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Standard Practice for For Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method¹

This standard is issued under the fixed designation C1662; 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 C1174).

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

C92 Test Methods for Sieve Analysis and Water Content of Refractory Materials

C169 Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass

C429 Test Method for Sieve Analysis of Raw Materials for Glass Manufacture

C693 Test Method for Density of Glass by Buoyancy

C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy

C1174 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

C1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste

C1285 Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase

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.

Glass Ceramics: The Product Consistency Test (PCT)

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1293 Test Methods for pH of Water

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1

3.1 Definitions:

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 *finer, 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/m³ and a minimal electrical resistivity of 16.67 MΩ•cm at 25°C (see Specification D1193 and Terminology D1129).

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 $C_i(i)$ is the steady-state concentration of component *i* measured in the effluent solution, C_i° is the background

concentration of component i in the 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 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 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 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 C1285 (see Section 19 in C1285; see also Test Methods C92 and C429 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 C1285). 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 C1220 (see Section 8 in C1220). 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 C169) 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

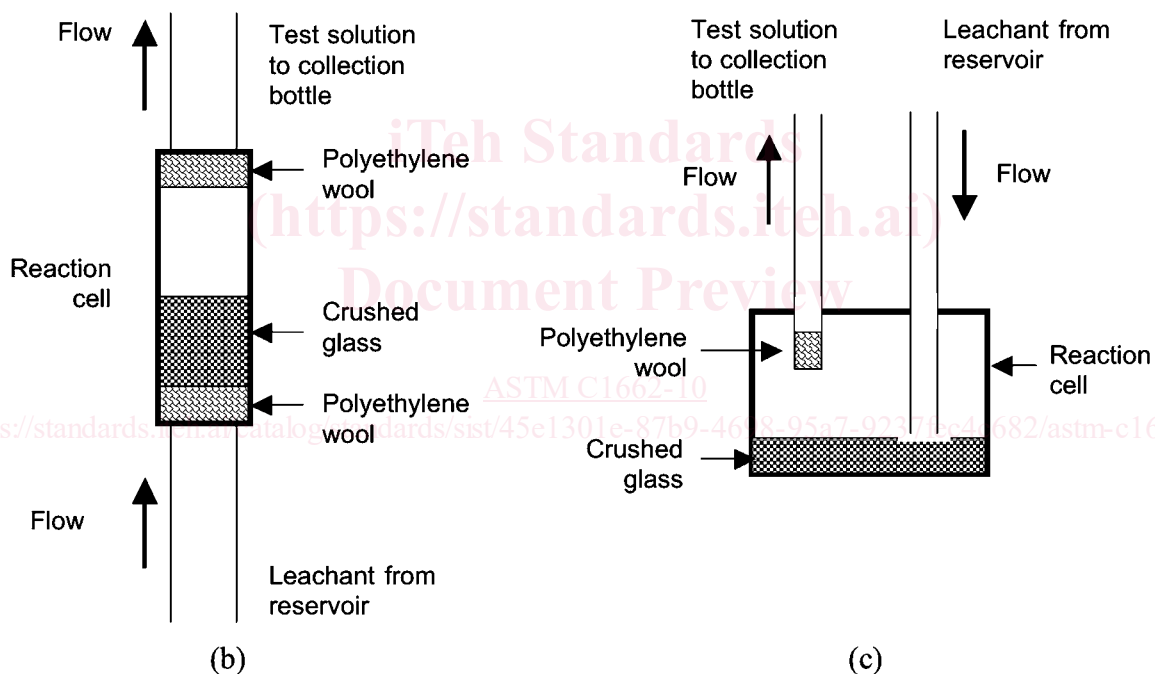
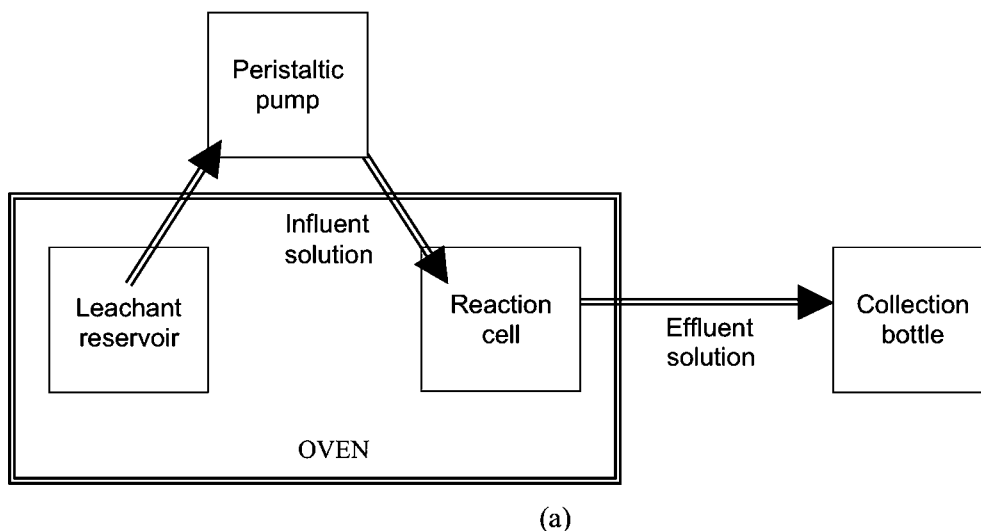


FIG. 1 (a) Schematic SPFT Design, (b) Basic Column Reactor Design and (c) Bottle Reactor Design.

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, C_i^0 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 An upper threshold 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. The value of the threshold flow rate depends on the glass dissolution rate and surface area in the test.

6.9.2 A lower threshold 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. The value of the threshold flow rate depends on the glass dissolution rate and surface area in the test.

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.~~

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6.10.1 Because the total amount of silica (or other selected component) in the effluent is used to represent the amount of glass that has dissolved, the effluent solutions are not filtered prior to analysis unless contaminants are observed in the solution. This is because the silica present in any colloidal or precipitated material that is removed by filtration represents dissolved glass.

6.10.2 If particulates of glass have been flushed out of the reaction cell and collected with the effluent solution, that sample should be discarded and the test terminated. Previous solutions are suspected of containing glass particles, even if none were seen, and the test results should be discarded. The test apparatus should be inspected and repaired to prevent the loss of glass particles in subsequent tests.

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 N₂) to mitigate against the effects of dissolved gases during the test (such as drift in pH due to the uptake of CO₂). 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-(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 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 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 1 h of the aliquot being collected (see Test Method D1293 regarding measurement of solution pH). Aliquots for additional analyses, e.g., for example, 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.