11. Summary of Rest Results for Participant G

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test No. 1 run 2 conducted with 0.199 g glass					
1(2)-1	2.0	9.91	26	8.70E-11	2.07E-08
1(2)-2	3.0	9.88	22	9.03E-11	2.14E-08
1(2)-3	4.0	8.64	19	9.17E-11	2.18E-08
1(2)-4	5.0	9.97	19	9.04E-11	2.15E-08
1(2)-5	6.0	9.62	19	9.10E-11	2.16E-08
1(2)-6	7.0	9.96	18	9.14E-11	2.17E-08
Test No. 1 run 5 conducted with 0.19839 g glass					
1(5)-1	2.0	9.77	26	6.35E-11	1.51E-08
1(5)-2	3.0	8.64	23	7.87E-11	1.87E-08
1(5)-3	4.0	9.50	23	6.84E-11	1.63E-08
1(5)-4	5.0	10.10	23	6.61E-11	1.58E-08
1(5)-5	6.0	10.00	23	6.73E-11	1.60E-08
1(5)-6	7.0	8.67		4.20E-11	1.00E-08
1(5)-7	9.0	8.70		3.99E-11	9.50E-09
Test No. 2 run 3 conducted with 0.2015 g glass					
2(3)-1	1.6	11.11	28	9.02E-11	2.12E-08
2(3)-2	3.4	11.26	30	9.56E-11	2.24E-08
2(3)-3	4.6	11.29	30	8.08E-11	1.89E-08
2(3)-4	5.6	11.32	31	1.04E-10	2.43E-08
2(3)-5	7.5	11.30	31	9.54E-11	2.24E-08
2(3)-6	9.4	11.30	32	9.60E-11	2.25E-08
2(3)-7	11.5	11.31	32	9.70E-11	2.28E-08
2(3)-8	13.7	11.28	32	9.75E-11	2.29E-08
Test No. 2 run 7 conducted with 0.2012 g glass					
2(7)-1	1.6	10.98	36	9.14E-11	2.15E-08
2(7)-2	3.4	11.2	47	9.59E-11	2.25E-08
2(7)-3	4.6	11.16	44	9.51E-11	2.23E-08
2(7)-4	5.6	11.29	45	1.04E-10	2.44E-08
2(7)-5	7.5	11.27	38	9.41E-11	2.21E-08
2(7)-6	9.4	11.31	32	9.55E-11	2.24E-08
2(7)-7	11.5	11.33	32	9.70E-11	2.28E-08
2(7)-8	13.7	11.25	32	9.69E-11	2.28E-08
Test No. 2 run 10 conducted with 0.1997 g glass					
2(10)-1	1.6	11.05	33	8.72E-11	2.06E-08
2(10)-2	3.4	11.24	34	9.34E-11	2.21E-08
2(10)-3	4.6	11.23	33	9.20E-11	2.18E-08
2(10)-4	5.6	11.33	34	1.04E-10	2.46E-08
2(10)-5	7.5	11.29	34	9.06E-11	2.14E-08
2(10)-6	9.4	11.29	33	8.63E-11	2.04E-08

Table 11. (continued)

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test No. 2 run 11 test blank					
2(11)-1	1.6	11.31	0.45	9.09E-11	
2(11)-2	3.4	11.39	0.40	9.10E-11	
2(11)-3	4.6	11.38	0.40	8.37E-11	
2(11)-4	5.6	11.45	0.40	8.63E-11	
2(11)-5	7.5	11.41	0.43	7.72E-11	
2(11)-6	9.4	11.32	0.40	3.67E-11	
2(11)-7	11.5	-	-	2.63E-14	
2(11)-8	13.7	-	-	2.26E-14	
Test No. 3 run 4 conducted with 0.0967 g glass					
3(4)-1	0.9	11.5	17.9	1.31E-10	6.40E-08
3(4)-2	1.9	11.5	22.0	5.28E-11	2.58E-08
3(4)-3	2.9	11.63	18.1	1.57E-10	7.68E-08
3(4)-4	4.7	11.66	17.1	1.43E-10	7.00E-08
3(4)-5	5.9	11.56	16.9	1.59E-10	7.75E-08
3(4)-6	6.9	11.53	17.3	1.60E-10	7.84E-08
3(4)-7	7.9	11.73	17.2	1.58E-10	7.71E-08
3(4)-8	8.9	11.62	17.2	1.61E-10	7.87E-08
3(4)-9	10.0	11.3	17.1	1.70E-10	8.32E-08
3(4)-10	11.7	11.79	16.9	1.52E-10	7.45E-08
3(4)-11	13.0	11.78	16.8	1.58E-10	7.73E-08
3(4)-12	14.0	11.8	16.9	1.52E-10	7.41E-08
3(4)-13	14.9	11.3	16.2	1.51E-10	7.40E-08
3(4)-14	15.9	11.4	15.6	1.58E-10	7.73E-08
Test No. 4 run 3 conducted with 0.0517 g glass					
4(3)-1	1.9	11.82	10.6	1.51E-10	1.38E-07
4(3)-2	3.0	11.84	11.1	2.00E-10	1.83E-07
4(3)-3	4.1	11.78	10.6	2.02E-10	1.85E-07
4(3)-4	5.1	11.71	10.4	2.04E-10	1.86E-07
4(3)-5	6.1	11.81	10.4	2.05E-10	1.87E-07
4(3)-6	7.5	11.86	10.5	1.90E-10	1.74E-07
4(3)-7	9.0	11.87	10.5	1.93E-10	1.76E-07
4(3)-8	10.1	11.73	10.4	2.09E-10	1.91E-07
4(3)-9	11.0	11.78	10.5	2.08E-10	1.90E-07
4(3)-10	12.2	11.71	10.5	2.08E-10	1.90E-07
4(3)-11	13.1	11.79	10.5	2.08E-10	1.90E-07
Test No. 4 run 5 conducted with 0.0507 g glass					
4(5)-1	1.9	11.81	9.8	1.50E-10	1.39E-07
4(5)-2	3.0	11.87	10.7	1.76E-10	1.64E-07
4(5)-3	4.1	11.86	9.7	1.77E-10	1.65E-07
4(5)-4	5.1	11.76	9.8	1.77E-10	1.65E-07
4(5)-6	6.5	11.81	10.4	1.78E-10	1.66E-07
Test No. 5 run 7 conducted with 0.289 g glass					
5(7)-1	1.9	11.87	32.6	9.30E-11	1.52E-08
5(7)-2	3.0	11.83	28.8	1.09E-10	1.78E-08
5(7)-3	4.1	11.1	30.0	1.07E-10	1.76E-08
5(7)-4	6.1	11.42	32.0	9.98E-11	1.63E-08
5(7)-5	8.9	11.48	31.5	1.02E-10	1.67E-08
5(7)-6	10.2	11.46	30.8	1.09E-10	1.78E-08
5(7)-7	12.5	11.37	30.8	1.07E-10	1.75E-08

Table 11. (continued)

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test No. 5 run 8 conducted with 0.2939 g glass					
5(8)-1	1.9	11.72	24.7	1.37E-10	2.21E-08
5(8)-2	3.0	11.63	29.0	1.10E-10	1.76E-08
5(8)-3	4.1	10.95	28.6	1.08E-10	1.74E-08
5(8)-4	6.1	11.32	28.4	1.09E-10	1.75E-08
5(8)-5	8.9	11.15	28.5	1.08E-10	1.74E-08
Test No. 6 run 1 conducted with 0.0495 g glass					
6(1)-1	1.0	11.79	6.54	2.34E-10	2.24E-07
6(1)-2	2.0	11.73	8.65	2.70E-10	2.58E-07
6(1)-3	3.3	11.98	8.15	2.72E-10	2.60E-07
6(1)-4	4.3	11.94	9.38	2.71E-10	2.59E-07
6(1)-5	5.1	11.94	9.21	2.72E-10	2.60E-07
6(1)-6	6.1	11.90	8.93	2.72E-10	2.60E-07
6(1)-7	7.0	11.94	9.32	2.71E-10	2.58E-07
6(1)-8	8.0	11.80	9.83	2.73E-10	2.61E-07
6(1)-9	8.9	11.90	9.21	2.69E-10	2.57E-07
6(1)-10	9.9	11.77	8.12	2.72E-10	2.60E-07
Test No. 6 run 4 conducted with 0.0509 g glass					
6(4)-1	1.0	not reported	10.9	3.01E-11	2.80E-08
6(4)-2	2.0	11.75	11.2	2.55E-10	2.36E-07
6(4)-3	3.3	11.92	11.1	2.69E-10	2.50E-07
6(4)-4	4.3	11.94	10.8	2.69E-10	2.50E-07
6(4)-5	5.1	11.97	11.0	2.68E-10	2.49E-07
6(4)-6	6.1	11.92	10.6	2.73E-10	2.53E-07
6(4)-7	7.0	11.93	11.0	2.70E-10	2.51E-07
6(4)-8	8.0	11.81	10.9	2.73E-10	2.54E-07
6(4)-9	8.9	11.89	10.7	2.71E-10	2.52E-07
6(4)-10	9.9	11.78	10.7	2.70E-10	2.51E-07
Test No. 6 run 11 conducted with 0.0503 g glass					
6(11)-3	1.2	not reported	14.7	2.68E-10	2.52E-07
6(11)-4	2.2	11.92	14.0	2.71E-10	2.54E-07
6(11)-5	3.0	11.95	13.6	2.62E-10	2.46E-07
6(11)-6	4.0	11.90	13.4	2.69E-10	2.53E-07
6(11)-7	5.0	11.91	13.9	2.70E-10	2.54E-07
6(11)-8	6.0	11.79	13.4	2.73E-10	2.56E-07
6(11)-9	6.9	11.87	13.5	2.72E-10	2.55E-07
6(11)-10	7.9	11.76	13.2	2.71E-10	2.55E-07
Test No. 7 run 21 conducted with 0.0305 g glass					
7(21)-1	0.9	11.67	8.07	3.39E-10	5.29E-07
7(21)-2	2.0	11.85	8.67	3.66E-10	5.67E-07
7(21)-3	3.0	11.86	8.89	3.71E-10	5.74E-07
7(21)-4	4.0	11.84	8.41	3.68E-10	5.71E-07
7(21)-5	4.7	11.75	8.26	3.73E-10	5.78E-07
7(21)-6	5.9	not reported	8.43	3.70E-10	5.74E-07
7(21)-7	7.0	11.89	8.19	3.64E-10	5.64E-07
7(21)-8	8.0	11.92	7.71	3.78E-10	5.85E-07
7(21)-9	9.1	11.85	7.60	3.72E-10	5.76E-07
7(21)-10	10.0	11.89	7.51	3.73E-10	5.79E-07

Table 11. (continued)

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test No. 7 run 25 conducted with 0.0301 g glass					
7(25)-2	1.0	11.86	6.68	3.52E-10	5.53E-07
7(25)-3	2.0	11.85	6.46	4.11E-10	6.46E-07
7(25)-4	2.8	11.73	6.38	3.56E-10	5.59E-07
7(25)-5	3.9	not reported	6.16	3.58E-10	5.62E-07
7(25)-6	5.0	11.90	5.93	3.59E-10	5.64E-07
7(25)-7	6.0	11.90	5.76	3.62E-10	5.69E-07
7(25)-8	7.1	11.90	5.70	3.60E-10	5.65E-07
7(25)-9	8.0	11.89	5.61	3.62E-10	5.68E-07
7(25)-10	9.0	11.89	5.55	3.60E-10	5.66E-07
Test No. 8 run 3 conducted with 0.0151 g glass					
8(3)-1	0.6	11.58	1.8	not reported	not reported
8(3)-2	0.9	11.64	2.0	1.14E-09	3.58E-06
8(3)-3	1.5	11.62	2.0	1.11E-09	3.47E-06
8(3)-4	2.0	11.64	1.9	1.13E-09	3.53E-06
8(3)-5	2.6	11.58	1.8	1.15E-09	3.59E-06
8(3)-6	2.9	11.66	1.8	1.14E-09	3.56E-06
8(3)-7	4.5	not reported	1.7	1.14E-09	3.56E-06
8(3)-8	5.6	11.25	1.4	1.14E-09	3.56E-06
8(3)-9	5.9	not reported	1.9	1.15E-09	3.59E-06
Test No. 8 run 4 conducted with 0.0206 g glass					
8(4)-1	0.6	11.60	2.1	not reported	not reported
8(4)-2	0.9	11.63	2.1	1.13E-09	2.58E-06
8(4)-3	1.5	11.58	2.6	1.10E-09	2.53E-06
8(4)-4	2.0	not reported	3.1	1.12E-09	2.56E-06
8(4)-5	2.5	11.59	3.0	1.14E-09	2.62E-06
8(4)-6	2.9	11.64	3.0	1.13E-09	2.60E-06
8(4)-7	4.5	not reported	2.6	1.14E-09	2.62E-06
8(4)-8	5.6	11.32	1.0	1.15E-09	2.64E-06
Test No. 8 run 5 conducted with 0.0264 g glass					
8(5)-1	0.6	11.47	4.2	not reported	not reported
8(5)-2	1.6	11.50	5.1	3.09E-10	5.53E-07
8(5)-3	2.0	not reported	4.9	3.12E-10	5.59E-07
8(5)-4	2.6	11.49	4.7	3.22E-10	5.76E-07
8(5)-5	3.0	not reported	4.7	3.16E-10	5.66E-07
8(5)-6	4.5	not reported	4.6	2.52E-10	4.50E-07
Test No. 9 run 43 conducted with 0.00647 g glass					
9(43)-1	0.6	11.39	0.354	2.06E-09	1.50E-05
9(43)-2	1.0	11.45	0.394	2.12E-09	1.54E-05
9(43)-3	1.8	not reported	0.422	2.07E-09	1.51E-05
9(43)-4	2.8	11.50	0.407	2.08E-09	1.52E-05
9(43)-5	3.6	11.53	0.414	2.12E-09	1.55E-05
9(43)-6	4.6	11.58	0.385	2.21E-09	1.61E-05
9(43)-7	5.6	11.55	0.486	2.29E-09	1.67E-05
9(43)-8	6.0	11.53	0.399	2.19E-09	1.60E-05
Test No. 9 run 44 conducted with 0.007958 g glass					
9(44)-1	0.6	11.36	0.601	2.28E-09	1.35E-05
9(44)-2	1.0	11.45	0.594	2.26E-09	1.34E-05
9(44)-3	1.8	not reported	0.558	2.26E-09	1.34E-05
9(44)-4	2.8	11.51	0.531	2.26E-09	1.34E-05
9(44)-5	3.6	11.51	0.538	2.26E-09	1.34E-05
9(44)-6	4.6	11.55	0.541	2.29E-09	1.35E-05
9(44)-7	5.6	11.53	0.534	2.27E-09	1.34E-05
9(44)-8	6.0	11.52	0.519	2.31E-09	1.37E-05

Table 11. (continued)

Sample Number	Reaction Time ^a , d	pH	Si, mg/L	Flow rate (m ³ /s)	F/S ^o , m/s
Test No. 9 run 45 conducted with 0.00488 g glass					
9(45)-1	0.6	11.39	0.525	2.47E-09	2.39E-05
9(45)-2	1.0	11.45	0.421	2.46E-09	2.39E-05
9(45)-3	1.8	not reported	0.401	2.46E-09	2.39E-05
9(45)-4	2.8	11.50	0.327	2.46E-09	2.38E-05
9(45)-5	3.6	11.53	0.296	2.45E-09	2.38E-05
9(45)-6	4.6	11.54	0.291	2.44E-09	2.37E-05
9(45)-7	5.6	11.54	0.267	2.45E-09	2.38E-05
9(45)-8	6.0	11.50	0.274	2.45E-09	2.38E-05
Test No. 9 run 46 conducted with 0.00791 g glass					
9(46)-1	0.6	11.40	0.472	2.11E-09	1.26E-05
9(46)-2	1.0	11.46	0.419	2.12E-09	1.27E-05
9(46)-3	1.8	11.50	0.451	2.12E-09	1.27E-05
9(46)-4	2.8	11.53	0.444	2.12E-09	1.27E-05
9(46)-5	3.6	11.53	0.406	2.13E-09	1.28E-05
9(46)-6	4.6	11.57	0.409	2.15E-09	1.28E-05
9(46)-7	5.6	11.57	0.377	2.10E-09	1.26E-05
9(46)-8	6.0	11.53	0.387	2.11E-09	1.26E-05

^aEstimated from data provided by Participant G.

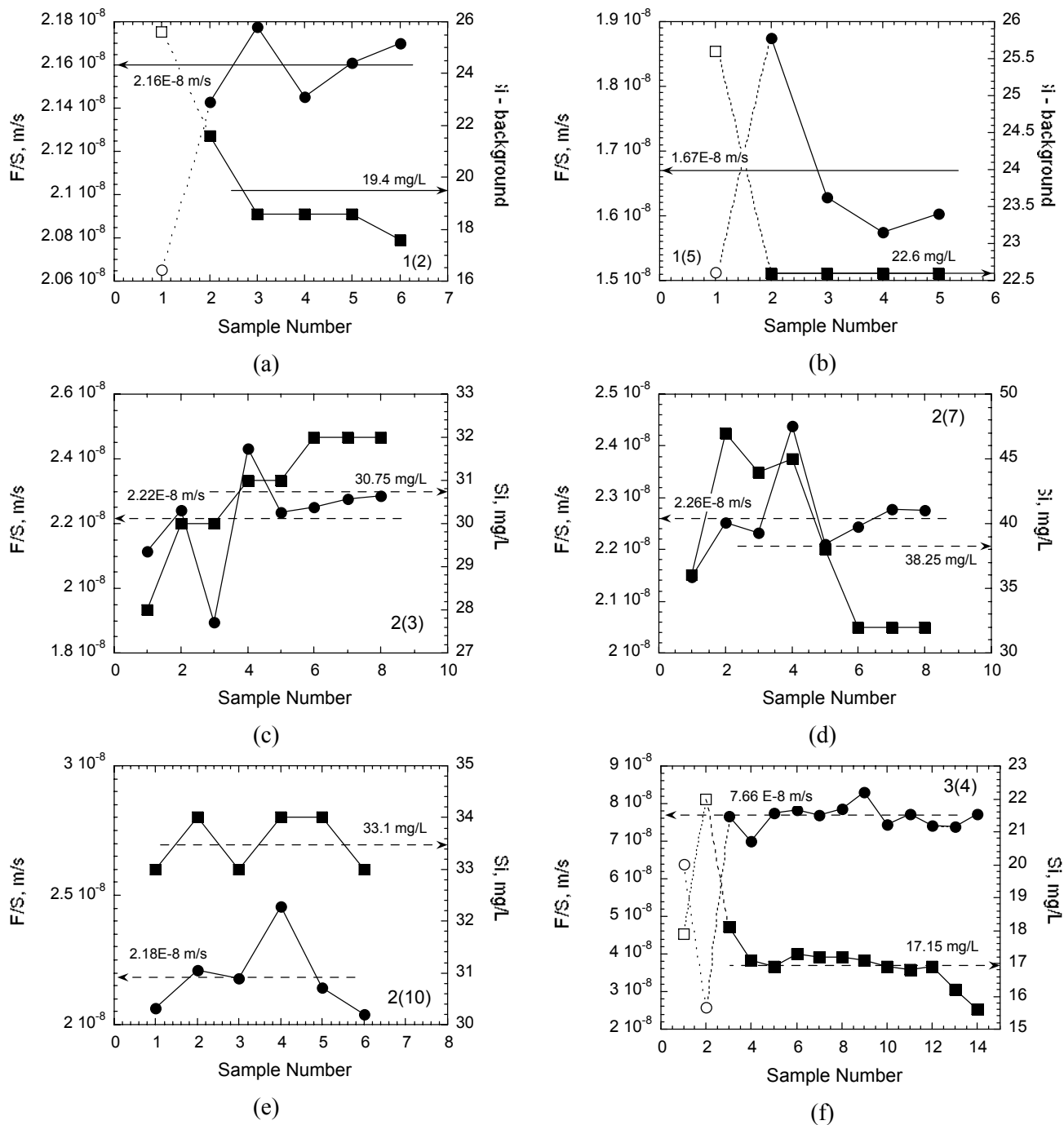


Fig. 14. Results from Participant G for Samples Taken in Tests (a) 1(2), (b) 1(5), (c) 2(3), (d) 2(7), (e) 2(10), (f) 3(4), (g) 4(3), (h) 4(5), (i) 5(7), (j) 5(8), (k) 2(11) blank test, (l) 6(1), (m) 6(4), (n) 6(11), (o) 7(21), (p) 7(25), (q) 8(3), (r) 8(4), (s) 8(5), (t) 9(43), (u) 9(44), (v) 9(45), and (w) 9(46): values of (●) F/S and (■) Si concentration. (Mean values are shown by dashed lines on plots. Results shown by open symbols were excluded from mean.)

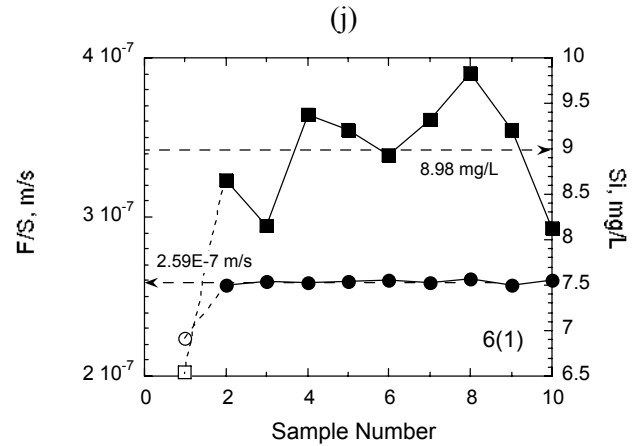
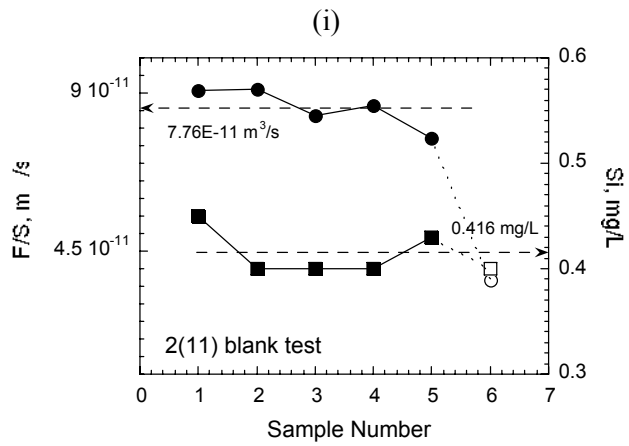
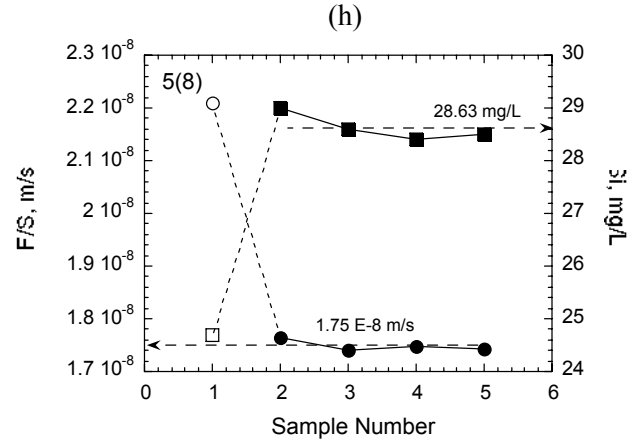
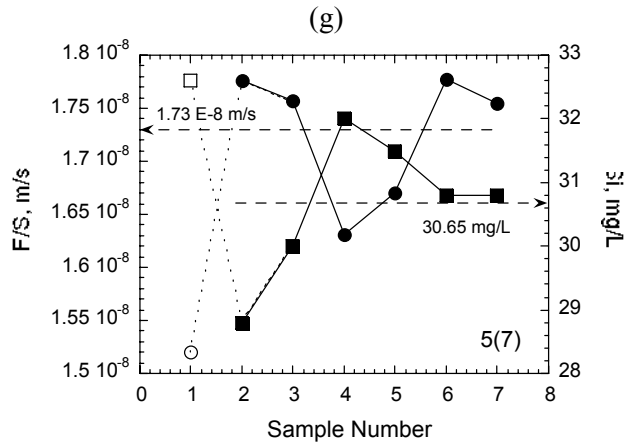
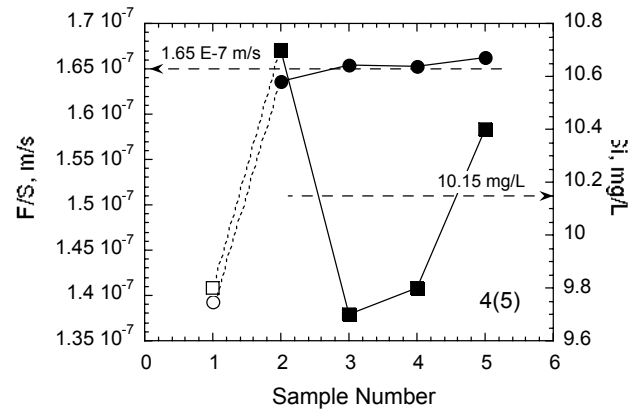
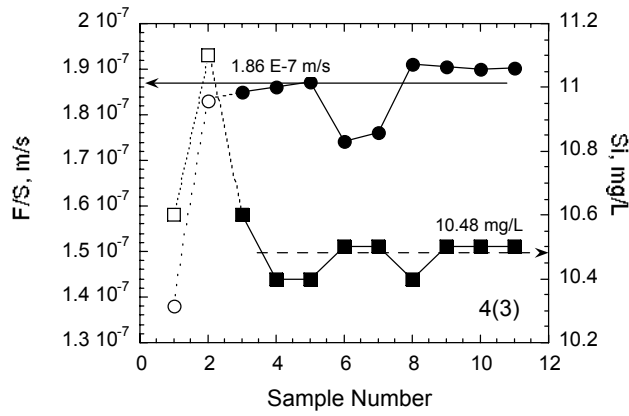


Fig. 14. (continued)

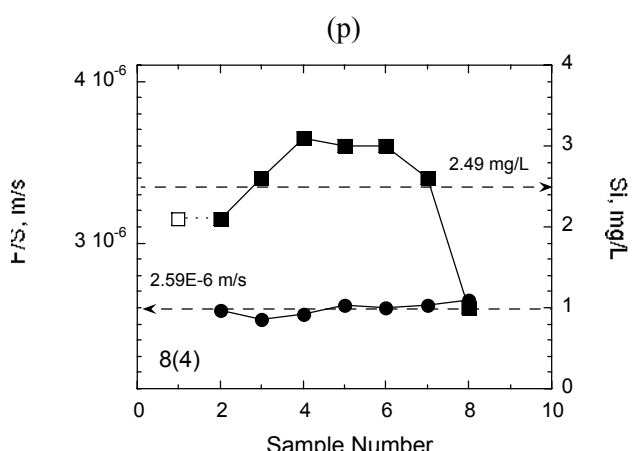
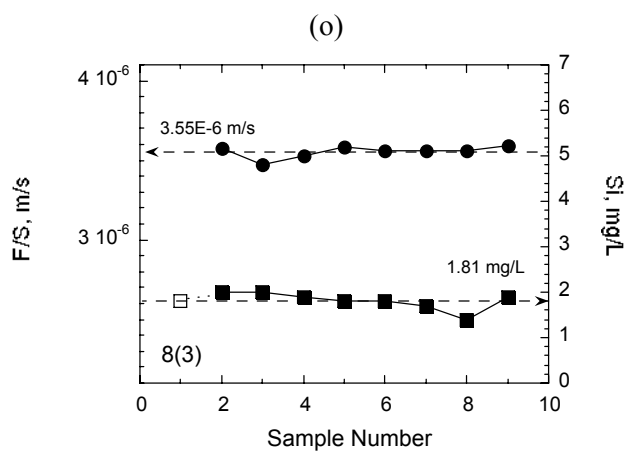
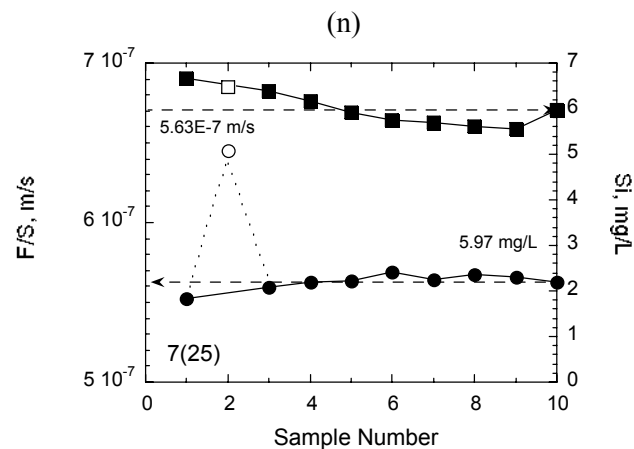
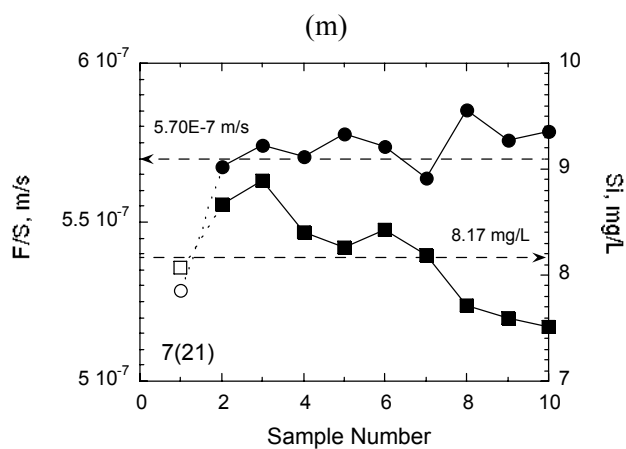
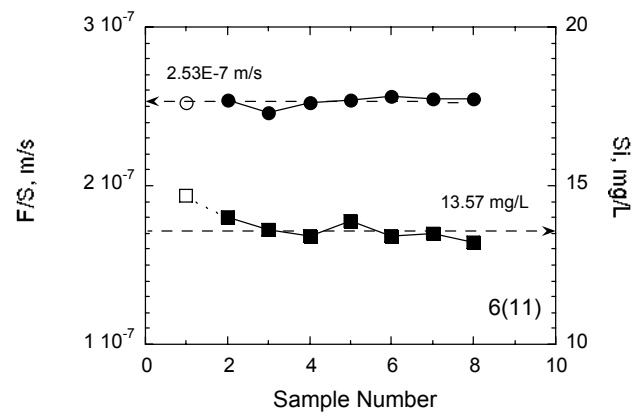
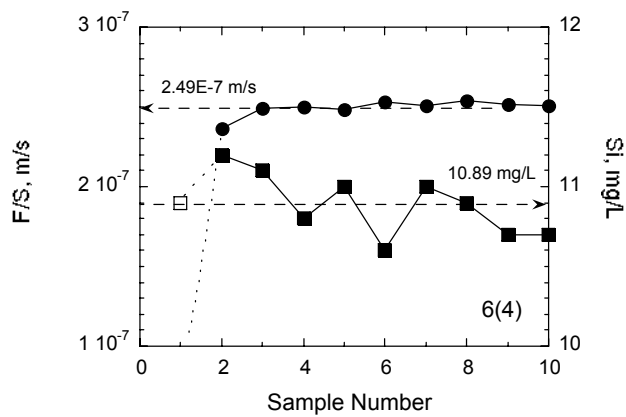
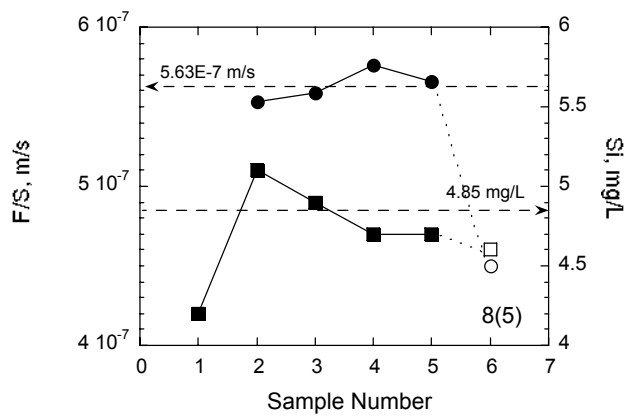
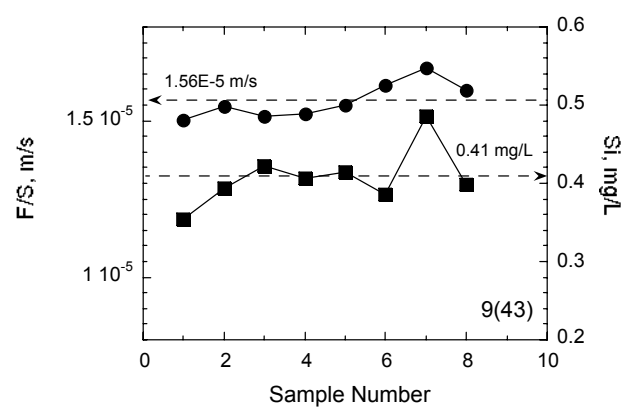


