Designation: C 1662 – 07

Standard Practice for
For Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method[1]

This standard is issued under the fixed designation C 1662; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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 periods (for example, see Practice C 1174).

1.8 This practice must be performed in accordance with all quality assurance requirements for acceptance of the data.

1.9 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.10 *This standard does not purport to address all of the safety concerns, if any, 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:* [2]

C 92 Test Methods for Sieve Analysis and Water Content of Refractory Materials
C 169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass
C 429 Test Method for Sieve Analysis of Raw Materials for Glass Manufacture
C 693 Test Method for Density of Glass by Buoyancy
C 1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy
C 1174 Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste
C 1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste
C 1285 Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)
D 1129 Terminology Relating to Water
D 1193 Specification for Reagent Water
D 1293 Test Methods for pH of Water
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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[1] This practice is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.13 on Spent Fuel and High Level Waste.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3. Terminology

3.1

3.1.1 *alteration phase*, *n*—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*, *n*—reaction between dissolved components and the glass surface to reform bonds that are broken during glass dissolution.

3.1.3 *chemical durability*, *n*—the resistance of a glass to dissolution under particular test conditions.

3.1.4 *continuous flow*, *n*—the continual replacement of solution in the reaction cell with fresh test solution.

3.1.5 *control test*, *n*—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*, *n*—small particles of glass produced by mechanically fracturing larger pieces of glass.

3.1.7 *dissolution*, *n*—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*, *n*—the solution exiting the reaction cell.

3.1.9 *fines*, *n*—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*, *n*—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*, *adj*—measured by change in mass.

3.1.12 *high-purity water*, *n*—ASTM Type I or Type II water with a maximum total matter content including soluble silica of 0.1 g/m^3 and a minimal electrical resistivity of 16.67 MΩ•cm at 25°C (see Specification D 1193 and Terminology D 1129).

3.1.13 *influent solution*, *n*—the solution entering the reaction cell.

3.1.14 *intrinsic rate constant*, *n*—the component of the forward rate constant that depends only on the glass composition

3.1.15 *leached layer*, *n*—residual material at the glass surface from which some or all soluble components have been leached.

3.1.16 *leaching* , *n*—the preferential loss of soluble components from a material.

3.1.17 *mesh size fraction* , *n*—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.

3.1.18 *pulsed flow*, *n*—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.

3.1.19 *reaction cell*, *n*—the container in which the sample remains during the test.

3.1.20 *secondary phase*, *n*—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.

3.1.21 *single-pass flow-through test (SPFT)*, *n*—a test in which solution is flushed from the system after contacting the test specimen and is not recirculated through the reaction cell.

3.1.22 *steady-state*, *adj*—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.

3.1.23 *stoichiometric dissolution*, *n*—release of elements into solution in the same proportion that they are in the glass.

3.1.24 *test solution*, *n*—the solution entering the reaction cell.

4. Summary of Practice

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 Eq 1:

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

where Ci (i) is the steady-state concentration of component i measured in the effluent solution, Ci° is the background concentration of component i in the influent solution measured in a blank test, F is the solution flow rate, S° is the initial surface area of the glass sample that is exposed to solution, and fi 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 dissolution rate.

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, and so forth. 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. Procedure

6.1 Fig. 1a shows a block diagram for a generic SPFT test assembly. The components of the system include a solution reservoir, transport lines, a pump, a reaction cell, and a collection bottle. The test solution is pumped from a reservoir through a reaction cell that contains the sample by a peristaltic

