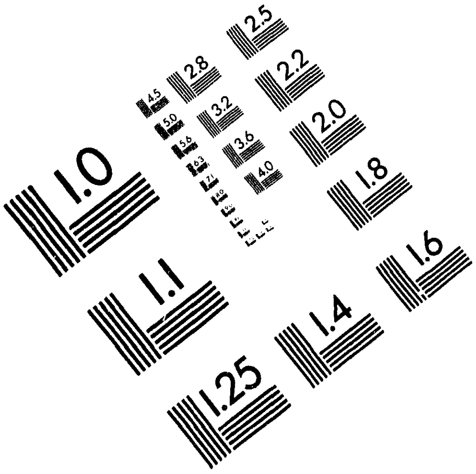

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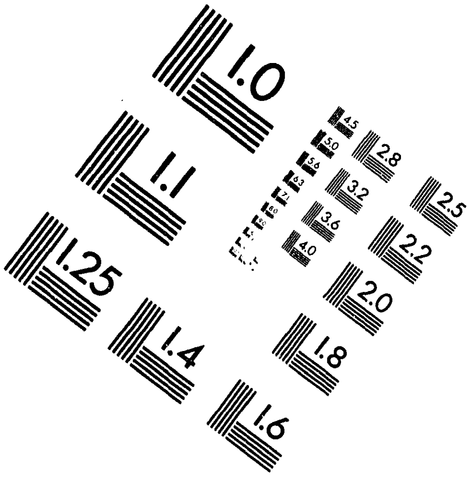

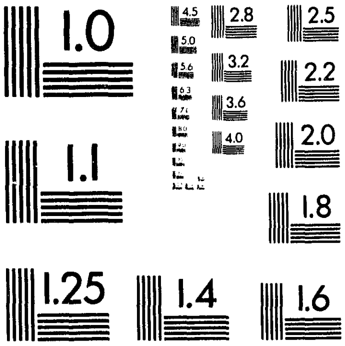

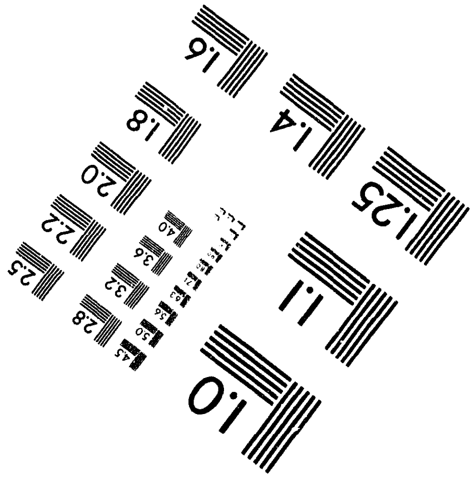

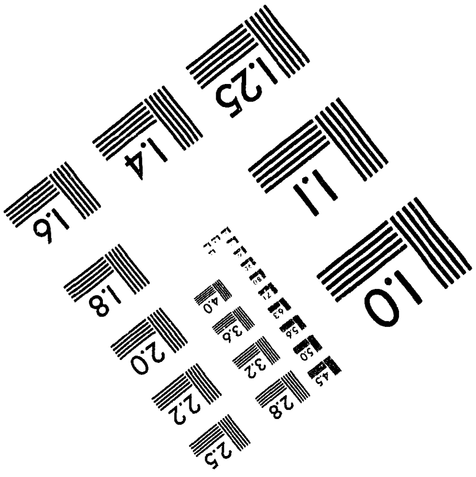

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WSRC-TR-90-539, REV 3

NUCLEAR WASTE GLASS PRODUCT CONSISTENCY TEST - VERSION 7.0

by
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DOE Contract No. **DE-AC09-89SR18035**

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WSRC-TR-90-539, Rev. 3
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NUCLEAR WASTE GLASS PRODUCT CONSISTENCY TEST (PCT) - VERSION 7.0 (U)

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Approved by

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Defense Waste Processing Technology

Publication Date: June 1994

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ABSTRACT

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass. The glass will be produced in the Defense Waste Processing Facility (DWPF), poured into stainless steel canisters, and eventually disposed of in a geologic repository. In order to comply with the Waste Acceptance Product Specifications (WAPS), the durability of the glass needs to be measured during production to assure its long term stability and radionuclide release properties.

A durability test, designated the Product Consistency Test (PCT), was developed for DWPF glass in order to meet the WAPS requirements. The response of the PCT procedure was based on extensive testing with glasses of widely different compositions. The PCT was determined to be very reproducible, to yield reliable results rapidly, and to be easily performed in shielded cell facilities with radioactive samples.