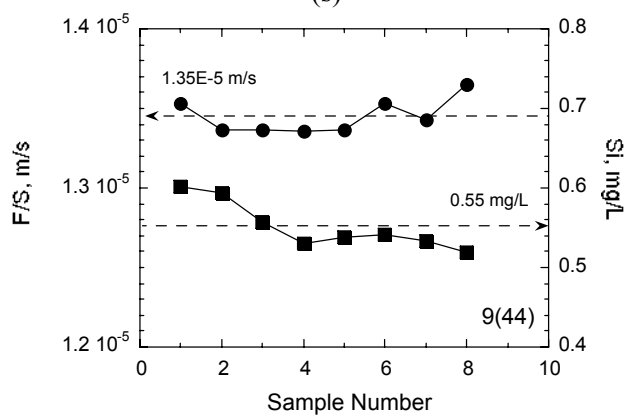
Fig. 14. (continued)



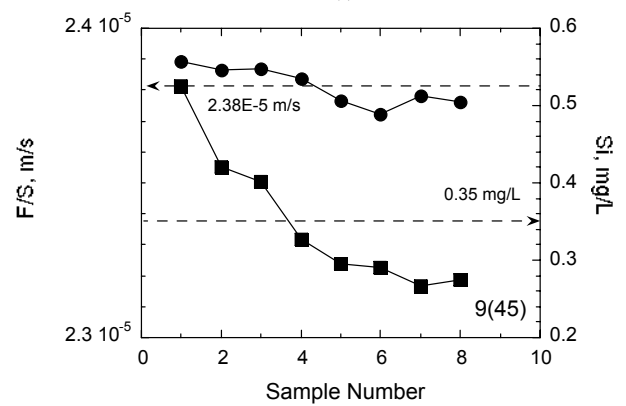
(s)



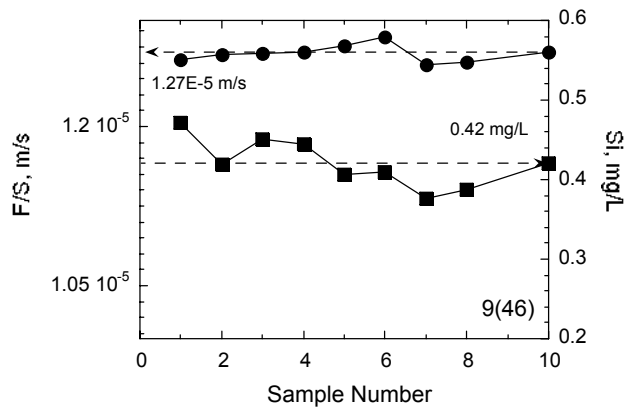
(t)



(u)



(v)



(w)

Fig. 14. (continued)

4. DISCUSSION

4.1 CALCULATION OF DISSOLUTION RATES WITH INDIVIDUAL DATA SETS

The dissolution rate for each test was calculated using Eq. 5. Substituting the mass fraction of Si in LRM glass (which is $f(Si) = 0.2533$) and rearranging the equation slightly gives the form of the equation used to calculate the rate from the test data:

$$rate = \frac{[C^{ss}(i) - C^o(i)] \cdot (F / S^o)}{0.2533} \quad (7)$$

Table 12 provides a summary of the results for the SPFT tests conducted by the seven participants, including the mean values and standard deviations for samples taken during each test. The mean values of $C^{ss}(Si)$ and F/S^o given in Table 12 were used as the steady state values to calculate the dissolution rates with Eq. 7. The background value that was used for $C^o(Si)$ in the rate calculation for each test is listed in Table 12. When they were available, the mean values of blank tests were used as background concentrations. Otherwise, the values measured in the leachant were used. The terms “leachant blank” and “test blank” are used to distinguish analyses of the leachant solution itself from those of test solutions collected from a blank test, respectively. The rates for each test are given in Table 12.

The draft ASTM standard called for flow rates to remain constant within 10%. This was achieved in most tests by most participants. The values of F/S^o in Table 12 indicate the consistency of the flow rates, since these values are calculated by simply dividing the flow rates by the initial surface area in the calculation. The standard deviation exceeded 10% of the mean value in the following tests: Participant B, tests L6 (10.1%), L7 (12.9%), L4-2 (20.0%), L5-2 (13.6%), and L6-2 (15.1%); Participant C, test 60-3 (13.2%); Participant E, test LRM IX (14.4%); Participant F, tests F31-3 (12.1%), F31-4 low rates (22.3%), F31-4 moderate rates (10.2%). The deviation was due to a single outlying data point in some cases (e.g., sample number 4 in LRM IX), while in other cases there was an apparent trend (e.g., F31-3). In most cases, a corresponding deviation was not seen in the Si concentrations when the sampled flow rate deviated from the mean. This suggests that the measured flow rate was in error or did not represent the average flow when the collected solution passed through the reaction cell. A smaller set of samplings than was used in the present analysis could have been selected for some tests to constrain the measured rate to a more constant flow rate. Other tests had significant scatter in both the flow rate and the Si concentration.

The scatter in the measured Si concentrations was greater than the scatter in the measured flow rates: the relative deviation from the mean Si concentration was greater than 10% in about one-third of the tests, whereas the relative deviation from the mean flow rate was greater than 10% in about one-tenth of the tests. This situation arises because scatter in the Si concentrations is due to both variance in the flow rate and uncertainty of the solution analyses. For example, the percent relative standard deviations in the Si concentrations in the 32 tests conducted by Participant A ranges from a low of 4.34% (LRM-3-E) to a high of 22.2% (LRM-3bO), with a mean of 10.7%.

When possible, the forward dissolution rates were determined from the results of each participant by plotting the data as rate vs. steady-state Si concentration and fitting the data by linear regression. The y-intercept of the fitted line gives the forward dissolution rate. The individual results from the data of Participants A, D, E, F, and G are discussed in Sections 4.1.1 through 4.1.5. The data sets provided by Participants B and C did not include a sufficient span of steady-state Si concentrations for regression or extrapolation. Those results were evaluated in combination with the other data sets to determine the forward rate from the combined data base, as discussed in Section 4.2.

Table 12. Summary of Test Results, All Participants

Participant	Test Number	Number of Samplings	Temp., °C	Initial mass glass, g	pH	Li, mg/L	F/S° x 10 ⁷ , m/s	Si steady-state C ^{ss} (Si), mg/L	Si background C°(Si), mg/L	Rate, g/(m ² d)
A-1	LRM-1-A	14	69.2 ± 0.3	test blank	11.27 ± 0.11	44.6 ± 2.9	-	0.157 ± 0.027	-	-
	LRM-1-B	14	69.2 ± 0.3	0.20	11.19 ± 0.07	37.1 ± 1.7	1.87 ± 0.02	9.46 ± 0.76	0.157	0.594
	LRM-1-C	14	69.2 ± 0.3	1.00	11.06 ± 0.07	41.2 ± 2.8	0.386 ± 0.006	24.7 ± 1.8	0.157	0.322
	LRM-1-D	14	69.2 ± 0.3	0.50	11.12 ± 0.06	43.6 ± 1.5	0.780 ± 0.009	18.9 ± 0.9	0.157	0.499
	LRM-1-E	14	69.2 ± 0.3	1.00	11.22 ± 0.06	42.8 ± 3.0	1.72 ± 0.01	13.5 ± 1.0	0.157	0.781
	LRM-1-F	14	69.2 ± 0.3	0.67	11.25 ± 0.08	40.9 ± 4.7	2.63 ± 0.03	9.79 ± 0.94	0.157	0.864
	LRM-1-G	14	69.2 ± 0.3	1.00	11.27 ± 0.06	46.5 ± 4.1	3.13 ± 0.02	8.77 ± 0.60	0.157	0.919
	LRM-1-H	14	69.2 ± 0.3	0.33	11.26 ± 0.09	45.2 ± 1.4	5.25 ± 0.02	6.10 ± 0.31	0.157	1.06
	LRM-1-I	14	69.2 ± 0.3	1.00	11.29 ± 0.05	41.6 ± 3.0	6.46 ± 0.08	4.47 ± 0.41	0.157	0.950
	LRM-1-J	14	69.2 ± 0.3	0.20	11.28 ± 0.07	43.6 ± 2.3	8.67 ± 0.05	4.07 ± 0.45	0.157	1.16
A-2	LRM-2-A	14	68.9 ± 0.3	test blank	11.27 ± 0.14	42.1 ± 3.8	-	0.184 ± 0.017	-	-
	LRM-2-B	14	68.9 ± 0.3	0.20	11.17 ± 0.15	47.3 ± 0.9	1.88 ± 0.02	12.5 ± 0.8	0.184	0.794
	LRM-2-C	14	68.9 ± 0.3	1.00	11.06 ± 0.15	41.3 ± 3.2	0.385 ± 0.010	26.8 ± 2.0	0.184	0.350
	LRM-2-D	14	68.9 ± 0.3	0.50	11.07 ± 0.14	43.1 ± 3.7	0.788 ± 0.008	20.8 ± 2.8	0.184	0.554
	LRM-2-E	14	68.9 ± 0.3	1.00	11.23 ± 0.14	38.2 ± 2.9	1.72 ± 0.02	14.3 ± 1.1	0.184	0.828
	LRM-2-F	14	68.9 ± 0.3	0.67	11.26 ± 0.14	41.0 ± 2.4	2.65 ± 0.02	11.2 ± 0.7	0.184	0.992
	LRM-2-G	14	68.9 ± 0.3	1.00	11.28 ± 0.13	42.9 ± 3.5	3.12 ± 0.04	9.42 ± 0.86	0.184	0.982
	LRM-2-H	14	68.9 ± 0.3	0.33	11.29 ± 0.14	41.5 ± 4.1	5.25 ± 0.06	6.03 ± 0.84	0.184	1.05
	LRM-2-I	14	68.9 ± 0.3	1.00	11.30 ± 0.13	41.3 ± 3.8	6.45 ± 0.05	4.99 ± 0.85	0.184	1.06
	LRM-2-J	14	68.9 ± 0.3	0.20	11.30 ± 0.12	40.9 ± 2.7	8.66 ± 0.06	3.08 ± 0.20	0.184	0.855
A-3	LRM-3-A	12	68.4 ± 0.4	test blank	11.26 ± 0.06	42.8 ± 7.2	-	0.169 ± 0.058	-	-
	LRM-3-B	10	68.4 ± 0.4	0.20	11.16 ± 0.08	43.3 ± 3.2	1.92 ± 0.02	11.2 ± 1.0	0.169	0.721
	LRM-3-C	10	68.4 ± 0.4	1.00	11.15 ± 0.10	42.2 ± 2.9	0.392 ± 0.004	27.8 ± 3.0	0.169	0.369
	LRM-3-D	10	68.4 ± 0.4	0.50	11.10 ± 0.08	39.1 ± 3.6	0.783 ± 0.007	18.2 ± 2.2	0.169	0.482
	LRM-3-E	7	68.4 ± 0.4	1.00	11.21 ± 0.06	39.7 ± 1.5	1.72 ± 0.02	11.7 ± 0.5	0.169	0.677
	LRM-3-F	7	68.4 ± 0.4	0.67	11.24 ± 0.06	41.5 ± 2.6	2.66 ± 0.01	9.49 ± 0.63	0.169	0.845
	LRM-3-G	7	68.4 ± 0.4	1.00	11.25 ± 0.07	40.0 ± 2.3	3.17 ± 0.05	8.15 ± 0.50	0.169	0.862
	LRM-3-H	7	68.4 ± 0.4	0.33	11.25 ± 0.07	41.6 ± 1.9	5.26 ± 0.05	5.08 ± 0.27	0.169	0.881
	LRM-3-I	7	68.4 ± 0.4	1.00	11.28 ± 0.06	44.3 ± 2.0	6.62 ± 0.10	5.72 ± 0.37	0.169	1.25
	LRM-3-J	9	68.4 ± 0.4	0.20	11.29 ± 0.07	45.1 ± 2.6	8.28 ± 0.27	4.50 ± 0.25	0.169	1.22
	LRM-3-K	12	68.4 ± 0.4	2.50	10.97 ± 0.08	44.5 ± 2.2	0.136 ± 0.003	42.6 ± 5.0	0.169	0.196
	LRM-3-L	15	68.4 ± 0.4	0.50	11.34 ± 0.04	49.1 ± 2.8	13.3 ± 0.2	3.20 ± 0.41	0.169	1.37
	LRM-3-M	15	68.4 ± 0.4	0.37	11.34 ± 0.05	37.6 ± 1.8	18.5 ± 0.5	2.19 ± 0.38	0.169	1.28
	LRM-3-N	15	68.4 ± 0.4	0.25	11.36 ± 0.04	48.9 ± 2.8	26.3 ± 0.4	1.64 ± 0.16	0.169	1.32
	LRM-3-O	15	68.4 ± 0.4	0.13	11.37 ± 0.03	51.0 ± 5.5	50.2 ± 1.2	0.818 ± 0.144	0.169	1.11

Table 12. (continued)

Participant	Test Number	Number of Samplings	Temp., °C	Initial mass glass, g	pH	Li, mg/L	F/S° x 10 ⁷ , m/s	Si steady-state, mg/L	Si background, mg/L	Rate, g/(m ² d)
B	L4 blank	7		test blank	10.49 ± 0.34	nr ^a	-	0.05 ± 0.00	-	-
	L5-1	7	70.0 ± 0.1	0.999	10.54 ± 0.33	nr	1.65 ± 0.11	6.66 ± 0.16	0.05	0.371
	L6-1	7	70.0 ± 0.1	1.003	10.57 ± 0.31	nr	1.69 ± 0.17	6.40 ± 0.25	0.05	0.366
	L7-1	7	70.0 ± 0.1	0.999	10.60 ± 0.30	nr	1.63 ± 0.21	7.54 ± 0.39	0.05	0.416
	L8 blank	9		test blank	10.65 ± 0.14	nr	-	0.668 ± 0.077	-	-
	L4-2	9	70.5 ± 0.2	0.750	10.48 ± 0.20	nr	1.65 ± 0.33	7.97 ± 0.10	0.668	0.411
	L5-2	9	70.5 ± 0.2	0.751	10.54 ± 0.17	nr	1.76 ± 0.24	7.35 ± 0.54	0.668	0.401
	L6-2	9	70.5 ± 0.2	0.749	10.61 ± 0.16	nr	1.79 ± 0.27	7.12 ± 0.38	0.668	0.395
C	10-BL-6	3		test blank	9.97 ± 0.14	nr	-	<0.12	-	-
	10-1	3	70 ± 2	0.2094	9.95 ± 0.14	nr	0.365 ± 0.015	34.3 ± 1.9	0.1	0.426
	10-2	3	70 ± 2	0.1967	10.11 ± 0.17	nr	0.567 ± 0.046	27.3 ± 2.1	0.1	0.524
	10-3	3	70 ± 2	0.2082	9.88 ± 0.14	nr	0.326 ± 0.013	34.7 ± 1.7	0.1	0.384
	25-BL-6	3		test blank	10.63 ± 0.07	nr	-	<0.12	-	-
	25-1	3	70 ± 2	0.2022	10.49 ± 0.04	nr	0.819 ± 0.026	26.0 ± 1.6	0.1	0.722
	25-2	3	70 ± 2	0.1947	10.54 ± 0.05	nr	0.866 ± 0.096	26.0 ± 0.8	0.1	0.767
	25-3	3	70 ± 2	0.2019	10.54 ± 0.06	nr	0.774 ± 0.067	24.0 ± 2.2	0.1	0.626
	60-BL-6	3		test blank	10.00 ± 0.14	nr	-	4.60 ± 0.22	-	-
	60-1	3	70 ± 2	0.1987	10.05 ± 0.04	nr	2.83 ± 0.19	6.40 ± 0.67	4.60	0.172
	60-2	3	70 ± 2	0.1966	10.05 ± 0.08	nr	3.09 ± 1.19	5.67 ± 1.44	4.60	0.058
	60-3	3	70 ± 2	0.1997	9.93 ± 0.09	nr	1.36 ± 0.18	9.73 ± 0.45	4.60	0.238
D	A-blank	1	nr	leachant blank	11.37	46.5	-	<0.1	-	-
	A	7	70.1 ± 0.0	0.1	11.28 ± 0.03	47.3 ± 0.7	8.16 ± 0.004	3.97 ± 0.33	0.1	1.08
	A'-blank	1	nr	leachant blank	11.41	47.1	-	<0.1	-	-
	A'	7	70.13 ± 0.05	0.1	11.28 ± 0.04	47.6 ± 0.9	8.23 ± 0.003	5.61 ± 0.30	0.1	1.55
	A2-blank	1	nr	leachant blank	11.12	49.9	-	<0.1	-	-
	A2	7	70.13 ± 0.15	0.1	11.04 ± 0.06	42.8 ± 7.0	7.51 ± 0.51	4.44 ± 0.87	0.1	1.11
	B2'-blank	1	nr	leachant blank	11.77	49.6	-	<0.1	-	-
	B2'	9	70.26 ± 0.14	0.1	11.85 ± 0.07	48.9 ± 0.9	21.8 ± 3.0	2.10 ± 0.77	0.1	1.48
	B3-blank	1	nr	leachant blank	11.91	49.6	-	<0.1	-	-
	B3	8	70.13 ± 0.15	0.1	11.80 ± 0.12	43.7 ± 6.8	22.7 ± 0.3	2.09 ± 0.29	0.1	1.54
	B4-blank	1	nr	leachant blank	11.85	48.8	-	<0.1	-	-
	B4	8	70.10 ± 0.14	0.1	11.87 ± 0.03	50.5 ± 1.8	22.7 ± 0.3	2.03 ± 0.14	0.1	1.49
	D-blank	1	nr	leachant blank	11.31	47.0	-	<0.1	-	-
	D	8	70.04 ± 0.08	0.1	11.31 ± 0.04	49.5 ± 1.6	4.70 ± 0.04	5.70 ± 0.30	0.1	0.898

Table 12. (continued)

Participant	Test Number	Number of Samplings	Temp., °C	Initial mass glass, g	pH	Li, mg/L	F/S° x 10 ⁷ , m/s	Si steady-state, mg/L	Si background, mg/L	Rate, g/(m ² d)
D (cont.)	D'-blank	1	nr	leachant blank	11.13	48.0	-	<0.1	-	-
	D'	8	70.04 ± 0.10	0.1	11.28 ± 0.07	49.5 ± 1.6	4.48 ± 0.21	5.70 ± 0.33	0.1	0.856
	E-blank	1	nr	leachant blank	11.92	47.5	-	<0.1	-	-
	E	8	70.13 ± 0.40	0.1	11.94 ± 0.05	52.6 ± 6.3	37.2 ± 0.1	1.55 ± 0.05	0.1	1.84
	E'-blank	1	nr	leachant blank	11.91	47.3	-	<0.1	-	-
	E'	8	70.09 ± 0.42	0.1	11.93 ± 0.05	50.7 ± 3.6	37.0 ± 0.1	1.36 ± 0.08	0.1	1.59
	E2-blank	1	nr	leachant blank	11.89	48.9	-	<0.1	-	-
	E2	8	70.09 ± 0.16	0.1	11.90 ± 0.02	50.5 ± 1.9	36.9 ± 0.3	1.48 ± 0.21	0.1	1.73
	G-blank	1	nr	leachant blank	11.89	44.4	-	<0.1	-	-
	G	8	70.29 ± 0.10	0.1	11.86 ± 0.03	45.2 ± 0.5	65.6 ± 0.5	0.77 ± 0.28	0.1	1.49
	G'-blank	1	nr	leachant blank	11.86	44.7	-	<0.1	-	-
	G'	8	70.30 ± 0.11	0.1	11.85 ± 0.03	45.2 ± 0.5	66.2 ± 0.7	0.85 ± 0.12	0.1	1.69
	G4-blank	1	nr	leachant blank	11.60	51.2	-	<0.1	-	-
	G4	8	69.66 ± 0.18	0.1	11.65 ± 0.03	50.8 ± 0.6	63.3 ± 1.9	0.72 ± 0.07	0.1	1.33
	H3-blank	1	nr	leachant blank	11.30	48.5	-	<0.1	-	-
	H3	8	69.74 ± 0.36	0.1	11.34 ± 0.04	50.3 ± 1.0	79.3 ± 0.6	0.69 ± 0.18	0.1	1.60
	H3'-blank	1	nr	leachant blank	11.28	48.9	-	<0.1	-	-
	H3'	8	69.76 ± 0.36	0.1	11.33 ± 0.04	50.3 ± 1.2	78.6 ± 2.2	0.71 ± 0.20	0.1	1.64
	H5-blank	1	nr	leachant blank	11.50	48.0	-	<0.1	-	-
	H5	8	69.76 ± 0.72	0.1	11.57 ± 0.12	50.4 ± 1.3	76.7 ± 0.9	0.81 ± 0.10	0.1	1.87
E	a-blank	2		leachant blank			-	1.45	-	-
	b-blank	2		leachant blank			-	0.07	-	-
	LRM I	30	70.0 ± 0.3	0.50063	11.70 ± 0.13		8.35 ± 0.68	3.34 ± 0.34	0.76	0.736
	LRM II	22	69.6 ± 0.3	0.50076	11.56 ± 0.02		4.59 ± 0.38	6.72 ± 0.56	0.76	0.934
	LRM III	22	70.1 ± 0.3	0.50060	11.57 ± 0.03		7.87 ± 0.18	3.98 ± 0.45	0.76	0.864
	LRM IV	24	69.9 ± 0.2	0.50036	11.48 ± 0.05	51.4 ± 1.45	4.47 ± 0.28	6.01 ± 0.90	0.76	0.800
	LRM V	24	70.4 ± 0.3	0.50039	11.49 ± 0.04		9.42 ± 0.21	8.24 ± 1.87	0.76	2.40
	LRM VI	23	70.5 ± 0.2	0.49979	11.49 ± 0.02		9.82 ± 0.29	4.81 ± 0.31	0.76	1.36
	LRM VIII	11	69.1 ± 1.1	0.49981	11.63 ± 0.09		0.983 ± 0.071	13.3 ± 2.5	↓	0.446
	LRM IX	11	70.0 ± 1.2	0.49982	11.63 ± 0.02		1.04 ± 0.15	14.9 ± 2.3	↓	0.529
F	blank		70.1	leachant blank	11.03		-	0.055	-	-
	F31-1 ^b	16	nr	0.1575	nr	nr	101 ± 5	1.19 ± 0.06	0.055	3.88
	F31-1 ^c	16	66.4-70.3	0.1575	nr	nr	5.98 to 448	-	0.055	3.99
	F31-2	14	nr	0.0975	nr	nr	283 ± 10	0.429 ± 0.013	0.055	3.60
	F31-3 ^d	18	nr	0.1125	nr	nr	199 ± 24	0.542 ± 0.066	0.055	3.31
	F31-3 ^e	25	nr	0.1125	nr	nr	238 ± 13	0.400 ± 0.054	0.055	2.80

Table 12. (continued)

Participant	Test Number	Number of Samplings	Temp., °C	Initial mass glass, g	pH	Li, mg/L	F/S° × 10 ⁷ , m/s	Si steady-state, mg/L	Si background, mg/L	Rate, g/(m ² d)
F (cont.)	F31-4 ^f	12	nr	0.1183	nr	nr	233 ± 4	0.250 ± 0.027	0.055	1.55
	F31-4 ^g	8	nr	0.1183	nr	nr	136 ± 3	0.349 ± 0.019	0.055	1.36
	F31-4 ^h	7	nr	0.1183	nr	nr	2.28 ± 0.51	8.34 ± 1.33	0.055	0.645
	F31-4 ⁱ	5	nr	0.1183	nr	nr	6.69 ± 0.68	4.29 ± 0.30	0.055	0.968
G	2(11)	6		test blank	11.38 ± 0.05	nr	-	0.416 ± 0.022	-	-
	1(2)	6	70	0.1990	9.55 ± 0.63	nr	0.216 ± 0.001	19.4 ± 1.5	0.42	0.135
	1(5)	7	70	0.1984	9.56 ± 0.67	nr	0.167 ± 0.014	23.0 ± 0.0	0.42	0.129
	2(3)	8	70	0.2015	11.30 ± 0.01	nr	0.222 ± 0.016	30.8 ± 1.4	0.42	0.230
	2(7)	8	70	0.2012	11.26 ± 0.06	nr	0.226 ± 0.008	38.3 ± 6.3	0.42	0.292
	2(10)	8	70	0.1997	11.24 ± 0.01	nr	0.218 ± 0.015	33.5 ± 0.5	0.42	0.246
	3(4)	14	70	0.0967	11.59 ± 0.18	nr	0.766 ± 0.035	16.9 ± 0.6	0.42	0.438
	4(3)	11	70	0.0517	11.78 ± 0.06	nr	1.86 ± 0.06	10.5 ± 0.7	0.42	0.637
	4(5)	6	70	0.0507	11.83 ± 0.05	nr	1.65 ± 0.01	10.2 ± 0.5	0.42	0.548
	5(7)	7	70	0.2890	11.44 ± 0.23	nr	0.172 ± 0.006	30.7 ± 1.1	0.42	0.178
	5(8)	5	70	0.2939	11.26 ± 0.29	nr	0.175 ± 0.001	28.6 ± 0.3	0.42	0.168
	6(1)	10	70	0.0495	11.88 ± 0.09	nr	2.59 ± 0.01	8.98 ± 0.57	0.08	0.786
	6(4)	10	70	0.0509	11.88 ± 0.08	nr	2.49 ± 0.05	10.9 ± 0.2	0.08	0.920
	6(11)	7	70	0.0503	11.87 ± 0.07	nr	2.53 ± 0.03	13.6 ± 0.3	0.08	1.17
	7(21)	10	70	0.0305	11.84 ± 0.08	nr	5.70 ± 0.16	8.17 ± 0.46	0.08	1.57
	7(25)	9	70	0.0301	11.87 ± 0.06	nr	5.63 ± 0.05	5.97 ± 0.40	0.08	1.13
	8(3)	9	70	0.0151	11.57 ± 0.16	nr	35.5 ± 0.4	1.81 ± 0.20	0.08	2.10
	8(4)	8	70	0.0206	11.55 ± 0.13	nr	25.9 ± 0.4	2.49 ± 0.74	0.08	2.13
	8(5)	6	70	0.0264	11.50 ± 0.02	nr	5.63 ± 0.10	4.85 ± 0.19	0.08	0.917
	blank			blank	leachant blank	nr	-	0.08	-	-
	9(43)	8	70	0.00647	11.50 ± 0.06	nr	156 ± 6	0.480 ± 0.038	0.08	1.75
	9(44)	8	70	0.007958	11.49 ± 0.07	nr	134 ± 1	0.552 ± 0.030	0.08	2.17
	9(45)	8	70	0.00488	11.49 ± 0.06	nr	238 ± 1	0.350 ± 0.091	0.08	2.20
	9(46)	8	70	0.00791	11.51 ± 0.06	nr	127 ± 1	0.421 ± 0.033	0.08	1.47
	blank			blank	leachant blank	nr	-	0.012	-	-

^aEntry of “nr” means no value was reported.^bSamples collected during the first 302.5 minutes of test F31-1.^cSamples collected between 306 and 540 minutes of test F31-1.^dSamples collected during the first 465.5 minutes of test F31-3.^eSamples collected between 300 and 4435 minutes of test F31-3.^fSamples collected between 33 and 333 minutes of test F31-4 at a very high flow rate.^gSamples collected between 333 and 448 minutes of test F31-4 at a high flow rate.^hSamples collected between 1445 and 10448 minutes of test F31-4 at a low flow rate.ⁱSamples collected between 10448 and 13516 minutes of test F31-4 at a moderate flow rate.^jOnly background-subtracted Si concentrations were provided for this test.