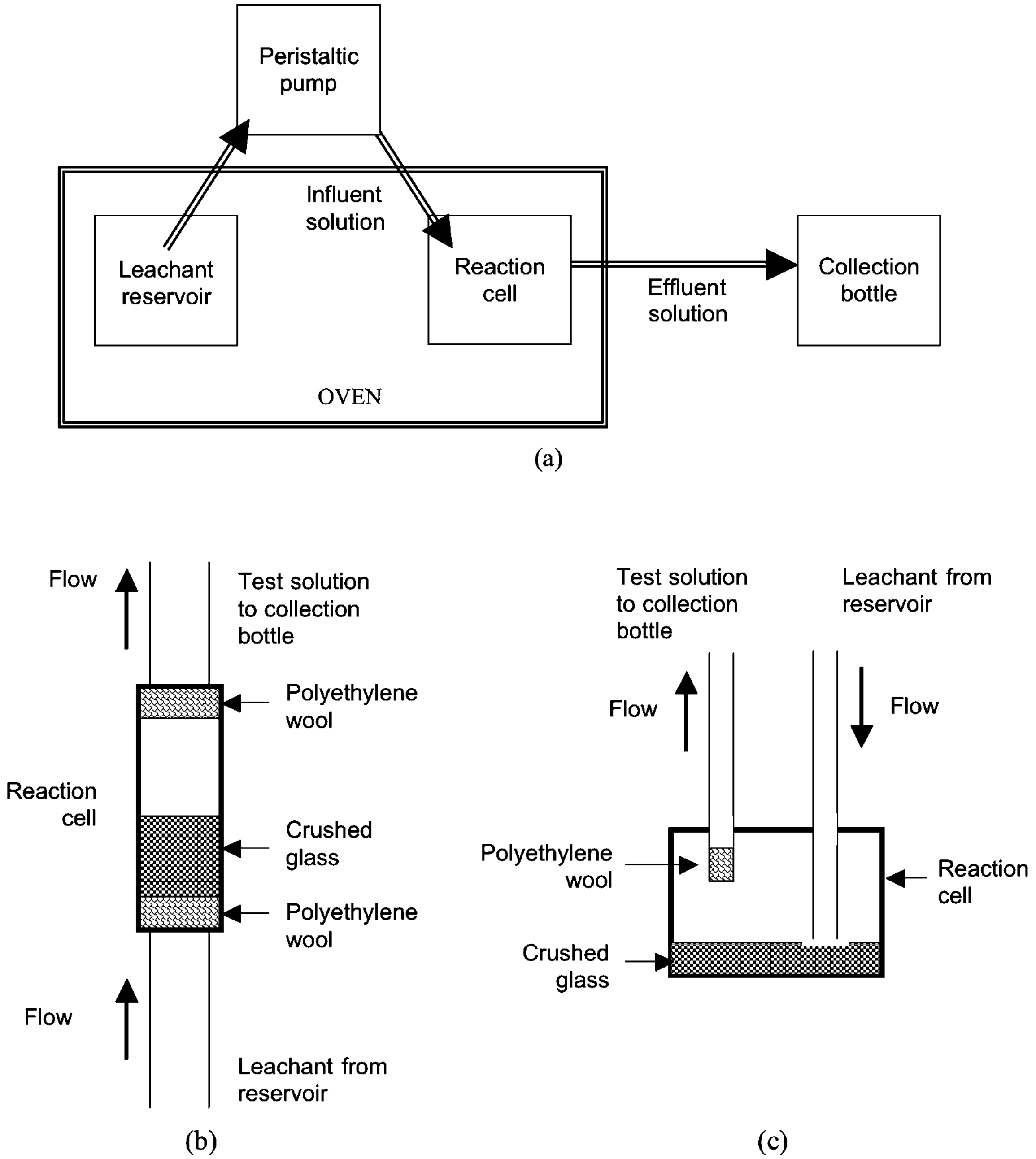

FIG. 1 (a) Schematic SPFT Design, (b) Basic Column Reactor Design and (c) Bottle Reactor Design.

pump or similar device. Depending on the temperature of interest, the reaction cell may be located in a constant temperature oven or water bath. The leachant in the reservoir can be heated to the test temperature in the same oven. As influent solution is pumped into the reaction cell, an equal volume of effluent solution will be displaced from the reaction cell. The effluent solution is sampled several times during the test 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. Separate tests are conducted at several flow rates and with several sample surface areas to measure the effect of the solution composition (primarily the dissolved silica concentration) on the measured glass dissolution rate.

6.2 Either column-type or bottle-type reaction cells can be used; these are shown schematically in Fig. 1. In the column cell design, the influent solution is pumped (usually upwards) through the crushed glass (or around a monolithic sample). In the bottle design, the influent solution is pumped into a cell filled with solution and displaces an equal volume of effluent solution. Polyethylene wool or an equivalent material can be used to prevent crushed glass particles from being flushed from the reaction cell during the test, or the effluent solution can be filtered after it is collected.

6.3 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 Test Method C 1285 (see Section 19 in C 1285; see also Test Methods 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 mass percent. The initial surface area can be calculated from the specific surface area and using the arithmetic average of the sizes of the sieve mesh and the density of the glass (see Appendix X1 in 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 represent the homogeneity of the glass 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 with different masses of glass or 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.

