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# Standard Test Method for Measurement of Glass Dissolution Rate Using Stirred Dilute Reactor Conditions on Monolithic Samples<sup>1</sup>

This standard is issued under the fixed designation C1926; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes a test method in which the dissolution rate of a homogenous silicate glass is measured through corrosion of monolithic samples in stirred dilute conditions.

1.2 Although the test method was designed for simulated nuclear waste glass compositions per Guide C1174, the method is applicable to glass compositions for other applications including, but not limited to, display glass, pharmaceutical glass, bioglass, and container glass compositions.

1.3 Various test solutions can be used at temperatures less than 100 °C. While the durability of the glass can be impacted by dissolving species from the glass, and thus the test can be conducted in dilute conditions or concentrated condition to determine the impact of such species, care must be taken to avoid, acknowledge, or account for the production of alteration layers which may confound the step height measurements.

1.4 The dissolution rate measured by this test is, by design, an average of all corrosion that occurs during the test. In dilute conditions, glass is assumed to dissolve congruently and the dissolution rate is assumed to be constant.

1.5 Tests are carried out via the placement of the monolithic samples in a large well-mixed volume of solution, achieving a high volume to surface area ratio resulting in dilute conditions with agitation of the solution.

1.6 This test method excludes test methods using powdered glass samples, or in which the reactor solution saturates with time. Glass fibers may be used without a mask if the diameter is known to high accuracy before the test.

1.7 Tests may be conducted with ASTM Type I water (see Specification D1193 and Terminology D1129), buffered water or other chemical solutions, simulated or actual groundwaters, biofluids, or other dissolving solutions.

1.8 Tests are conducted with monolithic glass samples with at least a single flat face. Although having two plane-parallel

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faces is helpful for certain step height measurements, it is not required. The geometric dimensions of the monolith are not required to be known. The reacted monolithic sample is to be analyzed following the reaction to measure a corroded depth to determine dissolution rate.

1.9 Tests may be performed with radioactive samples. However, safety concerns working with radionuclides are not addressed in this test method.

1.10 Data from these tests can be used to determine the value of kinetic rate model parameters needed to predict glass corrosion behavior over long periods of time. For an example, see Practice C1662, section 9.5.

1.11 This test method must be performed in accordance with all quality assurance requirements for acceptance of the data.

1.12 *Units*—The values stated in SI units are regarded as the standard. Any values given in parentheses are for information only.

1.13 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.14 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

C693 Test Method for Density of Glass by Buoyancy

C859 Terminology Relating to Nuclear Materials

C1174 Guide for Evaluation of Long-Term Behavior of Materials Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste

<sup>2</sup> 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.

- C1220** Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste  
**C1662** Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method  
**D859** Test Method for Silica in Water  
**D1129** Terminology Relating to Water  
**D1193** Specification for Reagent Water  
**D1293** Test Methods for pH of Water  
**D7778** Guide for Conducting an Interlaboratory Study to Determine the Precision of a Test Method  
**E177** Practice for Use of the Terms Precision and Bias in ASTM Test Methods  
**E691** Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 3. Terminology

#### 3.1 Definitions:

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

3.1.2 *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 condensation reactions.

3.1.3 *glass coupon, n*—a mechanically sectioned monolith of glass containing at least one flat surface; the flat surface should be polished to a finish of 3000 nm or better.

3.1.4 *gravimetric, adj*—measured by change in mass.

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

3.1.6 *reaction vessel, n*—a sealed container made of an inert material containing the contacting solution and glass sample.

3.1.7 *step height, n*—the difference in height between an un-corroded portion of a glass monolith sample and the bulk corroded surface.

3.1.8 *test solution, n*—the solution contacting the glass during the experiment.

3.2 Definitions not listed here can be found in Terminology **C859**.

### 4. Summary of Test Method

4.1 Based on Test Method **C1220**, Practice **C1662**, and the work of Icenhower and Steefel (2015) (**1**)<sup>3</sup>, monolithic glass specimens are contacted by a solution by suspending the glass coupon in a well-agitated reaction vessel at a low surface area to volume ratio, to maintain dilute conditions. A portion of the glass coupon surface is masked with an inert material during the solution exposure. Following the exposure, the inert material is removed from the surface or accounted for in the height measurement. The height difference between the protected, un-corroded surface and the receded corroded surface is then measured. This step height is used to calculate the dissolution rate of the glass by using Eq 1:

$$rate = \frac{h \times p}{t} \quad (1)$$

<sup>3</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

where:

*rate* = dissolution rate of the glass, g/m<sup>2</sup>·d,

*h* = depth of surface recession, m,

*p* = density of the glass (that is, by Test Method **C693**), g/m<sup>3</sup>, and

*t* = experimental duration in days, d.

