



Designation: C1220 – 17

# Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste<sup>1</sup>

This standard is issued under the fixed designation C1220; 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 provides a measure of the chemical durability of a simulated or radioactive monolithic waste form, such as a glass, ceramic, cement (grout), or cermet, in a test solution at temperatures  $<100^{\circ}\text{C}$  under low specimen surface-area-to-leachant volume (S/V) ratio conditions.

1.2 This test method can be used to characterize the dissolution or leaching behaviors of various simulated or radioactive waste forms in various leachants under the specific conditions of the test based on analysis of the test solution. Data from this test are used to calculate normalized elemental mass loss values from specimens exposed to aqueous solutions at temperatures  $<100^{\circ}\text{C}$ .

1.3 The test is conducted under static conditions in a constant solution volume and at a constant temperature. The reactivity of the test specimen is determined from the amounts of components released and accumulated in the solution over the test duration. A wide range of test conditions can be used to study material behavior, including various leachant composition, specimen surface area-to-leachant volume ratios, temperatures, and test durations.

1.4 Three leachant compositions and four reference test matrices of test conditions are recommended to characterize materials behavior and facilitate interlaboratory comparisons of tests results.

1.5 Specimen surfaces may become altered during this test. Although not part of the test method, it is recommended that these altered surface regions be examined to characterize chemical and physical changes due to the reaction of waste forms during static exposure to solutions.

1.6 This test method is not recommended for evaluating metallic materials, the degradation of which includes oxidation reactions that are not controlled by this test method.

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

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *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.* For a specific hazard statement, see 7.3.2.

1.10 *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>
- C859 Terminology Relating to Nuclear Materials
  - C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy
  - C1174 Practice for Evaluation of the Long-Term Behavior of Materials Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste
  - D1193 Specification for Reagent Water
  - D1293 Test Methods for pH of Water
- 2.2 *EPA Document:*<sup>3</sup>
- SW-846A Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

<sup>1</sup> This test method 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> SW846A, 3rd Ed., Revision 1, U.S. Environmental Protection Agency, Washington, DC, December 1987.

### 3. Terminology

3.1 Please refer to Terminology **C859** for additional terminology that may not be listed below.

#### 3.2 Definitions:

3.2.1 *accumulated dose, n*—the sum of the absorbed doses received by the system considered regardless of whether it is exposed to radiation in a continuous or discontinuous fashion.

3.2.2 *actinide, n*—any element with atomic number of 89 to 103.

3.2.3 *high-purity water, n*—purified water conforming with the requirements given in Specification **D1193** for Type I or Type II water.

3.2.4 *leachate, n*—in *leach tests*, general term for the solution resulting from a test in which a solid is contacted by a solution and leaches or dissolves.

3.2.5 *leaching, v*—the preferential loss of soluble components from a solid material into a solution leaving a residual phase that is depleted in those components, but structurally unchanged.

3.2.6 *monolithic specimen, n*—specimen that is physically one coherent piece, as opposed to powdered specimens that consist of many small pieces of irregular configuration. A monolithic specimen may consist of several individual phases, but they must be bound in a stable coherent configuration.

3.2.7 *nuclear waste form, n*—solid material in which radioactive wastes have been immobilized.

3.2.8 *precision of a measurement process, n*—the expected dispersion of values obtained using a measurement process under prescribed conditions, usually represented as a standard deviation or relative standard deviation.

#### 3.3 Abbreviations:

3.3.1 *EDX*—energy-dispersive x-ray fluorescence (instrument or analysis).

3.3.2 *ISE*—ion selective electrode.

3.3.3 *PTFE*—polytetrafluoroethylene.

3.3.4 *SEM*—scanning electron microscopy (or microscope).

3.3.5 *TEM*—transmission electron microscopy (or microscope).

3.3.6 *XRD*—x-ray diffraction (or diffractometer).

### 4. Summary of Test Method

4.1 A specimen of known geometric surface area ( $S$ ) is immersed in a known volume of leachant ( $V$ ) in a test vessel that is sealed and placed in an oven (or other controlled-temperature device) set at a defined temperature for a defined time period without agitation. After the prescribed time interval, the vessel is removed from the oven and allowed to cool before being opened. Aliquots of the leachate solution are removed and analyzed for pH and various dissolved and colloidal components that were released from the specimen during the test. The concentrations of dissolved soluble components are used to determine the extent of reaction. A separate test is conducted to provide data for each test condition (duration, temperature,  $S/V$  ratio, leachant composition, etc.).

Although it is not a part of the test method, it is recommended that the reacted test specimens be examined for changes in the composition and structures of the near-surface regions for correlations with the solution results and to study the reaction mechanism.

### 5. Significance and Use

5.1 This test method can be used to provide a measure of the reactivity of a material in a dilute solution in which the test response is dominated by the dissolution or leaching of the test specimen. It can be used to compare the dissolution or leaching behaviors of candidate radioactive waste forms and to study the reactions during static exposure to dilute solutions in which solution feed-back effects can be maintained negligible, depending on the test conditions.

5.2 The test is suitable for application to natural minerals, simulated waste form materials, and radioactive waste form material specimens.

5.3 Data from this test may form part of the larger body of data that is necessary in the logical approach to long-term prediction of waste form behavior, as described in Practice **C1174**. In particular, measured solution concentrations and characterizations of altered surfaces may be used in the validation of geochemical modeling codes.

5.4 This test method excludes the use of crushed or powdered specimens and organic materials.

5.5 Several reference test parameter values and reference leachant solutions are specified to facilitate the comparison of results of tests conducted with different materials and at different laboratories. However, other test parameter values and leachant solution compositions can be used to characterize the specimen reactivity.

5.5.1 Tests can be conducted with different leachant compositions to simulate groundwaters, buffer the leachate pH as the specimen dissolves, or measure the common ion effect of particular solutes.

5.5.2 Tests can be conducted to measure the effects of various test parameter values on the specimen response, including time, temperature, and  $S/V$  ratio. Tests conducted for different durations and at various temperatures provide insight into the reaction kinetics. Tests conducted at different  $S/V$  ratio provide insight into chemical affinity (solution feed-back effects) and the approach to saturation.

5.6 Either aerated or deaerated solutions may be used in this test method except when testing highly radioactive specimens. Deaerated solutions are mandatory in tests conducted with highly radioactive specimens to minimize the effects of nitrogen radiolysis. Preparation of deaerated leachants is addressed in **7.2.2**.