6.4 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 Test Method C 1220 (see Section 8 in 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.

6.5 The mass fractions of elemental silicon in the glass must be known to determine the glass dissolution rate (see also 9.4.5). This may be determined by direct analysis of the glass (see Test Method C 169) or based on the as-batched composition of the glass.

6.6 The flow rate of the solution through the reaction cell is calculated by dividing the mass of test solution 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. Samplings in which the flow rate differs by more than 10 % shall not be used in determining the steady-state concentrations for that test. The average flow rate measured in a test is used as the flow rate to calculate the glass dissolution rate in that test.

6.7 A small change in the solution 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. Changes in the solution concentrations of the elements of interest with subsequent samplings (that is, with reaction time) should be noted.

6.8 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 is to be used as background concentration for element i in tests with glass, that is, Ci^{o} in Eq 1. The solution from the control test is also used to confirm that neither the influent solution nor the effluent solution was contaminated due to interactions with the apparatus.

6.9 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.

6.9.1 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.

6.9.2 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.

6.9.3 The glass dissolution rate is expected to vary with the solution flow rate when the flow rate is between these extreme values.

6.10 To determine the forward dissolution rate, tests 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 (a dissolved silica concentration of zero) to determine the forward glass dissolution rate.

6.11 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 test solution should not interact with the apparatus. 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 of the solution needed to complete the control test and the tests with glass. Solutions may be purged with an inert gas (such as N_2) to mitigate against the effects of dissolved gases during the test (such as drift in pH due to the uptake of CO_2). The solution reservoir may be placed in an oven set at or near the test temperature so gases that exsolve and form the solution as it is heated are retained within the solution reservoir. The reservoir can be placed in the same oven or water bath used for the reaction cell.

7.3 The mechanism for transferring the solution from the reservoir to the reaction cell (that is, 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 remain within 1 °C of 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 (that is, 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 and recorded at the beginning and end of the test. It is recommended that the temperature be recorded prior to each sampling of the test solution.

7.6 For bottle type reaction cells, influent 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.

7.6.1 For tests at low flow rates and low temperatures, an inert magnetic stirring bar can be used. However, it must be situated such that it does not contact the glass.

7.7 Effluent solution shall be collected as soon as possible after it exits the reaction cell to minimize the time difference between when the solution was in the cell and when it is collected. Separate aliquots shall be collected for measurement of the solution pH and the dissolved glass components.

7.7.1 Effluent solution exiting the system during the first day of the test or prior to the first system volume exchange 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 1 h after the aliquot is collected to minimize effects of dissolved carbon dioxide. The aliquot used to measure the pH may be sparged with an inert gas if the influent solution was sparged.

7.7.3 Aliquots of effluent 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 and 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 measured solution concentrations.

7.8 The system shall be airtight to prevent the formation of air bubbles. Outgassing of the solution during the test can be minimized by maintaining the solution reservoir at or near the test temperature, so that most exsolved gases collect in the reservoir rather than in the pump line or reaction cell. An air trap may be incorporated into the influent line.

7.9 The length of the transfer line exiting the reaction cell shall be as short as possible to minimize the delay in collecting the solution after it exits the reaction cell.

7.10 Polypropylene or quartz wool may be used to prevent crushed glass from being flushed out of the reaction cell; the same material 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. This can be accomplished using a Teflon screen support.

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^o (see 8 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 HNO_3), 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/m^3).

8.2.6 Calculate the flow rate (m^3/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 8.2.2-8.2.7 as necessary to achieve desired flow rate.

8.2.8 The final volume of effluent solution may be retained for analysis and used to determine background concentrations in lieu of a control test.

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 HNO_3), 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 1 h of the aliquot being collected (see Test Method D 1293 regarding measurement of solution pH). Aliquots for additional analyses, e.g, for analysis of anions, can be collected separately or taken from this aliquot.

8.3.5 Record the date and time that the aliquot collection was started.

8.3.6 Determine and record the duration, in seconds, that the effluent sample for element analysis was collected.

8.3.7 Determine and record the mass of effluent solution that was collected for element analysis and the bottle tare mass.

8.3.8 Calculate and record the mass of effluent by subtracting the bottle tare from the total mass.

8.3.9 Calculate and record the volume of effluent for element analysis collected by dividing the mass of effluent solution by the density of the solution.

8.3.10 Calculate and record the flow rate (m^3/s) by dividing the volume of the effluent that was collected by the duration of its collection.