4.1.1 Rates from Participant A

The results of the three series of tests conducted by Participant A are shown in Figs. 15a, 15b, and 15c with linear regression fits. Uncertainty bars are drawn at 10% for the Si concentration and about 15% for the rate, based on propagation of uncertainties (see Appendix C). The y-intercepts of the regression equations give forward dissolution rates of 1.25, 1.29, and 1.35 $\text{g}/(\text{m}^2\text{d})$ for the three test series. For the combined results of tests LRM-1, LRM-2, and LRM-3 that are fitted in Fig. 15d, $m = -0.0392 \text{ g}/[(\text{m}^2\text{d})(\text{mg/L})]$ and $b = 1.29 \text{ g}/(\text{m}^2\text{d})$. The regression coefficient of $R^2 = 0.858$ indicates that 85.8% of the variations in the data base is explained by the regression equations (i.e., the relationship between the rate and the steady-state Si concentration). The remaining variation (14.2%) is due to uncertainty about the mean (i.e., the uncertainty in the rate measured at each Si concentration). This is consistent with the propagated uncertainty of about 15% in each rate.

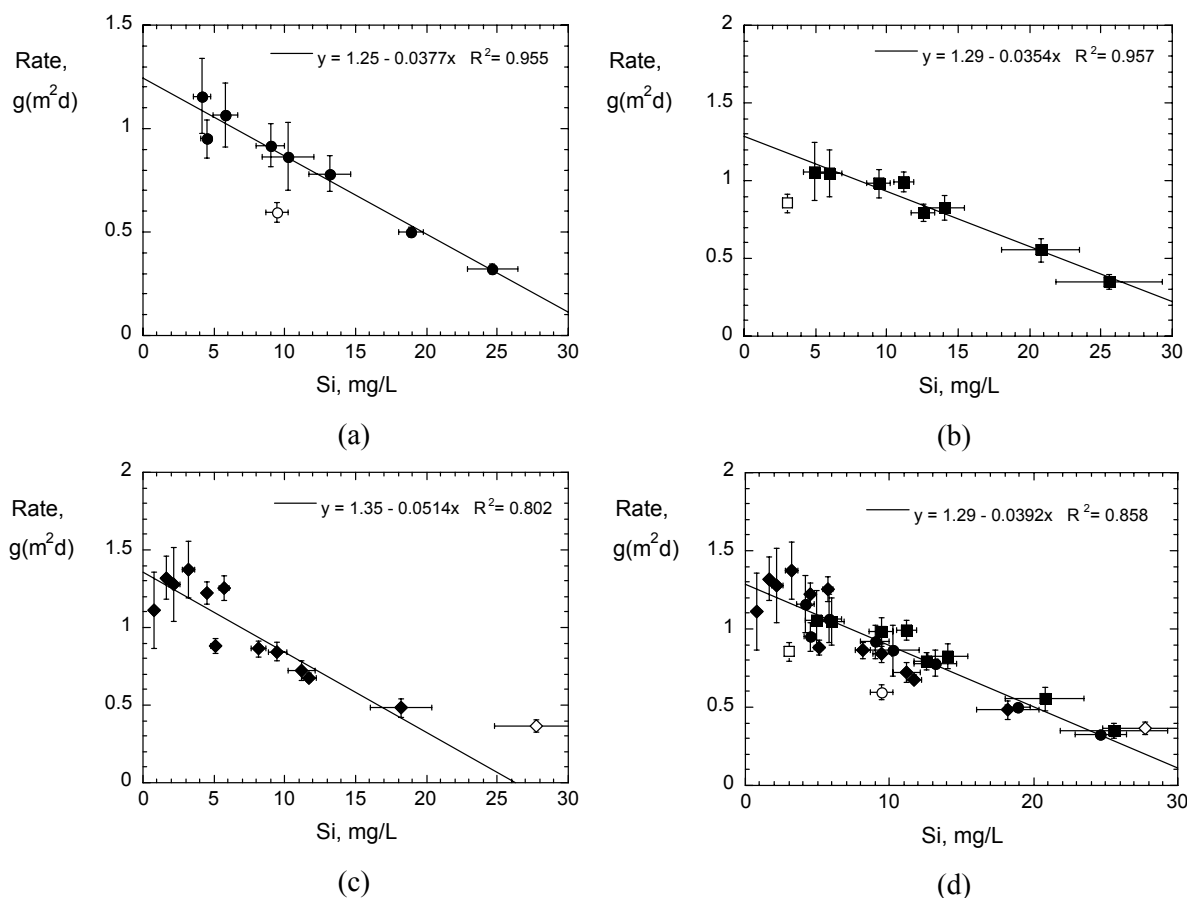


Fig. 15. Results of Rates Measured by Participant A in Tests (a) LRM-1, (b) LRM-2, (c) LRM-3, and (d) combined results for LRM-1 (●), LRM-2 (■), and LRM-3 (◆). (All rates are based on Si. Open symbols were excluded from regressions.)

4.1.2 Rates from Participant D

The rates calculated with the results provided by Participant D are plotted in Fig. 16, with linear regression of all data. Generic error bars are drawn at 10% of the Si concentration and 15% of the rate. The equation of the regression line is $y = 1.75 - 0.121x$, which indicates the forward rate is 1.75 g/(m²d). The range of measured solution pH values (at room temperature) is relatively large for this data set (11.04 to 11.94), although the rates and pH values are not correlated (see Section 4.3.4). All tests resulted in low Si concentrations and small feedback effects, and the value of the correlation coefficient is low: $R^2 = 0.569$.

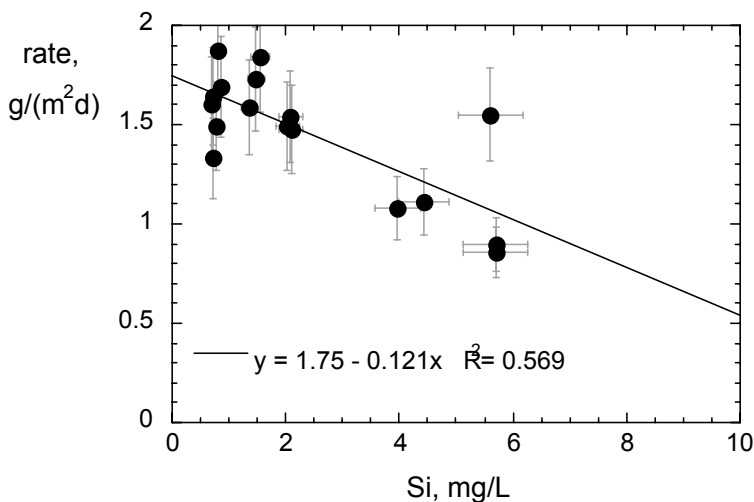


Fig. 16. Results of Rates Measured by Participant D.

4.1.3 Rates from Participant E

The rates calculated with the results provided by Participant E are plotted in Fig. 17, with linear regression of all data except LRM V (rate = 2.40 g/m²d and Si = 8.24 mg/L), which is excluded as an outlier. The equation of the regression line is $y = 1.14 - 0.044x$, with $R^2 = 0.461$, and the forward rate from the regression is 1.14 g/(m²d). However, there is high uncertainty in this value because of scatter in the rates measured at Si concentrations between about 3 and 7 mg/L.

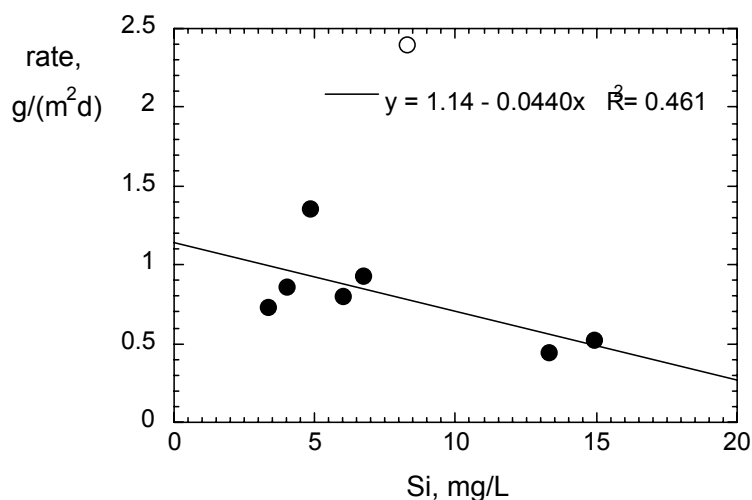


Fig. 17. Results of Rates Measured by Participant E.

4.1.4 Rates from Participant F

The test methods used by Participant F were not consistent with the method called for in the ILS, in that (1) solutions were collected for analysis immediately after tests were started, rather than waiting for about three days to allow high-energy surface sites to dissolve, and (2) tests were not conducted to measure steady-state values. However, the results of tests conducted by Participant F can be compared with results from other participants to better understand the effects of the initial surface finish and other factors that may contribute to bias in the SPFT test method.

The samplings in tests F31-1, F31-2, and F31-3 during the first 300 minutes (5 hours) in the column reactor indicate a transient period of high glass reactivity. Using the mean values in Fig 11, the results provided in short-term samplings of three tests in column reactors give rates F31-1 = 3.88 g/(m²d), F31-2 = 3.60 g/(m²d), and F31-3 = 3.31 g/(m²d) for tests through 465.5 minutes. Samplings of test F31-3 at longer test durations (at a constant flow rate) give a lower average rate of 2.80 g/(m²d) between about 5 hours and three days. It can be seen in Fig. 11d that the Si concentration decreases after the transient increase during the initial 5 hours of reaction. This is attributed to the generation of a more uniform surface finish after sharp edges on the fractured glass have dissolved.

The flow rate was varied in Test F31-1 after the initial 300 minutes (data are plotted in Fig. 12). The variation in flow rates gives different Si concentrations between subsequent samplings, which can be used to calculate the dissolution rate. Although the single sampling provides no confidence that steady state was achieved, this data set can be plotted and extrapolated to zero concentration to provide an estimate of the forward rate. The dissolution rates calculated from the results of test F31-1 in single samplings beyond the first 300 minutes are plotted against the Si concentration in the sample in Fig. 18a. The results of tests at the four highest F/S values (the four lowest Si concentrations) were excluded from the regression because the leachant solution was not sufficiently heated during these samplings, and the rates are probably lowered by the temperature effect. The excluded data are shown by open symbols. The regression equation is $y = 4.06 - 0.371x$, with $R^2 = 0.945$. The forward rate is 4.06 g/(m²d).

Test F31-4 was conducted in a stirred reactor. Rates were calculated for the individual samplings taken in test F31-4 at the very high, high, low, and moderate flow rates shown in Fig. 13. The individual rates are plotted in Fig. 18b for the initial tests at very high and high flow rates through 537 minutes, and in Fig. 18c for the tests at low and moderate flow rates through 4450 minutes (74 hours and 10 minutes). The rates are plotted against the Si concentrations measured in samplings at the different flow rates in Fig. 18d. The line in Fig. 18d is regressed to the dissolution rates at high, moderate, and low flow rates. There is significant scatter in the rates measured at very high flow rates, which range from about 0.3 to 1.8 g/(m²d). The regression line passes through the center of that range. The regression equation is $y = 1.36 - 0.0858x$, with $R^2 = 0.866$. The forward rate is 1.36 g/(m²d).

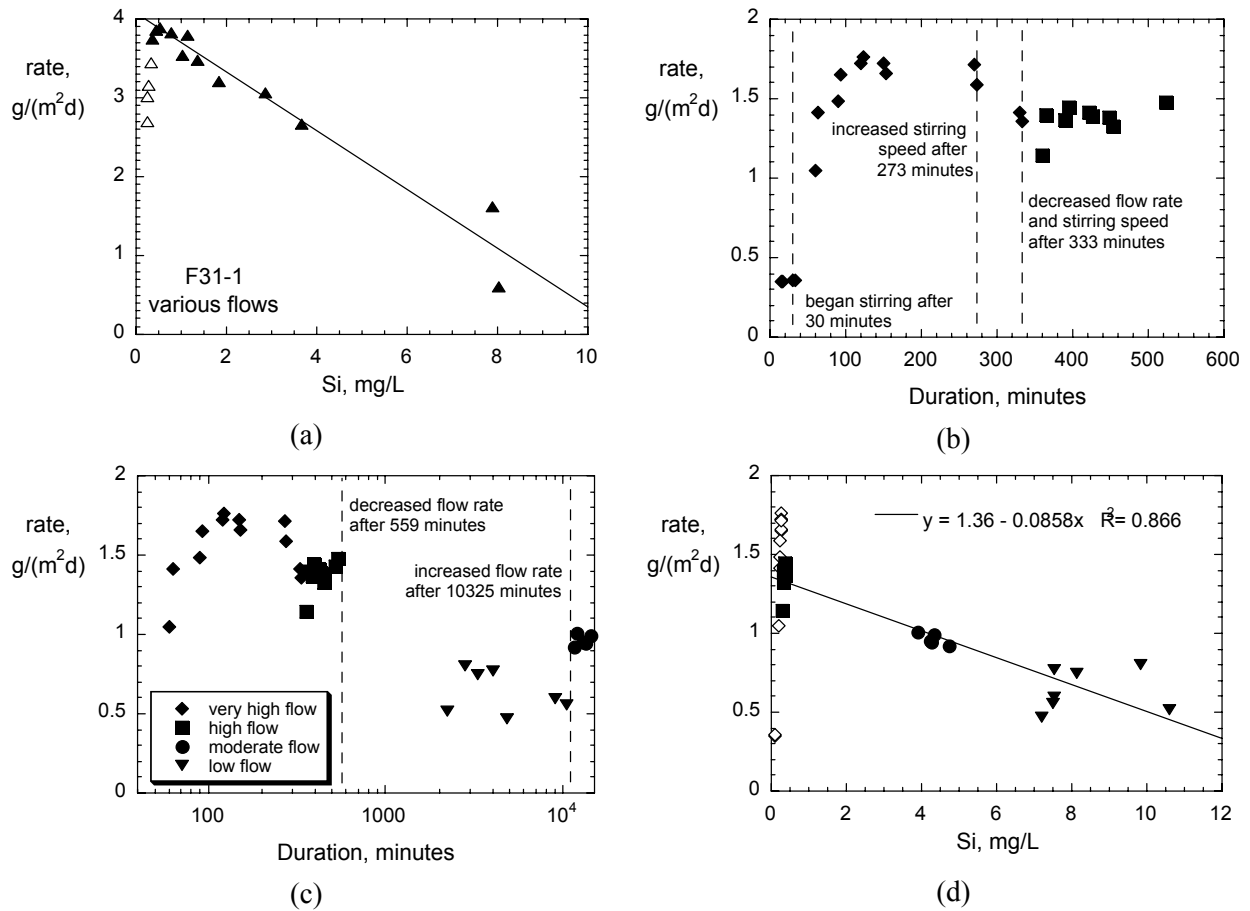


Fig. 18. (a) Results for Continuation of Test F31-1 at Various Flow Rates: dissolution rate vs. Si concentration. Rates for individual samplings in Test F31-4: (b) short duration samples, (c) long-duration samples, and (d) rates from (c) plotted vs. steady-state Si concentration: (◆) very high initial flow rate (33 to 333 minutes), (■) high flow rate (333 to 453 minutes), (▼) low flow rate (1,445 to 10,448 minutes), (●) moderate flow rate conditions (10,448 to 13,516 minutes), and (▲) various flow rates. (All rates are based on Si. Results shown by open symbols were excluded from regression.)

4.1.5 Rates from Participant G

The rates calculated with the results of tests conducted by Participant G are plotted in Fig. 19. The results of tests 1(2) and 1(5) are excluded from the plot because of the low pH values measured in these tests. The set of test results shows a difference in behavior at Si concentrations above and below about 20 mg/L. Although there is scatter, the rates decrease as the steady-state Si concentrations increase up to about 20 mg/L, and are nearly constant at higher Si concentrations. Linear regression is shown for tests in which the steady-state Si concentrations were less than 23 mg/L. Based on the results of Participant A, it is likely that Si concentrations greater than about 23 mg/L provide significant feedback. The equation of the regression line for Si concentrations less than about 23 mg/L is $y = 1.91 - 0.0896x$, with $R^2 = 0.759$, and the forward rate (from the y-intercept of the regression line) is 1.91 g/(m²d).

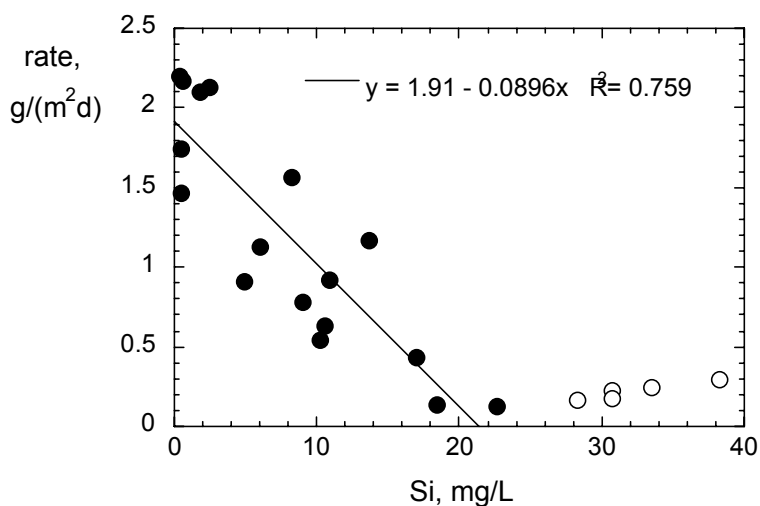


Fig. 19. Results for Participant G in Individual Tests. (Open symbols were excluded from regression.)

4.1.6 Summary of Forward Rates

The rates determined from the results provided by each participant are summarized in Table 13. Rates were not determined from the results of Participants B and C. The average of the rates measured in three tests by Participant A is 1.30 g/(m²d) and the average of the rates measured in replicate tests F31-1, F31-2, and F31-3 by Participant F is 3.60 g/(m²d). The average and standard deviation of the measured rates (excluding tests F31-1, F31-2, and F31-3) is 1.44 ± 0.28 g/(m²d). The rates measured in tests F31-1, F31-2, and F31-3 are excluded from the average because these rates are strongly affected by the transient dissolution of glass at sharp points and edges soon after the tests were initiated. The average of the rates from tests F31-1, F31-2, and F31-3 is 2.5 times the average of the other rates.

Table 13. Summary of Forward Rates

Participant	Forward rate, g/(m ² d)	Participant	Forward rate, g/(m ² d)
A1	1.25	F31-1	3.88
A2	1.29	F31-2	3.60
A3	1.35	F31-3	3.31
D	1.75	F31-4	1.36
E	1.14	G	1.91

4.2 CALCULATION OF FORWARD RATE AND SPFT TEST PRECISION WITH COMBINED RESULTS

The forward rate and the precision of the SPFT test were determined from the combined results of all participants to include variations in the reactor designs and methods used for solution analyses, uncertainties in test execution, such as mass measurements, and factors that were not taken into account in the analyses, such as small differences in the test temperatures.

The rates measured in individual test runs by all participants under all test conditions are plotted in Fig. 20a. The three tests conducted by Participant F in the column apparatus are shown as F-1 and the test conducted in the stirred reactor is shown as F-2. The F-1 results give rates that are significantly higher than other tests. This is probably attributable to the higher initial reactivity of glass due to the surface topology of the glass grains. Tests conducted by other participants that were sampled soon after the tests were started also showed initial dissolution rates that were significantly higher than those attained at longer reaction times when steady state was attained. Those samples were excluded from steady-state Si concentrations used to determine the dissolution rate.

Some of the tests conducted by Participants B and C gave rates that were significantly lower than others. The tests by Participant C had very high background concentrations measured in the blank tests; for example, the three samplings of the blank test 60-BL gave background concentrations of 4.3, 4.7, and 4.8 mg/L. The other blank tests conducted by Participant C at lower flow rates had Si concentrations <0.12 mg/L. If the 60 BL blank test solutions are all assumed to have been contaminated and tests with glass are not background-subtracted, the rate would be about 0.45 g/(m²d), which is similar to the rates measured by Participant B at a similar pH.

As seen in the results from Participant G, the plot in Fig. 20a shows a much greater sensitivity of the rate to the Si concentration below about 15 mg/L than at higher concentrations. Figure 20b provides an expanded view of the rates measured at low Si concentrations, excluding all of the results from Participant C and the anomalously high rate measured by Participant E in Test V. The results of tests by Participant F in the column reactor are also excluded because the test method was different, and the measured rates probably reflect the dissolution rate of sharp points and edges (see Section 4.3.5). The rates measured by Participant F in the stirred reactor beyond 350 days are included in the regression because the method is similar to that used by other participants and the results of Test F31-3 suggest that most of the glass at sharp points and edges had probably dissolved during the first 300 minutes. The equation of the regression line is $y = 1.64 - 0.111x$, with $R^2 = 0.461$. The y -intercept gives the forward dissolution rate predicted by the combination of the rates, which is 1.64 g/(m²d). All rate measurements are weighted equally in this analysis.

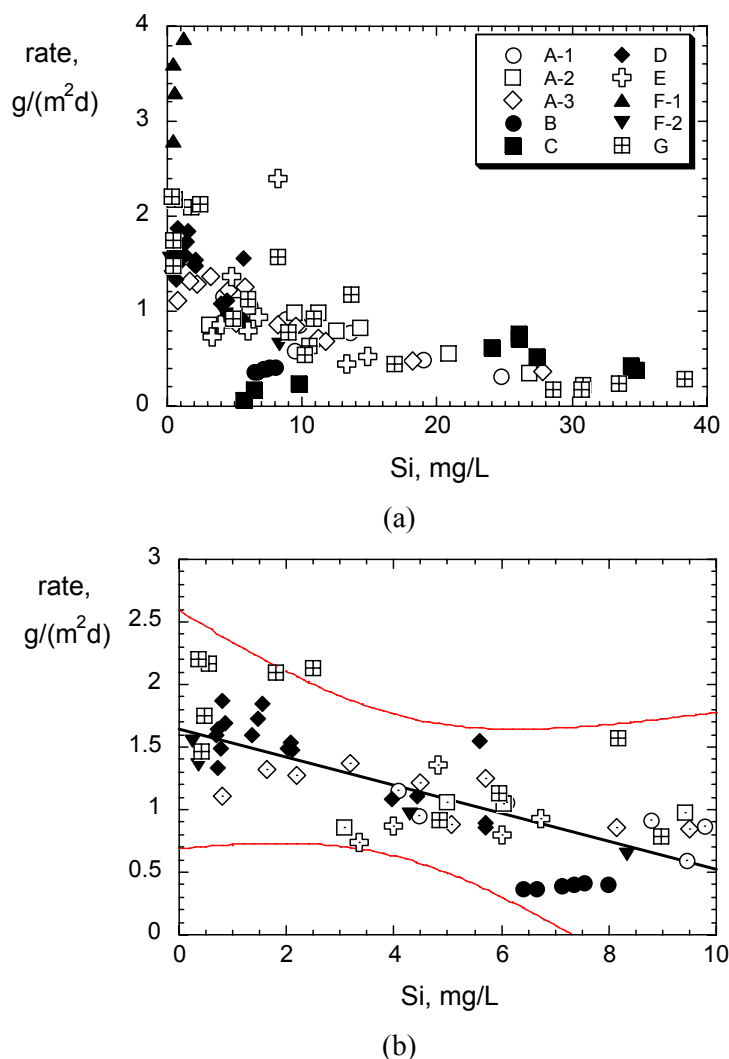


Fig. 20. (a) Combined Results from All Participants and (b) Subset of Results with Rates <2.3 g/(m²d) and Steady-state Si Concentrations <10 mg/L (all of the results plotted in (b) are included in the regression fit).

The uncertainty in the y -intercept of the regression of the combined data set provides a measure of the precision of the rate at any Si concentration, including the value extrapolated to $\text{Si} = 0$ and used as the forward rate. The precision of the forward dissolution rate determined from any data set can be expressed as the expanded uncertainty, which is calculated as the product of the standard uncertainty and t -distribution constant (or coverage factor). The values of the estimated standard error (s.e.) in the slope and y -intercept of the linear regression of a data set are calculated using the formulae

$$s.e. \text{ in slope} = \left\{ \frac{s^2}{\Sigma(X_i - \bar{X})^2} \right\}^{1/2} \quad (8)$$

$$s.e. \text{ in } y\text{-intercept} = \left\{ \frac{s^2 \Sigma X_i^2}{n \Sigma(X_i - \bar{X})^2} \right\}^{1/2} \quad (9)$$

where X_i is the steady-state Si concentration measured in the i^{th} test, n is the number of rates used in the regression, \bar{X} is the mean of all steady-state Si concentrations in the regressed data set, and s is the standard deviation (Draper and Smith 1966). The estimated standard error in the predicted value (i.e., the value calculated with the regression line at any concentration X) is

$$s.e. \text{ in predicted value } \hat{Y} = s \left\{ \frac{1}{n} - \frac{(X_k - \bar{X})^2}{\Sigma(X_i - \bar{X})^2} \right\}^{1/2} \quad (10)$$

The standard deviation is calculated from the regressed rates as

$$s = \left\{ \Sigma Y^2 - \Sigma 2mXY - \Sigma 2Yb + \Sigma m^2 X^2 + \Sigma 2mXb + \Sigma b^2 \right\}^{1/2} \quad (11)$$

where m is the slope and b is the y -intercept of the regression line. Using the reduced data set and regression line plotted in Fig. 20b, the standard deviation is 4.59 g/(m²d). The estimated standard error in the slope is 0.188 [g/(m²d)]/(mg/L) and the estimated standard error in the y -intercept is 0.952 g/(m²d). The uncertainty hyperbolae are drawn at the estimated standard error about the regression line as $Y \pm s.e.$ in Fig. 20b. The regression coefficient value of $R^2 = 0.461$ indicates that the linear regression accounts for only 46.1% of the scatter; the remaining 53.9% is scatter around the mean.

Assuming the uncertainty about the mean has a normal distribution, the t -distribution value for the 66 measured rates that were regressed is 2.00, so that the expanded uncertainty is 1.90 g/(m²d). The forward rate determined by the data set in Fig. 20b is 1.64 ± 1.90 g/(m²d) at the 95% confidence level. The relative uncertainty is $1.90/1.64 = 116\%$.

4.3 OTHER ANALYSES

4.3.1 Repeatability

The three test series conducted by Participants A (LRM-1, LRM-2, and LRM-3) and F (the initial samplings of F31-1, F31-2, and F31-3) provide a measure of the repeatability that can be compared with the reproducibility measured by the combined results. The results of the three test series provided by Participant A (see Fig. 15) give the following rates: LRM-1 = 1.25 g/(m²d), LRM-2 = 1.29 g/(m²d), and LRM-3 = 1.35 g/(m²d). The mean and standard deviation for the three tests by Participant A is 1.30 ± 0.05 g/(m²d), and the relative standard deviation is 3.8%. The mean values from the results provided by Participant F for short-term samplings of three tests in column reactors (see Fig 11) give the following rates: F31-1 = 3.88 g/(m²d), F31-2 = 3.60 g/(m²d), and F31-3 = 3.31 g/(m²d). The mean and standard deviation for the three tests is 3.60 ± 0.29 g/(m²d), and the relative standard deviation is 7.9%. The slightly higher uncertainty in the tests by Participant F is attributed to the much lower solution concentrations that were measured in those tests. Although the rates measured in tests F31-1, -2, and -3 are believed to be dominated by the dissolution of fracture edges that dissolve faster than the bulk glass, the repeatability of the tests is similar.

The precision of the results of tests from Participant A giving Si concentrations less than 20 mg/L was evaluated for comparison with the precision of the combined results of all participants. The results from tests LRM-1, LRM-2, and LRM-3 attaining steady-state Si concentrations less than 20 mg/L were used to determine the uncertainty (see Fig. 15d). The slope of the regression line is $m = -0.0392$ g/[(m²d)(mg/L)], and the y-intercept is $b = 1.29$ g/(m²d). The values used to calculate the standard errors with Eqs. 10 and 11 are summarized in Appendix D, Table D.2. The standard deviation, estimated standard error in the slope, and estimated standard error in the y-intercept for the combined data set are 0.558 g/(m²d), 0.0160 g/[(m²d)(mg/L)], and 0.190 g/(m²d), respectively. The *s.e.* in the predicted mean values at a particular steady-state Si concentration were calculated using Eq. 10 for concentrations between 0 and 20 mg/L, and the uncertainty in the regression is plotted as $\hat{Y} \pm s.e.$ in Fig. 21. (Results shown by open symbols were

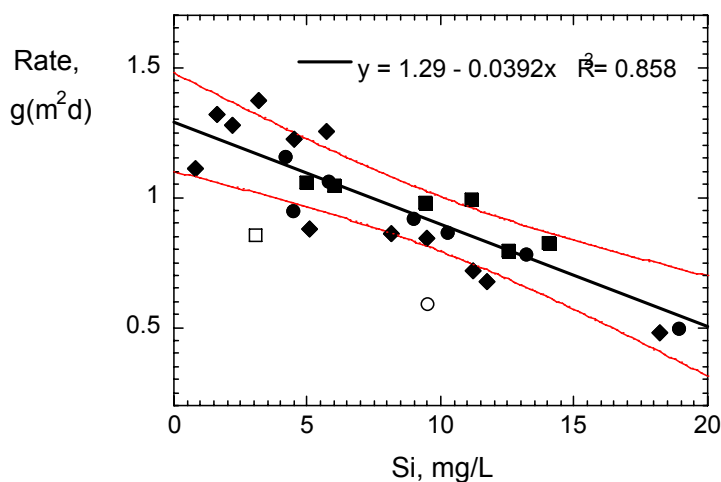


Fig. 21. Results of Tests Conducted by Participant A with Steady-state Si Concentrations <20 mg/L (all plotted results are included in the regression fit).

excluded from the uncertainty calculations.) The confidence limit in the rate predicated at any Si concentration is the product of the estimated standard error and the t -distribution value for the appropriate degrees of freedom for the data base ($n-2$) and desired probability level. For example, the 90% and 95% confidence intervals for values at the y -intercept are calculated to be 0.324 and 0.390 g/(m²d), respectively, using $t_{0.05, n-2} = 1.706$ and $t_{0.025, n-2} = 2.056$ (for $n = 28$ rates). Therefore, at the 95% confidence level, the forward rate is measured to be 1.29 ± 0.39 g/(m²d) in the 3 test series from Participant A. The relative uncertainty is $0.39/1.29 = 30.2\%$.