5.7 Control of the oxygen fugacity is not part of this test method. Such control and measurement may be required for specific uses of test data but are beyond the scope of this test method.

5.8 Tests can be conducted using vessels compatible with the test specimen, leachant, and test environment. Corrosion resistant materials shall be used for tests with corrosive brines.

Radiation-resistant materials shall be used for tests in radiation fields wherein the accumulated absorbed dose will exceed  $10^4$  rad (see **Note 1**).

**NOTE 1**—Additional requirements to the test method apply when using a highly radioactive waste form specimen, as indicated in the procedure.

## 6. Apparatus and Analytical Requirements

6.1 **Fig. 1** illustrates the basic features of the test equipment. The specimen is held near the centroid of the leachant volume hanging from a PTFE Teflon monofilament attached to the vessel lid or set on a coarsely woven support screen.

6.2 **Oven**—The test oven must be capable of controlling the temperature of the test vessels to within  $1^\circ\text{C}$  of the test temperature.

6.2.1 When radioactive specimens are used, take into account self-heating when selecting the oven temperature to achieve the desired leaching temperature. Identify zones within the chamber where vessels can be located that are constant within  $1^\circ\text{C}$  of the target temperature using at least ten points of temperature measurement.

6.2.2 A temperature recorder or other monitoring device must be provided to ensure that the desired temperature is maintained for the duration of the test. Brief fluctuations from the desired temperature (for example, 5 min.) are allowed when specimens are placed in or removed from the test oven, when thermocouples are checked, etc. The cumulative time that the oven temperature fluctuates more than  $1^\circ\text{C}$  from the target temperature must be kept to a minimum. The thermal mass of the vessel and leachate are expected to moderate the variance in the specimen temperature, but the oven should remain closed as much as possible.

6.2.3 The locations of test vessels should be mapped to facilitate their retrieval when the tests are terminated. Placements should minimize the need to disturb neighboring vessels when retrieving vessels.

6.3 **Test Vessel and Specimen Support**—Steel, titanium, fused silica, or polytetrafluoroethylene (PTFE) Teflon vessels and specimen supports (**Fig. 2**) can be used. Vessels shall be selected to be compatible with the test specimen material, leachant, and the radiation field.

6.3.1 When testing is performed in radiation fields expected to yield an absorbed dose of less than  $10^4$  rad, PTFE vessels shall be qualified for use (see 6.4). PTFE vessels shall not be used if the integrated dose to any PTFE component from all radiation (alpha, beta, or gamma) is predicted to exceed  $10^4$  rad (100 Gy). Doses below  $10^4$  rad have been shown to not damage PTFE.<sup>4</sup> The total absorbed dose of each PTFE test vessel may not exceed  $10^4$  rad (100 Gy) during the lifetime of the vessel. For this reason, a record of the absorbed dose received must be maintained for every vessel that is reused. The use of PTFE test vessels may result in the release of  $\text{F}^-$  from the vessel to the solution. The primary reason for limiting the integrated dose to PTFE vessels and specimen supports to  $10^4$  rad and requiring that the PTFE vessels be qualified for use is to ensure that excessive fluoride releases do not occur. For PTFE vessels that meet the qualification requirements of this test method (see 6.4), the amount of release at radiation levels  $<10^4$  rad have not been demonstrated to have an effect on leaching behavior.<sup>4</sup> Nevertheless, analysis for  $\text{F}^-$  concentration is a requirement for all tests in which PTFE vessels or components are used. Teflon vessels are pervious to carbon dioxide, which could affect the solution pH, and some water loss may occur. The use of Teflon vessels is not recommended for test durations beyond 91 days.

6.3.2 If the integrated dose to the test vessel and specimen support is expected to exceed  $10^4$  rad, Type 304L stainless steel or fused silica vessels and specimen supports can be used except when brine leachants are used. Fused silica vessels and components must be used in tests with highly radioactive waste forms in brine leachants because of the corrosion of stainless steel by the brine. Stainless steel and fused silica vessels are impervious to carbon dioxide and water loss is usually negligible.

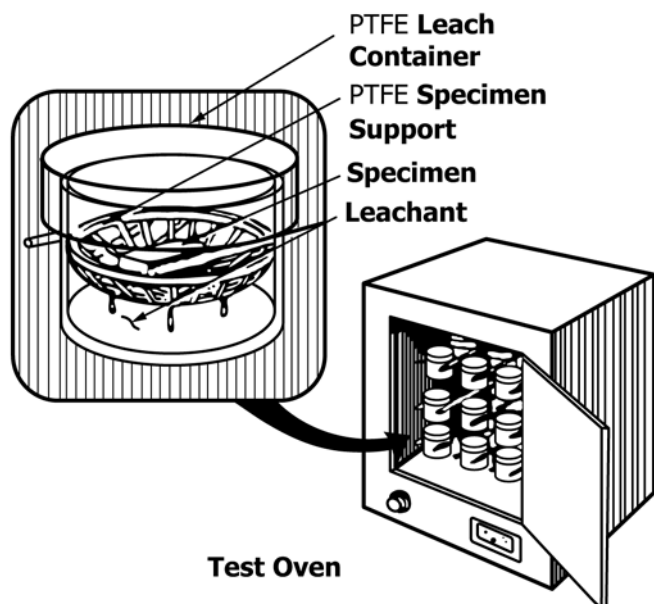
6.3.3 Vessels made of the same material shall be used throughout a test matrix to allow interactions between the vessel and the leachate to be evaluated and taken into account, for example, the release of silicon from fused silica.

6.3.4 The vessels must have sufficient volume to accommodate the leachant, specimen, and specimen support. Test vessel volumes will generally be between 20 mL and 1 L. The vessels shall have a tightly fitting lid and be sufficiently impervious to water to limit the loss during the test to less than 10 % of the initial volume (mass) of leachant.

6.3.5 The specimen support shall be constructed of the same material as the vessel or of an equally inert material and designed to hold the specimen near the centroid of the leachate volume throughout the test, but must not contact more than 5 % of the specimen surface area.

6.3.6 Vessel identification and the cleaning history of each vessel must be maintained during testing if the vessels are reused.

<sup>4</sup> Strachan, D. M., "Effect of Gamma Irradiation on Simulated Waste Glass Leaching and on the Leach Vessel," *Journal of the American Ceramic Society*, Vol 66 [9], C-158-C-160, 1983.