8.3.11 If the calculated flow rate deviates by more than 10 % from the target flow rate, adjust the pump speed and record new pump setting.

8.3.12 If particulate material is observed or suspected, the solution collected for analysis must 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 precipitate from the test solution, determine if and how the measured glass dissolution rate is expected to be affected.

8.3.13 Acidify the effluent that was collected for element analysis by adding 3 to 5 drops of ultrapure concentrated nitric acid.

8.3.14 Determine and record new total mass of aliquot.

8.3.15 Record the temperature of the reaction cell.

8.3.16 Repeat 8.3.3-8.3.14 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 HNO_3) 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 HNO_3) to flush the system with at least three system volumes.

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 A sample of the effluent can be collected in a clean solution bottle when the flush with the nitric acid solution is started for composition analysis. This may be done to verify that the component used to calculate the glass dissolution rate does not become fixed on the apparatus during the test.

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 (see Practice C 1109).

9. Data Analysis

9.1 *Calculate the initial surface area of crushed glass in the reaction cell (S^o)*—The surface area of a crushed sample 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 Test Method C 693 for measurement of density) is:

$$S_p = \frac{6}{\rho \times d} \tag{2}$$

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, $d = 3.38 \times 10^{-4}$ m. If the density of the glass is 2500 kg/m^3, the specific surface area is $S_p = 6 \div (2500 \text{ kg/m}^3 \times 3.38 \times 10^{-4} \text{ m}) = 7.10$ m^2/kg. If 0.0005 kg of glass is used in the test, the initial surface area is $S^o = 0.0005 \text{ kg} \times 7.10 \text{ m}^2\text{/kg} = 3.55 \times 10^{-3} \text{ m}^2$.

9.2 *Calculate the initial surface area of monolith sample in the reaction cell (S^o)*—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 by the time it was collected. 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, a test solution is collected for 1 h, 25 min (which is 510 s) and the mass of the solution bottle with test solution is 26.01 g. If the mass of an empty solution bottle is 7.46 g, the mass of solution is (26.01 – 7.46) = 18.55 g. If the density of the solution is 1000 kg/m^3(1.000 g/mL), the volume of solution collected is 18.55 mL. The flow rate is calculated to be 18.55 mL/510 s = 3.64×10^{-3} mL/s (which is 3.64×10^{-9} m^3/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 Eq 1. (A sample determination of the dissolution rate is included in Annex A1.) Selection of the glass components used to track the dissolution rate should consider abundance, solubility, structural role, and release mechanism. Boron and silicon are commonly used to track dissolution of borosilicate glasses. The use of alkali metals is not recommended because they may be released faster than dissolution of the glass matrix under some test conditions, since 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 element *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):

$$\text{flow rate, m}^3\text{/s} = \text{mass collected, kg/}(1000 \text{ kg/m}^3 \cdot t\text{, s}) \tag{3}$$

9.4.3 Plot [*i*] versus time or aliquot number. 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 element *i* with time (or aliquot number) may be an indication that the glass is dissolving fast enough 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 (that is, alkali metals and boron) be monitored. Differences in the rates calculated using different elements may provide added insight to the dissolution mechanism, for example, whether dissolution nonstoichiometric under the particular test conditions. (This may be confirmed by examination of the reacted solids at the end of the test.) Elements present in high concentrations in the leachant solution (that is, 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^o, C_{Si}, $C_i - C_i^o$, and the calculated rate for each test in the test series.

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

9.4.8 If the data plotted in 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, that is, 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 can be calculated using the forward glass dissolution rates measured at various temperatures and pH values in a mechanistic rate expression such as that given in Eq 4:

$$rate = k_0 \cdot 10^{\eta pH} \cdot exp\left(\frac{-E_a}{RT}\right) \cdot \left(1 - \frac{Q}{K}\right) \tag{4}$$

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 *Ea* can be determined by regressing data in a plot of log rate versus pH at the various temperatures, if it is assumed that the value of η is independent of temperature and the value of *Ea* is independent of pH.

9.5.2 Note that different values of η and *Ea* may be appropriate for acidic and alkaline solutions for some glasses. For many glasses, the pH dependence 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:

$$log\ k_0 = log\ rate - \eta \cdot pH + \frac{E_a}{2.303\ RT} \tag{5}$$

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 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, since the 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.

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 known[3].