There is a small amount of bias in the forward rate depending on which measured rates are included in the extrapolation. For the results in Fig. 21, the forward rate is 1.30 g/(m²d) if only the rates from tests with steady-state Si concentrations less than 15 mg/L are used, and 1.32 g/(m²d) if only the rates from tests with steady-state Si concentrations less than 10 mg/L are used. The difference is well within the uncertainty.

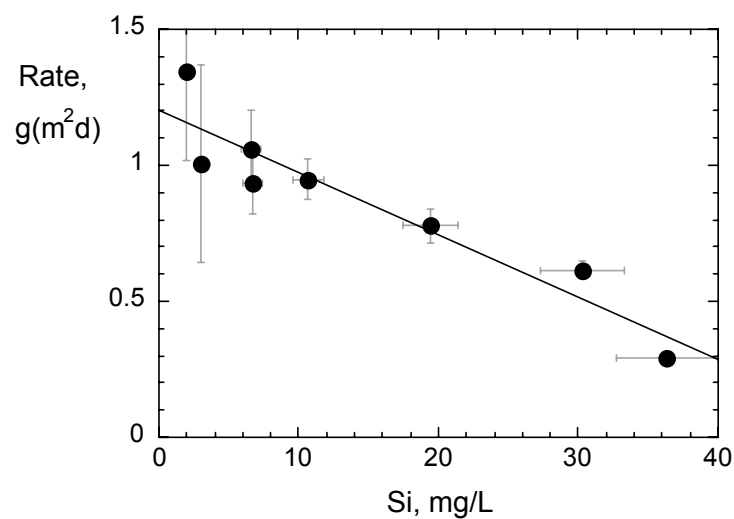
4.3.2 Effect of Glass Particle Size

Participant A conducted Test Series A-4 using –80 +100 mesh size glass, which has a specific surface area of about 0.14 m²/g, based on the arithmetic average of the sieve mesh openings. The test results are summarized in Table 14. The rates are plotted in Fig. 22. The uncertainty bars show the propagated errors in the rates and analytical uncertainties of 10% in the measured Si concentrations. The equation of the regression line is $y = 1.20 - 0.0229x$, with $R^2 = 0.884$, and the forward rate from the regression is 1.20 g/(m²d). Note that Si concentrations up to 36 mg/L do not appear to have a significant effect on the dissolution rate. This is in contrast to tests with smaller particles, which were affected by Si concentrations greater than about 20 mg/L.

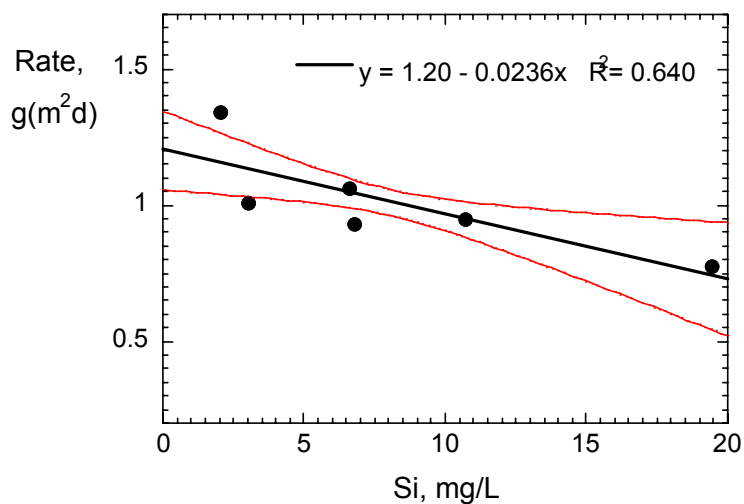
The equation of the regression line, considering only the results with Si concentrations less than 20 mg/L is $y = 1.20 - 0.0236x$, with $R^2 = 0.640$, and the forward rate from the regression is 1.20 g/(m²d) (see Fig. 22b). The standard deviation, standard error in the slope, and standard error in the y -intercept for this data set are 0.252 g/(m²d), 0.0169 g/[(m²d)(mg/L)], and 0.168 g/(m²d), respectively. (Data used to calculate the confidence limits for Test LRM-4 are summarized in Appendix D Table D.4.) The 90% and 95% confidence intervals for the y -intercept are 0.358 and 0.467 g/(m²d), respectively, using $t_{0.05, n-2} = 2.132$ and $t_{0.025, n-2} = 2.776$ (for $n = 6$ rates). The forward dissolution rate in tests conducted with –80 +100 mesh size glass was determined to be 1.18 ± 0.47 g/(m²d) at the 95% confidence limit. This is in excellent agreement with the rate of 1.29 ± 0.39 g/(m²d) measured by Participant A with –100 +200 mesh size glass.

Table 14. Summary of Results for Test Series A-4 with –80 +100 Mesh Size Glass

Test Number	Number of Samplings	Mass Glass, g	F/S° x 10 ⁷ , m/s	Si steady-state, mg/L	Si background, mg/L	Rate, g/(m ² d)
LRM-4-A	10	test blank		<0.05		
LRM-4-C	10	1.00	0.593 ± 0.025	30.3 ± 1.6	0.00	0.613
LRM-4-D	10	0.50	1.17 ± 0.02	19.5 ± 1.6	0.00	0.777
LRM-4-E	10	1.00	2.60 ± 0.04	10.7 ± 0.8	0.00	0.948
LRM-4-F	10	0.67	4.06 ± 0.08	6.75 ± 0.81	0.00	0.934
LRM-4-G	10	1.00	4.71 ± 0.05	6.59 ± 0.85	0.00	1.06
LRM-4-K	10	2.50	0.237 ± 0.006	36.3 ± 2.2	0.00	0.294
LRM-4-L	10	0.50	19.7 ± 0.2	2.00 ± 0.48	0.00	1.34
LRM-4-I	10	1.00	9.78 ± 0.13	3.02 ± 1.08	0.00	1.01



(a)



(b)

Fig. 22. Results of Tests LRM-4. (Rates based on Si.)

4.3.3 Effect of Temperature

The effects of temperature were measured by Participant F. After the first 240 minutes of sampling Test F31-2, the oven temperature was varied while the test was continued at a constant flow rate. The test data are given in Table 15. The value of F/S remained essentially constant, $2.81 \pm 0.06 \times 10^{-5}$ m/s, as the temperature was varied. A background Si concentration of 0.055 mg/L was used for calculation of all dissolution rates. The Si concentrations measured in tests at 31.9 and 39.7°C were below the background level, and rates were not calculated at those temperatures. Figure 23a shows the flow rates and Si concentrations measured in Test F31-2 for samples collected beyond 240 minutes (4 hours) of reaction.

The temperatures and calculated rates are plotted against the test duration when the samples were collected in Fig. 23b. The results are shown in an Arrhenius plot of \ln rate vs. $1/RT$ in Fig. 23c. The plot

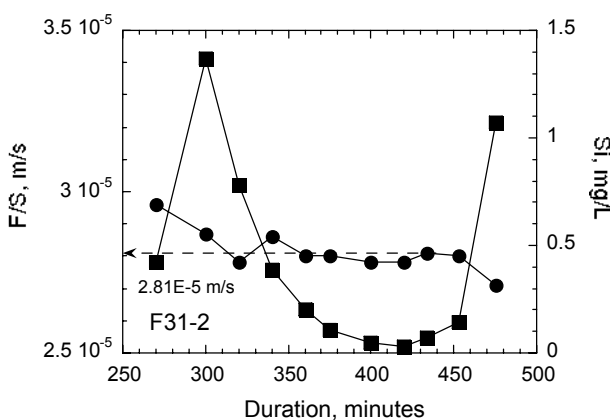
Table 15. Test F31-2 Conducted at Different Temperatures

Sample Number ^a	Reaction Time, minutes	Temperature, °C	Si, mg/L	Flow rate, m ³ /s	F/S, ^b m/s	Dissolution rate, ^c g/m ² d
F31-2-14	270	69.9	0.42	5.77E-08	2.96E-05	3.69
F31-2-15	300	90.1	1.37	5.60E-08	2.87E-05	12.9
F31-2-16	320	79.4	0.78	5.42E-08	2.78E-05	6.87
F31-2-17	340	69.2	0.388	5.59E-08	2.86E-05	3.25
F31-2-18	360	59.1	0.205	5.46E-08	2.80E-05	1.43
F31-2-19	375	50.2	0.110	5.45E-08	2.80E-05	0.524
F31-2-20	400	39.7	0.047	5.42E-08	2.78E-05	-
F31-2-21	420	31.9	0.028	5.42E-08	2.78E-05	-
F31-2-22	434	44.9	0.070	5.49E-08	2.81E-05	0.144
F31-2-23	453	54.9	0.145	5.46E-08	2.80E-05	0.859
F31-2-24	475	84.5	1.07	5.29E-08	2.71E-05	9.39

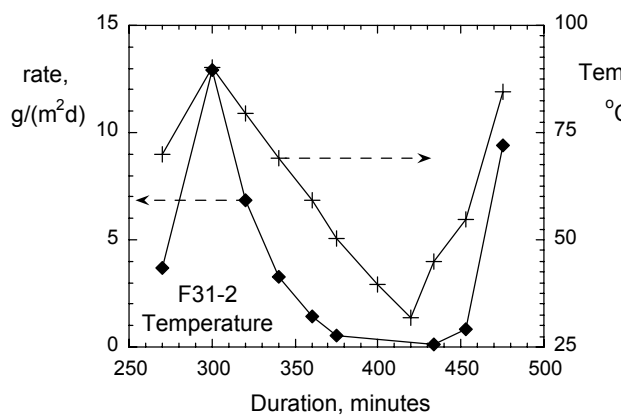
^aSample numbers assigned for this report.

^bValues calculated using data provided by Participant F.

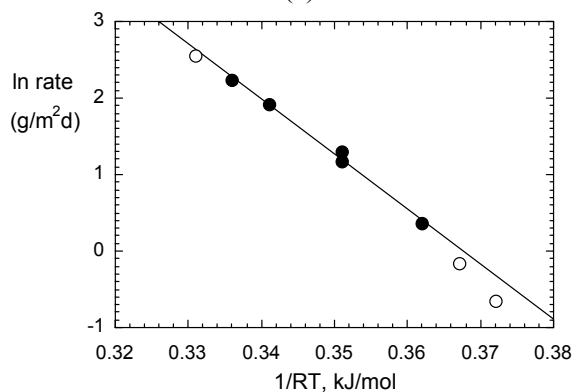
^cRates calculated by assuming a background concentration of 0.055 mg/L.



(a)



(b)



(c)

Fig. 23. Results for Continuation of Test F31-2 at Different Temperatures: (a) values of (●) F/S and (■) Si concentrations, (b) values of (◆) rate and (+) temperature, and (c) Arrhenius plot of ln rate vs. 1/RT.

of the entire data set has negative curvature, and only the results for samples collected between 59.1 and 84.5 °C are included in the regression. Results at 50.2, 54.9, and 90.1 °C, which are excluded from the regression, are shown by open symbols. The negative of the slope of the plot gives the activation energy as 72.0 kJ/mol. The curvature in the plot is probably due to the differences in the impact of solution feedback in tests at different temperature. Using an activation energy of 72.0 kJ/mol, the dissolution rates at 68 and 72 °C are 0.862 and 1.16 times the rate at 70 °C, respectively. That is, the temperature range of 70 ± 2 °C allowed in the ILS can result in a variation in the dissolution rate of about 30%. Participants reported the test temperatures to different degrees of precision: some reported the temperature to within 0.01 °C and others simply reported the temperature was within the 70 ± 2 °C range that was called for in the instructions. The ASTM SPFT test method should call for a specification of the test temperature to within 1 °C.

4.3.4 Variation in pH and Li Concentration during the Test

Although it was expected that the pH and Li concentration would be correlated because the initial pH was imposed by a LiOH/LiCl solution, the test results indicate that they are not correlated. Figures 24a and 24b show the variance in the pH and Li concentrations measured in the blank tests for the three test series conducted by Participant A. Uncertainty bars are drawn at 0.02 pH units in Fig. 24a and at 10% of the measured concentrations in Fig. 24b to represent analytical uncertainty. Solid, dotted, and dashed lines are drawn to show the mean values for tests series A-1, A-2, and A-3, respectively. Note that at least two batches of LiOH/LiCl solution were used during each test series, that the test series were conducted sequentially over several months, and that the solutions from each series were analyzed at different times. The pH increases slightly after the first three collections in all three test series, and then becomes nearly constant. The Li concentrations show nearly uniform scatter for the three test series, although the concentrations for collections 8, 9, and 10 are all (probably fortuitously) higher than the averages.

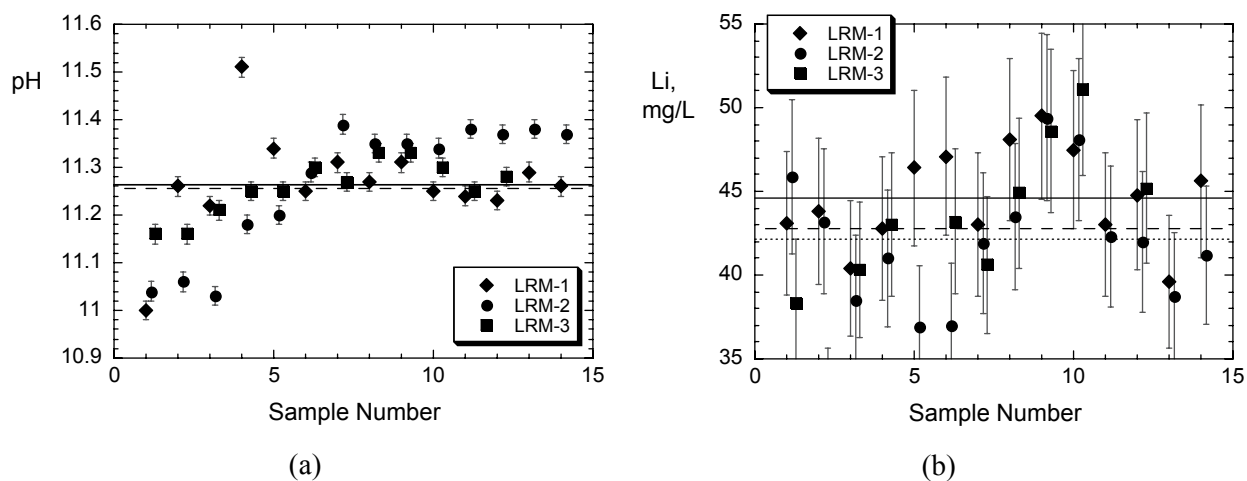


Fig. 24. Measured Values for Blank Test Solutions Reported by Participant A: (a) pH and (b) Li concentration (sample numbers of LRM-2 and LRM-3 are offset for clarity).

Figure 25 shows a plot of the Li concentrations against the pH for the three blank tests conducted by Participant A and the blank tests conducted by Participant D. The results from Participant D show less scatter in the Li concentrations than those from Participant A, but a wider range of pH values. Neither shows a correlation between the Li concentration and the pH.

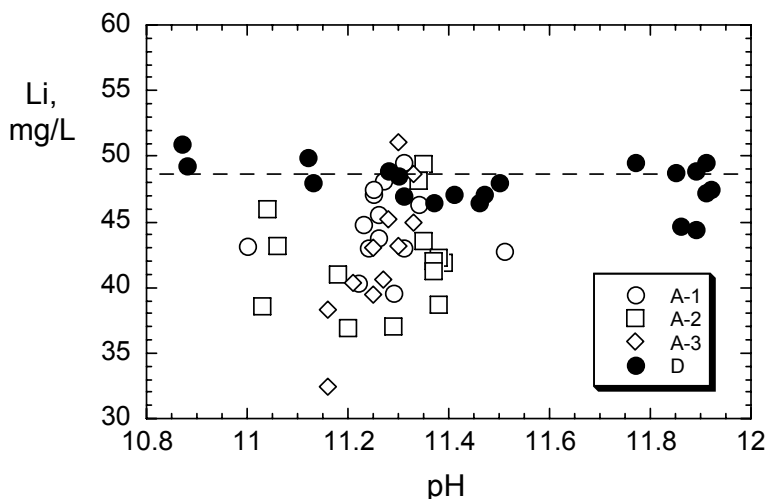


Fig. 25. Correlation between Li Concentration and pH for Blank Test Solutions Reported by Participants A and D

The ILS was conducted with a specific solution composition to ensure that all tests were conducted at the same pH. Nevertheless, a fairly wide range of pH values was measured in the test solutions. From the results summarized in Table 12, the pH values ranged from a low value of 9.55 by Participant G in Test 1(2) to a high value of 11.94 by Participant D in Test E.

Tests having pH values less than 10.33 were deemed too low to use in the analysis. The average pH value of the remaining tests (excluding blanks) is 11.33, and the median is 11.28. In alkaline solutions, the rate is expected to increase with the pH by a factor of $\log_{10} \text{rate} = 0.5 \times \text{pH}$, which is a factor of 2 as the pH increases from 10.33 to 11.94. Glass dissolution was expected to have a negligible impact on the pH under the flow conditions that would be used in the SPFT tests, but this may not be the case for tests in which dissolved glass components accumulated in the test solutions. As mentioned elsewhere, solution feedback may become significant at Si concentrations above about 15 mg/L.

The relationships between the steady-state Si concentration and the pH are plotted in Fig. 26 for tests conducted by Participants A, D, E, and G. The results of Participant A show a negative correlation between the Si concentration and pH. The highest concentrations in tests by Participants D and G also correspond to the lowest pH values, but the results of Participant E do not show a correlation between the Si concentration and pH. More scatter is expected in solutions with low Si concentrations. An initial transient stage of glass dissolution occurs that is dominated by dealkalization reactions, which raises the pH. This is expected to be short-lived in the SPFT tests, but it may be responsible for the higher pH values attained in some tests.

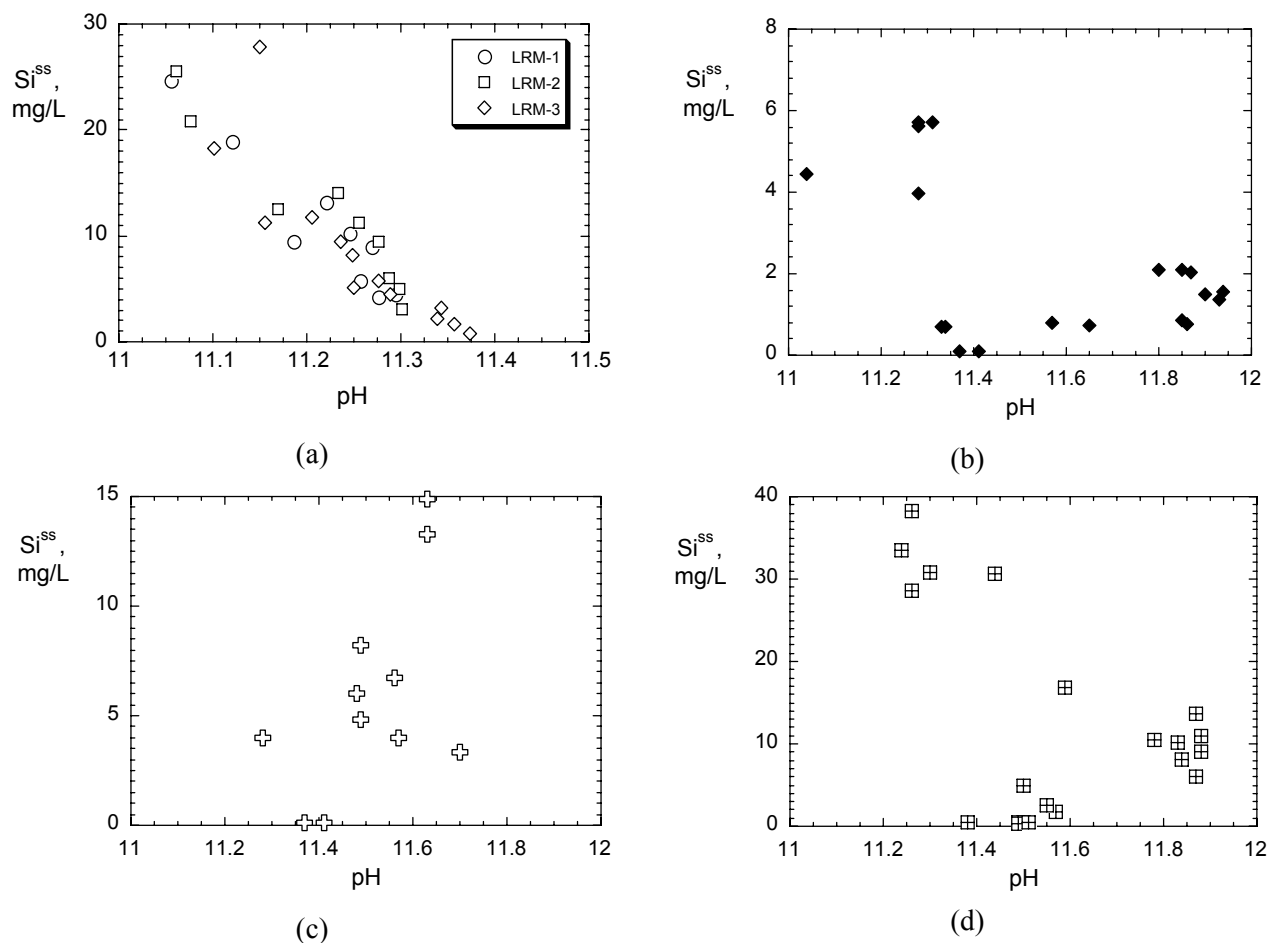
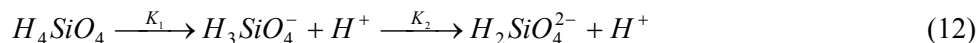


Fig. 26. Correlation between Steady-state Si Concentrations and pH Values: (a) Participant A, (b) Participant D, (c) Participant E, and (d) Participant G.

The dissolution of alkali borosilicate glasses in most leachants under static conditions results in an initial increase in the solution pH due to dealkalization reactions that generate hydroxide. Under the SPFT test conditions, the hydroxide that is generated by dealkalization early in the reaction is flushed from the system and does not affect the solution pH thereafter. This is the purpose of the solution flow. Under the alkaline conditions imposed in the ILS tests, glass dissolution could result in a slight decrease in the pH in tests conducted at low F/S ratios due to the accumulation of dissolution products and the dissociation of orthosilicic acid



The equilibrium constants for these reactions are $\log K_1 = -9.46$ and $\log K_2 = -12.56$ (at room temperature). At an imposed initial pH of about 11.2, the orthosilicic acid released as the glass dissolves will dissociate to $H_3SiO_4^-$ and neutralize an equal amount of LiOH, thereby lowering the pH. The decrease in pH is expected to parallel the increase in the Si concentration, and both are expected to be sensitive to the F/S ratio of the test. Small changes in the solution pH are expected as the solution re-equilibrates after cooling from 70 °C to room temperature. In addition, acidification of the test solutions

due to the absorption of atmospheric CO₂ during sample collection and analysis may also lower the pH values.

As given in Eq. 1, the glass dissolution rate is expected to be proportional to the pH as

$$rate \propto 10^{\eta pH} \quad (13)$$

where the value of η is near 0.5 for most borosilicate glasses in alkaline solutions. Therefore, the forward rates measured at pH 12 are expected to be about 10 times higher than the forward rates measured at near pH 10. The rates measured in the ILS are plotted against the pH in Fig. 27a. The uncertainty in the pH denotes the range of pH values measured for different samplings in a test. Participant F did not report pH values for individual tests. Most tests with glass resulted in pH values between about 11 and 12 (all measured at room temperature). Figure 27b compares the results to the pH dependence predicted by Eq. 13 (note that the rates are plotted on a logarithmic scale). In Fig. 27b, a line with slope 0.5 is drawn to intersect the highest rates over the pH range. Most of the measured rates fall below the line due to the slowing effect of dissolved Si, which is represented by the term $\left(1 - \frac{Q}{K}\right)$ in Eq. 1. The results are consistent with the model.

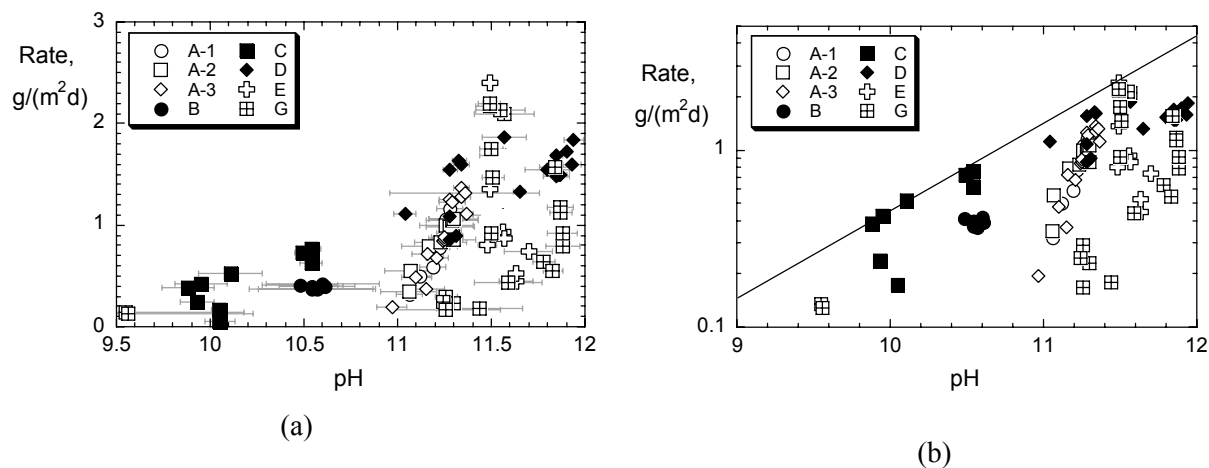


Fig. 27. Measured rates vs. measured pH values (a) showing range of pH values measured in each test and (b) compared with modeled pH dependency $\log rate = 0.5 pH$ (note logarithmic scale).

The rates measured by Participant G at the two lowest pH values were not included in the determination of the forward rate in the ILS. The results of Participant B were included in the determination of the forward rate, even though these tests had anomalously low pH values. The agreement between the rates measured by Participant C and the line drawn in Fig. 26b suggest that these are the forward rates at these pH values. However, these results were excluded from the consensus forward rate due to the lack of evidence that steady state was attained in these tests (see Section 3.3) and the anomalously low pH values that were attained in the test.

4.3.5 Change in Surface Area as Glass Dissolves

A shrinking core model is commonly used to take the loss of surface area as a glass dissolves into account (e.g., McGrail et al. 1997), and the draft SPFT test procedure recommends that the change in surface area be estimated by modeling the particles as shrinking spheres. In this model, the final surface area of the reacted glass, S_f , is calculated using the expression

$$S_f = \left\{ \frac{6}{\rho \cdot d_o} \right\} \cdot m_o^{1/3} \cdot m_f^{2/3} \quad (14)$$

where ρ is the density of the glass, d_o is the initial diameter of the glass particle, m_o is the initial mass of the sample, and m_f is the final mass of the sample, which is calculated from the dissolution rate and reaction time. A 100 mesh sieve has an opening of 1.5×10^{-4} m, and a 200 mesh sieve has an opening of 7.5×10^{-5} m. The arithmetic average of the sieve openings is $(d_{\max} + d_{\min})/2 = 1.125 \times 10^{-4}$ m; this is used as the diameter of a spherical particle of LRM glass within the -100 +200 mesh size fraction in the present analysis. The density of LRM glass is assumed to be the same as that of the LRM-1 prototype glass, which is 2516 ± 9 kg/m³ (Wolf et al. 1998). The mean dissolution rate of 1.64 g/(m²d) is used for this calculation. For a test conducted with 1.00 g glass, the initial surface area is 1.00 g \times 0.021 m²/g = 0.021 m². The final mass is calculated from the initial mass, specific surface area, dissolution rate, and a reaction time of 14 days:

$$m_f = 1.00 - 1.00 \text{ g} \cdot \left\{ \frac{0.021 \text{ m}^2}{\text{g}} \right\} \cdot \left\{ \frac{1.64 \text{ g}}{\text{m}^2 \cdot \text{d}} \right\} \cdot 14 \text{ d} = 0.518 \text{ g} \quad (15)$$

Substituting these values into Eq. 14 gives

$$S_f = \left\{ \frac{6}{2.516 \times 10^6 \text{ g/m}^3 \cdot 1.125 \times 10^{-4} \text{ m}} \right\} \cdot 1.00^{1/3} \cdot 0.518^{2/3} = 0.01367 \text{ m}^2 \quad (16)$$

The final surface area is predicted to be only 65% of the initial surface area after 14 days. Such a large decrease in the surface area (35%) should be reflected by a proportional decrease in the Si solution concentrations measured over the course of the experiment if the glass dissolves at a constant rate. Decreases in the Si concentration are seen in tests conducted at high F/S ratios. If the glass dissolves at a constant rate, the rate at which surface area is lost will increase with the reaction time. For example, about 94% of the initial surface area is calculated to remain after 3 days of reaction, 84% after 7 days, 76% after 10 days, and 65% after 14 days. Complete dissolution is calculated to occur after a little more than 29 days at a dissolution rate of 1.64 g/(m²d). Although the test durations were not reported by all participants, it is assumed that mean Si concentrations occurred after about 7 days of reaction. Recalculating the dissolution rates using a surface area of $0.84 S_o$ will increase the mean rate to $1.64 \div 0.84 = 1.95$ g/(m²d). For comparison, the glass is calculated to completely dissolve within 12 days if the dissolution rate is 4 g/(m²d).

Small decreases in the Si concentrations were seen over time in tests conducted under high F/S conditions. None of the participants reported that the glass had completely dissolved in any of the tests. The accuracy of the rate calculated using the initial surface area (as in Eq. 6) decreases as the measured rate increases because the loss of surface area occurs faster; the calculated rates will be too low because the initial surface area used in the calculation is too large. The accuracy can be improved by using a more

representative surface area to calculate the rate, which will depend on the test duration. Because the surface area continually decreases as the glass dissolves, a compromise in the test duration is needed to balance the uncertainty in the steady-state Si concentration value with the uncertainty in the glass surface area. For example, the loss of surface area predicted by the shrinking core model becomes significant in tests with -100 +200 mesh glass within about 7 days when the rates are higher than about 1 g/(m²d). Steady-state Si concentrations were attained under most test conditions within 7 days.