**FIG. 1** Example Apparatus for Static Leach Test Method



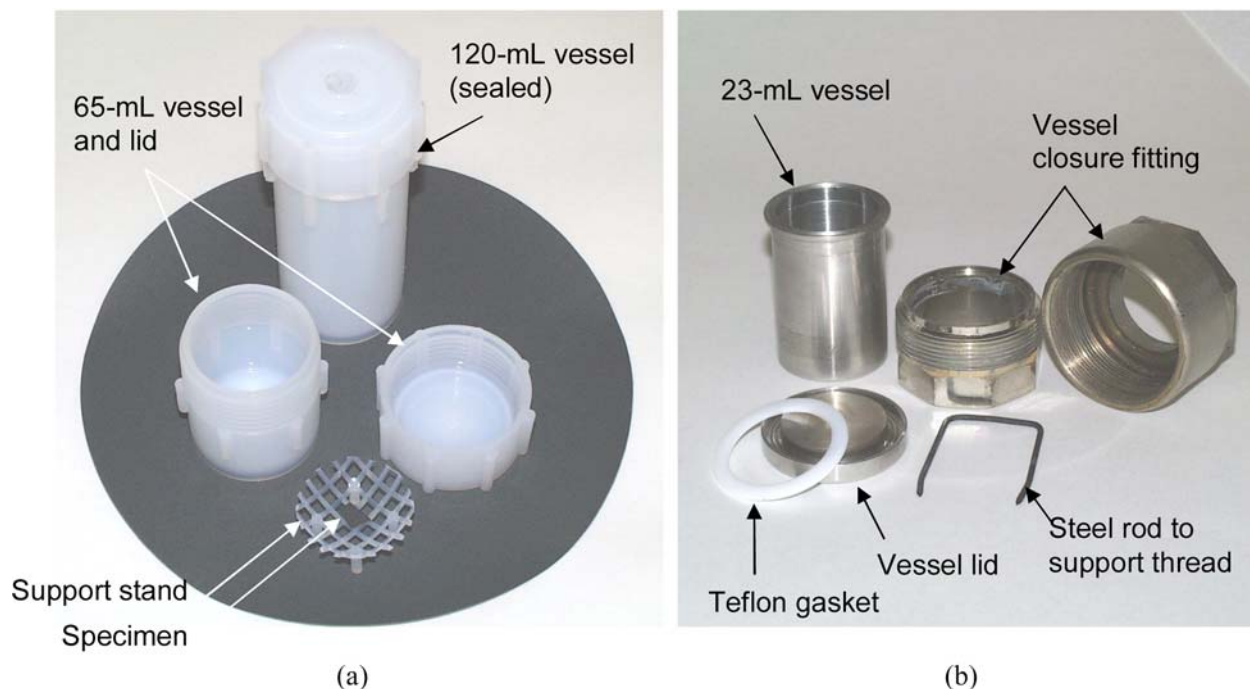


FIG. 2 Photograph of (a) PTFE Teflon Vessel and Support and (b) Type 304L Steel Test Vessel, Support, and Closure Fitting

6.3.7 A unique identifying number should be permanently marked on each leach vessel and lid. This number is used to identify tests in the oven and to track the cleaning and use history of each vessel and lid.

6.3.8 It is usually convenient to clean several vessels and lids at the same time. This facilitates tracing any inconsistent test responses to improper cleaning of a batch of vessels or to a problem vessel. Each batch of cleaned vessels shall be identified using a unique batch number. It is recommended that a log book of the leach vessel number and date of cleaning be kept. The date can be used as the batch number identifier if only one batch has been cleaned on that date. Alternatively, a separate batch number can be assigned and recorded.

6.4 *Qualification of PTFE Teflon Test Vessels and Supports*—Variations in manufacturing practice may cause particular lots of PTFE Teflon to release unacceptable amounts of fluoride during leach tests. Therefore, the vessels from a particular lot must be qualified for use by performing a blank test for 28 days to ascertain and document that the fluoride release is acceptably low. In addition, the fluoride level must always be checked for tests and blanks conducted in PTFE Teflon vessels. It is recommended that the vessels used in a test series be from the same lot. Measurement of pH shall also be determined in these qualification tests, as well as in the analyses of test leachates. The test matrices in Section 9 require the use of blanks, which will provide additional evidence that excessive  $F^-$  release from the vessel has not occurred during testing.

6.4.1 To qualify a lot of PTFE vessels and supports, clean three randomly selected vessels from the lot as described in 6.5.

6.4.1.1 Fill each vessel (with the support in place) to about 85 % capacity with demineralized water and seal the vessel.

6.4.1.2 Place each vessel in a 90°C oven and leave undisturbed for 28 days.

6.4.1.3 After 28 days, let the vessel cool then open and withdraw aliquots for pH and  $F^-$  concentration measurements.

6.4.1.4 Measure the pH and  $F^-$  concentrations in each aliquant.

6.4.1.5 If the pH is in the range of 5.0 to 7.0 and the  $F^-$  is below 0.5  $\mu\text{g/mL}$ , the lot of PTFE is acceptable for use. If the pH is not within the range of 5.0 to 7.0 or the  $F^-$  concentration is not below 0.5  $\mu\text{g/mL}$ , repeat the cleaning procedure in 6.5 until both values are within the acceptable range for all three vessels.

6.4.1.6 Clean the remaining vessels with the same number of repeated steps required for the three vessels.

6.5 *Cleaning PTFE Vessels and Supports*—New PTFE vessels and supports must be cleaned to reduce the amount of  $F^-$  released during testing. PTFE vessels can be reused after testing provided they are cleaned before reuse and were not used in tests with actinide-doped specimens. This is because actinides are difficult to remove from PTFE and may not be sufficiently removed by leachate acidification and the vessel/specimen support structure cleaning procedure. As these dopants may be present in very low concentrations in the leachates of subsequent tests, contamination due to leaching from the vessel walls could be significant. Clean new PTFE Teflon vessels and supports following steps 6.5.1 – 6.5.22.

6.5.1 Heat new PTFE test vessels and supports, but not fine monofilament used to suspend test specimens, in a  $200 \pm 10^\circ\text{C}$  oven for one week prior to cleaning.

6.5.2 Rinse vessels, lids, and supports with fresh high-purity water at ambient temperature. Use at least three vessel volumes to rinse each vessel.