10.4 *Interactions Between Solution and the Apparatus*—It must be verified that the solution has not become contaminated through interactions with the apparatus. This can be evaluated by analyzing the aliquot of test solution collected during the pretest flush of the apparatus in 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 (that is, 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 pretest cleaning of the apparatus immediately after the test in question, see 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 in the line between the reservoir and the reaction cell. The formation of bubbles in the tubing or reaction cell can 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 generally proceed faster than the 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 both too high. To reduce the likelihood of fines being collected, the test solution should not be sampled to determine the steady-state concentrations until an amount of solution equal to the system volume has flowed to flush fines from the sample and apparatus (see 8.3.2). The time required to flush fines from the reaction cell will depend on the flow rate.

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[3] L. A. Currie, "Limits for Qualitative Detection and Quantitative Determination," Analytical Chemistry 40, pp. 586 – 593 (1968).

10.11 *Selection of Solutions*—The influent 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 Specification 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 1. Buffer solutions must be prepared with water that meets the requirements of ASTM Type I water (see Specification D 1193). Buffers should be selected to avoid strong complexants and solutes known to affect the dissolution rate. Glass components that are also components 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.

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^{o}, 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 An interlaboratory study (see E 691) was conducted to measure the precision with which the test method described in this practice can be conducted[4]. In that study, tests were conducted by seven participants to measure the dissolution rate of a borosilicate glass (LRM glass) at 70 ºC in a LiOH/LiCl solution having a pH that is near 11 at room temperature and assumed to be near 10 at 70 ºC. The LRM glass was developed as a standard test material and has been used in previous interlaboratory studies[5], [6]. In the interlaboratory study, one participant (Participant A) conducted three series of tests from which the forward dissolution rates were determined to be 1.25, 1.29, and 1.35 g/(m^{2}d). This provides a measure of the intralaboratory precision (repeatability) of 1.29 ± 0.39 g/(m^{2}d) at the 95 % confidence level. The results of two participants (Participants B and C) were not sufficient to determine forward dissolution rates. The rates determined from the data sets provided by Participants D, E, F, and G were 1.75, 1.14, 1.36, and 1.91 g/(m^{2}d), respectively. The forward rate determined from the combined results of Participants A, D, E, F, and G was 1.64 g/(m^{2}d) with an estimated uncertainty of 0.90 g/(m^{2}d). This gives a measure of the interlaboratory precision (reproducibility) of 1.64 ± 1.80 g/(m^{2}d) at the 95% confidence level.

12.2 The precision of the rates measured in the interlaboratory study did not include the uncertainty in the surface area of the crushed glass. A geometric approximation was used to calculate the glass surface area[4]. Subsequent tests were conducted with LRM glass following Test Method C 1220 at the same temperature and using the same leachant composition that was used in the interlaboratory study[7]. Those tests were conducted with monolithic specimens having measured geometric surface areas. The forward dissolution rate determined from those test results was 1.67 g/(m^{2}d). The excellent agreement between the forward dissolution rates measured in the SPFT tests with crushed glass and in the C 1220 tests with

TABLE 1 Compositions of pH Buffer Solutions

Composition	Ionic Strength	20 °C	40 °C	70 °C	90 °C
0.005 m Potassium hydrogen phthalate + 0.004	0.0132	5.92	5.91	5.90	5.89
0.005 m H_3BO_3 + 0.0003 m LiOH	0.0003	8.06	7.91	7.71	7.62
0.005 m H_3BO_3 + 0.0020 m LiOH	0.0019	9.07	8.91	8.70	8.59
0,005 mm H_3BO_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

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[4] W. L. Ebert, Interlaboratory Study of the Reproducibility of the Single-Pass Flow-Through Test Method: Measuring the Dissolution Rate of LRM Glass at 70 ºC and pH 10, Argonne National Laboratory report ANL-05/33 (2005).

[5] W. L. Ebert and S. F. Wolf, "An Interlaboratory Study of a Standard Glass for Acceptance Testing of Low-Activity Waste Glass," *Journal of Nuclear Materials* Vol. 282, pp. 112 – 124 (2000).

[6] Samples of LRM glass are available for use in SPFT test to compare results with the interlaboratory study; contact ASTM.

[7] W. L. Ebert, Comparison of the Results of Short-Term Static Tests and Single-Pass Flow-Through Tests with LRM Glass, Argonne National Laboratory report ANL-06/51 (2006).

monolithic specimens gives confidence in the surface area calculated for the crushed glass. It also indicates that negligible bias is introduced in the SPFT test method by using crushed glass.