The rate at which the surface area decreases will be lower in tests with larger glass particles. The same dissolution rate was measured with -80 +100 mesh glass as with -100 +200 mesh glass (within experimental uncertainty). However, the initial diameter of the -80 +100 mesh glass is about 1.5 times that of the -100 +200 mesh glass and, according to Eq. 14, the change in surface area is expected to be about 66% less after the same mass has dissolved. The shrinking sphere model probably over-estimates the decrease in surface area, although the present data base is not sufficient to evaluate the accuracy.

Although the shrinking core model implicitly assumes the glass dissolution rate remains constant, this may not always be the case. For example, glass at sharp points and edges on fractured glass particles will dissolve faster than glass on smooth surfaces because of added strain. Glass dissolved from points and edges will dominate the test response (i.e., the solution concentrations) immediately after a test is started, but will become insignificant as the test proceeds and the sharp edges become smoothed. The loss of surface area is not expected to be significant when glass at points and edges dissolve because these features account for only a small fraction of the total surface area. However, the loss of mass due to the dissolution of fracture edges can be significant compared with the amount of glass that dissolves from smooth surfaces. In SPFT tests, the dissolution of glass at sharp points and edges is evidenced by a high rate during the initial few samplings followed by a lower rate at subsequent samplings. In the draft ASTM standard SPFT test procedure, it is recommended that sample collection begin a few days after the test is started and after most of the sharp points and edges have dissolved. (The time required to dissolve away the fracture surfaces will depend on the glass dissolution rate.)

The tests conducted by Participant F demonstrate the change in reaction rate from the initial high transient rate to the more stable longer-term rate. The results of Test F31-3 show the behavior expected from the initial dissolution of sharp edges (see Fig. 11c): the Si concentration increases rapidly during the first 100 minutes, remains nearly constant through about 300 minutes, then decreases slowly. Compared with the Si concentrations measured in samplings at longer reaction times (see Fig. 11d), the decrease between about 300 and 400 minutes occurs quickly. This indicates that most of the sharp edges have dissolved away and only the smooth surfaces are dissolving beyond about 400 minutes (6.7 hours). The slow decrease in the Si concentrations between about 400 and 4450 minutes (6.7 and 74 hours) is due to the dissolution of the smooth surfaces. The concentration in Test F31-3 was 0.46 mg/L after 480 minutes and 0.35 mg/L after 4450 minutes.

Several tests conducted by other participants showed similar behavior. For example, Test 9(45) by Participant G (see Fig. 14v) was conducted at $F/S = 2.4 \times 10^{-5}$ m/s, which is about the same F/S value used by Participant F beyond 360 minutes in Test F31-3. These results show a rapid decrease in the Si concentration for the first 5 samplings, then a slower decrease in the Si concentration for the rest of the test. The decrease is probably due to the decrease in the amount of glass in high-energy fracture sites and the decrease in the surface area.

4.3.6 Examination of Reacted Solids

Some participants reported the observation that the appearance of some of the reacted glass grains had changed from the initial light green color to a dark orange or red. Participant E conducted geochemical simulations that indicated test solutions could be saturated with respect to iron and silicate phases and provided an SEM image showing the initial formation of an iron-rich corrosion layer. Figure 28a shows images obtained with a scanning electron microscope of a typical green-colored grain, and Figs. 28b and 28c show red-colored grains recovered from Test LRM-1-I provided by Participant A. Participant A estimated that about 2% of the reacted grains were red and noted that other tests contained fewer red grains than LRM-1-I. The green grain in Fig. 28a looks similar to the unreacted glass in Fig. 1, except that what were probably sharp edges initially (indicated by arrows) have become pitted.

The reacted grains had an outer layer of red material overlying a yellowish core. Inspection with an optical microscope of an archived sample of the crushed glass used in the ILS revealed the presence of a small number of yellowish grains mixed with the greenish colored grains. However, inspection of the source glass from which the crushed glass was prepared gave no indication of a second glass phase.

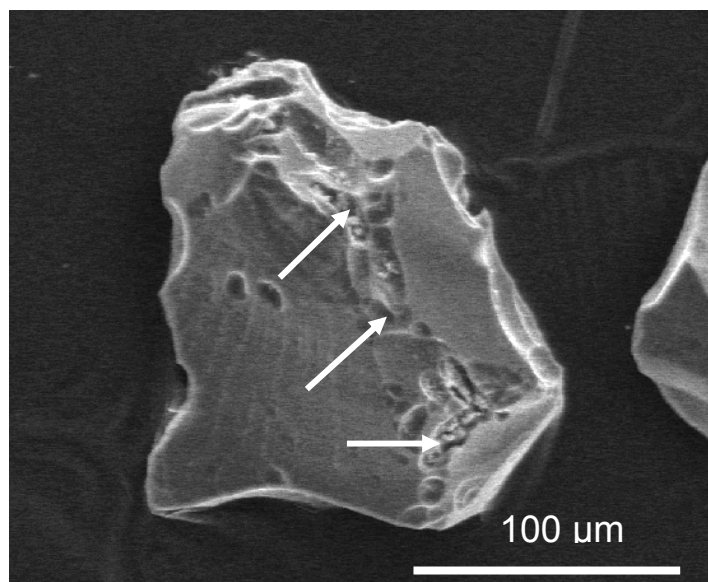
The results of x-ray emission spectroscopy analyses conducted by Participant A on normal (green) grains, the red layers, and the yellowish cores are given in Table 16. The red material was enriched in Fe relative to the core material, but it was clearly not an iron oxide coating. The yellow grains and core material were enriched in Zn relative to the green grains. The LRM glass was not formulated to include Zn and was not analyzed for Zn (Ebert and Wolf 2000). While it is possible that the LRM glass was contaminated during crushing and sieving, it is very unlikely that it would be contaminated to such a high extent as 2%. Figures 28b and 28c indicate the red layer is several micrometers thick.

The presence of a second glass phase only became evident in these SPFT tests in highly dilute solutions. There was no indication of a second phase in previous dissolution tests with LRM glass (Wolf et al. 1998; Ebert and Wolf 2000), but the formation of red alteration layers on about 2% of the crushed glass particles in these tests clearly indicates that the LRM glass sample is not compositionally homogeneous.

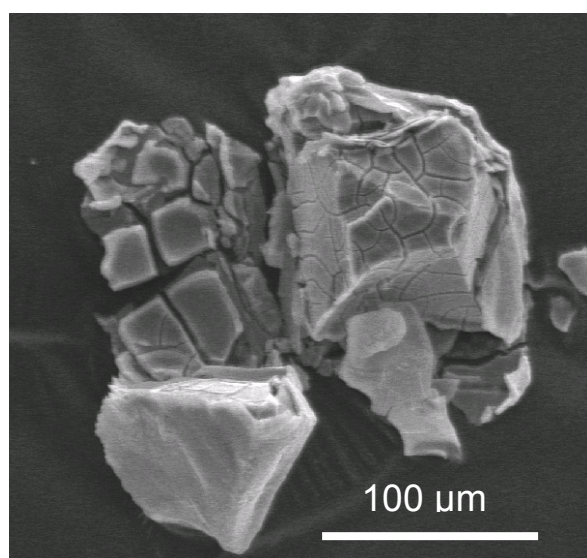
Table 16. Composition Analysis of LRM Glass Particles with EDS, in atom %

Analyzed Solid	Al	Fe	Na	Si	Zn
Green particle, unreacted	4.6	0.79	14	21	nd ^a
Green particle after 2-week test	4.5	1.1	12	22	nd
Yellow particle, unreacted	5.4	2.1	16	16	1.5
Surface of red particle after 1 day test	4.6	4.0	12	15	1.4
Surface of red particle after 2-day test	3.7	6.3	7.5	14	2.0
Surface of red particle after 2-week test	0.51	17	2.7	6.6	4.6
Yellow interior of red particle after 2-week test	5.5	1.7	16	16	1.7

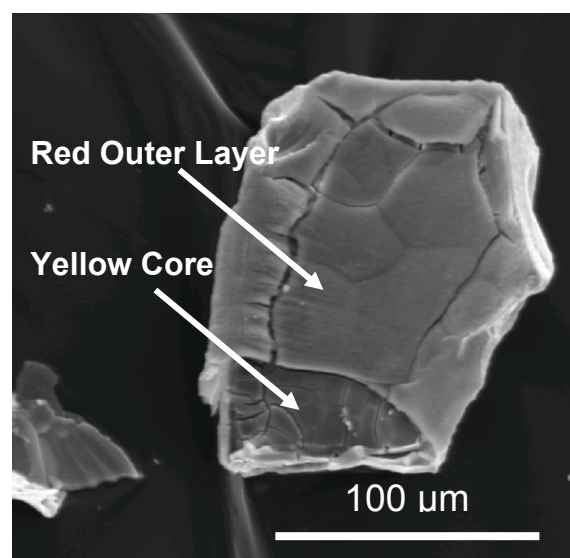
^a“nd” indicates element not detected.



(a)



(b)



(c)

Fig. 28. SEM Photomicrographs of (a) Reacted Green Particle, (b) Three Red Pparticles with Fractured Outer Layers, and (c) Red Particle with Partially Spalled Outer Layer Revealing Yellow Core

4.4 COMMENTS FROM PARTICIPANTS REGARDING PROCEDURE

One participant commented that the method should not be based on a theoretical model (Eq. 5 in this report and Eq. 1 in the draft ASTM standard), which may not apply to some materials, and should instead emphasize that the underlying objective is to provide a flow rate that does not affect the dissolution rate independent of the dissolution mechanism. The equation given in the draft ASTM standard (Eq. 5 in this report) is needed to calculate the glass dissolution rate from the test data. It is not based on a mechanistic expression for the glass dissolution rate. Equation 1 is a mechanistic expression used to estimate the

effects of temperature and pH on the glass dissolution rate; it is not used to determine the rate from the SPFT test results. Instead, the rate is calculated simply as the time evolution of a soluble component i normalized to the surface area of the glass sample and the concentration of i in the glass (see Eq. 5) and is independent of Eq. 1.

One participant commented that “it is not correct to make a hypothesis on a mechanism [namely, the first-order dependence of the rate on the Si concentration underlies the extrapolation] in the context of an experimental procedure.” The comment was made with regard to the practice of extrapolating the rates measured at various Si concentrations to zero concentration, and that it would be better to measure the rate directly by selecting a flow rate high enough to measure the dissolution rate directly (i.e., at the lowest attainable Si concentration). In fact, Participant F conducted several tests at very high flow rates with the intent of directly measuring the forward rate rather than extrapolating test results to a Si concentration of zero (Tests F31-1, -2, and -3 through about 3 hours). As seen in the results of Participant F (Fig. 19) and Participant G (Fig. 20), there is significant scatter in the rates measured in several tests at low Si concentrations. This is due, in part, to the fact that the measured concentrations are only slightly higher than the background concentrations in the leachant. Even if they are not used to extrapolate the measured rates, tests at other F/S ratios provide confidence that the appropriate test conditions (e.g., a high enough flow rate) were selected to measure the forward rate. The ASTM standard recommends that the rate be measured at several Si concentrations to address the conflicting needs to maintaining low enough concentrations to minimize solution feedback effects and maintaining high enough solution concentrations for reliable analyses. The rates measured in tests at lower F/S ratios (at slightly higher steady-state Si concentrations) provide added confidence in the reported forward rate. However, the rates measured in tests that attain significantly higher Si concentrations do not increase confidence in the forward rate.

One participant commented that the procedure should make a recommendation regarding filtering the test solutions prior to analysis to ensure that colloids are not included in the analyzed solutions. Filtering was specifically excluded in the protocol due to potential to lower the solute concentrations by sorption to the filtering medium and removing colloidal material. Elements released from the glass must be measured to correctly calculate the amount of glass that has dissolved, regardless of their chemical state. The procedure does recommend that polyethylene wool (or equivalent) be placed at the exit line to prevent *glass* from being flushed from the reaction cell. One participant recommended “the use of mesh sieves with apertures slightly smaller than the size of the grains” rather than quartz or polyethylene wool.

It was suggested that the amount of nitric acid added to acidify the test solutions be better defined. The draft procedure calls for 3-5 drops. For example, Participant routinely added 0.04 mL of nitric acid. The solutions are acidified to ensure the solutes remain dissolved, and the exact and precise amount of nitric acid added is presumed not to be crucial.

4.5 ADEQUACY OF THE ASTM TEST METHOD AND LESSONS LEARNED

The ILS results indicate that the draft ASTM SPFT test method provides adequate guidance for a first-time user to conduct the test. The method controls the major variables that affect the forward dissolution rates of borosilicate waste glasses, namely, temperature, pH, and dissolved Si concentration. The draft SPFT test method calls for the temperature of the reaction cell to be monitored with a thermocouple (step 7.5), but does not provide a tolerance range. The range of ± 2 °C used in the ILS is too large. Based on the rates measured at several temperatures by Participant F, a range of 4 °C contributed about 30% uncertainty to the rate. A range of ± 1 °C is probably appropriate. The pH of the test solution is affected by the glass dissolution rate and the solution flow rate. The leachant solution used in the ILS did not provide significant buffering capacity so the pH decreased under some test conditions. The effect of glass dissolution on the pH can be mitigated by using leachants with greater buffering capacity. The draft SPFT

test method does not provide a tolerance range for pH drift during the tests. From the results discussed in Section 4.3.4, a tolerance of ± 0.3 pH units should be achievable. The ratio of rates in solutions that differ in pH by 0.6 pH units is expected to be about $10^{0.5 \times 0.6} = 2.00$, which is slightly higher than the uncertainty in the consensus rate. The leachant composition was specified for the ILS rather than the pH due to concerns regarding the reproducibility of pH measurements and different temperature dependencies of buffer solutions that could have been selected by different participants if only the pH was specified. From the summary in Table 12, the pH values of the leachant solution (0.004 molal LiCl and 0.003 molal LiOH) and test solutions that were measured by participants varied significantly, and by more than 0.6 pH units in some cases. The lowest and highest pH values measured for the leachant (or in control tests) and test solutions are summarized in Table 17. The range of pH values measured for the test solutions is due, in large part, to glass dissolution. Tests conducted at low F/S ratios, which resulted in relatively high Si concentrations, typically have low pH values. The range of pH values measured for the leachant reflects the uncertainty in measuring the pH (e.g., due to day-to-day variations in the meter/electrode calibration), the uptake of CO₂ (for solutions that were not sparged), and small differences in making up the solutions.

The ASTM draft standard acknowledges the uncertainty in the surface area of crushed glass but does not address it. This is a major issue for all tests conducted with crushed glass because the dissolution rate is usually reported on a per-unit-surface area basis, and the surface area of the crushed glass is not accurately known—neither the initial surface area nor the rate at which the surface area changes during the test are known. The approach recommended in the ASTM SPFT test method is to use the geometric surface area based on sieve fraction to calculate the initial surface area. This approach is consistent with that used in other ASTM methods (e.g., C1285) and allows for comparison of materials that have similar fracturing behaviors. However, the surface area remains the greatest uncertainty in the calculation of the rate. The data generated in the ILS provide some insight regarding the loss in surface area as the glass dissolves. If the glass is dissolving at a constant rate (e.g., near the forward rate), the steady-state Si concentration should be proportional to the surface area. Although the total surface area is not known accurately, changes in the surface area should result in changes to the steady-state Si concentration if the flow rate remains constant (see Eq. 7). A few tests at high F/S ratios showed a decrease in the steady-state Si concentration (Participant A test LRM-3-L, -M, -N; Participant F test 31-3; Participant G test 9(45)).

Table 17. Range of pH Values Measured for Leachant and Test Solutions

Participant	Leachant		Test Solutions	
	Lowest	Highest	Lowest	Highest
A	11.26 \pm 0.06	11.27 \pm 0.14	10.97 \pm 0.08	11.37 \pm 0.03
B	10.49 \pm 0.34	10.65 \pm 0.14	10.48 \pm 0.20	10.61 \pm 0.16
C	9.97	10.93	9.88 \pm 0.14	10.54 \pm 0.06
D	11.12	11.92	11.04 \pm 0.06	11.94 \pm 0.05
E	Not reported		11.48 \pm 0.05	11.70 \pm 0.13
F	11.03 ^a		Not reported	
G ^b	11.38 \pm 0.05		11.24 \pm 0.01	11.88 \pm 0.08

^aOnly one value was reported.

^bTests 1(2) and 1(5) were excluded from analysis.

More work is needed to provide a better measure of the surface area of crushed glass and to take into account the effects of fracture surfaces on the dissolution rates that are measured. Because of the uncertainty in the surface area of crushed glass, the results of SPFT tests with crushed glass may be best suited for measuring the dependence of the forward dissolution rate on pH and temperature (and the Si concentration). Tests with monolithic samples with directly measurable surface areas may provide a more accurate measure of the dissolution rate when combined with the dependencies measured in SPFT tests.

The ASTM draft standard includes requirements that the flow rate be constant within 10% relative standard deviation for the samplings used to determine the steady-state Si concentration (see steps 6.5, 7.3, and 8.3.10) and that the Si concentration be constant within 15% (see step 9.4.4), both calculated as the percent relative standard deviation. The percent relative standard deviation calculated with the means and standard deviations of the steady-state Si concentrations and flow rates given in Table 12 are summarized in Table 18. The values of the flow rate are constant within 10% for all but a few tests (e.g., L6-1, L7-1, L5-2, L6-2, L7-2, and LRM IX). The values for the steady-state Si concentrations exceed 15% for several tests. If the flow rate remains sufficiently constant in a test, variance in the Si concentration may indicate changes in the surface area or reactivity of the glass. This occurs in several tests conducted at high F/S ratios (LRM-3-M, LRM-3-O, F31-3, A2, B2', G, H3, H3', LRM IV, 2(7), 8(4), and 9(45), as well as in several tests in which the variance was less than 15%) and can be seen in the data plotted for these tests in Figs. 3–9 and 11–14. The scatter in the data from a few tests exceeds 15% and is random (e.g., LRM-1-F, LRM-2-I, LRM V, LRM VIII, and LRM IX). Note that data in several test series were subjectively excluded as outliers and are not included in this analysis. The requirements that the flow rate remains constant within 10% and the Si concentration remains constant within 15% for determination of the steady-state Si concentration are readily achievable.

The determination of the forward rate in Sections 4.1 and 4.2 *did not* exclude the results from tests in which the variance in the Si concentration exceeded 15% or that in the flow rate exceeded 10%. If the rates from those tests were eliminated from the data set in Fig. 20, the forward rate would be 1.57 g/(m²d) and the regression coefficient would decrease slightly: $R^2 = 0.417$. The rate decreases slightly because most of the rates that are excluded were measured at low Si concentrations when the glass was dissolving at near the forward rate. Those rates are included in the present analysis to obtain the most reliable forward rate from the available data set. In practice, the test conditions should be adjusted to better maintain steady state and mitigate the impact of the loss of surface area during the test. For example, the test could be repeated at the same F/S ratio but using a larger size fraction of crushed glass. Alternatively, the rate could be calculated using only the samplings taken early in the test, if it was certain that the initial samplings were not significantly affected by the dissolution of fracture surfaces. The attainment of steady state provides the best evidence that a representative rate is being measured.

Table 18. Relative Standard Deviations in Steady-State Si Concentrations and Flow Rates

Test Number	Relative Standard Deviation, %		Test Number	Relative Standard Deviation, %	
	Si Concentration	Flow Rate		Si Concentration	Flow Rate
Results from Participant A			Results from Participant D		
LRM-1-B	8.08	1.12	A	8.19	0
LRM-1-C	7.18	1.58	A'	5.39 ^a	0
LRM-1-D	4.59 ^a	1.15	A2	19.49 ^a	6.81
LRM-1-E	11.11	0.73	B2'	20.52 ^a	7.99
LRM-1-F	17.80	1.01	B3	13.65 ^a	1.69
LRM-1-G	11.06	0.55	D	5.05	0.87
LRM-1-H	14.81	0.40	D'	5.55	4.68
LRM-1-I	9.14	1.28	E	3.45	0.20
LRM-1-J	14.56	0.59	E'	5.80	0.31
LRM-2-B	6.50	1.11	E2	13.92 ^a	0.87
LRM-2-C	7.65	2.58	G	58.52 ^a	0.81
LRM-2-D	13.26	1.01	G'	13.63 ^a	1.02
LRM-2-E	7.61	0.93	G4	9.92	3.01
LRM-2-F	6.03	0.64	H3	25.94 ^a	0.71
LRM-2-G	9.12	1.14	H3'	27.89 ^a	2.70
LRM-2-H	13.91	1.16	H5	12.46 ^a	1.22
LRM-2-I	17.07	0.69	Results from Participant E		
LRM-2-J	6.37	0.73	LRM I	10.28 ^a	8.14
LRM-3-B	8.88	1.09	LRM II	8.26 ^a	8.26
LRM-3-C	10.63	1.08	LRM III	11.34	2.31
LRM-3-D	11.82	0.82	LRM IV	15.03 ^a	6.18
LRM-3-E	4.28	1.06	LRM V	22.66	2.25
LRM-3-F	6.64	0.55	LRM VI	6.39	2.88
LRM-3-G	6.14	1.49	LRM VIII	18.68	7.20
LRM-3-H	5.38	1.05	LRM IX	15.15	14.34
LRM-3-I	6.40	1.52	Results from Participant G		
LRM-3-J	5.62	3.31	1(2)	7.82	0.67
LRM-3-K	11.79	2.31	1(5)	0	8.26
LRM-3-L	12.77 ^a	1.75	2(3)	4.52	7.10
LRM-3-M	17.26 ^a	2.65	2(7)	16.46 ^a	3.75
LRM-3-N	9.51 ^a	1.54	2(10)	1.63	6.91
LRM-3-O	17.57 ^a	2.45	3(4)	3.57 ^a	4.22
Results from Participant B			4(3)	0.64	3.42
L4 blank	0	7.59	4(5)	4.72	0.46
L5-1	2.37	6.48	5(7)	3.70	3.63
L6-1	4.04	10.22	5(8)	0.92	0.88
L7-1	5.21	12.58	6(1)	6.40	0.45
L8 blank	11.47	8.27	6(4)	1.86	2.01
L4-2	12.8 ^a	18.71	6(11)	2.11	1.35
L5-2	7.38 ^a	12.39	7(21)	5.91 ^d	1.13
L6-2	5.38	14.81	7(25)	5.20	0.60
Results from Participant F			8(3)	10.81	1.13
F31-1	5.22	4.99	8(4)	29.78 ^a	1.45
F31-2	8.72	6.52	8(5)	3.95	1.79
F31-3	18.44 ^b	12.76	9(43)	9.29	3.77
F31-3	5.98 ^c	3.24	9(44)	5.47 ^a	0.81
			9(45)	25.96 ^a	0.38
			9(46)	7.78	0.71

^aSi concentration decreases with time in test with nearly constant flow rate.^bSi concentration increases then decreases over first 350 minutes of test.^cSi concentration decreases beyond 350 minutes with nearly constant flow rate.

5. CONCLUSIONS

The draft ASTM method provides a practicable standardized procedure for conducting SPFT tests. Most of the participants had not conducted SPFT tests previously, and the results they provided for the ILS represent the efforts of competent scientists following the written procedure. Conclusions from this work are presented separately for measurement of the dissolution rate and evaluation of the draft test method.

LRM Glass Dissolution Rate:

Results of SPFT tests with LRM glass at 70 °C in a LiCl/LiOH solution that imposed a pH near 11.3 (at room temperature) were provided by 7 participants. The dissolution rates were calculated from the Si concentrations and solution flow rates measured in several samplings of the test solution taken over several days (in most cases). The data sets provided by 5 participants were sufficient to determine the forward rates by linear regression of the rates measured at steady-state Si concentrations below about 30 mg/L. The forward rate was also determined from the combined rates from all participants at steady-state Si concentrations below about 10 mg/L.

- The dissolution rate decreased nearly linearly with an increase in the steady-state Si concentrations up to about 15 mg/L, and was nearly constant at higher Si concentrations. This reflects the dependence of the dissolution rate on the chemical affinity term.
- The consensus forward rate based on the combined results is 1.64 g/(m²d) at 70 °C and pH 11.3 (room temperature). This was determined from the set of tests with steady-state Si concentrations <10 mg/L. The inter-laboratory uncertainty based on the standard deviation of the combined results is 1.90 g/(m²d) at the 95% confidence level. The relative uncertainty for SPFT test is 116 %—this is the reproducibility of the test.
- The average forward rate from three sets of measurements by a single participant (Participant A) was 1.29 g/(m²d). The intra-laboratory uncertainty based on the standard deviation of the combined results is 0.39 g/(m²d) at the 95% confidence level. The relative uncertainty for SPFT test is 30.2 %—this is the repeatability of the test.
- Glass dissolution lowers the solution pH under test conditions with low F/S ratios and the dissolution rate decreased as the pH decreased. The LiOH/LiCl leachant solution did not buffer the test solutions. The pH is lowered as glass dissolves due primarily to the dissociation of orthosilicic acid that is generated.
- Dissolution of glass at sharp points and edges dominates the initial reaction and occurs faster than dissolution of flat surfaces. The sharp points and edges are artifacts from crushing the glass and do not represent the intrinsic dissolution behavior of the glass. The analysis and interpretation of test results must take into account the initially high rate due to the dissolution of glass at sharp points and edges and the loss of surface area at longer reaction times.
- Analyses of the reacted glass indicated that the LRM glass is not homogeneous. About 2% of the glass dissolves at a higher rate than the rest of the glass. It is presumed that charges of glass used in all tests by all participants had the same proportion of faster-dissolving glass, and that the inhomogeneity of the LRM glass does not invalidate the comparisons made in the ILS.
- The uncontrolled factors that may have contributed to the relative uncertainty in the forward dissolution rate determined in the ILS include the reaction cell design, the technique used to measure the Si concentration, sample handling, sparging vs. not sparging the leachant and test

solutions, and the possible nonuniformity of the glass samples (i.e., the relative amounts of the secondary phase in the lots provided to each participant). Test variables that were inadequately controlled include temperature, solution pH, and the sampling schedule. Comparison of the inter-laboratory uncertainty of 116 % and intra-laboratory uncertainty of 30.2 % suggests that variance in the uncontrolled and inadequately controlled test factors resulted in a 4-fold increase in the uncertainty of the forward rate.

SPFT Test Method:

Based on the experiences of the participants and analysis of the results, the following recommendations are offered for improving the ASTM protocol for the SPFT test:

- A glass size fraction larger than –100 +200 mesh may be required to reduce the impact of the loss of surface area during the test on the measured rate.
- The test duration at which samples are collected should be reported. How the reaction time is quantified should be standardized (e.g., by reporting the times of day when sample collection was started and completed). Although the elapsed reaction time is not used to calculate the dissolution rate, it is needed to calculate the mass dissolved for estimating the change in surface area and to assess if and when the fracture surfaces (i.e., the sharp points and edges) have been dissolved.
- The need for subjectivity in determining the steady-state Si concentrations should be discussed in test results and minimized. The method should call for all test results to be reported, including those not used in the determination of the steady-state Si concentration, to support the determination of the dissolution rate.
- The requirements that the variance in the values used to determine the steady-state Si concentration be within 15% *rsd* and the flow rates be within 10% *rsd* are reasonable and achievable.
- The use of polyethylene wool (or equivalent) in the exit tube should be required as part of the ASTM protocol (it is currently a recommendation). However, the solutions should not be filtered to remove colloidal material, since the total amount of Si released from the glass is used to calculate the glass dissolution rate.
- The shrinking core model (which is included in the Appendix of the draft standard) should be applied with caution, and should be limited to the dissolution of a small amount of glass, e.g., less than 20 mass%. Tests in which the Si concentration decreases significantly with time should be repeated with a sample having a larger mesh size.
- The importance of conducting a control test (without glass) needs to be emphasized. Several participants only measured the composition of the leachant solution before or after the test was conducted (those samples are referred to as leachant blanks in this report). In addition to monitoring changes in the leachant, e.g., due to concentration gradients in the leachant reservoir and interactions with the apparatus, analyses of solutions from control tests (test blanks) can be used as a measure of the analytical uncertainty. This is especially important for tests at high F/S ratios in which the Si concentrations in the test solutions are only slightly higher than the background concentrations in the leachant.
- The test temperature should be monitored throughout the test and reported to the nearest 1 °C.