Version 7.0 of the PCT procedure is attached. This draft version has been submitted to ASTM for full committee (C26, Nuclear Fuel Cycle) ballot after being balloted successfully through subcommittee C26.13 on Repository Waste Package Materials Testing.

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NUCLEAR WASTE GLASS PRODUCT CONSISTENCY TEST (PCT) - VERSION 5.0 (U)

INTRODUCTION

A durability test, designated the Product Consistency Test (PCT), has been developed for glasses produced in the Defense Waste Processing Facility (DWPF).[1] The test is designed to meet the requirements of the Waste Acceptance Product Specifications (WAPS) 1.3 and 1.4.[2] Specification 1.3 requires the DWPF to demonstrate control of the radionuclide release properties of the final waste form. Changes in phase composition due to devitrification do not greatly alter the rate of release of material from the glass[3] of the type which will be produced in DWPF. However, the WAPS Specification 1.4 requires that the release properties of devitrified glass be similar to those determined in Specification 1.3. The DWPF is responsible for relating the results of the PCT to a repository site-specific release test, or, alternatively, for performing the repository site-specific release tests.

The PCT has been developed, in part, to satisfy the WAPS requirements by providing a test which is (1) sensitive to glass composition and homogeneity, (2) can be routinely performed during production, and (3) has the potential to be related to repository site-specific release tests. The test was designed to provide confirmation of the consistency of DWPF glass while considering the following:

- sensitivity of the test to glass composition and homogeneity
- time necessary to demonstrate product quality
- ease of sample preparation for radioactive glass
- ease of test procedure for remote operation
- precision of the test results
- acceptance by waste form developers and repository projects

The PCT production protocol was developed using a controlled glass particle size. The sample size was limited to U.S. Standard 100-200 mesh (149-74mm) crushed glass because leaching of finer mesh sizes can cause overestimation of saturation concentrations, e.g. if finer powders are used, mass balance calculations need to be used to determine the maximum saturation concentration expected from a given particle size.[4] Fine particles also contribute larger errors to the estimation of the sample surface area than coarser sized samples. Moreover, use of a coarser mesh crushed glass simplifies sample preparation for radioactive service.

One test temperature, 90°C, was chosen for the production PCT protocol. This temperature is representative of the anticipated temperature in a high level nuclear waste repository because of the heat of decay of the radionuclides in DWPF waste glass. A single leachant, ASTM Type I water, was specified so that the test would be dominated by elemental species leached from the glass.

The V_{soln}/m_{solid} ratio for the PCT was chosen as 10 mL/g and test durations of 1, 3, 7, 14, and 28 days were evaluated. Seven days was chosen as the minimum test duration which optimized test precision but did not sacrifice test discrimination.[1]

Leachate filtration to <0.45 µm was determined to improve the precision of the PCT. Filtering is advantageous because it removes colloidal species which would otherwise dissolve during the leachate acidification step and erroneously be measured as soluble elemental species. Filtering the leachate also removes the potential for fine glass particulates becoming entrained in the leachate acidification.[5] Such a dissolved particulate of glass would give an erroneously high soluble leachate concentration or contribute excessive radioactivity to the leachate.

PCT sample preparation specifies that the sieved glass should be washed in ASTM Type I water and absolute ethyl alcohol to remove electrostatically adhering fine particles. Comparisons of Brunuaer-Emmet-Teller (B.E.T.) specific surface area measurements of alcohol washed and unwashed crushed basalt demonstrated that there was less than a 5% difference in the total surface area.[5] Other studies[6-9] have demonstrated that the <1mm fine particles only affect the initial non-linear kinetics of dissolution, e.g. the first 24 hour period. Thereafter, the fines are consumed with no further effect on the bulk dissolution. However, the amount of fines adhering to a glass sample is an uncontrollable quantity and, hence, sample washing was included in the PCT. Later experimental studies verified that sample washing improved the precision and the accuracy of the PCT.

An SRL internal round robin[1] and a seven laboratory external round robin were completed[10] in order to determine the precision and accuracy of the PCT. Confirmatory testing on radioactive samples was also performed.[11] These studies indicated that the PCT was very reproducible, yielded reliable results rapidly, and could be easily performed in shielded cell facilities with radioactive samples.