13. Keywords

13.1 glass dissolution rate

ANNEX

(Mandatory Information)

A1. Sample Calculations

A1.1 Example of Dissolution Rate Calculation

A1.1.1 As an example, consider the fictitious set of results in Tables A1.1 and A1.2. Table A1 gives the results of 13 samplings in Test 4, which was conducted with a sample of glass having a surface area of 0.0210 m^{2}and at a flow rate of 3.61 × 10^{-9} m^3/s. The $F/S°$ ratio is 1.72 × 10^{-7} m/s. 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_{Si} = 0.2533 kg(Si)/kg(glass) for this example, and the background concentration of silicon in the solution used in all tests is $C_{Si}°$= 0.157 kg/m^3. The steady-state silicon concentration is determined from a plot of C_{Si} versus time, which is shown in Fig. A1.1 for Test 4. For Test 4, the steady-state silicon concentration is 13.8 mg/L, which is the mean concentration of the data points in Fig. A1.1. (The relative standard deviation for these 13 data points is 7.4 %.) The glass dissolution rate in Test 4 is calculated as:

$$rate\,\frac{g}{m^2 s} = (C^i - C^{i\circ})\,\frac{mg}{L}\cdot\left(\frac{1g}{1000\,mg}\right)\cdot\left(\frac{1000\,L}{m^3}\right)\cdot\left(\frac{F}{S^\circ}\right)\frac{m}{s}/f_i \tag{A1.1}$$

$$= (13.8 - 0.157)\,\frac{mg}{L}\cdot\left(\frac{1g}{1000\,mg}\right)\cdot\left(\frac{1000\,L}{m^3}\cdot(1.72\times 10^{-7})\,\frac{m}{s}/0.2533\right.$$

$$= 9.04 \times 10^{-6}\ g/(m^2 s) \tag{A1.2}$$

Similar calculations for the dissolution rates in tests at other $F/S°$ values are summarized in Table A1.2. The rates are plotted against the steady state silicon concentrations (C_i) in Fig. A1.2. Uncertainty bars are drawn at 13 % for the rate and 10 % for the Si concentration to represent analytical uncertainties. Linear regression is used to determine the y-intercept, which is the forward glass dissolution rate. The rate measured in Test 1 was excluded from the regression as an outlier. The y-intercept of the regression line fit to the remaining rates is 1.44 × 10^{-5} g/(m^2 • s), which is 1.24 g/(m^2 • d). This is the forward dissolution rate at this particular test temperature and pH (the average pH for the eight tests included in the regression is 11.22). The uncertainty in the forward rate includes uncertainty in the measured rates and in the regression. Note that while the background-corrected silicon concentrations were used to calculate the amount of glass dissolved in each test, the total silicon concentration is used to extrapolate the rates to zero silicon concentration. This is because the rate is affected by all of the silicon present in the solution contacting the glass, not only the silicon that was released from the glass.

A1.2 Example of Surface Area Calculation

A1.2.1 A test with 0.0005 kg of –40 +60 mesh glass (3.59 × 10^{-3} m^2 initial glass surface area) was run 1.5 × 10^5 s. The forward dissolution rate was 2.0 × 10^{-10} kg/(m^2 • s), so 1.08 × 10^{-7} 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

$$S_f = \left\{\frac{6}{\rho\cdot d_o}\right\}\cdot m_o^{\frac{1}{3}}\cdot m_f^{\frac{2}{3}} \tag{A1.3}$$

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, ρ = 2500 kg/m^3, d_o = 3.38 × 10^{-4} m, m_o = 0.0005 kg, and m_f = 0.00049989 kg. Solving Eq A3 with these values gives:

$$S_f = \left\{\frac{6}{2.500\times 10^6\ g/m^3\cdot 3.38\times 10^{-4}\ m}\right\}\cdot(5\times 10^{-4})^{1/3}\cdot(4.9989$$
$$\times 10^{-4})^{2/3}$$
$$= 3.55\times 10^{-3}\ m^2 \tag{A1.4}$$