6.5.3 Fill vessels approximately 90 % full with 5 wt % NaOH solution and tighten lids.

6.5.4 Place PTFE vessels rated to 0.5 MPa or higher in an oven preheated to  $110 \pm 10^\circ\text{C}$ . Place PTFE vessels not rated to 0.5 MPa in an oven preheated to  $95 \pm 2^\circ\text{C}$ .

6.5.5 Retighten the vessel lids after 12 to 24 h in oven.

6.5.6 After 7 days in oven, remove vessels and allow to cool to room temperature.

6.5.7 Remove lids carefully and dispose of NaOH solution.

6.5.8 Rinse vessels and lids in fresh high-purity water two times.

6.5.9 Place vessels and lids in fresh, boiling high-purity water for a minimum of 1 h.

6.5.10 Remove vessels and lids and discard water.

6.5.11 Repeat steps 6.5.8 – 6.5.10.

6.5.12 Allow vessels and lids to air dry for a minimum of 16 h at  $90 \pm 10^\circ\text{C}$ .

6.5.13 Fill vessels about 90 % full with fresh high-purity water at ambient temperature.

6.5.14 Tighten lids and place vessels in oven preheated to  $90 \pm 2^\circ\text{C}$  for a minimum of 16 h.

6.5.15 Remove vessels and allow to cool to room temperature.

6.5.16 Take an aliquant of liquid from each vessel and measure pH.

6.5.17 If the pH is below 5, repeat steps 6.5.1 – 6.5.16 until the pH is above 5.

6.5.18 If the pH is above 7, repeat steps 6.5.8 – 6.5.16.

6.5.19 If the pH is between 5.0 and 7.0 take an aliquant and measure the  $\text{F}^-$  concentration.

6.5.20 If the  $\text{F}^-$  concentration is  $>0.5 \mu\text{g/mL}$ , repeat steps 6.5.8 – 6.5.19.

6.5.21 If the  $\text{F}^-$  is still  $>0.5 \mu\text{g/mL}$  after performing steps 6.5.8 – 6.5.19 twice, repeat steps 6.5.1 – 6.5.19.

6.5.22 If the  $\text{F}^-$  concentration is  $<0.5 \mu\text{g/mL}$ , a vessel is acceptable for use.

6.6 *Cleaning of New PTFE Gaskets*—Clean new PTFE Teflon gaskets to be used with stainless steel vessel following steps 6.6.1 – 6.6.6.

6.6.1 Handle the gaskets only with clean tongs, forceps, or gloves.

6.6.2 Clean each gasket ultrasonically in 95 % ethanol for approximately 10 min.

6.6.3 Clean each gasket with high-purity water at ambient temperature for approximately 3 min.

6.6.4 Bake each gasket in an oven at  $200 \pm 10^\circ\text{C}$  for a minimum of 4 h.

6.6.5 Immerse each gasket in fresh high-purity water in a boiling water bath for a minimum of 2 h.

6.6.6 Dry gaskets at  $90 \pm 10^\circ\text{C}$  for a minimum of 16 h and store in a clean environment until needed.

6.7 *Clean Used PTFE Teflon Vessels and Supports*—Clean used PTFE vessels and supports following steps 6.7.1 – 6.7.11.

6.7.1 Rinse vessels, lids, and supports with fresh high-purity water. Use at least three vessel volumes of water for each vessel.

6.7.2 Soak vessels and supports for 1 h in 0.16 M  $\text{HNO}_3$  (1 wt %  $\text{HNO}_3$ ) at  $90 \pm 10^\circ\text{C}$ .

6.7.3 Remove vessels and supports and discard acid soak solution.

6.7.4 Rinse vessels and supports again as specified in step 6.7.1.

6.7.5 Soak vessels and supports for 1 h in high-purity water at  $90 \pm 10^\circ\text{C}$ .

6.7.6 Remove vessels and supports and allow to dry.

6.7.7 Fill the vessels with supports in place approximately 90 % full with fresh high-purity water. Close the lids and hold for at least 16 h at  $90 \pm 2^\circ\text{C}$  and then measure the pH of the water in each vessel.

6.7.8 Take an aliquant of the water from at least two vessels from each vessel batch and measure the  $\text{F}^-$  concentration.

6.7.9 Repeat steps 6.7.4 – 6.7.8 until the pH is in the range of 5.0 to 7.0 and the  $\text{F}^-$  concentration is  $<0.5 \mu\text{g/mL}$ .

6.7.10 If the pH and fluoride requirements cannot be achieved after three repetitions of steps 6.7.4 – 6.7.8, then repeat the cleaning procedure starting at step 6.7.1.

6.7.11 Dry vessels and lids at  $90 \pm 10^\circ\text{C}$  for a minimum of 16 h and store inside a clean environment until used.

6.8 *Clean New Fused Silica Vessels*—Clean fused silica vessels following steps 6.8.1 – 6.8.10.

6.8.1 Rinse vessels, lids, and supports with fresh high-purity water. Use at least three vessel volumes of water for each vessel.

6.8.2 Soak vessels and supports for 1 h in 0.16 M  $\text{HNO}_3$  (1 wt %  $\text{HNO}_3$ ) at  $90 \pm 10^\circ\text{C}$ .

6.8.3 Rinse again as specified in 6.8.1.

6.8.4 Soak for 1 h in high-purity water at  $90 \pm 10^\circ\text{C}$ .

6.8.5 Remove vessels and discard water. Allow vessels to dry.

6.8.6 Fill the vessels approximately 90 % full with fresh high-purity water with support in place. Close the lids and hold for at least 16 h at  $90 \pm 2^\circ\text{C}$ .

6.8.7 Take an aliquant of the water from each vessel and measure the pH.

6.8.8 Repeat steps 6.8.4 – 6.8.7 until the pH is in the range of 5.0 to 7.0.

6.8.9 If the pH requirement cannot be achieved by three repetitions of steps 6.8.4 – 6.8.7, then repeat the cleaning procedure starting at step 6.8.1.

6.8.10 Dry vessels and lids at  $90 \pm 10^\circ\text{C}$  for a minimum of 16 h and store inside a clean environment until used.

6.9 *Clean New Stainless Steel Vessels*—Clean new stainless steel vessels using steps 6.9.1 – 6.9.13.

6.9.1 Degrease new Type 304L stainless steel vessels and lids without gaskets and ultrasonicate in 95 % ethanol for approximately 5 min to remove any residual grease or oil left from machining operations:

6.9.2 Rinse vessels and lids three times in high-purity water.

6.9.3 Submerge vessels and lids in 0.16 M  $\text{HNO}_3$  (1 wt %  $\text{HNO}_3$ ) for 1 h at  $90 \pm 10^\circ\text{C}$ .