The PCT production protocol is test method A, e.g. PCT-A. PCT-A is a crushed glass durability test limited to 7 days ±3.5 hours and performed at 90±2°C in a leachant of ASTM-Type I water. The test method is static and conducted in stainless steel vessels. Test method A can specifically be used to evaluate whether the durability and elemental release characteristics of waste glasses have been consistently controlled during production. This method is applicable to radioactive and simulated waste glasses.

In order to allow for longer tests in various types of groundwaters at varying temperatures, PCT test method B (PCT-B) was co-developed. PCT-B is a crushed glass durability test that allows testing of waste glasses at varying test durations, test temperatures, ratios of glass surface area (S) to leachant volume (V), and leachant types. This method is static and can be conducted in stainless steel and/or PFA Teflon® vessels. Test Method B can specifically be used to evaluate the relative durability characteristics of homogeneous and/or devitrified glasses. This method is applicable to radioactive and simulated waste glasses. Test Method B cannot be used as a consistency test for production of high level radioactive waste glass.

SUMMARY

Version 7.0 of the PCT procedure is attached. This draft version has been submitted to ASTM for full committee (C26, Nuclear Fuel Cycle) ballot after being balloted successfully through subcommittee C26.13 on Repository Waste Package Materials Testing.

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1. C. M. Jantzen and N. E. Bibler, "**Product Consistency Test (PCT) and Test Protocol,**" USDOE Report DPST-87-575, Savannah River Laboratory, Aiken, SC (1987).

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6. G.R. Holdren, Jr. and R.A. Burner, "**Mechanism of Feldspar Weathering I. Experimental Studies,**" Geochim. Cosmochim. Acta, 43, 1161-1171 (1979).

7. D.E. Grandstaff, "**The Dissolution Rate of Forsterite Olivine from Hawaiian Beach Sand,**" Proceedings of the Third International Symposium on Water-Rock Interactions, Alberta Research Council, Edmonton, 72-74 (1980).

8. P.M. Tole, A.C. Lasaga, C. Pantano and W.B. White, "**The Kinetics of Dissolution of Nepheline ($NaAlSiO_4$),**" Geochim.Cosmochim. Acta, 50[3],379-392 (1986).

9. V.N. Fleer "**The Dissolution Kinetics of Anorthite ($CaAl_2Si_2O_8$) and Synthetic Strontium Feldspar ($SrAl_2Si_2O_8$) in Aqueous Solutions at Temperatures Below 100°C: With Applications to the Geological Disposal of Radioactive Wastes**" Ph.D. Thesis, The Pennsylvania State University, University Park (1982).

10. G. F. Piepel, T. E. Jones, D. L. Eggett, G. B. Mellinger, "**Product Consistency Test Round Robin Conducted by the Materials Characterization Center - Summary Report,**" USDOE Report PNL-6967, Materials Characterization Center, Battelle Pacific Northwest Laboratories, Richland, WA (1989).

11. N. E. Bibler and J. K. Bates, "**Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glasses,**" Scientific Basis for Nuclear Waste Management, XIII, V. M. Oversby and P. W. Brown (Eds.), Materials Research Society, Pittsburgh, PA, 327-338 (1990).

Attachment A

STANDARD TEST METHODS FOR DETERMINING CHEMICAL DURABILITY OF NUCLEAR WASTE GLASSES: THE PRODUCT CONSISTENCY TEST (PCT)

Version 7.0

April 19, 1994

C. M. Jantzen, N. E. Bibler, D.C. Beam and W.G. Ramsey
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Aiken, South Carolina 29808

STANDARD TEST METHODS FOR DETERMINING CHEMICAL DURABILITY OF NUCLEAR WASTE GLASSES:

THE PRODUCT CONSISTENCY TEST (PCT)

1. Scope

1.1 These Product Consistency Test methods (A and B) evaluate the chemical durability of homogeneous and devitrified glasses by measuring the concentrations of the chemical species released from a crushed glass to a test solution.

1.1.1 Test Method A is a 7 day crushed glass durability test performed at 90±2°C in a leachant of ASTM-Type I water. The test method is static and conducted in stainless steel vessels. Test method A can specifically be used to evaluate whether the durability and elemental release characteristics of waste glasses have been consistently controlled during production. This method is applicable to radioactive and simulated waste glasses.

1.1.2 Test Method B is a crushed glass durability test that allows testing of waste glasses at varying test durations, test temperatures, ratios of glass surface area (S) to leachant volume (V), and leachant types. This method is static and can be conducted in stainless steel and/or PFA Teflon® vessels. Test Method B can specifically be used to evaluate the relative durability characteristics of homogeneous and/or devitrified glasses. This method is applicable to radioactive and simulated waste glasses. Test Method B cannot be used as a consistency test for production of high level radioactive waste glass.