4.2 The step height measurements are to be collected from samples where the dilution of species dissolving from the glass remain at concentration below which they can impact the dissolution of the glass. In doing so, the forward glass dissolution rate at infinite dilution can be determined.

### 5. Significance and Use

5.1 This test method provides a description of the design of the Stirred Reactor Coupon Analysis (SRCA) apparatus and identifies aspects of the performance of the SRCA tests and interpretation of the test results that must be addressed by the experimenter to provide confidence in the measured dissolution rate.

5.2 The SRCA methods described in this test method can be used to characterize several aspects of glass corrosion that can be included in mechanistic models of long-term durability of glasses, including nuclear waste glasses.

5.3 Depending on the test parameters investigated, the SRCA results can be used to measure the intrinsic dilute glass dissolution rate, as well as the effects of conditions such as temperature, pH, and solution chemistry on the dissolution rate.

5.4 Due to the scalable nature of the method, it is particularly applicable to studies of the impact of glass composition on dilute-condition corrosion. Models of glass behavior can be parameterized by testing glass composition matrices and establishing quantitative structure-property relationships.

5.5 The step heights present on the corroded sample can be measured by a variety of techniques including profilometry (optical or stylus), atomic force microscopy, interferometry or other techniques capable of determining relative depths on a sample surface. The sample can also be interrogated with other techniques such as scanning electron microscopy to characterize the corrosion behavior. These further analyses can determine if the sample corroded homogeneously and possible formation of secondary phases or leached layers. Occurrence of these features may impact the accuracy of glass dissolution. This test method does not address these solid-state characterizations.

### 6. Procedure

#### 6.1 Sample Preparation:

6.1.1 Monolithic glass samples are used in SRCA testing and require at least one flat face for surface recession measurements. The dimensions and shape of the monolith are irrelevant, although it must be able to fit through the sample ports of the reaction vessel. A coupon size of ~15 mm by 5 mm by 2 mm has been found to be convenient for the example vessel shown in Fig. 1.

6.1.2 The surface finish of the flat face(s) of the monolith is important and should be polished to ensure that the surface

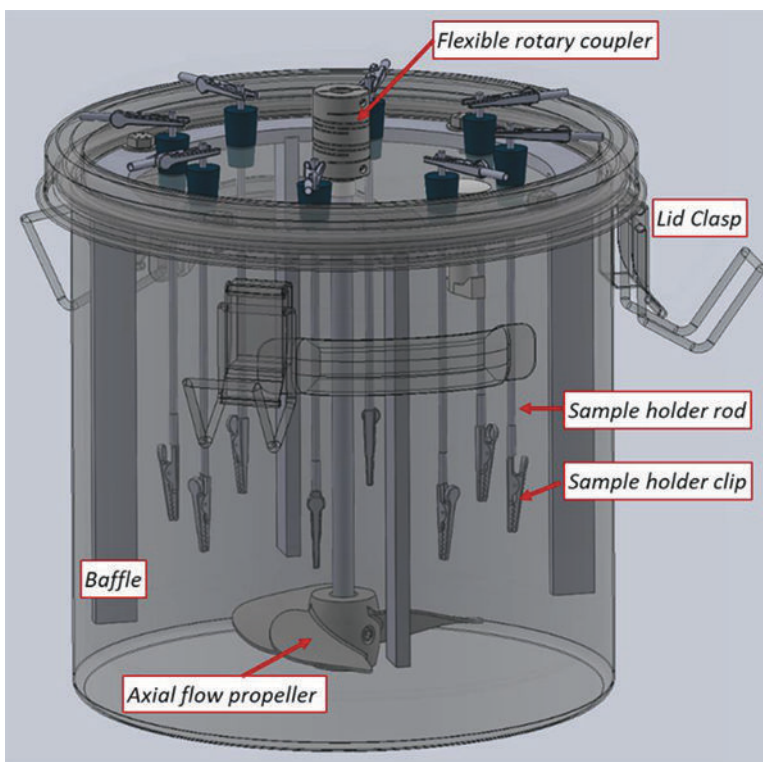


FIG. 1 Schematic of the Dilute Reactor SRCA Design used for Round Robin Testing

recession will not be hidden within the polishing lines. A final polish of  $3\ \mu\text{m}$  or better is recommended. The procedure for polishing the monolith samples shall be documented with the tests. An example preparation procedure for monolithic glass samples is given in Test Method C1220.