TABLE A1.1 Fictitious SPFT Test Results for Test 4

Aliquot No.	pH	[Si], kg/m^3	Flow Rate, m^3/s
1	11.07	13.9	3.64 × 10^{-6}
2	11.21	12.5	3.58 × 10^{-6}
3	11.26	13.7	3.60 × 10^{-6}
4	11.29	13.0	3.62 × 10^{-6}
5	11.27	12.9	3.60 × 10^{-6}
6	11.20	13.4	3.61 × 10^{-6}
7	11.17	11.5	3.60 × 10^{-6}
8	11.27	13.7	3.58 × 10^{-6}
9	11.20	13.4	3.62 × 10^{-6}
10	11.22	15.6	3.59 × 10^{-6}
11	11.20	18.3	3.62 × 10^{-6}
12	11.27	17.4	3.57 × 10^{-6}
13	11.22	17.5	3.59 × 10^{-6}

TABLE A1.2 Fictitious SPFT Test Results

Test No.	F/S°, m/s	pH	C_{Si}, kg/m^3	$C_{Si} - C_{Si}°$, kg/m^3	Rate, g/m^2 · s)
1	1.87 × 10	11.19	9.46	9.31	6.88×10^{-6}
2	3.86 × 10	11.06	24.7	24.5	3.73×10^{-6}
3	7.80 × 10	11.12	18.9	18.8	5.78×10^{-6}
4	1.72 × 10	11.22	13.8	13.3	9.04×10^{-6}
5	2.63 × 10	11.25	9.79	9.64	1.00×10^{-5}
6	3.13 × 10	11.27	8.77	8.61	1.06×10^{-5}
7	5.25 × 10	11.26	6.10	5.95	1.23×10^{-5}
8	6.46 × 10	11.29	4.47	4.31	1.10×10^{-5}
9	8.67 × 10	11.28	4.07	3.92	1.34×10^{-5}

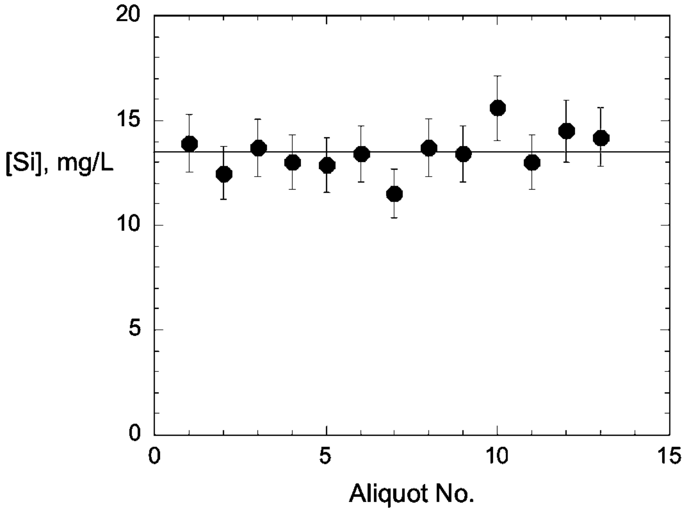

FIG. A1.1 Plot of Measured Concentrations of Si for Samplings in Tests No. 4.

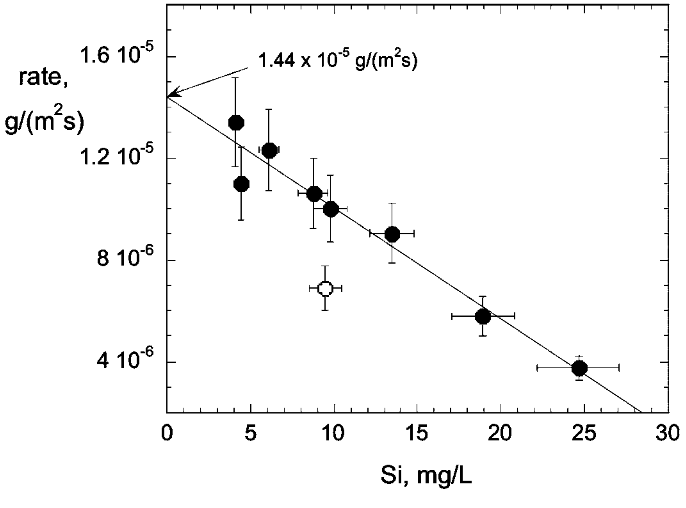

FIG. A1.2 Plot of Glass Dissolution Rate (calculated from the silicon concentration) versus Steady- State Silicon Concentration.

The final surface area is 98.9 % of the initial surface area. In this example, the change in surface area during the test is insignificant compared to the uncertainty in the steady state concentrations used to calculate the dissolution rates.

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