1.2 These test methods must be performed in accordance with all quality assurance requirements for acceptance of the data.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C92	Standard Test Methods for Sieve Analysis and Water Content of Refractory Materials[1]
C 162	Standard Terminology of Glass and Glass Products[1]
C 169	Standard Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass[1]
C225	Standard Test Methods for Resistance of Glass Containers to Chemical Attack[1]
C 429	Standard Test Method for Sieve Analysis of Raw Materials for Glass Manufacture[1]
C371	Standard Method for Wire-Cloth Sieve Analysis of Nonplastic Ceramic Powders[1]
C 1109	Standard Test Methods for Analysis of Aqueous Leachates from Nuclear Waste Materials using Inductively Coupled Plasma-Atomic Emission Spectrometry[2]
C 1174	Standard Practice for Prediction of the Long Term Behavior of Waste Package Materials Including Waste Forms Used in the Geologic Disposal of High-Level Nuclear Waste[2]
D 1129	Definitions of Terms Relating to Water[3]
D 1193	Specification for Reagent Water[3]
D 1293	Standard Test Methods for pH of Water[3]
D 1125	Test Methods for Electrical Conductivity and Resistivity of Water[3]
D4327	Standard Test Method for Anions in Water by Ion Chromatography[3]

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[1] *Annual Book of ASTM Standards, Vol 15.02*
[2] *Annual Book of ASTM Standards, Vol. 12.01*
[3] *Annual Book of ASTM Standards, Vol. 11.01*

E7	Standard Terminology Relating to Metallography[4]
E 177	Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]
E456	Standard Terminology Relating to Quality and Statistics[5]
E1402	Standard Terminology Relating to Sampling[5]
E 691	Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

2.2 *Other Documents:*

ASTM Manual on Presentation of Data and Control Chart Analysis[6]

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW846A (latest version or equivalent)[7]

Product Consistency Test Round Robin Conducted by the Materials Characterization Center- Summary Report[8]

Product Consistency Test (PCT) for DWPF Glass, Part I. Test Development and Protocol,[9]

Evaluation of Experimental Factors That Influence the Application and Discrimination Capability of the Product Consistency Test[10]

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[4] *Annual Book of ASTM Standards, Vol. 03.01*

[5] *Annual Book of ASTM Standards, Vol. 14.02*

[6] *ASTM Special Technical Publication 15D*

[7] *SW846A 3rd Edition, Revision 1, U.S. Environmental Protection Agency,Washington, DC, December, 1987.*

[8] *U.S. DOE Report PNL-6967* Battelle *Pacific Northwest Laboratory, Richland, WA, September 1989.*

[9] *U.S. DOE Report DPST-87-575, Savannah River Laboratory, Aiken, SC 29808, July 30, 1987.*

[10] *U.S. DOE Report WSRC-TR-90-526, Westinghouse Savannah River Co. (October, 1990).*

Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material[11]

3. Definitions

anneal - to prevent or remove materials processing stresses in glass by controlled cooling from a suitable temperature (after ASTM C162)

annealing - a controlled cooling process for glass designed to reduce thermal residual stress to an acceptable level, and, in some cases, modify structure (after ASTM C162)

ASTM Type I water - purified water with a maximum total matter content including soluble silica of 0.1 g/m^3, a maximum electrical conductivity of 0.06μmho/cm at 25°C, a minimum electrical resistivity of 16.67 MΩ•cm at 25°C, (see ASTM D 1193 and D 1129)

chemical durability - in this method, the resistance of a glass test specimen to the release of its constituents to an aqueous solution under the specific conditions of this test. Note: the response of glass under other conditions is outside the scope of this document.

closed system tests - a system that precludes the transport of matter either into or out of the system

consistently controlled - to verify with a high degree of accuracy, as an experiment, by comparison with a standard or a target, or by other experiments[12]

devitrified glass - glass that has crystallized during cooling and/or due to thermal heat treatment

glass - an inorganic product of fusion that has cooled to a rigid condition without crystallizing (see ASTM C162).

leachant - the solution that is being used, or is intended for use in a durability test

leachate - the solution resulting from a durability test

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[11] *U.S. DOE Report WSRC-TR-92-346, Rev. 1, Westinghouse Savannah River Co. (June, 1993).*