6.9.4 Remove vessels and lids and discard acid soak solution.

6.9.5 Rinse vessels and lids three times with high-purity water at ambient temperature.

6.9.6 Remove vessels and lids and discard water. Allow vessels and lids to dry.

6.9.7 Submerge the vessels and lids in fresh high-purity water for 1 h at  $90 \pm 10^\circ\text{C}$ .

6.9.8 Rinse with fresh high-purity water at ambient temperature.

6.9.9 Fill the vessel 80 to 90 % full with high-purity water. Close the lid and leave in a  $90 \pm 2^\circ\text{C}$  oven for a minimum of 16 h.

6.9.10 Remove the vessels from the oven and let cool to room temperature. Take aliquant of the water and measure the pH.

6.9.11 If the pH is not in the range of 5.0 to 7.0, repeat steps 6.9.5 – 6.9.10

6.9.12 If the pH is not in the range of 5.0 to 7.0 after 3 repetitions of steps 6.9.5 – 6.9.10, repeat the cleaning steps starting at step 6.9.1.

6.9.13 Dry the vessels in a  $90 \pm 10^\circ\text{C}$  oven for a minimum of 16 h and then cool to room temperature. If the vessels are not used immediately, close the vessels and store in a clean environment until needed.

**6.10 Cleaning Used Stainless Steel and Used Fused Silica Vessels**—When stainless steel or fused silica vessels are used in tests with radioactive specimens, residual contamination may be present. The vessels shall be cleaned before reuse using 0.16 M  $\text{HNO}_3$  (1 wt %  $\text{HNO}_3$ ) and high-purity water until the level of the radioactive element of interest in the water is below the detectable level using the analytical method to be employed for concentration measurement of the leachate. Stainless steel vessels are also checked for Si contamination before reuse. Clean used stainless steel vessels using steps 6.10.1 – 6.10.11.

6.10.1 Rinse the vessel and lid with high-purity water.

6.10.2 Fill the vessel 80 to 90 % full with 0.16 M  $\text{HNO}_3$  (1 wt %  $\text{HNO}_3$ ). Seal the vessel and place in an oven at  $90 \pm 2^\circ\text{C}$  to digest for a minimum of 16 h to dissolve radionuclides adhering to the interior of the vessel.

6.10.3 Check the resulting solution for radioactivity. Repeat step 6.10.2 until the radioactivity of the solution is reduced to below the background levels.

6.10.4 Remove the gasket and discard. Rinse vessels and lids thoroughly with high-purity water at ambient temperature. Take precautions to prevent contamination of the vessel interior with any radionuclides present on the exterior of the vessel or in the work environment.

6.10.5 Fill the vessel 80 to 90 % full with fresh high-purity water. Close the lid using a new, cleaned gasket (see step 6.6) and place in oven at  $90 \pm 2^\circ\text{C}$  for at least 24 h.

6.10.6 Remove vessels from oven, then take an aliquant of the water and measure the pH.

6.10.7 Take another aliquant and measure the radioactivity.

6.10.8 For stainless steel vessels, take an aliquant to measure the Si content of the solution.

6.10.9 If the pH is not in the range of 5.0 to 7.0, the measured radioactivity is not at the background level, or Si > 1 ppm is detected for stainless steel vessels, repeat steps 6.10.2 – 6.10.8.

6.10.10 If three repetitions of steps 6.10.2 – 6.10.8 do not result in a pH within the range of 5.0 to 7.0, radioactivity below detection, and Si < 1 ppm for stainless steel vessels, then repeat the cleaning starting at step 6.10.1.

6.10.11 Dry vessels, lids, and gaskets at  $90 \pm 2^\circ\text{C}$  for a minimum of 16 h and store in a clean environment until needed.

**6.11 Cleaning Solution Bottles**—Solution bottles that will be used to contain analytical samples should be cleaned before use. Clean solution bottles using steps 6.11.1 – 6.11.3.

6.11.1 Rinse bottles three times with a dilute nitric acid solution (~2 wt %). For each rinse, fill bottle to about 10 % bottle volume, place cap on bottle, and shake to rinse all surfaces. Dispose of solution.

6.11.2 Rinse bottles three times with reagent grade (demineralized) water. For each rinse, fill bottle to about 25 % bottle volume, place cap on bottle, and shake to rinse all surfaces. Dispose of rinse water.

6.11.3 Dry bottle and cap in oven, then place cap on bottle and store until use.

**6.12 Mass Measurement**—Material masses shall be determined with balances that provide the following accuracies, depending on the materials being weighed:

**TABLE 1 Required Accuracy for Mass Determinations**

Leachant and vessels	within 0.25 % of the leachant mass
Chemical reagents used to prepare leachant	within 1 % of the reagent mass
Test specimens	within 0.5 mg

**6.13 Volume Measurement**—Measure leachant volumes gravimetrically or with pipettes, burettes, or flasks calibrated as described in Table 1.

**6.14 Solution Analysis**—Measure solute concentrations using equipment standardized with standards traceable to NIST, preferably, or other recognized organizations, such as EPA or USGS.

6.14.1 Determine and report precision and bias for analyses. Although analytical results should normally be accurate within 10 % when checked by individual measurements on reference solutions, this may not be possible when concentrations in the solution are near detection limits. The detection limits for each analysis must accompany the reported result.

6.14.2 Various analytical techniques can be used to determine the solute concentrations in leachates, including inductively coupled plasma spectroscopy (see Practice C1109 or EPA SW-846A, or both), direct current plasma spectroscopy, atomic absorption emission spectroscopy, and neutron activation. Selection of a specific technique depends on specific test objectives and the particular solutes of interest. For radioactive elements such as actinides and fission products, where small amounts may be of interest, radiochemistry/radiation counting may be needed or desirable.

6.14.3 Analyzing blanks and simulated leachates with test solutions helps ensure that high-quality data are obtained.

**6.15 pH Measurement**—Measure the pH to an accuracy of 0.1 unit using an electrode and meter calibrated with commercial buffers or buffers obtained from NIST. Follow Test Method D1293, Method A to make this measurement.