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APPENDIX A. DRAFT SPFT TEST METHOD PROVIDED TO ILS PARTICIPANTS

Draft Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Method

1. Scope

- 1.1 This practice describes a single-pass flow-through (SPFT) test method that can be used to measure the dissolution rate of a homogeneous silicate glass, including nuclear waste glasses, in various test solutions at temperatures less than 100°C. Tests may be conducted under conditions in which the effects from dissolved species on the dissolution rate are minimized to measure the forward dissolution rate at specific values of temperature and pH, or to measure the dependence of the dissolution rate on the concentrations of various solute species.
- 1.2 Tests are conducted by pumping solutions in either a continuous or pulsed flow mode through a reaction cell that contains the test specimen. Tests must be conducted at several solution flow rates to evaluate the effect of the flow rate on the glass dissolution rate.
- 1.3 This practice excludes static test methods in which flow is simulated by manually removing solution from the reaction cell and replacing it with fresh solution.
- 1.4 Tests may be conducted with demineralized water, chemical solutions (such as pH buffer solutions, simulated groundwater solutions, and brines), or actual groundwater.
- 1.5 Tests may be conducted with crushed glass of a known size fraction or monolithic specimens having known geometric surface area. The reacted solids may be examined to provide additional information regarding the behavior of the material in the test and the reaction mechanism.
- 1.6 Tests may be conducted with glasses containing radionuclides. However, this test method does not address safety issues for radioactive samples.
- 1.7 Data from these tests can be used to determine the values of kinetic model parameters needed to calculate the glass corrosion behavior in a disposal system over long times (for example, see Standard C 1174).
- 1.8 This standard practice must be performed in accordance with all quality assurance requirements for acceptance of the data.
- 1.9 This standard does not purport to address the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards

- C 92 Test Methods for Sieve Analysis and Water Content of Refractory Materials¹
- C 169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass²
- C 429 Test Method for Sieve Analysis of Raw Materials for Glass Manufacture²
- C 693 Standard Test Method for Density of Glass by Buoyancy²
- C 1109 Test Method for Analysis of Aqueous Leachates from nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy³
- C 1174 Practice for Prediction of the Long-Term Behavior of Waste Package Materials Including Waste Forms Used in the Disposal of High-Level Nuclear Waste³
- C 1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste³
- C 1285 Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)³
- D 1129 Terminology Relating to Water⁴
- D 1193 Specification for Reagent Water⁴
- D 1293 Test Methods for pH of Water⁴

- E 177 Practice for use of the Terms Precision and Bias in ASTM Test Methods⁵
 E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁵

¹Annual Book of ASTM Standards, Vol 15.01

²Annual Book of ASTM Standards, Vol 15.02

³Annual Book of ASTM Standards, Vol 12.01

⁴Annual Book of ASTM Standards, Vol 11.01

⁵Annual Book of ASTM Standards, Vol 14.02

3. Terminology

3.1 Definitions

- 3.1.1 *alteration phase*-a solid phase formed as a result of corrosion, including phases precipitated from solution, leached layers, and phases formed within leached layers.
- 3.1.2 *Back reaction*-reaction between dissolved components and the glass surface to reform bonds that are broken during glass dissolution.
- 3.1.3 *chemical durability*-the resistance of a glass to dissolution under particular test conditions.
- 3.1.4 *continuous flow*-the continual replacement of solution in the reaction cell with fresh test solution.
- 3.1.5 *control test*-test conducted without specimen to measure background concentrations in the test solution and from interactions between test solution and apparatus.
- 3.1.6 *crushed glass*-small particles of glass produced by mechanically fracturing larger pieces of glass.
- 3.1.7 *dissolution*-the result of reactions in which chemical bonds are broken and species are released from the glass and become dissolved in the test solution.
- 3.1.8 *effluent solution*-the solution exiting the reaction cell.
- 3.1.9 *finest*-small pieces of glass that adhere to the glass particles prepared for use in the test that are not removed by sieving.
- 3.1.10 *forward glass dissolution rate*-the rate at which glass dissolves into solution at specific values of the temperature and pH in the absence of back reactions.
- 3.1.11 *gravimetric*-measured by change in mass.
- 3.1.12 *high-purity water*-ASTM Type I or Type II water with a maximum total matter content including soluble silica of 0.1 g/m³, a minimal electrical resistivity of 16.67 MΩ•cm at 25°C (see Specification D 1193 and Terminology D 1129).
- 3.1.13 *intrinsic rate constant*-the component of the forward rate constant that depends only on the glass composition.
- 3.1.14 *leached layer*-residual material at the glass surface from which some or all soluble components have been leached.
- 3.1.15 *leaching*-the preferential loss of soluble components from a material.
- 3.1.16 *mesh size fraction*-a designation of the size range of crushed glass given by the combination of the smallest mesh size that the glass is passed through (prefixed by a negative sign) and the largest mesh size that it does not pass through (prefixed by a positive sign). For example, the -40 +60 mesh size fraction will pass through a 40 mesh sieve but will not pass through a 60 mesh sieve.
- 3.1.17 *pulsed flow*-the replacement of solution in the reaction cell with fresh test solution due to the regular periodic action of a mechanical pump. Excludes manual replacement of the test solution
- 3.1.18 *reaction cell*-the container in which the sample remains during the test.
- 3.1.19 *secondary phase*-any phase that is not present in the glass being tested that is formed in solution or on the surface of the sample or apparatus by combination of components released from the glass as it dissolved or present in the test solution.

- 3.1.20 *single-pass flow-through test (SPFT)*-a test in which solution is flushed from the system after contacting the test specimen and is not recirculated through the reaction cell.
- 3.1.21 *steady-state*-in this standard, the condition in which the concentration of a dissolved glass component remains constant due to the opposing effects of solution flow to remove the components from the vicinity of the sample and glass dissolution to add components to solution. In the present context, dissolution of the glass may proceed at a steady-state rate that is fixed by the solution flow rate, temperature, solution pH, and other rate-affecting processes.
- 3.1.22 *stoichiometric dissolution*-release of elements into solution in the same proportion that they are in the glass.
- 3.1.23 *test solution*-the solution entering the reaction cell.

4. Summary of Test Method

- 4.1 Crushed or monolithic glass specimens having a known surface area are contacted by a solution that continuously flows at a known flow rate and at a constant temperature through a reaction cell that contains the glass sample. The concentration of a soluble glass component (*i*) in the effluent solution exiting the sample cell is used to calculate the amount of glass that has dissolved. The flow rate is determined by dividing the mass of solution that is collected for analysis by the duration over which it was collected. The dissolution rate of the glass is calculated by using Equation A-1:

$$\text{rate} = \frac{(C_i - C_i^\circ) \cdot \left(\frac{F}{S^\circ}\right)}{f_i} \quad (\text{A-1})$$

where C_i is the steady-state concentration of component *i* measured in the effluent solution, C_i° is the background concentration of component *i* in the initial test solution measured in a blank test, *F* is the solution flow rate, *S* is the surface area of the glass sample that is exposed to solution, and f_i is the mass fraction of component *i* in the glass. Several samples of the effluent solution are collected during the test to determine the steady-state concentrations of dissolved glass components at a particular solution flow rate. Because the glass dissolution rate will likely be affected by the steady-state concentrations of dissolved silica and other solutes, tests must be conducted at several solution flow rates to provide data that can be extrapolated to zero concentration to determine the forward glass dissolution rate at infinite dilutions.

5. Significance and Use

- 5.1 This practice provides a prescriptive description of the design of a SPFT test apparatus and identifies aspects of the performance of SPFT tests and interpretation of test results that must be addressed by the experimenter to provide confidence in the measured dissolution rate.
- 5.2 The SPFT test method described in this practice can be used to characterize various aspects of glass corrosion behavior that can be utilized in a mechanistic model for calculating long-term behavior of a nuclear waste glass.
- 5.3 Depending on the values of test parameters that are used, the results of SPFT tests can be used to measure the intrinsic dissolution rate of a glass, the temperature and pH dependencies of the rate, and the effects of various dissolved species on the corrosion behavior.
- 5.4 The reacted sample recovered from a test may be examined with surface analytical techniques, such as scanning electron microscopy, to further characterize the corrosion behavior. Such examinations may provide evidence regarding whether the glass is dissolving stoichiometrically, if particular leached layers and secondary phases were formed on the specimen surface, etc.

These occurrences may impact the accuracy of the glass dissolution rate that is measured using this method. This practice does not address the analysis of solid reaction materials.

6. General Procedure

- 6.1 Figure 1 shows a flow diagram for a generic SPFT test assembly. The components of the system include a solution reservoir, transport lines, a reaction cell, and a pump. The test solution is pumped from a reservoir through a reaction cell that contains the sample. Solution is pumped directly with a peristaltic pump or similar device. Depending on the temperature of interest, the reaction cell may be located in a constant temperature oven or water bath. As test solution is pumped into the reaction cell, an equal volume of effluent solution will be displaced from the reaction cell. Aliquots of the effluent solution are collected periodically for analysis. The mass of effluent that is collected for analysis and the collection time are used to calculate the solution flow rate for that aliquot. Chemical analysis of the effluent solution is performed to measure the concentration of the components used to calculate the dissolution rate. The concentrations of several glass components can be tracked to determine whether the glass is dissolving stoichiometrically. Tests are conducted at several flow rates and with several sample surface areas to take into account the effect of the flow rate on the measured glass dissolution rate.
- 6.2 Crushed glass can be used to provide high surface area samples. Crushed glass is to be prepared following the procedure for crushed sample preparation in Standard C 1285 (see section 19 in Standard C 1285; see also Standards C 92 and C 429 for sieving methods). The surface area of crushed and sieved glass is estimated based on the size fraction that is used in the test. The particle size of crushed samples must be large enough that the decrease in surface area during the test is less than 15%. The initial surface area can be calculated from the specific surface area and the mass of glass used in the test. The specific surface area can be calculated based on the arithmetic average of the sizes of the sieve mesh and the density of the glass (see section Appendix X1 in Standard C 1285). The final surface area can be calculated based on the amount of glass that dissolved during the test if the particles can be modeled to have geometric shapes. The crushed glass used in a series of SPFT tests must be from the same source to ensure homogeneity on the scale of the test sample size. (A series of SPFT tests refers to tests conducted with the same glass and test solution but at different flow rates.) It is recommended that a small amount of the crushed glass be examined with a scanning electron microscope prior to testing to document the size of the particles and the absence of fines with a photomicrograph.
- 6.3 Monolithic samples can be used to provide samples with low surface areas. Samples can be prepared with any shape for which the geometric surface area can be measured directly. Monolithic samples are to be prepared following the sample preparation procedure in Standard C 1220 (see section 8 in Standard C 1220). Enough monolithic glass samples shall be prepared for use in a series of SPFT tests. The surface finishes of the monoliths to be used in the series of tests shall be consistent and shall be reported with the test results. For example, if the faces of the samples are polished with silica carbide paper, the grit and lubricating fluid shall be reported. To facilitate comparison of tests with different glasses, a final polish of 600-grit is recommended.
- 6.4 The mass fractions of elemental silicon in the glass must be known to determine the glass dissolution rate (see also section 9.4.5). This may be determined by direct analysis of the glass (e.g., see Standard C 169) or based on the as-batched composition of the glass.
- 6.5 The flow rate of the solution through the reaction cell is calculated by dividing the mass of test solution that is collected by the duration over which it was collected. Although the flow rate is set before the sample is placed in the reaction cell, the flow rate measured with the sample in place is used for the calculations. The flow rate is likely to vary slightly with each aliquot that is taken during a test. A test is acceptable if the flow rates determined for the aliquots collected during a test vary by 10% or less. The average flow rate measured in a test is used as the flow rate to calculate the glass dissolution rate in that test.

- 6.6 A small change in the steady-state concentration may occur over time due to a change in glass surface area. The surface area may decrease as the sample dissolves or increase as the surface roughens.
- 6.7 A control test is to be conducted under the same conditions of temperature, flow rate, and test solution that are used in the tests with glass, except that no sample is included in the test. The average of the solution concentrations of an element i that are measured in the control test are to be used as background concentration for element i in tests with glass, i.e., C_i^0 in Equation 1. The solution from the control test is also used to confirm that neither the test solution nor the effluent solution was contaminated due to interactions with the apparatus.
- 6.8 The steady-state condition established in a flow-through test depends on the dissolution rate of the glass and the flow rate of test solution through the reaction cell. The glass dissolution rate will depend on the concentrations of dissolved glass components in the solution contacting the glass and, therefore, on the rate at which these solutes are flushed from the vicinity of the sample over a range of flow rates.
 - 6.8.1 A value of the flow rate exists for which a glass will dissolve at a maximum rate at a particular temperature and pH. Further increases in the flow rate will not affect the glass dissolution rate, although the steady-state concentrations will become lower as the flow rate is increased.
 - 6.8.2 A value of the flow rate exists below which the glass dissolution rate will be independent of the flow rate and will dissolve as if the system was static. Further decreases in the flow rate will not affect the glass dissolution rate.
 - 6.8.3 The glass dissolution rate is expected to vary with the solution flow rate when the flow rate is between these extreme values.
- 6.9 Tests to determine the forward dissolution rate must be conducted at several flow rates to measure the effect of the flow rate (which occurs through the effect of the solution composition) on the glass dissolution rate. A plot of the measured dissolution rates against the steady-state concentration of dissolved silica (which are measured in tests conducted at different solution flow rates) is used to extrapolate the glass dissolution rate to an infinitely dilute solution composition to determine the forward glass dissolution rate.
- 6.10 If a leached layer is observed on the reacted glass, the possible effect of that layer on the measured dissolution rate should be investigated.

7. Requirements of the Apparatus

- 7.1 The apparatus should not interact with the test solution. A control test must be conducted to detect interactions between the test solution and the apparatus and, if necessary, adjust test results to take the interactions into account.
- 7.2 The solution reservoir must be large enough to contain all the solution needed to complete the tests with glass and the control test. Solutions may be purged with an inert gas (e.g., N_2) to mitigate against the effects of dissolved gases (e.g., drift in pH) during the test. The solution reservoir may be placed in an oven set at or near the test temperature so gases that exsolve from the solution as it is heated are contained within the solution reservoir.
- 7.3 The mechanism for transferring the solution from the reservoir to the reaction cell (i.e., the mechanical pump or other device) must maintain an average flow rate that is constant within 10% over the entire test duration.
- 7.4 The temperature of the solution entering the reaction cell shall be at the desired test temperature. This can be accomplished by placing at least the final 0.5 m of the inlet line inside the temperature control device (i.e., the oven or water bath) and by maintaining the temperature of the solution reservoir near the test temperature.
- 7.5 The temperature of the reaction cell shall be monitored with a thermocouple or similar device.

- 7.6 Solution injected into the reaction cell must mix with the solution in the cell to minimize concentration gradients. Mixing that results naturally as solution enters the cell at high flow rates or convection at high test temperatures will likely be adequate under most test conditions.
- 7.7 Effluent solution shall be collected as soon after it exits the reaction cell as possible to minimize the difference between the time the solution was in the cell and the time it is collected. Separate aliquots shall be collected for measurement of the solution pH and dissolved glass components.
 - 7.7.1 Aliquots collected during the first day of the test shall not be used to determine the glass dissolution rate. This is because the composition of the effluent early in the test will likely be affected by the dissolution of fines and initial surface roughness.
 - 7.7.2 Aliquots of effluent solution that are taken for measurement of the pH shall be stored in sealed containers and the pH must be measured within one hour after the aliquot is collected to minimize effects of dissolved carbon dioxide.
 - 7.7.3 Aliquots of test solution taken to measure dissolved glass components are used to determine the solution flow rate.
 - 7.7.4 The use of some solution pumps may result in pulsed flow through the reaction cell. The solution concentrations in the reaction cell may vary between pulses. The aliquot of test solution shall be collected for a duration long enough to include several solution pulses to minimize the effects of pulsed flow on the solution concentrations.
- 7.8 The system shall be air tight to prevent the formation of air bubbles. Outgassing of the solution during the test can be minimized by maintaining the solution reservoir at near the test temperature so that exsolved gases collect in the reservoir rather than in the pump line or reaction cell.
- 7.9 The length of the transfer line exiting the reaction cell shall be as short as possible to minimize the time between when the solution was in the reaction cell and when it is collected.
- 7.10 Quartz wool may be used to prevent crushed glass from being flushed out of the reaction cell; quartz wool must then also be used in the control test.
- 7.11 Monolithic samples shall be positioned or supported in the reaction cell so that at least 98% of the surface is contacted by solution.
- 7.12 The tubing and reaction cell shall be cleaned between tests.

8. Test Method

- 8.1 Pre-Test system cleaning. The system is flushed with the test solution prior to running a test with glass. Inspect tube connections to detect leaks during the system flushes.
 - 8.1.1 Place inlet line in reservoir of test solution.
 - 8.1.2 Pump at least three system volumes of test solution through system with the system at the highest test temperature to be used. The system volume can be estimated from the length of tubing and the volume of the reaction cell or measured based on the volume of water required to fill the system initially. Test solution can be pumped at a higher rate during the flushing steps than the rate at which the test is to be run. Collect effluent in a waste container and discard.
- 8.2 Pre-Test Flow Rate Determination
 - 8.2.1 Determine the flow rate and sample surface area required to attain the desired quotient F/S (see 9.1 for calculation of surface area for crushed glass).
 - 8.2.2 Set pump to desired flow rate and pass test solution through system.
 - 8.2.3 Collect effluent in a clean, tared, and labeled solution bottle and determine the duration, in seconds, that effluent was collected. Solution bottles are to be cleaned by rinsing with a dilute nitric acid solution (approximately 0.1 M HNO₃) then three rinses with demineralized water and air dried prior to use.
 - 8.2.4 Determine the mass of effluent solution that was collected.

- 8.2.5 Determine the volume of effluent collected by dividing the mass of effluent solution by the density of the solution (for most test solutions, the density can be approximated as 1000 kg/m³).
 - 8.2.6 Calculate the flow rate (m³/s) by dividing the volume of effluent that was collected by the duration it was collected.
 - 8.2.7 Adjust the pump rate and repeat steps 8.2.2 through 8.2.7 as necessary to achieve desired flow rate.
 - 8.2.8 Retain the final volume of effluent solution for analysis and use as control test sample for determination of background concentrations.
 - 8.2.9 Record flow rate.
- 8.3 Test with Glass
- 8.3.1 Place glass sample in reaction cell.
 - 8.3.2 Pump at least one system volume of test solution through the system before collecting first aliquot of effluent solution. The time required for this is calculated by dividing the system volume by the flow rate.
 - 8.3.3 Collect effluent for element analysis in a tared solution bottle labeled to identify test and date and time aliquot was collected. This aliquot is used to determine the flow rate. Amount of effluent collected must be sufficient to meet analytical requirements. Solution bottles are to be cleaned by rinsing with a dilute nitric acid solution (approximately 0.1 M HNO₃) then three rinses with demineralized water and air dried prior to use.
 - 8.3.4 Collect a separate aliquot of effluent solution in a clean, labeled container for measurement of pH. The pH must be measured within one hour of the aliquot being collected (see Standard D 1293 regarding measurement of solution pH). Aliquots for additional analyses can be collected as needed, for example, for analysis of anions.
 - 8.3.5 Determine and record the duration, in seconds, that effluent for element analysis was collected.
 - 8.3.6 Determine and record the mass of effluent solution for element analysis that was collected and the bottle tare mass.
 - 8.3.7 Calculate and record the mass of effluent by subtracting the bottle tare from the total mass.
 - 8.3.8 Calculate and record the volume of effluent for element analysis collected by dividing the mass of effluent solution by the density of the solution.
 - 8.3.9 Calculate and record the flow rate (m³/s) by dividing the volume of the effluent that was collected by the duration for which it was collected.
 - 8.3.10 If the calculated flow rate deviates by more than 10% from the target flow rate, adjust the pump speed and record new pump setting.
 - 8.3.11 If particulate material is observed or suspected, the solution may be passed through a filter. Record filter pore size. The origin of the particulates should be evaluated. Whether the particles are test materials flushed from the reaction cell or alteration phases that precipitates from the test solution, it must be determined if and how the measured glass dissolution rate is affected.
 - 8.3.12 Acidify the effluent that was collected for element analysis by adding 3-5 drops of ultrapure concentrated nitric acid.
 - 8.3.13 Determine and record new total mass.
 - 8.3.14 Record the temperature of the reaction cell.
 - 8.3.15 Repeat steps 8.3.3 through 8.3.14 at least every two days for a 14-day period. Initial tests with a glass require frequent analyses of the effluent solution to assure that the steady-state solution concentration is determined. Collection intervals and overall test duration can be modified in subsequent tests as insight into the dissolution rate is gained.

- 8.4 Post-Test system cleaning. The system is flushed sequentially with a dilute nitric acid solution (approximately 0.1 M HNO₃) and demineralized water. The system can be flushed at a higher flow rate than the flow rate at which the test was run.
- 8.4.1 Prepare enough nitric acid solution (approximately 0.1 M HNO₃) to flush the system with at least three system volumes and place in bottle.
 - 8.4.2 Remove the inlet line from the test solution reservoir and place in the bottle of nitric acid solution.
 - 8.4.3 Remove all glass from reaction vessel.
 - 8.4.4 Pump at least three system volumes of nitric acid solution through system.
 - 8.4.5 Collect a sample of the effluent in a clean solution bottle when the flush with the nitric acid solution is started for composition analysis. This is done to verify that the component used to calculate the glass dissolution rate does not become fixed on the apparatus during the test. Solution bottles are to be cleaned by rinsing with a dilute nitric acid solution (approximately 0.1 M HNO₃) then three rinses with demineralized water and air dried prior to use.
 - 8.4.6 Collect and discard remaining flush effluent.
 - 8.4.7 Place inlet line in bottle of demineralized water.
 - 8.4.8 Pump at least three system volumes of demineralized water through system.
 - 8.4.9 Collect and discard effluent.
 - 8.4.10 Submit control test sample and effluent samples for analysis of key glass components, including silicon (e.g., see Standard C 1109)

9. Data Analysis

- 9.1 *Calculate the initial surface area of crushed glass in the reaction cell (S⁰)*– If a crushed sample is used, the surface area is calculated as the product of the specific surface area and the mass of glass used in the test. The specific surface area is calculated based on the mesh size of the fraction used in the test and the density of the glass. The particles of glass are modeled as spheres with diameter (d) equal to the arithmetic average of the openings of the sieves used to isolate the material. The specific surface area (S_p) of a glass having a density ρ (see Standard C 693 for measurement of density) is

$$S_p = \frac{6}{\rho \cdot d} \quad (\text{A-2})$$

For example, the openings of 40 and 60 mesh sieves (U.S. Series Designation) are 425 μm and 250 μm, respectively; the arithmetic average opening is 338 μm. Therefore, $d = 3.38 \times 10^{-4} \text{ m}$. If the density of the glass is 2500 kg/m³, the specific surface area is $S_p = 6 / (2500 \text{ kg/m}^3 \cdot 3.38 \times 10^{-4} \text{ m}) = 7.10 \text{ m}^2/\text{kg}$. If 0.0005 kg of glass is used in the test, the initial surface area is $S^0 = 0.0005 \text{ kg} \cdot 7.10 \text{ m}^2/\text{kg} = 3.55 \times 10^{-3} \text{ m}^2$.

- 9.2 *Calculate the initial surface area of monolith sample in the reaction cell (S⁰)*– If a monolithic sample is used, the surface area is calculated geometrically using dimensions measured with calibrated calipers. The surface finish of a monolithic sample and application of a surface roughness factor must be documented.
- 9.3 *Calculate the flow rate (F)*– The flow rate is calculated by dividing the mass of solution that is collected over a time duration by the time duration. Determine the mass of the empty solution bottle. Collect test solution for a duration t . Determine the mass of the solution bottle with solution then subtract the mass of the empty bottle to determine the mass of solution that was collected. Divide the mass of solution collected by the density of the solution to obtain the volume of solution. Divide the volume of solution collected by the duration it was collected to calculate the solution flow rate (F). For example, the mass of the empty solution bottle is 10.90

g. Test solution is collected for 27 hours and 38 minutes (which is 9.95×10^4 seconds). The mass of the solution bottle with test solution is 11.33 g. The mass of solution is $(11.33 - 10.90) = 0.43$ g. The density of the solution is assumed to be 1000 kg/m^3 (1.000 g/mL), so the volume of solution collected is 0.43 mL. The flow rate is calculated as $0.43 \text{ mL} / 9.95 \times 10^4 \text{ seconds} = 4.3 \times 10^{-6} \text{ mL/s}$ (which is $4.3 \times 10^{-12} \text{ m}^3/\text{s}$).

9.4 *Determine the glass dissolution rate*– The dissolution rate is calculated from the measured solution concentrations of key glass components, flow rate, and glass surface area by using Equation 1. (A sample determination of the dissolution rate is included in Appendix A.1.) The selection of which glass components to track should consider abundance, solubility, structural role, and release mechanism. In general, boron and silicon are commonly used to track dissolution of borosilicate glasses. The use of alkali metals are not recommended. The release of alkali metals may occur faster than dissolution of the glass matrix, because their release is by ion exchange rather than matrix dissolution.

9.4.1 Tabulate the mass of solution collected, the collection time, and the concentrations of i and Si measured in each sample aliquot.

9.4.2 Calculate the flow rate for each aliquot by dividing the mass collected (in kg) by the density of the test solution (which can be assumed to be 1000 kg/m^3 for most test solutions) and dividing by the collection time t (in seconds)

$$\text{flow rate, } \frac{\text{m}^3}{\text{s}} = \frac{\text{mass collected, kg}}{1000 \frac{\text{kg}}{\text{m}^3} \bullet t, \text{s}} \quad (\text{A-3})$$

9.4.3 Plot $[i]$ verses time. Identify the data to be used to determine the steady-state concentration based on visual examination of the data. Exclude data that precede the attainment of steady-state conditions. Determine the steady-state concentration (C_i) from those concentrations. Record the mean and standard deviation.

9.4.4 A continual decrease in the concentration of i with time may be an indication that the glass is dissolving at a high enough rate that the surface area of the glass is decreasing significantly during the test. The relative standard deviation (the standard deviation divided by the mean) of the calculated steady-state concentration must be less than 0.15 for the test results to be acceptable.

9.4.5 It is recommended that the concentrations of other soluble components besides silicon (e.g., alkali metals and boron) be monitored. Differences in the rates calculated using different elements may provided added insight to the dissolution mechanism, for example that dissolution is nonstoichiometric. (This may be confirmed by examination of the reacted solids at the end of the test.) Elements present in high concentrations in the test solution (e.g., in a component of a pH buffer) should not be used to measure the glass dissolution rate.

9.4.6 Tabulate the values of F/S^0 , C_{Si} , $C_i - C_i^0$, and the calculated rate for each test in the test series.

9.4.7 Plot the calculated rate versus C_{Si} and extrapolate to $C_{\text{Si}} = 0$ to deconvolute the effect of the flow rate on the measured rate. The rate at $C_{\text{Si}} = 0$ is the forward glass dissolution rate. If the test is being conducted in a test solution with a non-zero Si concentration (e.g., a groundwater), then the rate should be extrapolated to that Si concentration to determine the dissolution rate.

9.4.8 If the data plotted in step 8.4.7 deviate from linearity, the rate may be affected by other solutes besides silicon. For example, the aluminum concentration is known to affect the dissolution rates of some aluminosilicate minerals and glasses. The rates may be plotted against various products of the concentrations of solutes suspected of affecting the rate, e.g., against $[\text{Si}]^{0.5}[\text{Al}]^{0.2}$, to attain a linear plot for extrapolation to infinite dilution.

- 9.5 *Calculate the intrinsic rate constant*– The intrinsic rate constant is calculated from the forward glass dissolution rates measured at various temperatures and pH values using Eq. (A-4):

$$rate = k_0 \cdot 10^{\eta pH} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (A-4)$$

where k_0 is the intrinsic rate constant, η is the pH dependence, E_a is the activation energy, R is the gas constant, and T is absolute temperature.

- 9.5.1 The values of η and E_a can be determined by regressing data in a plot of log rate vs. pH at the various temperatures if it is assumed that the value of η is independent of temperature and the value of E_a is independent of pH.
- 9.5.2 Note that different values of η and E_a may be appropriate for acidic and alkaline solutions for some glasses. The pH dependence of many glasses has a “V” shape with a minimum rate at near-neutral pHs and higher rates at lower and higher pHs.
- 9.5.3 Calculate the value of log k_0 using the expression

$$\log k_0 = \log rate - \eta \cdot pH + \frac{E_a}{2.303RT} \quad (A-5)$$

10. Possible complications

- 10.1 Incongruent dissolution– Dissolution may occur due to the simultaneous action of more than one reaction process that may proceed at different rates and reactions to release some components may occur faster than reactions to release other components. For example, sodium and boron are often released faster than silicon in the early stages of dissolution under some conditions. This may be a transient phenomenon, formation of diffusion barriers may slow the release of sodium and boron as the reaction progresses. This should be borne in mind when selecting components to measure the dissolution rate and when evaluating the process for which the rate was measured.
- 10.2 Phase-separated glasses– The dissolution rate measured for a nonhomogeneous glass may be the result of the simultaneous dissolution of more than one phase. It may be possible to distinguish the dissolution rates of different phases using the release of elements that are unique to one phase. In some cases, the dissolution rate of an inclusion phase may be deemed negligible compared to the dissolution rate of the host glass phase. For example, the dissolution of magnetite inclusions will be much slower than the dissolution of a host borosilicate glass, as may be determined based on the release of iron.
- 10.3 Limit of quantitation– Under the highly dilute conditions necessary to measure the forward glass dissolution rate, it is likely that the solution concentrations of many species will be near the detection limits of the analytical instrument used to measure the solution concentrations. The limit of quantitation for an analyte used to calculate the glass dissolution rate should be determined as ten times the standard deviation of the measured concentration of that analyte in an instrumental blank solution. This gives the lowest concentration for which the measured concentration is quantifiable at the 95% confidence level when the instrumental blank is well known.⁶
- ⁶L. A. Currie, “Limits for Qualitative Detection and Quantitative Determination,” *Analytical Chemistry* **40**, 586-593 (1968).
- 10.4 Interactions between Solution and the Apparatus– It must be verified that the solution has not become contaminated by interactions with the apparatus. This can be evaluated by analyzing the aliquot of test solution collected during the pre-test flush of the apparatus in step 8.2.8. The performance of some of the materials used in the testing apparatus may be degraded by interactions with some solutions. For example, tubing used with peristaltic pumps may soften and expand due to interactions with some test solutions (e.g., brines). Degraded materials must be replaced as required to maintain proper performance of the test apparatus.
- 10.5 Accumulation of Released Material on Apparatus Walls– Material released from the glass may become fixed on the walls of the apparatus by sorption, plating, or being absorbed into the walls of the apparatus. The extent of this interaction will depend on the element. Whether or not this

- occurs can be evaluated by analyzing the aliquot of the acid solution that is passed through the apparatus after the test is completed (in the pre-test cleaning of the apparatus immediately after the test in question, see step 8.4.5) and analyzed for comparison with the results of control tests.
- 10.6 Self-Abrasion of Sample During Test– Severe agitation of crushed samples may result in chipping, sloughing, or fracture of the material as a result of particle collisions under turbulent flow conditions. Evidence of abrasion may include generation of fines in the test solution or formation of uneven layers on the reacted solids. Self-abrasion may result in a significant increase in the surface area and an overestimate of the dissolution rate. Turbulent flow should be avoided, and if abrasion is suspected, an aliquot of the effluent solution should be checked for the presence of fines. This can be done comparing the concentrations before and after passing the solution through a 0.1 micrometer pore size filter.
 - 10.7 Bubble Formation in Solution– Temperature differences between the solution in the solution reservoir and in the reaction cell may result in bubble formation from outgassing of the solution. Bubbles may be removed from the solution stream before entering the reaction cell by including a ballast to collect the gas between the reservoir and the reaction cell. The formation of bubbles in the tubing or reaction cell can also be reduced or eliminated by heating the test solution in the reservoir to the test temperature so that outgassing occurs within the reservoir and gases are not pumped through the system. Bubbles may also form due to leaks at joints in the apparatus. Such leaks should be sealed before conducting tests.
 - 10.8 Layer Formation– Surface layers that are chemically and physically distinct from the glass may form if a glass dissolves nonstoichiometrically. For example, this often occurs during the dissolution of alkali glasses because ion exchange reactions proceed faster than reactions leading to the dissolution of the glass matrix. Because of this, the dissolution rates calculated based on the measured solution concentrations of alkali metals are often significantly higher than those calculated based on the measured solution concentrations of silicon. Different steady-state rates will be measured for components released at different rates. That a glass dissolves nonstoichiometrically can be verified by examination of the reacted glass at the end of a test.
 - 10.9 Alteration Phase Formation– Some components may become sequestered in alteration phases that precipitate from the test solution and are not collected in the aliquots that are analyzed. Dissolution will appear to be nonstoichiometric if this occurs. Alteration phases may form on the test samples, in the solution, or on the apparatus walls. They may be detected by examination of the reacted glass at the end of a test or by solids removed from the effluent solution by filtration.
 - 10.10 Fines– Glass fines may be flushed from the sample during the test and collected in the aliquots of test solution collected to measure the dissolution rate. Inclusion of fines in the effluent solution that is analyzed will result in solution concentrations and calculated dissolution rates that are too high. To reduce the likelihood of fines being collected, the test solution should not be sampled until an amount of solution equal to the system volume has flowed to flush fines from the sample and apparatus (see step 8.3.2).
 - 10.11 Selection of Solutions– The test solutions to be used will be determined by the objective of the tests to be conducted.
 - 10.11.1 Demineralized water. Tests can be conducted using demineralized water as the test solution. The water must meet the requirements of ASTM Type I water (see Standard D 1193).
 - 10.11.2 pH buffers. Buffer solutions are used to maintain a constant solution pH to measure the dissolution rate at a particular pH value. Examples of buffer solutions that can be used in tests covering a range of pH and temperatures are summarized in Table A.1. Buffer solutions must be prepared with water that meets the requirements of ASTM Type I water (see Standard D 1193). Buffers should be selected to avoid strong complexants and solutes known to affect the dissolution rate. Glass components that are also a component of the buffer in concentrations that are significant with respect to the

concentrations generated due to release from the glass should not be used to determine the dissolution rate of the glass.