[12] *Websters New Twentieth Century Dictionary, Unabridged, 2nd Edition, The World Publishing Co., New York, 1973.*

mixed waste - waste containing both radioactive and hazardous components regulated by the Atomic Energy Act (AEA)[13] and the Resource Conservation and Recovery Act (RCRA),[14] respectively. The term "radioactive component" refers only to the actual radionuclides dispersed or suspended in the waste substance. [15]

mixed waste glass - a glass comprised of glass forming additives and hazardous waste that contains radioactive constituents

nuclear waste glass - a glass comprised of glass forming additives and radioactive waste

open system tests - a system that permits the transport of matter into or out of the system, e.g. O_2 and/or CO_2 diffusion into or out of the system.

radioactive - of or exhibiting radioactivity;[16] a material giving or capable of giving off, radiant energy in the form of particles or rays, as alpha, beta, and gamma rays, by the disintegration of atomic nuclei; said of certain elements, such as radium, thorium, and uranium, and their products[12]

radioactivity - spontaneous nuclear disintegration with emission of corpuscular or electromagnetic radiation, or both (consult D 1129)

sample blank - a cleaned test vessel that has been filled with the same amount of leachant as the sample vessels but contains no glass sample

sensitization - in austenitic steels such as Types 304 and 316, the precipitation of chromium carbide at the grain boundaries in a temperature range of 400-900°C (after ASTM E7). Note: this constitutes the greatest single threat to their corrosion resistance[17]

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[13] *Federal Register 52FR May 1, 1987, page 15937, Dept of Energy 10CFRPart962 Final Rule.*

[14] *Environmental Protection Agency Federal Regulation 40 CFR 261*

[15] *DOE Order 5400.3*

[16] *The American Heritage Dictionary, Houghton Mifflin, 2nd Edition, The World Publishing Co., New York, 1973*

[17] *C. A. Zapffe, "Stainless Steels," The American Society for Metals, Cleveland, OH (1949).*

set of samples - samples tested simultaneously in the same oven

simulated waste glass - a glass comprised of glass forming additives with simulants of, and/or actual chemical species in radioactive wastes, and/or in mixed nuclear wastes

standard - to have the quality of a model, gauge, pattern, or type[12]

standardize - to make, cause, adjust, or adapt to fit a standard;[13] to cause to conform to a given standard, e.g. to make standard or uniform[12]

unsensitized austenitic steel - stainless steel which is not sensitized; see sensitization

verify - to determine or test the accuracy of, as by comparison investigation, or reference, e.g. to conduct experiments to verify a hypothesis[14]

vitrification - the process of fusing waste with glass making chemicals at elevated temperatures to form a waste glass (see ASTM C162)

4. Significance and Use

4.1 These test methods provide data useful for evaluating the chemical durability of glasses as measured by elemental release. Accordingly, it may be applicable throughout manufacturing, research, and development.

4.1.1 Test Method A can specifically be used to obtain data to evaluate whether the durability of waste glasses have been consistently controlled during production (see Table I).

4.1.2 Test Method B can specifically be used to measure the durability of glasses under various leaching conditions, e.g. varying test durations, test temperatures, ratio of glass surface area (S) to leachant volume(V) (see Appendix I), and leachant types (see Table I). Data from this test may form part of the larger body of data that are necessary in the logical approach to long-term prediction of waste form behavior (see ASTM C1174).

5. Summary of the Test Methods A and B

Test Method A is the Product Consistency Test (PCT-A), which was developed specifically to test the durability of radioactive waste glasses during production (Table I).[9] It can also be used to test simulated waste glasses. The method is easily reproducible, can be performed remotely on highly radioactive samples and can yield results rapidly. The glass does not need to be annealed prior to testing. In this method the glass is crushed and sieved to U.S. Standard ASTM -100 to +200 mesh (0.149-0.074mm), the particles are cleaned of adhering fines, and an amount of sized and cleaned glass that is greater than or equal to 1 gram is placed in a Type 304L stainless steel vessel. An amount of ASTM Type I water equal to 10 cc/gram of sample mass (m_{solid}) is added and the vessel is sealed. The vessel is placed in a constant temperature devices at 90±2°C. The vessels must be placed in the constant temperature devices so that there is ample convection around the samples and even heat distribution (Figure 1). After 7 days ±3.4 hours the vessel is removed from the oven and cooled to ambient temperature. The pH is measured on an aliquot of the leachate and the temperature of the aliquot at the time of the pH measurement is also recorded. The remaining leachate is filtered and sent for analysis.