6.15.1 When measuring the pH of a deaerated solution, conduct the measurement under an argon atmosphere.



**TABLE 2 Required Calibration Schedule**

Measurement	Device	Frequency Check and Methods
Temperature	thermocouple or thermometer	6 months NIST standard or ice/boiling water
Voltage	electronics or temperature probe (without sensor)	6 months against a calibrated millivolt source
Length	micrometer	6 months standard foils, gage blocks
Mass	balance	3 months NIST standard masses
Chemical concentration	analytical method	3 months NIST standards, where possible, 2 times daily (routine), secondary standards before use with commercial or NIST buffer solutions, and at intervals of 60 min during measurements
pH	pH meter	See Test Methods D1293 and 6.11 for guidance
Volume	volumetric flasks	use certified flasks or before use by measuring the mass of pure water contained
Activity	pipettes counting techniques	before use by measuring the mass of pure water transferred twice a day, before and after counting NIST or NIST-traceable standard isotope source for radionuclide of interest

6.15.2 When measuring the pH of a brine solution, the measured value will be affected by a significant liquid junction potential that is sensitive to the ionic strength and the activity coefficient of hydrogen that will differ significantly from unity. These effects lead to large uncertainties in the measured values. They are discussed in more detail in [Appendix X1](#).

6.16 *Calibration and Standards*—Calibrate all instruments used in these tests prior to use and check periodically to minimize possible errors due to drift. [Table 2](#) shows the methods and the minimum frequency of calibration for the various devices used. Use standardized procedures that are published by recognized authorities such as NIST or ASTM.

## 7. Leachant Preparation and Storage

7.1 *General Chemicals and Procedures*—Use chemicals of reagent grade or better that conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> It is recommended that the assays of each chemical be assessed to determine if impurities, once the leachant is prepared, will exceed detection limits of the analysis system to be used. If impurities will cause detection limits to be exceeded, obtain a different batch of the chemical or use an ultrapure chemical. Good laboratory practice should be used at all times to minimize contamination of the leachant.

7.1.1 Although any leachant can be used in tests, recipes for a reference brine leachant and a reference silicate leachant are provided to facilitate comparisons of test results from different laboratories. The reference brine and silicate leachant compositions are not intended to represent any particular ground waters.

<sup>5</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.1.2 Blank tests must be conducted with all leachants to measure the stability of the leachant under the test conditions and interactions with the vessel and support.

7.1.3 The density of all leachants should be measured to permit the addition of leachant to the individual leach tests by weight rather than by volume.

7.2 *Demineralized Water*—The water referred to in this procedure is air-saturated reagent water Type I or II conforming to Specification D1193, with a total impurity level, including organics, of less than 0.1 mg/L.

7.2.1 Radiolysis of gases dissolved in water can become an important factor in tests with radioactive materials. Therefore, deaerated leachants should be used in tests with radioactive specimens.

7.2.2 To deaerate demineralized water for use in leachant preparation, boil high-purity water for 15 min while purging with argon. Immediately place the hot water under an argon atmosphere to cool. Prepare the leachants as described below using the cooled, deaerated water in an argon atmosphere.

7.2.3 The density of pure air-free water at 23°C is 0.9976 g/cm<sup>3</sup>.

7.3 *Preparation of Reference Brine Leachant*—Prepare the reference brine by dissolving 48.2 g KCl, 90.0 g NaCl, and 116.0 g MgCl<sub>2</sub> (247.9 g MgCl<sub>2</sub>·6H<sub>2</sub>O) in enough demineralized water to make approximately 900 mL of solution. Adjust the pH to fall within the range of 6.4 to 6.6 by dropwise addition of 0.01 M NaOH or 0.01 M HCl. Then add water to make 1.00 L of solution. Analyze the leachant to verify the composition and to determine impurity concentrations. Discard the leachant if the concentration of any constituent is in error by more than 10 % from the recipe concentration, which is 35.4 g Na<sup>+</sup>/L, 54.9 mg K<sup>+</sup>/L, 29.6 mg Mg<sup>2+</sup>/L, and 164 mg Cl<sup>-</sup>/L (neglecting the Na and Cl added as NaOH and HCl).

7.3.1 The density of the brine leachant should be measured to permit the addition of aliquots of brine leachant to the individual leach tests by weight rather than by volume.

**7.3.2 Caution**—When using brine in radiation fields, hydrogen gas will be generated and may pressurize the test vessel. Take the appropriate precautions when making such studies. Use appropriate pressure-rated test vessels or vessels with gas vents, or both. Also, since chloride brines can become very corrosive under high radiation fields, use caution when selecting the test vessel material.

**7.4 Preparation of Reference Silicate Water Leachant**—Prepare the silicate water leachant by dissolving 0.179 g  $\text{NaHCO}_3$  and 0.096 g  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  in enough demineralized water to make about 900 mL of solution. Adjust the pH to within 0.1 unit of 7.5 with 0.01 M HCl. Add water to make 1.00 L of solution.

**7.4.1** Analyze an aliquant of the leachant to verify the composition (27.1 mg Si/L) and to determine impurity concentrations. Discard the leachant if the concentration of any constituent is in error by more than 10 %.

**7.4.2** The density of the silicate water leachant should be measured to permit the addition of aliquots of leachant to the individual leach tests by weight rather than by volume.

**7.5 Repository Water Leachants**—When actual ground waters or leachants that are representative of specific repository waters are used, the rigor with which the data characterizing the water are obtained must be the same as for the three reference leachants. Record the type of repository water used, where and when it was obtained or how it was prepared if made up in the laboratory, results of its chemical composition analysis, the presence of colloidal material, etc. of any precipitates that may have been formed in the blanks during the test.

**7.5.1** Analyze an aliquant of the leachant to measure the composition.

**7.5.2** The density of the ground water should be measured to permit the addition of aliquots to the individual leach tests by weight rather than by volume.

**7.6 Other Leachants**—Other leachant solutions are useful when using the test to study the waste form degradation mechanism and measuring model parameters. For example, pH buffer solutions can be used to measure the effect of pH on the test response and leachants with added components can be used to measure common ion (solution feed-back) effects.

**7.7 Leachant Storage**—Use polyethylene or polypropylene bottles with tight-fitting lids to store the leachants. Clean bottles before use following the cleaning steps given in 6.11.

**7.7.1** Use the leachant immediately or store in a sealed vessel until beginning the test. If the leachant is not used within one month after it is prepared, report the storage time and verify the composition by analysis before use in tests. Natural groundwaters should be stored in a dark location to prevent the growth of algae.

**7.7.2** Store deaerated solutions in a tightly sealed container with an argon atmosphere above the liquid level and for no longer than one week.