6.1.3 Following polishing of the face, a mask will be applied to the flat surface of the monolith. The mask shall be made of an inert material and is used to protect the area below the mask from dissolution. Suggested masks include room temperature vulcanizing silicone and sputter deposited chromium metal. Before use of a mask material, a control test to determine the stability of the mask material in the solution of interest shall be performed and documented.

6.1.3.1 When using a removable mask material, such as silicone, post-reaction treatment of the masked area shall be consistent. The mask shall be removed manually to expose the protected surface. Additional cleaning of the protected area may be required to remove any residual mask material. For example, isopropyl or ethyl alcohol with agitation from a cotton swab has been shown to be sufficient for removing residual silicone.

6.1.3.2 For use of more permanent masking materials, such as sputtered Cr, no post reaction treatment is required. The mask will remain undisturbed during the test and can be analyzed as is. The thickness of such films should be documented and subtracted from the analyzed step height.

6.1.4 If a leached layer is observed on the monolith following the reaction, the impact of such a layer on glass dissolution should be investigated.

## 6.2 Dilute Condition Reactor:

6.2.1 In order for forward rate conditions to be present, the contacting solution for the monolithic glass sample must be representative of an infinitely dilute solution. Fig. 1 shows a schematic of a dilute reactor SRCA design. Alternative designs that achieve a dilute, well-mixed condition can be used as well. 7.1 and Annex A1 should be used to guide reactor design.

6.2.2 A reservoir of solution is contained within an appropriately sized vessel made of an inert material (example: polytetrafluoroethylene (PTFE) or stainless steel). The monolithic glass samples are then suspended within the vessel. The vessel can be placed within an oven or water bath to attain steady temperature within the vessel.

6.2.3 Preparation of the monolith samples shall be performed using the steps outlined in 6.1.

6.2.4 The volume of solution to use should be determined based on the resulting concentration of species that can influence glass dissolution if the entire inventory of glass in the reactor were to dissolve. A ratio of glass surface area  $5\ \text{cm}^2$  to 1 L of solution is recommended. A resulting concentration of  $<1\ \text{ppm Si}$  if the entire glass inventory dissolved is recommended.

6.2.5 An aliquot may be collected from the dilute reaction vessel at the conclusion of each test for measurement to ensure chemical concentrations remained at dilute conditions.

## 7. Requirements of the Apparatus

### 7.1 Requirements for SRCA Vessel Design:

7.1.1 It is important to use a vessel that maintains dilute and well mixed solution conditions. It is also important that the solution not interact with the vessel. Examples of inert vessel



materials may include polypropylene, polytetrafluoroethylene (PTFE), or stainless steel, but the vessel material should be chosen to be inert with respect to the individual solution/glass combination to be tested and to remain stable at the desired test temperature.

7.1.2 The solution volume should be such that at least 1 L of solution will be present for every 5 cm<sup>2</sup> of exposed glass surface area for all samples. An exact measurement is not required, with conservatism suggested to ensure that the limit is not reached. The vessel size should be chosen such that with typical coupon sizes (15 mm by 5 mm by 2 mm), the volume required to fulfill the requirement can be safely contained with a reasonable head space to allow for safe handling of the vessel.

7.1.3 The vessel should be designed such that turbulent mixing is achieved. Mixing calculations to aid in this design are found in [Annex A1](#).

## 7.2 Requirements for Test Solution and Monitoring:

7.2.1 Although the instructions here are targeted towards dilute aqueous systems, other fluids, such as groundwaters or biofluids, could conceivably be used. In all cases, the test solution should not interact with any part of the test apparatus, including sample hangers, baffles, and the mixing apparatus. If a change in material of the system components is made, a control test to ensure no interactions occur must be performed. Any interactions leading to a change in system material shall be documented.