Test Method B is the Product Consistency Test (PCT-B), which was developed to test the durability of radioactive, mixed, or simulated waste glasses.[9] The method is easily reproducible, can be performed remotely if necessary, and can yield results rapidly. The glass does not need to be annealed prior to testing. In this method the glass is crushed and sieved to U.S. Standard ASTM -100 to +200 mesh (0.149-0.074mm) or to the size range of interest as long as the glass particles are less than U.S. Standard ASTM 40 mesh (0.420 mm). The particles are cleaned of adhering fines,[18] and an amount of sized and cleaned glass greater than or equal to 1 gram is placed in either a Type 304L stainless steel vessel or a PFA Teflon® vessel. An amount of ASTM Type I water equal to 10 cc/gram of sample mass (m_{solid}) is added and the vessel is sealed. Other ratios of solution volume to sample mass are allowed and other leachants are allowed. The vessel is placed in a constant temperature device at 90±2°C. Other test temperatures are permissable. It is desirable that inter-comparison of test responses be conducted at different temperatures indicate whether the reaction mechanism changes over the temperature range investigated. The vessels must be placed in the oven so that there is ample convection around the samples and even heat distribution (Figure 1). After 7 days ±3.4 hours, or other optional test durations,

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[18] *devitrified glasses containing soluble secondary phases require special handling procedures (see Sections 18.6.1 and 21.6.1)*

Table I. Summary of Test Methods A and B

	Test Method A	Test Method B
Type of Glass	**Radioactive Mixed Simulated**	**Radioactive Mixed Simulated**
Usage	**During production for rapid analysis and for waste compliance[20]**	**Scoping tests; Crystallization studies;[19] Comparative waste form evaluation**
Test Vessel	**Unsensitized Type 304L stainless steel; vessels rated to > 0.5 Mpascals[23]**	**Unsensitized Type 304L stainless steel or PFA Teflon®[21] vessels rated to > 0.5 Mpascals[23]**
Test Duration	**7 days ±3.4 hours times**	**7 days ±3.4 hours or varying**
Leachant	**ASTM Type I water solutions**	**ASTM Type I water or other**
Condition	**Static**	**Static**
Sample Mass	**> 1 gram**	**> 1 gram**
Particle Size	**U.S. Standard ASTM -100 to +200 mesh (0.149-0.074mm)**	**U.S. Standard ASTM -100 to +200 mesh (0.149-0.074mm) or other sizes which are < 40 mesh (0.420 mm)**
Leachant Volume	**10 cc/gram of sample mass**	**10 cc/gram of sample mass or varying m_{solid} to volume ratios[22]**
Temperature	**90 ±2°C**	**90 ±2°C or other temperatures provided that any observed changes in reaction mechanism are noted**
Atmosphere	**Air**	**Air or CO2 free air (See Section 10)**
Type of System	**Closed to transport**	**Open to transport in Teflon; Closed to transport in stainless steel**

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[19] *devitrified glasses containing soluble secondary phases require special handling procedures (see Sections 18.6.1 and 21.6.1)*

[20] *Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms, U.S. DOE Report EM-WAPS, Revision 0 (February, 1993).*

[21] *PFA Teflon® is perfluoralkoxy teflon; labware of PFA Teflon® is manufactured by Savillex® without plasticizers or organic additives*