## 8. Test Specimen Preparation

**8.1** Test specimens may be either fabricated individually or cut from larger samples of the waste-form material.

**8.1.1** When cutting a specimen from a larger sample, avoid the use of wax or adhesives to hold the sample being cut. If adhesive materials must be used, none of the surfaces of the resulting test specimen shall be surfaces to which the adhesive was applied.

**8.1.2** Sawing and cutting test specimens for tests to be conducted in deaerated solutions need not be done in an argon atmosphere. However, a final specimen cleaning step must be carried out under an argon atmosphere using deaerated deionized water.

**8.1.3** The surfaces of individually fabricated test specimens may not be representative of the bulk material due to formation of a surface skin, and the responses of such specimens may not be representative of the bulk material. If separate specimens are cast for each test, the user should determine the effect of the as-cast surface by comparing results of tests conducted with an as-cast specimen and a cut specimen without the outer layer has been removed.

**8.2 Characterization of Source Material**—The source material is the sample from which test specimens are extracted. If possible document the fabrication method and fabrication conditions for the source material and provide information on how test specimens were selected. The researcher must include information on the chemical and radiochemical (if applicable) composition and compositional variations of the source material. This information should be obtained from bulk chemical and radiochemical analyses. Include information on chemical-composition variations within the fabricated material, as well as within and between specimens. For certain radioactive samples, autoradiography may be necessary to determine the distribution of alpha-emitting isotopes. The researcher may also wish to characterize the source material with optical microscopy, XRD, SEM-EDX, TEM, or other analytical methods to document microcracking, phase identification, relative concentrations of phases, and homogeneity between test specimens.

**8.2.1** For specimens in which an as-fabricated surface is to be leached, analysis of a surface cross-section by SEM-EDX or other applicable surface spectroscopy techniques is also required to determine whether the surface composition differs from the bulk composition. If differences do exist, the possible effects on the test results should be discussed with the test results.

**8.2.2** When the waste form source material is a heterogeneous or multiphase material, it may not be possible to produce test specimens exposing equal amounts of all phases to the leachants in a test series. In this case, the test operator must document the differences between the test specimens that are used to ensure that the test specimens contain a representative distribution of the different phases. This should be documented with optical microscopy, SEM-EDX, or other applicable techniques. Individual particles of component phases may be large enough relative to the dimensions of the test specimen to estimate the exposed area.

**8.3 Test Specimens**—The test specimen is preferably prepared as a regularly shaped monolith, either a tablet (with six flat surfaces) or a disk such that the surface area exposed to the



leachant can be easily calculated from the geometry and measured dimensions.

8.3.1 All surfaces must be prepared in a consistent manner using either an abrasive saw or an alternative technology to provide a reproducible surface finish (200, 320, 600 grit or other surface finish). The surface finish will affect the test response of many materials.

8.3.1.1 Samples having a tabular shape allow for the best control of the surface finish.

8.3.1.2 The preferred surface finish will depend on the material being tested.

8.4 *Specimen Cutting*—When specimens are prepared from a larger sample, use a saw to prepare tabular specimen or a core drill and saw to prepare disk samples.

8.4.1 The saw blade should be appropriate for the material being cut. For example, a 200-grit diamond-impregnated cutting surface is appropriate for most glasses.<sup>6</sup>

8.4.2 Use water as the cutting fluid unless the material is known or suspected to contain a water-soluble phase, in which case absolute ethanol or another polar fluid (for example, kerosene or cyclohexane) should be used as the cutting fluid. Experiments can be conducted to measure the extent to which the sample dissolves in the cutting fluid.

8.4.3 The size or exact shape of the specimen is not critical, provided the geometric surface area can be determined, but a surface area of about 400 mm<sup>2</sup> is recommended. This size is easily handled during sample preparation and requires 40 mL leachant for a standard test conducted at a S/V ratio of 10 m<sup>-1</sup>.

8.4.4 A metal-bonded diamond core drill with an inner diameter of about 1 cm can be used to remove a core sample from the source material.<sup>7</sup> The diameter of the core can be polished by carefully chucking it in a low-speed drill. Specimen disks can then be cut from the core.

8.4.5 Tabular specimens can be produced by cutting a bar from the source material and polishing the four sides. Specimen tablets can then be cut from the bar and the faces polished. The recommended technique using a Buehler low-speed saw is provided in [Appendix X2](#).

8.5 *Specimen Polishing*—The saw-cut specimens are polished using successively finer grit paper with water (or absolute alcohol) lubrication. Saw-cut specimens will have a surface finish similar to 200-grit, depending on the hardness of the material, the condition of the wafering blade, and the cutting speed. The use of a mechanical polishing wheel is recommended to provide uniform surface finish. Typically, specimens can be polished successively with 240-grit, 320-grit, 400-grit, and 600-grit paper (and with finer grits) to produce a uniform and reproducible surface finish. Jigs can be con-

structed to hold specimens during polishing and automatic polishers can be used.

8.5.1 Place polishing paper of desired grit on polishing wheel and lubricate well with water (or absolute alcohol). Gently press sample face to be polished near center of paper and start wheel at low speed. Maintaining sample orientation, slowly rotate the sample around the paper in direction counter to wheel rotation moving towards the outside edge of wheel and then back towards the center. This motion subjects the sample to polishing in all directions. The force needed to hold the sample will vary with the hardness of the material, the grit size of the polishing paper, and the speed of the wheel. Because it is likely that hand-held samples will be pulled loose during polishing (especially when using coarse grit paper), drains in the tray beneath the wheel should be covered with a screen to prevent the loss of samples. The speed of the polishing wheel should be kept low enough to avoid binding and pulling the specimen, but high enough to effectively polish it.

8.5.2 Rinse the specimen with water (or absolute ethanol) and inspect the scratches on the specimen for uniformity in depth and directional randomness.

8.5.3 Repeat steps [8.5.1](#) and [8.5.2](#) with a finer grit size paper. The polishing times required to achieve a uniform surface usually increase with finer grit paper. For example, 10 seconds may be adequate for achieving a 240-grit finish whereas several minutes may be required to attain a 600-grit finish.

8.5.4 For typical glasses, a 600-grit finish will have a mirror finish to the naked eye with shallow scratches visible using a jeweler's loupe. Failure to remove surface scratches within a reasonable polishing time may require brief repolishing with a coarser grit.