7.2.2 It is important to note that the pH of the contacting solution is a highly impactful variable to the test. It is important that the pH of the solution at test temperature be well understood through testing or modeling, or both. Any inconsistency or drift in pH should be monitored or adjusted, or both, throughout the test.

7.2.3 It is recommended that the pH be monitored for a period of one day or for the expected test duration, whichever is shorter, to establish or correct any drift before test initiation. The solutions may be purged with an inert gas, such as N<sub>2</sub>, to prevent drifting of the pH due to ingress of CO<sub>2</sub>.

7.2.4 If a pH series is being done, it is recommended that the effect of any change in buffering agent over the series should be evaluated by performing measurements at the same pH with both buffering agents.

7.2.5 The temperature of the reaction vessel solution shall be measured and monitored with a thermocouple or similar device. Within a large oven, a representative solution in a separate vessel may be monitored if there are concerns about thermocouple materials interacting with the test solution. At a minimum, temperature should be recorded at the beginning of the test immediately before glass addition and at the conclusion of the test before removal of the glass samples. For longer tests, a daily temperature check regimen or online monitoring is suggested. Temperatures shall be within 2 °C of the desired temperature of the test throughout the duration.

7.2.6 Aliquots of solution collected for analysis shall be stored in sealed containers. If pH is to be measured per Test Methods [D1293](#), it shall be measured no later than 1 hour following collection.

7.2.7 The solution within the reaction vessel requires light agitation through use of an impeller, ensuring turbulent flow (Reynold's number > 10 000), but preventing vortex formation in the reactor to disturb any potential diffusion layers near the glass monolith surface.

7.2.8 At higher temperatures, evaporation of the solution is possible. It suggested that the solution level be monitored through manual observation. Suggested methods include comparing level to a known mark in the chamber, an inert dipstick, or the use of a sight tube. Lost solution can be replaced with ASTM Type I water. Unreplaced evaporation of >10 % of the original volume shall result in termination of the test.

## 8. Test Method

### 8.1 Stirred Reactor Test Protocol:

8.1.1 The reactor parts (vessel, baffles, sample holders, agitator), shall be cleaned by rinsing with dilute nitric acid (~0.1 mol/L) and demineralized water, in that order, before use.

8.1.2 Add the calculated volume of reaction solution to the reaction vessel.

8.1.3 Place reactor vessel in oven or water bath, if being used, to establish consistent temperature before glass sample introduction. Temperature shall be monitored by a thermocouple or other temperature recording device.

8.1.4 Begin agitation of the reaction vessel solution.

8.1.5 When the target temperature has been reached, measure solution pH (see Test Methods [D1293](#)).

8.1.6 Suspend the masked glass monolith samples in the reaction vessel solution with an inert rigid hanging system or placement on a rack made of inert material.

8.1.6.1 Monolithic glass samples are to be suspended such that 100 % of the surface to be investigated for height recession is exposed to the contacting solution. Attachment with a hanging design made of an inert material is recommended, [Fig. 1](#), but this can also be achieved by placement of the monolith on a rack made of inert material.

8.1.7 During testing, particularly for tests lasting longer than 2 days, the temperature and pH (see Test Methods [D1293](#)) of the contacting solution should be monitored on a regular basis. The pH should be measured with a recently calibrated pH meter on an aliquot of solution removed from the vessel and discarded following measurement to avoid any contamination from the pH meter. The aliquot can be cooled to room temperature to maintain a consistent baseline temperature for pH monitoring. If solution pH drifts, careful adjustment of the pH with the same buffer system is allowed.

8.1.8 It is important to acknowledge that the pH measurement taken at room temperature will differ from that at the testing temperature. Geochemical modeling or measuring the pH at test temperature can be used to establish the conditions in the vessel.

8.1.9 Following the set test time, measure solution pH (see Test Methods [D1293](#)) and remove the masked glass monolith sample. Treat sample according with [8.2](#). Removing subsets of the sample group and allowing the rest to continue is allowed, but the solution pH should be measured at each sample termination.

8.1.10 If re-use of the solution is desired, collect a sample of the reaction vessel solution and place into a clear, tared bottle labelled with the test identification information and submit for analysis (by ICP-OES or similar solution analysis technique) for crucial components such as Si (see Test Method D859) and Al. If ion concentrations are below a determined concentration, the solution inside the reaction vessel can be re-used for subsequent tests.