[22] *see Appendix I*

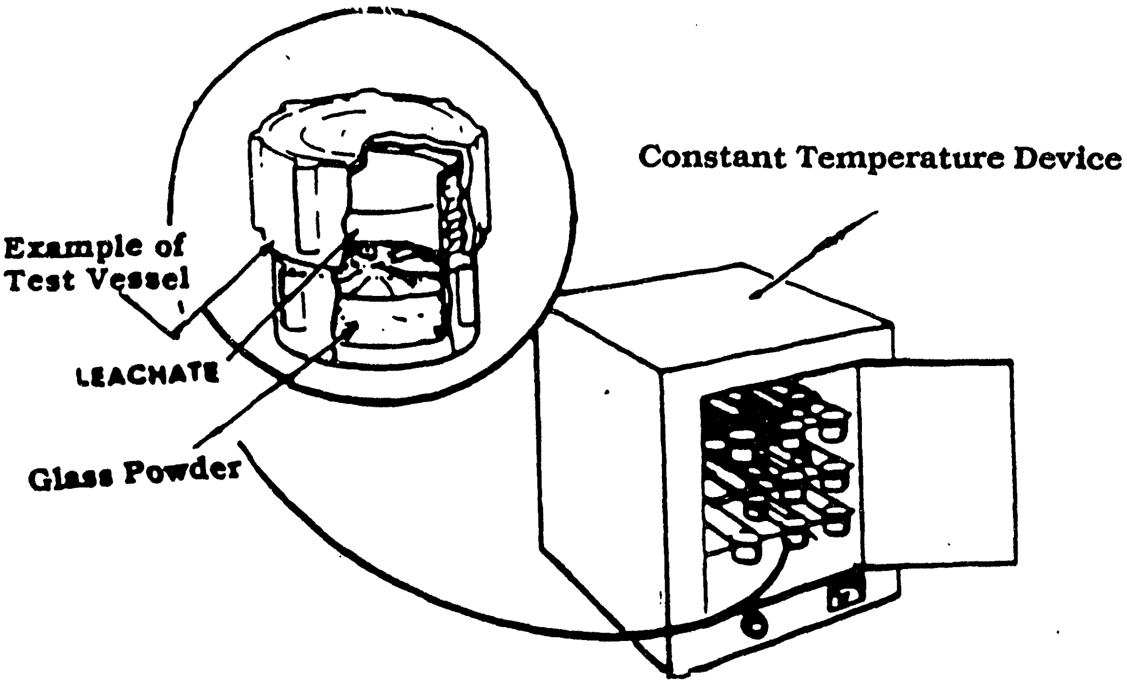

Figure 1. Schematic of Test Apparatus

the vessel is removed from the constant temperature oven device and cooled to ambient temperature. The pH is measured on an aliquot of the leachate and the temperature of the aliquot at the time of the pH measurement is also recorded. The remaining leachate is filtered and sent for analysis.

6. Apparatus

6.1 *Test Vessels for Method A* - The production test method requires the use of unsensitized Type 304L stainless steel leach vessels of > 20mL capacity designed to take internal pressures of >0.5 Mpascals without leaking (See Section 10).[23]

The stainless steel vessels require a gasket material in order to

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[23] *All appropriate precautions for operation of pressurized equipment must be taken. To ensure safe operation, the leach containers should be designed to withstand the vapor pressure of water at the test temperature with an appropriate safety factor. The thermal expansion of water must be taken into account when filling the leach containers. For example, between 4 °C and 100 °C, water expands by 4 volume %. Overfilling, e.g. filling a 60mL vessel to 55 mL, may lead to pressures inside the container that exceed the design limits and could lead to the failure of one or more parts of the vessel.*

remain sealed. Teflon® gaskets, available commercially, are acceptable for test durations of < 28 days since Teflon® is chemically inert and exposure to radiation doses up to 1 x 10^5 rad of beta or gamma radiation have been shown[24] not to damage Teflon®. If higher radiation doses are present, degradation of the Teflon® gasket can compromise the seal and/or contaminate the leachate with fluoride as F- and HF.[21,25] In high radiation doses, special gaskets fabricated from metals such as copper, gold, lead or indium are recommended. High radiation doses will not be experienced with simulated waste glasses.

6.2 *Test Vessels for Method B* - Test Method B allows for the use of either unsensitized Type 304L stainless steel or PFA Teflon® leach vessels of > 20 mL capacity designed to take internal pressures of > 0.5 Mpascals without leaking (See Section 10).[20]

The stainless steel vessels require a gasket material in order to remain sealed. If radioactive glass is tested in stainless steel vessels with Teflon® gaskets the same constraints that are noted in Section 6.1 for radioactive usage in Test Method A apply.

High radiation doses (>1 x 10^5 rad of beta or gamma radiation) will not generally be experienced with hazardous, mixed or simulated nuclear waste glasses. Teflon® vessels, available commercially, can be used in the absence of high radiation doses[21] since Teflon® is chemically inert when properly cleaned.[26]

6.3 ***Constant Temperature Devices*** - Laboratory ovens or water baths capable of maintaining ±2.0°C uniformity throughout the entire interior of the device, including the samples, at the test temperature are to be used for sample leaching and sample drying. These devices must be equipped with an over-temperature control.

6.4 *Conventional Oven* - Optional laboratory or drying ovens,

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[24] *D.M. Strachan, "Effect of Gamma Irradiation on Simulated Waste Glass Leaching and on the Leach Vessel," J. Am. Ceram. Soc. 66[9], C-158-C-160 (1983).*

[25] *N.E. Bibler, "Leaching Fully Radioactive SRP Nuclear Waste Glass in Tuff Groundwater in Stainless Steel Vessels," Nuclear Waste Management, II, D.E. Clark et. al. (Eds), Advances in Ceramics , 20, American Ceramic Society, Westerville , OH, 619-626 (1986).*

[26] *H.M. Kingston and L. B. Jassie (Eds.), Introduction to Microwave Sample Preparation, Theory and Practice, ACS, Washington, DC, 263p , 1988.; J. Goodman and L. Mudrak, "Chemical Carryover from PFA Process Wafer Carriers, Solid State Technology, October, 1988.*

capable of maintaining ±10°C, can be used for vessel cleaning and sample drying.