8.5.5 Care should be taken to avoid rounding the faces at the edges during polishing.

8.6 *Specimen Cleaning*—Clean the specimens using the following procedure:

8.6.1 Subject specimens to 5-min ultrasonic wash in high-purity water or other appropriate fluid.

8.6.2 Subject specimens to three 5-min ultrasonic washes in fresh absolute ethanol or other appropriate fluid.

8.6.3 Dry specimens to constant mass and record mass. Use a drying technique that has been demonstrated to be applicable to the specific waste form being tested. Drying for one hour at 110°C is sufficient for most nonporous waste forms. Porous waste forms may require higher temperatures and longer times.

8.6.4 When performing experiments using deaerated solutions, additionally wash the specimen three times using deaerated high-purity water under an argon atmosphere and store the specimen under argon until it is placed in the test vessel.

8.7 *Specimen Handling*—All handling of specimens after preparation and cleaning must be done with tongs, tweezers, or lint- and dust-free plastic or rubber gloves.

8.8 *Specimen Dimensions and Surface Area*—The dimensions of each specimen shall be measured with a calibrated device (for example, digital calipers) to the nearest 0.01 cm. The measured dimensions are used to calculate the geometrical

<sup>6</sup> The Buehler Isomet Low Speed Saw with standard accessories, Buehler part number 11-1180 with Arbor Diamond Wafering Blades, low diamond concentration (200 grit), 5-in. diameter × 0.015-in. thickness, part number 11-4255, or 4-in. diameter × 0.012-in. thickness, part number 11-4254, Buehler dressing Sticks, part number 11-1190, and Buehler Isomet dressing chuck, part number 11-1196, available from Buehler, 41 Waukegan Rd., Lake Bluff, IL 60044, (or equivalent) are recommended.

<sup>7</sup> Suitable diamond core drills are available for Starlite Industries, Inc., 1111 Lancaster Ave., Rosemont, PA 19010, Part #102135, ½ inch.

surface area, which is used in calculations to be performed with the test results. The porosity of a test specimen is not taken into account within this procedure, but the effects can be assessed by the user based on additional measurements that are performed in addition to this procedure.

8.8.1 For disk-shaped specimens, at least two measurements of the diameter and two measurements of the height shall be made at diametrically opposite locations. The geometric surface area and volume are calculated by modeling the specimen as a right circular cylinder and using the arithmetic averages of the measured diameters and heights.

8.8.2 For tabular-shaped specimens (that is, specimen with six flat faces and unequal edge lengths), the lengths of each edge and the length of one diagonal shall be measured.

8.8.3 The surface area is calculated based on the measured dimensions and the geometric shape of the test specimen.

8.8.4 If the specimen face has a regular geometric shape, calculate the area from the measured dimensions.

8.8.5 If it does not have a regular shape, the surface area can be determined as described in [Appendix X3](#).

8.8.6 The calculated surface area can be modified to take into account deviations in the specimen shape from an ideal right circular cylinder or tablet based on additional measurements and geometric calculations. For example, the specimen may have a nicked edge.

8.8.7 Although the use of a single monolithic specimen in each test is preferred, up to four monoliths can be used to provide the desired surface area, if necessary, provided that each can be placed in the test vessel without contacting another specimen.

8.8.8 The uncertainty in the surface area of the specimens contributes to the uncertainty in the normalized mass loss calculated from the test response and should be quantified, for example, by using the propagation of errors method or, preferably, the method developed by the International Committee for Weights and Measured (CIPM) and promulgated by NIST, see [Appendix X4](#).

8.8.9 Weigh each test specimen to an accuracy of 0.5 mg.

## 9. Test Matrices

9.1 A series of several tests, referred to as a matrix of tests, is usually conducted with a material of interest to address a particular issue.

9.1.1 Tests are often conducted for a series of durations to determine the kinetics, at several temperatures to determine the activation energy, at several S/V ratios to determine chemical affinity effects, etc.

9.1.2 The matrix identifies the sets of test parameters to be used, the number of replicate tests, and the series blank tests to be conducted.

9.1.3 If Type 304L stainless steel test vessels are used, it is recommended that key tests and blanks be performed in duplicate because high chloride levels, which may have a significant effect on test results, have occasionally been observed in tests conducted using stainless steel vessels. By conducting tests in duplicate, the researcher is reasonably assured of having at least one reliable data point for each test condition.

9.2 Blank tests conducted without a test specimen are required in most matrices.

9.2.1 Blank tests serve to monitor interactions between the leachant and the test vessel and changes in the leachant composition under the test conditions.

9.2.2 The results of blank tests are used to provide background concentrations of solutes to adjust the results of tests with specimens.

9.2.3 If several test matrices with one or more waste forms using the same batch of leachant are started simultaneously in the same oven, the same blank tests may be used for each matrix.

9.3 *Reference Test Matrices*—Four reference test matrices with specific test conditions are provided to facilitate the direct comparisons of tests conducted with different materials and at different laboratories. The reference test matrices are summarized in [Table 3](#) and discussed below. These represent the series of tests recommended to support the determination and comparisons of waste form behavior, including replicate tests conducted to determine intralaboratory precision. The test period must be controlled to within 2 % of the target test duration for direct comparisons of test results. Additional tests can be conducted to supplement each matrix and meet the user’s needs. The matrices and their purposes are described in steps [9.3.1 – 9.3.4](#).

9.3.1 *Matrix A: 7-day Tests at, 90°C*—This matrix is intended for screening tests used during waste form development, where the specific objective could be measuring the qualitative effects of composition variations, waste loading, processing parameters, etc., on the chemical durability of the waste form.

9.3.1.1 The test temperature is 90°C.

9.3.1.2 The leachant is demineralized water.

9.3.1.3 The test specimen surface finish is 600 grit.

9.3.1.4 The S/V ratio is 10 m<sup>-1</sup>.

**TABLE 3 Reference Test Matrices**

Reference Matrix	A	B	C	D
Leachant	Demineralized Water	Demineralized Water, Brine, or Silicate Water	Demineralized Water, Brine, or Silicate Water	pH Imposing Solutions
S/V ratio, m <sup>-1</sup>	10	10	10	2
Temperature, °C	90	90	20, 40, 70, 90	20, 40, 70, 90
Test Durations, d	7(3)	28(3)	3, 7, 14, 28, 56, 91, 182, and 364, then 6-month intervals	0.67, 1(3), 1.67, 2, 3, 4, 5, 6, 7, 10, and 14(2)
Blank Durations, d	none	28(2)	28, 91, 364	7 and 14