8.1.11 Properly dispose of reaction solution. Clean the vessel with rinses of dilute nitric acid followed by demineralized water.

8.2 Treatment of Glass Monolith Samples:

8.2.1 Remove the glass monolith from solution and immediately rinse three times with demineralized water. Shake to remove excess water between rinses. Next rinse the glass monolith three times with ethanol, shaking to remove excess between rinses.

8.2.2 Immediately following the ethanol rinse, place the glass monolith in an oven set between 20 °C and 50 °C to allow the ethanol to evaporate. This temperature is selected as to not alter any hydrated gel layers present on the glass monolith.

8.2.3 For a removable mask for which no baseline measurement was made before corrosion, manually remove the mask from the glass sample using tweezers or other method determined to not harm the glass sample or the step produced by corrosion. Solvents that are not expected to alter the sample specimen such as ethanol or acetone, are permitted, as is gentle wiping such as with a cotton swab.

8.2.4 For a mask which a baseline height measurement was taken, such as sputter deposited metal, visually inspect to ensure mask remained intact.

8.2.5 Analyze the step height which exists between the protected and corroded surfaces of the glass monolith. Techniques such as profilometry, atomic force microscopy, white light interferometry, or confocal laser microscopy are suggested for such measurements, depending on the depth resolution required. Microscopy of a sample cross section is another potential method, although care must be taken to avoid damage to the step during sample preparation.

8.2.6 Following step height analysis, the glass monolith sample can be polished again and used in further tests.

9. Calculation or Interpretation of Results

9.1 Calculations related to effluent collection and analyses are covered in Practice C1662, Section 9.

9.2 Determination of Glass Dissolution Rate from Step Height:

9.2.1 The dissolution rate is determined from the recession of the glass surface over a period of exposure using Eq 1. This method overcomes challenges in selecting proper element tracers for glass dissolution.

9.2.2 Tabulate the measured step heights of the samples (m) and the start time and sampling time of the monolithic sample.

9.2.3 Subtract the sampling time from the starting time to determine the duration of the test.

9.2.4 Determine the dissolution rate, in g/m<sup>2</sup> per unit time using Eq 1.

9.2.5 The intrinsic rate constant can be determined using Eq 2:

$$rate = k_0 \times 10^{\eta pH} \times \exp\left(-\frac{E_a}{RT}\right) \times \left(1 - \frac{Q}{K}\right) \quad (2)$$

where:

- $k_0$  = intrinsic rate constant,
- $\eta$  = pH dependence,
- $E_a$  = activation energy,
- $R$  = gas constant, and
- $T$  = absolute temperature.

9.2.5.1 The method of solving for the intrinsic rate constant are discussed in 9.5 of Practice C1662.

10. Possible Complications

10.1 Phase Separated Glasses—The dissolution rate measured for a phase separated glass may be incorrectly influenced by preferential dissolution of a single phase. Sections of the glass monolith would then recede farther than others, and if not observed before measurement lead to an incorrect step height. Imaging the protected:corroded interface at a lower magnification before step height measurement will aid in identifying such phase separation.

10.2 Alteration Layer Formation—Some glasses in some conditions may form alteration layers during testing. An example of this is given in Fig. 2, where alteration layers were seen on a zinc-bismuth-borate glass and a high-Al waste glass simulat after being tested concurrently with the round robin SRCA study (Ryan et al., 2022) (2). In both cases, the alteration layers were very fragile and powdery and were removed with the masks. The step height measurements were not affected by these layers.

10.2.1 Some step height measurement techniques may not be sensitive to the presence of particularly durable alteration

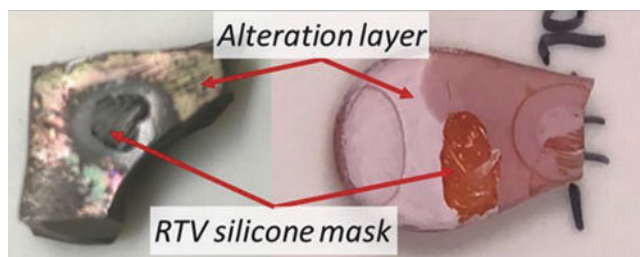


FIG. 2 Samples of a High-Al Simulated Waste Glass (Left) and a Zinc-Bismuth-Borate Glass (Right) that both Exhibited Delicate Alteration Layers After a SRCA Test