- 10.11.3 Solute species. Specific elements may be added to the solution used in the test to determine if their presence affects the glass dissolution rate. The effect of added species is determined by comparison to the dissolution rates measured in solutions without that species at the same temperature, pH, and flow rate. Possible effects of the counter ion should also be considered. In general, elements that are present in the glass and are also added to the solution should not be used to determine the dissolution rate of the glass.
- 10.11.4 Actual or synthetic groundwater. Tests may be conducted in actual or synthetic groundwater solutions. Such tests will show the combined effects of pH and several solute species.

Table A.1. Compositions of pH Buffer Solutions⁷

Composition	Ionic Strength	20°C	40°C	70°C	90°C
0.005 m Potassium Hydrogen Phthalate + 0.004 m LiOH	0.0132	5.92	5.91	5.90	5.89
0.005 m H ₃ BO ₃ + 0.0003 m LiOH	0.0003	8.06	7.91	7.71	7.62
0.005 m H ₃ BO ₃ + 0.0020 m LiOH	0.0019	9.07	8.91	8.70	8.59
0.005 m H ₃ BO ₃ + 0.0044 m LiOH	0.0044	10.05	9.80	9.46	9.25
0.004 m LiCl + 0.001 m LiOH	0.0050	11.11	10.50	9.77	9.39
0.005 m LiCl + 0.0107 m LiOH	0.0153	12.12	11.50	10.78	10.39

⁷Buffer compositions and calculated pH values taken from B.P. McGrail, et al., "Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste," Journal of Nuclear Materials Vol 249, 175-189 (1997).

11. Report

11.1 Report the test conditions including

- 11.1.1 Glass composition as measured or as-batched.
- 11.1.2 Composition of test solution used in each test.
- 11.1.3 Temperature of reaction vessel for each test.
- 11.1.4 Measured background concentration of silicon in control test solutions.
- 11.1.5 Table of measured flow rates, pH, and solute concentrations (of silicon and other components being tracked) for individual aliquots taken during each test.

11.2 Report the calculated values

- 11.2.1 Table of calculated or measured sample surface area, F/S, and dissolution rates.
- 11.2.2 Plot of dissolution rate versus steady-state silicon concentration (or product of silicon and other component, if appropriate) with linear extrapolation to determine y-intercept.

11.3 Report any deviations from the test method and discuss the expected effect on the results.

12. Precision and Bias

- 12.1 Data are not yet available to evaluate either the intra-laboratory or inter-laboratory precision and bias of the test method described in this practice.
- 12.2 This practice can be used in an interlaboratory study to determine the intra-laboratory and inter-laboratory precision and bias of the test method (see Standard E 691).

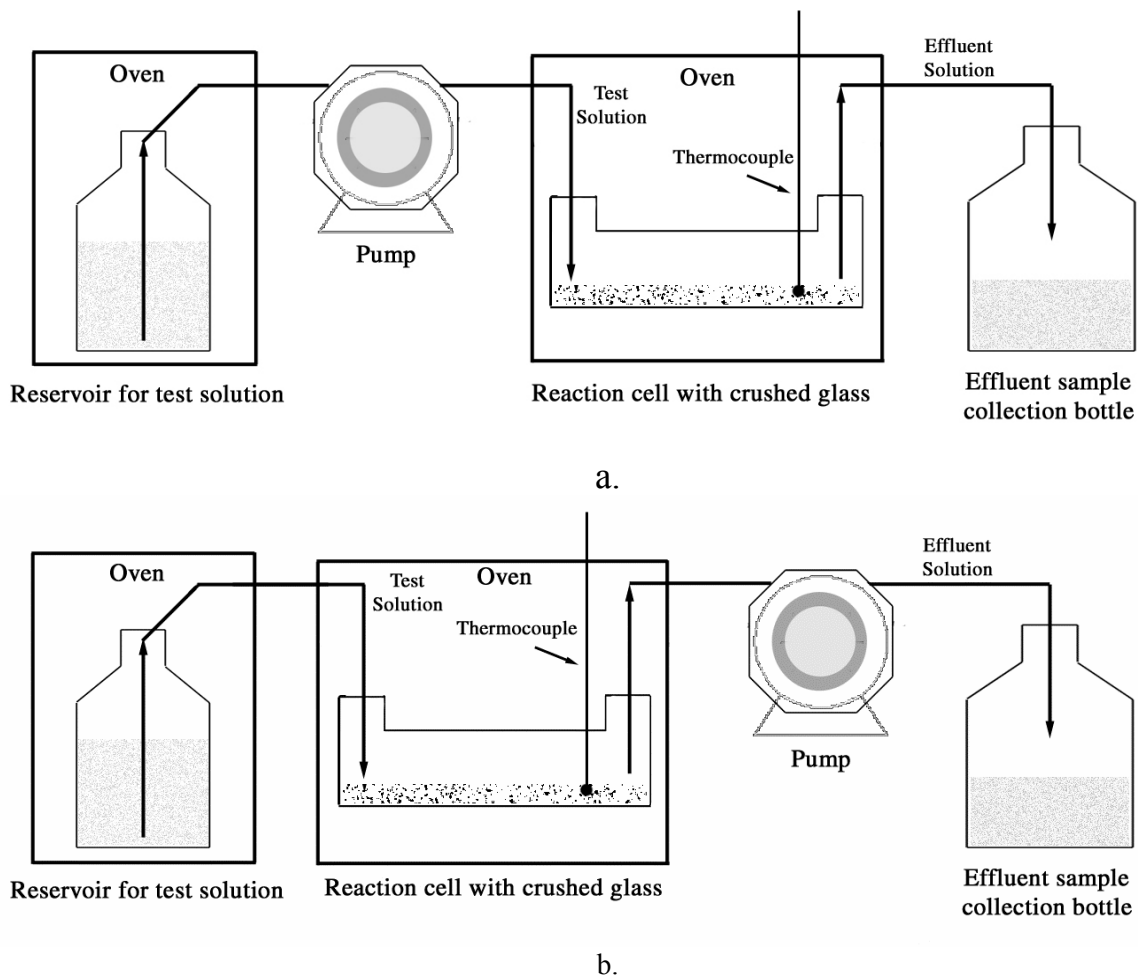


Fig. A.1. Schematic Drawing of SPFT Apparatus with Pump (a) Before and (b) After Reaction Cell. The lines and arrows represent tubing and direction of solution flow.

APPENDIX B. EXAMPLE OF DISSOLUTION RATE CALCULATION

As an example, consider the fictitious set of results in Tables B.1 and B.2. Table B.1 gives the results of Test 1, which was conducted with a sample of glass having a surface area of $3.55 \times 10^{-3} \text{ m}^2$ and at an average flow rate of $4.34 \times 10^{-12} \text{ m}^3/\text{s}$. The ratio F/S is $1.21 \times 10^{-9} \text{ m/s}$ for Test 1. The silicon concentrations are used to determine the glass dissolution rate in this example. The silicon content of the glass is defined to be $f_{\text{Si}} = 0.260 \text{ kg(Si)/kg(glass)}$ for this example, and the background concentration of silicon in the solution used in all tests is defined to be $C_{\text{Si}}^0 = 0.040 \text{ kg/m}^3$. (In practice, f_{Si} is to be measured by analysis of the glass, e.g., see Standard C 169, or estimated based on the as-batched glass composition, and C_{Si}^0 is determined from the sample of effluent taken at the end of the control test.) The steady-state silicon concentration is determined from a plot of C_{Si} versus time, which is shown in Fig. B.1 for Test 1. For Test 1, the steady-state silicon concentration is 3.50 mg/L , which is the mean concentration of the final seven data points in Fig. B.2. (The relative standard deviation for these seven points is 2.4%). The higher concentrations measured in the first three samples are attributed to the dissolution of fines and to surface roughness. The glass dissolution rate in Test 1 is calculated as

$$\text{rate} \frac{\text{g}}{\text{m}^2 \bullet \text{s}} = (C_i - C_i^0) \frac{\text{mg}}{\text{L}} \bullet \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \bullet \left(\frac{1000 \text{ L}}{\text{m}^3} \right) \bullet \left(\frac{F}{S^0} \right) \frac{\text{m}}{\text{s}} \div f_i \quad (\text{B-1a})$$

$$\text{rate} \frac{\text{g}}{\text{m}^2 \bullet \text{s}} = (3.50 - 0.04) \frac{\text{mg}}{\text{L}} \bullet \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \bullet \left(\frac{1000 \text{ L}}{\text{m}^3} \right) \bullet (1.21 \times 10^{-9}) \frac{\text{m}}{\text{s}} \div 0.260 \quad (\text{B-1b})$$

$$\text{rate} = 1.61 \times 10^{-8} \text{ g}/(\text{m}^2 \bullet \text{s})$$

Similar calculations for the dissolution rates in tests at other F/S values are summarized in Table B.2. The rates are plotted against the steady-state silicon concentrations (C_i) in Fig. B.2. Linear regression of all the data is used to determine the y-intercept, which is the forward glass dissolution rate. For the data plotted in Fig. B.2, the y-intercept of the regression line is $1.6 \times 10^{-7} \text{ g}/(\text{m}^2 \bullet \text{s})$. This is the forward dissolution rate at the particular test temperature and pH 8.89, which is the average pH for the 10 tests in Table A.3. Note that while the background-corrected silicon concentrations are used to calculate the glass dissolution rate, the total silicon concentration is used to extrapolate the rate to zero silicon concentration. This is because the rate is affected by all the silicon present in the solution contacting the glass, not only the silicon that was released from the glass.

Table B.1. Fictitious SPFT Test Results for Test 1

Aliquot No.	Time, s	pH	[B], kg/m ^{3a}	[Na], kg/m ³	[Si], kg/m ³	Flow Rate, m ³ /s
1	8640	8.98	0.211	0.432	0.500	4.1 x 10 ⁻¹²
2	17300	8.90	0.130	0.315	0.390	4.3 x 10 ⁻¹²
3	25900	9.02	0.0900	0.270	0.350	4.2 x 10 ⁻¹²
4	34600	9.00	0.0950	0.275	0.355	4.5 x 10 ⁻¹²
5	43200	8.95	0.0910	0.265	0.340	4.4 x 10 ⁻¹²
6	60500	8.96	0.0860	0.253	0.339	4.0 x 10 ⁻¹²
7	77800	8.94	0.0850	0.265	0.342	4.2 x 10 ⁻¹²
8	95000	9.01	0.0845	0.255	0.355	4.3 x 10 ⁻¹²
9	1.30 x 10 ⁵	8.92	0.0850	0.260	0.360	4.6 x 10 ⁻¹²
10	1.47 x 10 ⁵	8.98	0.0880	0.265	0.345	4.4 x 10 ⁻¹²

^a 1 kg/m³ = 1 mg/L.

Table B.2. Fictitious SPFT Test Results

Test No.	F/S ^o , ^a m/s	pH ^a	C _{Si} , kg/m ³	C _{Si} - C _{Si} ^o , kg/m ³	rate, g/(m ² •s)
1	1.2 x 10 ⁻⁹	8.97	3.50	0.346	1.6 x 10 ⁻⁸
2	5.2 x 10 ⁻⁹	8.89	2.59	0.255	5.1 x 10 ⁻⁸
3	1.7 x 10 ⁻⁸	8.90	1.55	0.151	1.0 x 10 ⁻⁷
4	2.3 x 10 ⁻⁸	8.89	1.11	0.107	9.5 x 10 ⁻⁸
5	4.0 x 10 ⁻⁸	8.92	0.71	0.067	1.0 x 10 ⁻⁷
6	8.5 x 10 ⁻⁸	8.95	0.51	0.047	1.5 x 10 ⁻⁷
7	9.7 x 10 ⁻⁸	8.87	0.46	0.042	1.6 x 10 ⁻⁷
8	1.9 x 10 ⁻⁷	8.82	0.25	0.021	1.5 x 10 ⁻⁷
9	3.7 x 10 ⁻⁷	8.84	0.14	0.010	1.4 x 10 ⁻⁷
10	3.8 x 10 ⁻⁷	8.88	0.16	0.012	1.7 x 10 ⁻⁷

^a Average for tests used to calculate the steady-state concentration.

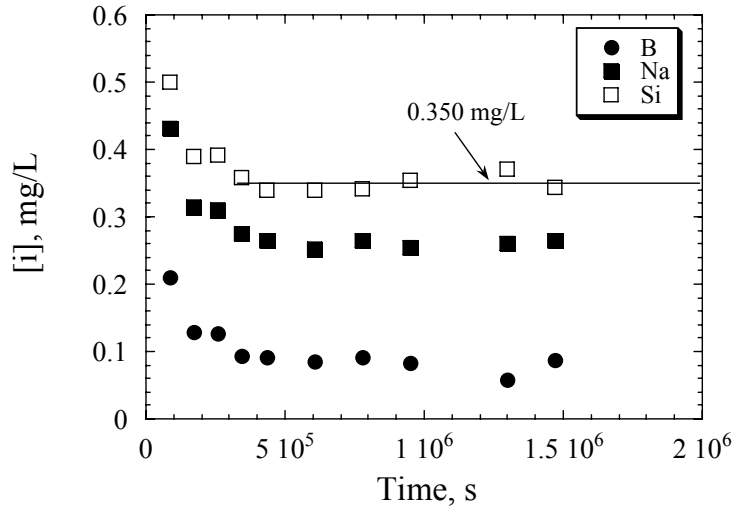


Fig. B.1. Plot of Measured Concentrations of B, Na, and Si as a Function of Time for Tests at $F/S = 1.2 \times 10^{-9} \text{ m/s}$.

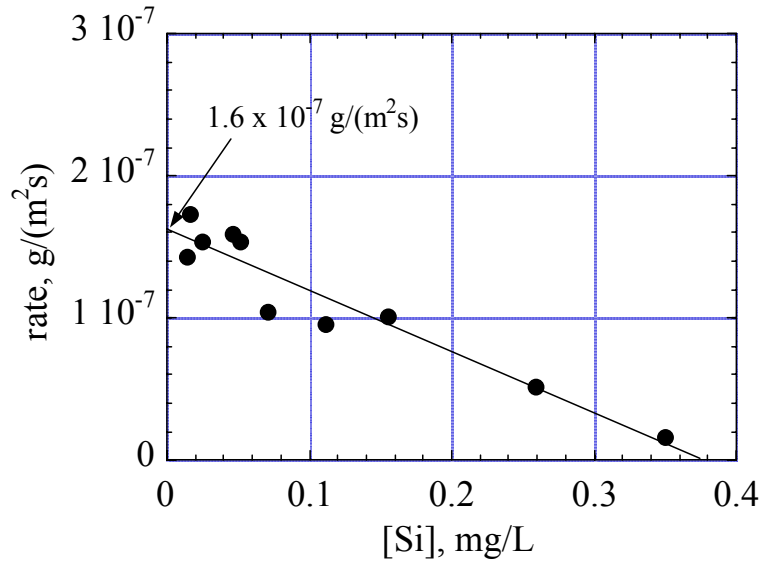


Fig. B.2. Plot of Glass Dissolution Rate (calculated from the silicon concentration) vs. Steady-State Silicon Concentration.

In the test with 0.0005 kg of -40 +60 mesh glass ($3.59 \times 10^{-3} \text{ m}^2$ initial glass surface area) that is run 1.5×10^5 seconds, and a dissolution rate of $2.0 \times 10^{-10} \text{ kg}/(\text{m}^2 \cdot \text{s})$, $1.08 \times 10^{-7} \text{ kg}$ of glass dissolved during the test. The surface area of the particles at the end of the test (S_f) can be calculated using the expression

$$S_f = \left(\frac{6}{\rho \cdot d_o} \right) \cdot m_o^{1/3} \cdot m_f^{2/3} \quad (\text{B-2})$$

where ρ is the density of the glass, d_o is the initial diameter of the glass particle, m_o is the initial mass of the sample and m_f is the final mass of the sample. For the present example, $\rho = 2500 \text{ kg/m}^3$, $d_o = 3.38 \times 10^{-4} \text{ m}$, $m_o = 0.0005 \text{ kg}$, and $m_f = 0.00049989 \text{ kg}$. Solving Eq. B-2 with these values gives

$$S_f = \left(\frac{6}{2500 \bullet 3.38 \times 10^{-4}} \right) \bullet 0.0005^{1/3} \bullet 0.00049989^{2/3} \quad (\text{B-3})$$

$$S_f = 3.55 \times 10^{-3} \text{ m}^3.$$

This is a loss of $4 \times 10^{-5} \text{ m}^2$, which is 1% of the initial surface area. In this example, the change in surface area during the test is insignificant compared with the uncertainty in the steady-state concentrations used to calculate the dissolution rates.

APPENDIX C. LETTERS TO PARTICIPANTS

This appendix includes the invitation letter sent to potential participants on August 24, 2002, and a correspondence letter sent January 28, 2003. These provided an introduction to the ILS with proposed test conditions, data needs, and expectations.

C.1. INVITATION LETTER SENT TO PARTICIPANTS ON AUGUST 24, 2002

Dear Colleague,

You are invited to participate in an interlaboratory study (ILS) testing program to evaluate the precision with which the dissolution rate of a borosilicate glass can be measured using a single-pass flow-through (SPFT) test method. A standard practice for conducting SPFT tests has been written for standardization through the American Society for Testing and Materials (ASTM). The standard has been successfully balloted through ASTM subcommittee C26.13 and will be included in the committee ballot in October, 2002. A copy of the practice is attached. There is currently no data base available to determine the precision of SPFT tests. The intralaboratory and interlaboratory precision measured in this ILS will be included in the precision and bias section of the first revision of the standard. You have been invited to participate either because you (or your laboratory) has published results of flow-through tests in the past or may be actively involved in research focused on glass waste forms.

The ILS will be conducted following ASTM D691. Participants are asked to perform three measurements of the forward glass dissolution rate of LRM glass at $70 \pm 2^\circ\text{C}$ and $\text{pH } 9.0 \pm 0.1$ (pH at 70°C). The forward glass dissolution rate is defined as the rate in the absence of feedback effects from dissolved silica. An obvious complication in measuring the forward glass dissolution rate is that the concentrations of glass components must be high enough to measure, but low enough not to affect the dissolution rate. The draft ASTM procedure calls for conducting several tests that result in steady-state concentrations of dissolved silica, then extrapolating those results to zero concentration.

Measurement of the forward glass dissolution rate will require conducting tests at between 5 and 10 different solution flow rate/glass surface area (F/S) ratios so that the effect of the solution flow rate can be separated from the measured dissolution rate to determine the forward glass dissolution rate. Several samplings (usually 10 or more over the course of two weeks) of the effluent solution will be required to determine the steady-state silicon concentration in tests at each F/S ratio. We recommend that solutions collected at a given F/S ratio be analyzed together to eliminate any small day-to-day variability of the analytical instrument. Typically, determining the forward glass dissolution rate at a single temperature and pH will require analysis of about 60 solutions. It is expected that the glass dissolution rate will approach a limiting value as the F/S ratio used in the test increases. This is because the steady-state Si concentration decreases as the F/S ratio increases. Although the rates measured in tests run at high F/S ratios are closer to the forward rate, analysis of the Si concentration becomes more difficult and results are usually scattered. Tests run at lower F/S ratios provide a constraint for taking the effect of dissolved silica into account and estimating the forward rate. (See draft ASTM procedure for a more detailed discussion on test design and analysis.)

The LRM (low-activity reference material) glass was developed as a test standard for low-activity waste glasses. It is a borosilicate glass that contains about 20 mass % Na_2O and small amounts

of other components that are either present in most waste streams or may be added to glass waste forms. The composition of LRM glass has been measured in a previous ILS [1]; the composition is given in Table C.1. Most of the components in LRM glass will be present in high-level waste (HLW) glasses, although at different concentrations. For example, LRM glass contains more sodium and less iron than HLW glasses. However, the purpose of this ILS is to evaluate the precision of the SPFT test method, not to measure the dissolution rate of a particular glass. The LRM glass contains small amounts of the RCRA metals Ba, Cd, Cr, and Pb, but no radionuclides. The glass itself has been shown to be non-hazardous per the TCLP [2].

We have prepared a single source of LRM glass for testing in the ILS program. About 25 g of crushed glass will be provided to each participant for use in the ILS; more or less glass will be provided if requested. Participants can isolate desired size fractions for testing. Although a particular size fraction is not specified in the ILS, the same size fraction must be used for the three tests to allow measurement of the intralaboratory precision. The mass of sample used in a series of tests can be varied to achieve the desired range of F/S ratios. Series of triplicate tests with different size fractions will be conducted at ANL to measure the effect of sample grain size. Additional tests by other participants are welcomed.

The draft ASTM procedure “Standard Practice for Measurement of the Glass Dissolution Rate using the Single-Pass Flow-Through Test Method” is to be followed. Key aspects of the ILS testing are summarized below:

- Triplicate measurements of the glass dissolution rate are to be made at 70°C ($\pm 2^\circ\text{C}$) and pH 9.0 (± 0.1 pH units; pH at 70°C). This is to allow calculation of the intralaboratory precision.
- The detailed design of the SPFT test apparatus is left to the discretion of the experimenter, within the requirements identified in the ASTM SPFT test procedure.
- All tests are to be conducted with the same size fraction of crushed glass. This is to eliminate any effects of the grain size on the test precision.
- A new sample must be used for every test. This is because the initial surface area, S° , will be used to calculate the dissolution rate. The initial surface area will be calculated from the sieve fraction. Grains will be modeled as spheres with a diameter equal to the arithmetic average of the sieve opening. The density of LRM glass is 2520 kg/m³. As described in the draft ASTM SPFT test procedure, the surface area of the crushed glass sample at the end of the test will be calculated based on the measured dissolution rate and total test duration to confirm that the loss of surface area due to dissolution during the test was negligible.
- The glass should be washed thoroughly with ethanol and/or water to remove fines prior to being placed in the reaction cell. Although fines will be flushed from the reaction cell during the first few days of the test, washing the glass prior to the test will minimize the number of fines that may become trapped in reaction cell (e.g., in a polyethylene wool plug) during the test.
- A control (blank) test must be conducted with the same buffer solution used in tests with glass for at least one solution flow rate. This will be used to measure the interactions between the solution and the apparatus.
- The composition of the buffer solution is left to the discretion of the experimenter. The buffer should not contain silicon.
- The oven temperature must remain within 2°C of the desired test temperature throughout the test.
- Solutions generated in the tests with glass and the blanks tests are to be filtered through 0.45- μm pore size filters, acidified with concentrated nitric acid, and then analyzed for Si. Estimated detection limits must be reported.
- The glass dissolution rate is to be calculated based on the release of Si.
- While a particular analytical method is not required for solution analysis, the method(s) that is used must be reported.

- A data sheet is provided in Fig. 2 to identify the data to be reported. Data should be reported in the same way and with the same number of significant figures as given in Fig. 2 to ensure uniformity in the reported results and facilitate the statistical analysis of the data. A sample of data entry is provided in Fig. 3. Data from all participants will be entered into an EXCEL spreadsheet for computations. Participants may provide data electronically or as hard copy.
- The dissolution rate will be calculated following the method given in the draft ASTM standard practice. This will include (1) determining the steady-state Si concentration at each F/S° , (2) calculating the dissolution rate at each F/S° , and (3) plotting the dissolution rate against the steady-state Si concentration and extrapolating to graphically determine the rate at $[Si] = 0$.

To facilitate design of the test matrix and eliminate the need for additional tests to determine the F/S° range of interest, participants should expect the dissolution rate to be about $1 \text{ g}/(\text{m}^2 \cdot \text{d})$ at pH 9 and 70°C . The range of F/S° values should be between an upper limit of $1 \times 10^{-6} \text{ m/s}$, where the steady-state Si concentration will be near or below the analytical detection limit, and a lower limit of $1 \times 10^{-9} \text{ m/s}$, where the system will be nearly static and the effects of the affinity term will be significant.

The dissolution rates measured at different laboratories will be analyzed to measure the reproducibility of the test method. These results will be documented in an Argonne National Laboratory report and a summary of the results will be published in the open literature. As has been done in previous ILS, participating laboratories will be recognized in all reports, but results will not be linked to specific laboratories.

We recognize that the SPFT is a labor and resource-intensive test method and that your participation represents a significant commitment by your laboratory. However, measurement of the glass dissolution rate provides key data used in assessing the long-term behavior of vitrified waste forms and calculating the performance of disposal systems for radioactive wastes. It is crucial that glass dissolution rates measured in the laboratory be reliable, since they will be used to predict waste glass degradation and the release of radionuclides for tens of thousands of years. A companion ASTM practice is being developed for measuring the dissolution rate of spent nuclear fuel. Participation in the ILS with glass will provide insight and credibility to laboratories who later use similar procedures to measure the dissolution of fuels and other materials.

We also recognize that only a small number of laboratories conduct SPFT tests routinely and that some participants will be running the tests for the first time. Laboratories that don't routinely conduct SPFT tests are encouraged to participate, because this will provide added insight to distinguish between the precision for measure the glass dissolution rate (based on the results of participants who are experienced in the SPFT test) and the precision of conducting the test (based on all results). The experience of participants who are new to the SPFT test method will also indicate where improvement and clarification are needed in the detailed ASTM procedure.

We request that results be reported to ANL before September 30, 2003. Participants will be provided compiled test results to verify correct transcription of their results prior to any communication or presentation of those results. If you are able to participate, and if you know of other scientists who may be interested in participating, please contact me by phone, fax, or e-mail:

Bill Ebert
Argonne National Laboratory
Phone: 630/252-6103
Fax: 630/252-5246
e-mail: ebert@cmt.anl.gov

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2. W.L. Ebert, S.F. Wolf, and D.M. Strachan, "Evaluation of a Standard Test Method and Material for Low-Activity Waste Product Acceptance," Proceedings of XVIII International Glass Conference, July 5-10, 1998, San Francisco, CA. Eds. M. K. Choudhary, N. T. Huff, and C. H. Drummond III. Available on CD-ROM from The American Ceramic Society, Westerville, OH.

Table C.1. LRM Glass Composition, in oxide mass %.

Oxide	mass %	Oxide	mass %	Oxide	mass %
Al ₂ O ₃	9.51	F	0.86	PbO	0.10
B ₂ O ₃	7.85	Fe ₂ O ₃	1.38	SO ₃	0.30
BaO	0.002	HgO	<0.002	SiO ₂	54.20
CaO	0.54	I	<0.002	SnO ₂	<0.1
CdO	0.16	K ₂ O	1.48	TiO ₂	0.10
Cl	<0.2	La ₂ O ₃	0.02	ZrO ₂	0.93
Cr ₂ O ₃	0.19	P ₂ O ₅	0.54		

Table C.2. SPFT Test Data Sheet for ILS with LRM Glass

Test Number: _____ Start Date: _____ Test Start Time: _____

Size fraction of glass: _____ Mass Glass: _____ Initial Surface Area of Glass: _____

Target flow rate: _____ Flow Rate Letter Designator: _____

Eluent Samplings:

Solution Number	Sampling Date	Temp., °C	Bottle Tare, g	Collection Time			Total Mass, g	Mass Eluent, g	Flow Rate, m ³ /s	F/S°, m/s	pH	[Si], mg/L
				Start	Stop	Total, s						

Table C.3. Sample SPFT Test Data Sheet for ILS with LRM Glass

Test Number: LRM-2 Start Date: 10-13-02 Test Start Time: 1300

Size fraction of glass: 75 – 150 μm Mass Glass: 0.95 g Initial Surface Area of Glass: 0.019 m^2

Target flow rate: $1 \times 10^{-10} \text{ m}^3/\text{s}$ Flow Rate Letter Designator: C

Eluent Samplings:

Solution Number	Sampling Date	Temp., $^{\circ}\text{C}$	Bottle Tare, g	Collection Time			Total Mass, g	Mass Eluent, g	Flow Rate, m^3/s	F/S $^{\circ}$, m/s	pH	[Si], mg/L
				Start	Stop	Total, s						
LRM-2-C-1	10-17-02	90.8	10.99	1130:00	1530:00	14400	12.17	1.38	9.6×10^{-11}	5.0×10^{-9}	8.96	0.310
LRM-2-C-2	10-19-02	90.6	10.98	1336:00	1606:00	9000	11.83	0.85	9.4×10^{-11}	5.0×10^{-9}	8.92	0.296
LRM-2-C-3	10-21-02	91.0	11.02	930:00	1130:20	7220	11.67	0.65	9.0×10^{-11}	4.7×10^{-9}	8.96	0.312

Test Number	Identify by replicate number (e.g., LRM-1, -2, -3)
Start Date:	Identify the calendar date the test is started
Start Time:	Identify the time of day the test is started
Size Fraction:	Identify the size fraction of crushed glass being used (by size of sieve openings)
Mass Glass:	Mass of glass added to reaction cell, in g
Surface Area:	Surface area of glass estimated from size fraction assuming glass particles are spheres with a diameter equal to the arithmetic average of sieve openings, in m ²
Nominal Flow Rate:	Target flow rate for experiment, in mL/s
Letter Designator:	Unique letter for nominal flow rate for test number (e.g., A, B, C, etc.)
Eluent Samples:	Data for collection of eluent samples for test number and flow
Sample Number:	Unique identifier for solution sample (e.g. LRM-1-A-1)
Sample Date:	Date solution sample was collected
Temperature:	Temperature of reaction cell when eluent is collected, in °C (report to nearest 0.1 °C)
Bottle Tare:	Mass of empty bottle (with lid) for sample collection, g (report to nearest 0.01 g)
Collection Time	
Start:	Time of day eluent collection started (report to nearest second)
Stop:	Time of day eluent collection stopped (report to nearest second)
Total:	Total time eluent was collected, in s
(Option: Duration that solution is collected can be measured directly using a timer and entered as “Time”)	
Total Mass:	Mass of solution bottle with eluent, in g (report to nearest 0.01 g)
Mass Eluent:	Mass of eluent collected, in g (report to nearest 0.01 g)
	Calculated as Total Mass – Bottle Tare, in g
Flow Rate:	Solution flow rate calculated based on mass of eluent collected and collection time assuming solution density is 1.00 g/mL (1×10^{-6} m ³ /g):
	Calculated as Flow Rate = (Total Mass, g – Bottle tare, g) • (1×10^{-6} m ³ /g) ÷ (Collection Time Stop – Collection Time Start, s).
F/S:	Solution flow rate-to- glass surface area ratio, in m/s
	Calculated as F/S = Flow Rate / Surface Area of Glass
pH:	pH of eluent measured at room temperature (report to nearest 0.01)
[Si]:	Concentration of silicon measured in eluent sample, in mg/L (report concentration to 3 significant figures)

C.2. CORRESPONDENCE LETTER TO PARTICIPANTS SENT JANUARY 28, 2003

Colleagues,

Thank you for your interest in participating in the interlaboratory study (ILS) of the single-pass flow-through test method. I presume that by now I have heard from all interested parties, though I will continue to encourage other possible participants. I have received a few comments regarding the study and suggestions for improvement. Listed below are the comments, responses, and modification to the ILS.

Comment: All participants should use the same mesh size fraction of crushed glass. Although the ASTM practice does not specify a size fraction, using the same size fraction in the ILS would remove that source uncertainty from the measured precision.

Response: The original intent was to include any effect of particle size in the measured precision so that the precision could be applied to tests with different size fractions. I agree the test results would better serve as a "precision standard" if a specific size is used.

Modification: Tests will be conducted with the -100 +200 mesh size fraction (0.075 mm - 0.150 mm). SPFT and other tests are commonly run with this size fraction. Besides its suitability for SPFT, specific surface areas of -100 +200 mesh glass measured for other tests can be utilized. ANL will provide crushed and sieved glass. ANL will run tests with at least one other size fraction to provide data on the effects of size fraction. ANL will provide a sample of another size fraction to any participant that wants to run other tests. I anticipate we won't be able to provide crushed glass until about mid-January 2003. My goal will be to provide approximately 20 g of -100 +200 mesh glass to each participant.

Comment: Tests should be conducted at a pH value other than 9. Running tests at pH 8 or 10 would avoid complications with silica chemistry near pH 9. Also, all participants should use the same buffer composition.

Response: The test conditions 70C and pH 9 were selected as being repository-relevant and providing measurable silicon concentrations under convenient laboratory conditions. The recommendation that all participants use the same chemicals to adjust the leachant pH will probably improve the use of the test results as a precision standard.

Modification: Tests will be conducted at the pH imposed by a mixture of 0.004 m LiCl + 0.003 m LiOH (0.1696 g LiCl + 0.0718 g LiOH per kg demineralized water). This mixture is expected have a pH value about pH 10 at 70C, based on the buffers listed in Table 2 of McGrail, et al., Journal of Nuclear Materials 249 (1997) 175-189. The composition of the leachant solution is to be controlled, not its pH. The pH of the leachant solution is to be measured prior to testing, and the pH of every sample is to measured when it is collected. The leachant solution does not have significant buffering capacity. Under the SPFT test conditions, glass dissolution is not expected to result in a significant pH increase except perhaps at low flow/surface ratios, where the silicon concentration will also affect the dissolution rate. Experience has shown these mixtures to maintain constant pH values. We expect the dissolution rate to be about 2X faster at pH 10 than at pH 9, so the slightly higher flow/surface area ratios than those suggested in the invitation letter may be needed.

Comment: The leachant solution should be treated to avoid acidification by absorbed carbon dioxide.

Response: The leachant solution can be sparged with nitrogen gas to remove dissolved air. However, it is not anticipated that this will affect the solution pH in these tests. The pH of every collected solution sample will be measured directly, so any pH drift that

occurs will be documented. Our experience is that the leachant solution pH will not be affected by dissolved air. We expect that the uncertainty in measuring the pH will be much greater than the effects of dissolved air.

Modification: None. Participants have the option to deareate the solutions if they desire.

Comment: Some participants requested monolithic samples for additional analyses of reacted glass.

Response: The LRM glass to be used in the ILS was received as crushed glass. No monoliths are available. However, several monoliths of the prototype glass that was made and studied at ANL prior to the manufacture of the LRM glass are available. ANL will provide monolithic samples of the prototype LRM material to participants.

Comment: Participants have limited resources they can apply to the ILS.

Response: I realize the significant resources needed to conduct this test and participate in the ILS, and that most will not participate in the full scope of the study. Some additional tests will be conducted at ANL to expand the scope and information provided by the study beyond the reproducibility of the SPFT test. Priorities are listed below, and participants can determine themselves how fully they can participate.

1. Conduct SPFT at 70 C with -100 +200 mesh LRM glass and LiCl/LiOH leachant solution.

Conduct tests using at least 5 different flow/surface area ratios. Either mass of glass, flow rate, or both can be varied. Fresh glass must be used for each test a a particular flow/surface area ratio. Glass cannot be reused. Additional glass will be provided, if necessary.

Measure pH (at room temperature) and composition of leachant solution (Li and Si).

Collect at least 6 test solution samples between day 3 and day 14 (e.g., after 3, 4.5, 6, 7.5, 11, and 14 days). (Collect more samples, if possible.) Measure mass of solution and collection time in order to calculate flow rate. Measure pH (at room temperature) and composition of test solutions (Li and Si).

Conduct control test without glass at lowest flow rate used to measure interactions with apparatus.

Measure pH (room temperature) and composition of leachant solution (Li and Si).

Record all data to data sheet and provide to ANL for analysis (either hard copy or in EXCEL spreadsheet).

2. Repeat measurements in 1 two times to determine intralaboratory precision.
3. Repeat measurements in 1 with different size fraction of glass.

Some elements were accidentally left out of the composition table provided with the invitation letter. The composition in mass %:

Al ₂ O ₃	9.51	MgO	0.10
B ₂ O ₃	7.85	MnO	0.08
BaO	0.00	MoO ₃	0.10
CaO	0.54	Na ₂ O	20.03
CdO	0.16	NiO	0.19
Cr ₂ O ₃	0.19	P ₂ O ₅	0.54
F	0.86	PbO	0.10
Fe ₂ O ₃	1.38	SO ₃	0.30
K ₂ O	1.48	SiO ₂	54.20
La ₂ O ₃	0.02	TiO ₂	0.10
Li ₂ O	0.11	ZrO ₂	0.93

In summary, the following modifications have been made to the ILS of the SPFT test method:

Tests will be conducted with -100 +200 mesh size LRM glass to be provided by ANL. Tests will be conducted using a 0.004 m LiCl + 0.003 m LiOH leachant solution.

I will try to provide the glass by mid-January and hope to have tests completed by the end of the calendar year.

Please continue to contact me with questions, concerns, suggested improvements, etc., and thank you again for your interest in this study.

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APPENDIX D. PROPAGATION OF ERRORS

The uncertainties in the rates calculated for individual tests within each test series were estimated from the measured test values, using the propagation-of-errors method. For a property P that is a function of measured values x_1, x_2, x_3 , etc., the probable error associated with P can be expressed in terms of the probable error in the means of the measured values as

$$Q_p^2 = \left(\frac{\partial P}{\partial x_1} \right)^2 \cdot Q_1^2 + \left(\frac{\partial P}{\partial x_2} \right)^2 \cdot Q_2^2 + \left(\frac{\partial P}{\partial x_3} \right)^2 \cdot Q_3^2 + \dots \quad (D-1)$$

The estimated uncertainties for measured and calculated values are listed below. The dissolution rate is calculated using Eq. D-2:

$$NR(i) = \frac{[C^{ss}(i) - C^o(i)] \times F}{S \times f(i)}. \quad (D-2)$$

The probable error in the rate calculated with Eq. D-2 is

$$Q_{NR(i)}^2 = \left(\frac{\partial NR(i)}{\partial C^{ss}(i)} \right)^2 \cdot Q_{C^{ss}(i)}^2 + \left(\frac{\partial NR(i)}{\partial F} \right)^2 \cdot Q_F^2 + \left(\frac{\partial NR(i)}{\partial S} \right)^2 \cdot Q_S^2 + \left(\frac{\partial NR(i)}{\partial f(i)} \right)^2 \cdot Q_{f(i)}^2. \quad (D-3)$$

The partial differential terms in Eq. D-3 are

$$\frac{\partial NR(i)}{\partial C^{ss}(i)} = \frac{F}{S \times f(i)}, \quad (D-4)$$

$$\frac{\partial NR(i)}{\partial F} = \frac{C^{ss}(i)}{S \times f(i)}, \quad (D-5)$$

$$\frac{\partial NR(i)}{\partial S} = \frac{-[C^{ss}(i) - C^o(i)] \times F}{S^2 \times f(i)}, \quad (D-6)$$

and

$$\frac{\partial NR(i)}{\partial f(i)} = \frac{-[C^{ss}(i) - C^o(i)] \times F}{S \times f(i)^2}. \quad (D-7)$$

The uncertainty terms are discussed below.

$Q_{f(Si)}$

The uncertainty in the elemental mass fraction is due to uncertainties in the mass of glass dissolved for analysis, the volume of the solution used to dissolve the glass, and the solution analysis. The uncertainties in the values of $f(i)$ in the LRM glass have been measured in a previous interlaboratory study (Ebert and Wolf 2000). The average SiO_2 content was determined in that study to be 54.20 mass % with a reproducibility standard deviation of 1.421 mass %. The corresponding mass fraction of Si is 0.253 ± 0.007 mass %, and the expanded uncertainty is taken to be 0.014 (two standard deviations).

Q_F

The uncertainty in the flow rate measured for each sampling of a test solution is the propagated error in the measurement of the solution mass M and the collection time t :

$$F = M/t. \quad (\text{D-8})$$

The variance is calculated as

$$Q_F^2 = \left(\frac{\partial F}{\partial M} \right)^2 \cdot Q_M^2 + \left(\frac{\partial F}{\partial t} \right)^2 \cdot Q_t^2 \quad (\text{D-9})$$

where $\frac{\partial F}{\partial M} = \frac{1}{t}$, $\frac{\partial F}{\partial t} = \frac{-M}{t^2}$.

The uncertainty in the collection time is due to uncertainty in how closely the recorded time corresponds to when solution was collected (for example, if the test solution was dripping out of the exit line). The uncertainty in the mass of test solution measured to the nearest 0.01 g is addressed by propagation of errors and is computed by applying Eq. D-3 to the difference between two measurements (the mass of the bottle with the test solution and the mass of the empty bottle):

$$M = \text{mass}_1 - \text{mass}_2 \quad (\text{D-8})$$

$$Q_M^2 = \left(\frac{\partial M}{\partial \text{mass}_1} \right)^2 \cdot Q_{\text{mass}_1}^2 + \left(\frac{\partial M}{\partial \text{mass}_2} \right)^2 \cdot Q_{\text{mass}_2}^2. \quad (\text{D-9})$$

If the uncertainty in each measured mass is 0.01 g, then $\frac{\partial M}{\partial \text{mass}_1} = 1$, $\frac{\partial M}{\partial \text{mass}_2} = -1$, and

$Q_1 = Q_2 = 0.01$. Inserting these values into Eq. D-9 gives

$$Q_M^2 = (1)^2 \cdot (0.01)^2 + (-1)^2 \cdot (0.01)^2 = 0.0002 \text{ g}. \quad (\text{D-10})$$

The uncertainty in the difference between the two masses to the nearest 0.01 g is $Q_M = (0.0002)^{0.5} = 0.014 \text{ g}$. The uncertainty in measuring the flow rate in each sampling is negligible compared with the variation in the flow rates in samplings taken during each test. Therefore, the uncertainty in the flow rate is taken to be the standard deviation of the series of samplings.

Q_{CSS(i)}

The uncertainty in the steady-state concentration is taken to be the standard deviation for the series of samplings, which is greater than the uncertainty in the individual solution analyses. For example, the uncertainty in the measured Si concentration is estimated to be 10% of the measured value for ICP-MS analyses, and it may be lower for other analytical methods. This is less than the standard deviation in the samplings used to determine the steady-state concentration for most tests. Deviations in the steady-state Si concentration of a test are confounded by real variations in the flow rate. Using the deviation in the measured Si concentrations, rather than the propagated error for individual samplings, captures this additional source of uncertainty.

Q_s

The uncertainty in the surface area includes uncertainty in the initial surface area plus uncertainty in how the surface area changes as the glass dissolves.

Initial surface area

The uncertainty in the initial surface area includes uncertainties in the specific surface area of the crushed glass and the measured mass of glass used in the test. Uncertainty in the specific surface area includes bias introduced by the method used to estimate the initial surface area of the crushed glass, which in the present analysis is done by using the arithmetic average of two sieve sizes. Although data are not available to estimate this bias for LRM glass, it has been addressed previously by comparing the results of tests with crushed glass with the results of tests with monolithic specimens of known geometric surface area and assuming that the crushed and monolithic glasses have the same specific reactivity (i.e., the same dissolution rate on a per unit surface area basis). These comparisons indicate the geometric surface area calculated based on sieve sizes is about 2 times too low.

The uncertainty in measuring the mass of glass used in the test is taken to be 0.014 g. Some masses were reported to the nearest 0.00001 g. The uncertainty in those measurements is 0.000014. The uncertainty in the initial surface area is dominated by the uncertainty in the specific surface area, which is taken to be 2 times the calculated surface area.

Changes in surface area

The loss of surface area as glass dissolves is modeled by using a shrinking core model (see Section 4.3.4). In that model, the glass dissolution rate is used to calculate the mass of glass that has dissolved, which is then used to calculate the remaining surface area. The glass dissolution rate is calculated from the Si concentration and the surface area (see Eq. 3). In effect, the uncertainty in the change in surface area is correlated with (and taken into account by) the uncertainty in the Si concentration.

NR(Si)

The uncertainties in the dissolution rates NR(Si) for tests by Participant A are summarized in Table D.1 for test series LRM-1, LRM-2, LRM-3, and LRM-3a and in Table D.2 for test series LRM-4. The separate contributions of the four terms in Eq. D-3, given in the tables, indicate that the uncertainty in the rate is almost entirely due to uncertainty in the steady-state Si concentration. The highest propagated uncertainties typically occur for the tests at the highest F/S values. The average propagated uncertainties are 0.095 g/(m²d) for the combined test series LRM-1, LRM-2, and LRM-3, and 0.140 g/(m²d) for test series LRM-4.

Estimated Standard Error

The values used to calculate the estimated standard error (see Eqs. 10 and 11) for the tests conducted by Participant A are summarized in Table D.3 for Tests LRM-1, LRM-2, and LRM-3, and in Table D.4 for Test LRM-4.

Table D.1. Propagated Uncertainties for Rates from Tests LRM-1, LRM-2, and LRM-3, Based on Si Concentrations

Test No.	Flow, m ³ /s		C _{ss} – C _{blank} , mg/L		$Q_C^2 \cdot (\partial NL / \partial C)^2$	$Q_F^2 \cdot (\partial NL / \partial F)^2$	$Q_S^2 \cdot (\partial NL / \partial S)^2$	$Q_{fSi}^2 \cdot (\partial NL / \partial f_{Si})^2$	$Q_{NR}^2, g/(m^2 s)$	$Q_{NR}, g/(m^2 s)$	$Q_{NR}, g/(m^2 d)$
	mean	uncertainty	mean	uncertainty							
LRM-1-B	7.86E-10	8.83E-12	9.305	0.764	3.20E-13	4.03E-17	6.27E-17	9.80E-16	3.21E-13	5.67E-07	0.049
LRM-1-C	8.11E-10	1.27E-11	24.493	1.769	7.28E-14	1.78E-17	1.43E-17	2.23E-16	7.31E-14	2.70E-07	0.023
LRM-1-D	8.19E-10	9.27E-12	18.750	0.869	7.18E-14	9.19E-18	1.41E-17	2.20E-16	7.20E-14	2.68E-07	0.023
LRM-1-E	3.61E-09	2.65E-11	13.032	1.465	9.88E-13	5.34E-17	1.94E-16	3.03E-15	9.92E-13	9.96E-07	0.086
LRM-1-F	3.70E-09	3.85E-11	10.059	1.818	3.57E-12	3.87E-16	7.00E-16	1.09E-14	3.58E-12	1.89E-06	0.164
LRM-1-G	6.57E-09	3.71E-11	8.830	0.994	1.51E-12	4.81E-17	2.96E-16	4.63E-15	1.52E-12	1.23E-06	0.106
LRM-1-H	3.64E-09	1.59E-11	5.632	0.858	3.16E-12	6.01E-17	6.20E-16	9.69E-15	3.18E-12	1.78E-06	0.154
LRM-1-I	1.36E-08	1.61E-10	4.313	0.409	1.09E-12	1.53E-16	2.13E-16	3.33E-15	1.09E-12	1.04E-06	0.090
LRM-1-J	3.64E-09	2.17E-11	4.031	0.610	4.37E-12	1.55E-16	8.56E-16	1.34E-14	4.38E-12	2.09E-06	0.181
LRM-2-B	7.91E-10	8.74E-12	12.359	0.815	3.68E-13	4.49E-17	7.21E-17	1.13E-15	3.69E-13	6.08E-07	0.053
LRM-2-C	8.09E-10	2.08E-11	25.373	3.720	3.21E-13	2.13E-16	6.29E-17	9.82E-16	3.22E-13	5.68E-07	0.049
LRM-2-D	8.27E-10	8.48E-12	20.602	2.756	7.37E-13	7.75E-17	1.44E-16	2.26E-15	7.40E-13	8.60E-07	0.074
LRM-2-E	3.61E-09	3.34E-11	13.873	1.385	8.86E-13	7.60E-17	1.74E-16	2.71E-15	8.89E-13	9.43E-07	0.081
LRM-2-F	3.72E-09	2.40E-11	10.992	0.674	4.96E-13	2.07E-17	9.72E-17	1.52E-15	4.98E-13	7.05E-07	0.061
LRM-2-G	6.55E-09	7.45E-11	9.233	0.859	1.12E-12	1.45E-16	2.20E-16	3.43E-15	1.12E-12	1.06E-06	0.092
LRM-2-H	3.64E-09	4.29E-11	5.843	0.838	3.02E-12	4.20E-16	5.93E-16	9.26E-15	3.03E-12	1.74E-06	0.150
LRM-2-I	1.36E-08	1.02E-10	4.805	0.852	4.72E-12	2.66E-16	9.25E-16	1.44E-14	4.73E-12	2.18E-06	0.188
LRM-2-J	3.64E-09	2.65E-11	2.895	0.196	4.50E-13	2.39E-17	8.83E-17	1.38E-15	4.52E-13	6.72E-07	0.058
LRM-3-B	8.05E-10	8.60E-12	11.023	0.993	5.66E-13	6.46E-17	1.11E-16	1.73E-15	5.68E-13	7.54E-07	0.065
LRM-3-C	8.24E-10	8.86E-12	27.581	2.950	2.09E-13	2.42E-17	4.10E-17	6.41E-16	2.10E-13	4.58E-07	0.040
LRM-3-D	8.22E-10	6.78E-12	18.061	2.155	4.45E-13	3.02E-17	8.72E-17	1.36E-15	4.46E-13	6.68E-07	0.058
LRM-3-E	3.60E-09	3.92E-11	11.560	0.502	1.16E-13	1.38E-17	2.28E-17	3.56E-16	1.17E-13	3.41E-07	0.029
LRM-3-F	3.74E-09	2.09E-11	9.324	0.630	4.37E-13	1.36E-17	8.57E-17	1.34E-15	4.39E-13	6.62E-07	0.057
LRM-3-G	6.65E-09	1.01E-10	7.980	0.500	3.92E-13	8.96E-17	7.69E-17	1.20E-15	3.94E-13	6.27E-07	0.054
LRM-3-H	3.65E-09	3.66E-11	4.911	0.273	3.22E-13	3.24E-17	6.32E-17	9.87E-16	3.24E-13	5.69E-07	0.049
LRM-3-I	1.39E-08	2.12E-10	5.556	0.366	9.17E-13	2.13E-16	1.80E-16	2.81E-15	9.20E-13	9.59E-07	0.083
LRM-3-J	3.48E-09	1.13E-10	4.336	0.253	6.86E-13	7.30E-16	1.34E-16	2.10E-15	6.89E-13	8.30E-07	0.072
LRM-3-K	7.13E-10	1.65E-11	42.415	5.020	1.13E-13	6.05E-17	2.22E-17	3.47E-16	1.14E-13	3.37E-07	0.029
LRM-3-L	1.40E-08	2.46E-10	3.026	0.408	4.60E-12	1.43E-15	9.01E-16	1.41E-14	4.61E-12	2.15E-06	0.186
LRM-3-M	1.44E-08	3.82E-10	2.021	0.378	7.68E-12	5.41E-15	1.51E-15	2.35E-14	7.71E-12	2.78E-06	0.240
LRM-3-N	1.38E-08	2.17E-10	1.473	0.156	2.63E-12	6.52E-16	5.15E-16	8.04E-15	2.64E-12	1.62E-06	0.140
LRM-3-O	1.37E-08	3.40E-10	0.649	0.144	8.15E-12	5.02E-15	1.60E-15	2.49E-14	8.18E-12	2.86E-06	0.247

Table D.2. Propagated Uncertainties for Rates from Test LRM-4, Based on Si Concentrations

Test No.	Flow, m ³ /s		C _{ss} – C _{blank} , mg/L		$Q_C^2 \bullet$ ($\partial NL / \partial C$) ²	$Q_F^2 \bullet$ ($\partial NL / \partial F$) ²	$Q_S^2 \bullet$ ($\partial NL / \partial S$) ²	$Q_{fSi}^2 \bullet$ ($\partial NL / \partial f_{Si}$) ²	Q_{NR}^2 , g/(m ² s)	Q_{NR} , g/(m ² s)	Q_{NR} , g/(m ² d)
	mean	uncertainty	mean	uncertainty							
LRM-4-C	8.31E-10	3.48E-11	30.290	1.622	1.45E-13	2.54E-16	2.84E-17	4.43E-16	1.46E-13	3.81E-07	0.033
LRM-4-D	8.19E-10	1.16E-11	19.450	1.579	5.34E-13	1.07E-16	1.05E-16	1.63E-15	5.36E-13	7.32E-07	0.063
LRM-4-E	3.64E-09	4.98E-11	10.694	0.814	6.98E-13	1.31E-16	1.37E-16	2.14E-15	7.00E-13	8.37E-07	0.072
LRM-4-F	3.81E-09	7.25E-11	6.747	0.813	1.70E-12	6.18E-16	3.34E-16	5.21E-15	1.71E-12	1.31E-06	0.113
LRM-4-G	6.60E-09	7.37E-11	6.595	0.852	2.52E-12	3.14E-16	4.93E-16	7.71E-15	2.53E-12	1.59E-06	0.137
LRM-4-K	8.29E-10	2.13E-11	36.330	2.194	4.23E-14	2.78E-17	8.28E-18	1.29E-16	4.24E-14	2.06E-07	0.018
LRM-4-L	1.38E-08	1.27E-10	1.999	0.481	1.40E-11	1.19E-15	2.74E-15	4.28E-14	1.40E-11	3.74E-06	0.323
LRM-4-I	1.37E-08	1.78E-10	3.018	1.081	1.75E-11	2.96E-15	3.43E-15	5.36E-14	1.75E-11	4.19E-06	0.362

Table D.3. Data for Calculating Confidence Limits for Forward Rate Measured in Tests LRM-1, LRM-2, and LRM-3

	ss Si (X)	Rate (Y)	Y^2	$(Y - \bar{Y})^2$	$2XY$	$2Y$	X^2	$2X$	$(X - \bar{X})^2$
LRM-1-C	24.6	0.322	1.04E-01	3.33E-01	1.59E+01	6.45E-01	6.08E+02	4.93E+01	2.18E+02
LRM-1-D	18.9	0.499	2.49E-01	1.61E-01	1.89E+01	9.98E-01	3.57E+02	3.78E+01	8.13E+01
LRM-1-E	13.2	0.781	6.09E-01	1.42E-02	2.06E+01	1.56E+00	1.74E+02	2.64E+01	1.09E+01
LRM-1-F	10.2	0.864	7.47E-01	1.24E-03	1.77E+01	1.73E+00	1.04E+02	2.04E+01	1.07E-01
LRM-1-G	8.99	0.919	8.45E-01	3.75E-04	1.65E+01	1.84E+00	8.08E+01	1.80E+01	8.14E-01
LRM-1-H	5.79	1.065	1.13E+00	2.72E-02	1.23E+01	2.13E+00	3.35E+01	1.16E+01	1.68E+01
LRM-1-I	4.47	0.950	9.03E-01	2.53E-03	8.49E+00	1.90E+00	2.00E+01	8.94E+00	2.94E+01
LRM-1-J	4.19	1.158	1.34E+00	6.67E-02	9.70E+00	2.32E+00	1.75E+01	8.38E+00	3.25E+01
LRM-2-B	12.5	0.794	6.30E-01	1.12E-02	1.99E+01	1.59E+00	1.57E+02	2.51E+01	7.04E+00
LRM-2-E	14.1	0.828	6.85E-01	5.19E-03	1.79E+01	6.99E-01	6.53E+02	5.11E+01	2.45E+02
LRM-2-F	11.2	0.992	9.84E-01	8.48E-03	2.30E+01	1.11E+00	4.32E+02	4.16E+01	1.19E+02
LRM-2-G	9.42	0.982	9.64E-01	6.76E-03	2.33E+01	1.66E+00	1.98E+02	2.81E+01	1.74E+01
LRM-2-H	6.03	1.046	1.09E+00	2.14E-02	2.22E+01	1.98E+00	1.25E+02	2.24E+01	1.66E+00
LRM-2-I	4.99	1.058	1.12E+00	2.50E-02	1.85E+01	1.96E+00	8.87E+01	1.88E+01	2.24E-01
LRM-3-B	11.2	0.721	5.19E-01	3.21E-02	1.61E+01	1.44E+00	1.25E+02	2.24E+01	1.70E+00
LRM-3-D	18.2	0.482	2.33E-01	1.74E-01	1.76E+01	9.65E-01	3.32E+02	3.65E+01	6.96E+01
LRM-3-E	11.7	0.677	4.58E-01	4.97E-02	1.59E+01	1.35E+00	1.38E+02	2.35E+01	3.39E+00
LRM-3-F	9.49	0.845	7.14E-01	3.02E-03	1.60E+01	1.69E+00	9.01E+01	1.90E+01	1.57E-01
LRM-3-G	8.15	0.862	7.44E-01	1.39E-03	1.41E+01	1.72E+00	6.64E+01	1.63E+01	3.03E+00
LRM-3-H	5.08	0.881	7.77E-01	3.33E-04	8.96E+00	1.76E+00	2.58E+01	1.02E+01	2.31E+01
LRM-3-I	5.72	1.254	1.57E+00	1.25E-01	1.44E+01	2.51E+00	3.28E+01	1.14E+01	1.73E+01
LRM-3-J	4.50	1.224	1.50E+00	1.05E-01	1.10E+01	2.45E+00	2.03E+01	9.01E+00	2.90E+01
LRM-3-L	3.20	1.373	1.88E+00	2.24E-01	8.77E+00	2.75E+00	1.02E+01	6.39E+00	4.48E+01
LRM-3-M	2.19	1.279	1.63E+00	1.44E-01	5.60E+00	2.56E+00	4.80E+00	4.38E+00	5.93E+01
LRM-3-N	1.64	1.320	1.74E+00	1.77E-01	4.34E+00	2.64E+00	2.70E+00	3.28E+00	6.80E+01
LRM-3-O	0.818	1.113	1.24E+00	4.55E-02	1.82E+00	2.23E+00	6.69E-01	1.64E+00	8.23E+01
average of values:	8.87	0.982							
sum of values:			2.49E+01	2.19E+00	4.03E+02	5.04E+01	3.96E+03	5.54E+02	1.22E+03

Table D.4. Data for Calculating Confidence Limits for Forward Rate in LRM-4 Tests

	ss Si (X)	Rate (Y)	Y^2	$(Y - \bar{Y})^2$	$2XY$	$2Y$	X^2	$2X$	$(X - \bar{X})^2$
LRM-4-D	19.450	0.777	6.03E-01	6.03E-01	3.02E+01	1.55E+00	3.78E+02	3.89E+01	9.14E+01
LRM-4-E	10.694	0.948	8.98E-01	8.98E-01	2.03E+01	1.90E+00	1.14E+02	2.14E+01	6.48E-01
LRM-4-F	6.747	0.934	8.73E-01	8.73E-01	1.26E+01	1.87E+00	4.55E+01	1.35E+01	9.87E+00
LRM-4-G	6.595	1.060	1.12E+00	1.12E+00	1.40E+01	2.12E+00	4.35E+01	1.32E+01	1.09E+01
LRM-4-L	1.999	1.342	1.80E+00	1.80E+00	5.36E+00	2.68E+00	4.00E+00	4.00E+00	6.23E+01
LRM-4-I	3.018	1.007	1.01E+00	1.01E+00	6.08E+00	2.01E+00	9.11E+00	6.04E+00	4.72E+01
<i>average of values:</i>	<i>8.084</i>	<i>1.011</i>							
<i>sum of values:</i>			<i>6.312</i>	<i>6.312</i>	<i>88.511</i>	<i>12.135</i>	<i>594.784</i>	<i>97.006</i>	<i>222.247</i>

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