6.5 *Temperature Measurement Device* - Resistance thermometers and/or thermocouples with a strip chart recorder or a data logger for periodic monitoring of the temperature of the convection oven during the test duration. The maximum period between temperature measurements should be 0.5 hours.

6.6 *Balance(s)* - Any balance that will provide the following sensitivity: 0.25% of the smallest masses to be measured including the mass of the reagents, sample, leachant, leachate, leach vessel, and any required combinations.

6.7 *Weight Calibration Set* - A standard weight calibration set covering the range to include the smallest and largest weights to be measured. The weight calibration set should be traceable to the National Institute of Standards and Technology (NIST).

6.8 *Crushing Device* - Any mechanical or manual crushing device that will avoid iron (mild steel) contamination in the crushed glass specimen.[27] Crushing and grinding devices made of tungsten carbide, agate, sapphire, stainless steel, or dense alumina are acceptable.

6.9 *Sieves* - A nest of U.S. Standard ASTM stainless steel or brass sieves. The nest shall include the covers and receptacle, including the largest and smallest sieves for the desired size range.

6.10 *Flasks* - Class A or calibrated volumetric laboratoryware

6.11 *Pipets* - Calibrated pipets. Pipet tips that have either been precleaned, sterilized, or individually packaged to avoid contamination from handling.

6.12 *Syringes and Syringe Filters* - Sterilized, precleaned, or individually packaged syringes and mono or bidirectional 0.45μm syringe filters.[28]

6.13 *Sample Vials* - Precleaned or individually packaged sample vials and caps.

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[27] *G.L. McVay and C.Q. Buckwalter, "Effect of Iron on Waste Glass Leaching," J. Am. Ceram. Soc., 66, 170-174 (1983).*

[28] *Cellulose acetate filters such as Nalgene #190-2045 and/or Gellman Sciences Supor Acrodisc 25, #4614 filters have been shown not to interfere with leachate analysis*

6.14 *pH meter* - pH meter with an accuracy of ± 0.1 pH units.

6.15 *Water Purification System* - Water purification system for producing ASTM-Type I water.

6.16 *Ultrasonic Cleaner*

6.17 *Analytic Equipment*- Equipment for measuring anion and cation content of the leachates and anion content of dilute solutions, e.g. Inductively Coupled Plasma-Atomic Emission Spectrometry (see ASTM C 1109 and/or EPA SW846A), Atomic Absorption Spectrometry, Ion Chromatography (consult ASTM D 4327 and/or EPA SW846A), and/or Ion Selective Electrodes.

7. Calibrations

7.1 *Calibrations* - Initially calibrate all instruments used in this test. Verify the calibrations during use of the instrument to indicate possible errors due to instrumental drift.

7.2 *Calibration and Standardization Schedule* -

7.2.1 *Temperature Measurement Devices* - Calibrate at least annually with standards traceable to NIST or an ice/boiling water bath.

7.2.2 *Balance* - Standardize before each use and after completion of all weighings with NIST standard masses. Have the balance calibrated on an annual basis.

7.2.3 *pH meter* - Standardize the pH meter before each use and after completion of all samples with commercial buffer solutions that bracket the solution pH values being measured. Standardize the pH meter at the same temperature as the leachate solutions being measured. If only an occasional pH determination is made, standardize the assembly each time it is used. In a long series of measurements, supplemental interim checks at regular intervals are recommended. In as much as commercially available pH assemblies exhibit different degrees of measurement stability, conduct these checks at intervals of 30 minutes, unless it is ascertained that less frequent checking is satisfactory to ensure the performance described in ASTM D 1293.

7.2.4 *Water Purification System* - Calibrate at least annually following the manufacturer's instructions. Standardize before every use with the 10 MΩ•cm at 25°C resistivity calibration cell on the water purification system (see ASTM D 1125).

8. Standards

8.1 *Reference Glass* - A reference glass[29] of choice, similar in composition to the glass being tested, is to be tested in triplicate along with each batch of glasses tested (see ASTM Manual on Presentation of Data and Control Chart Analysis). The reference glass composition should be traceable to NIST, or to a comparable source.

8.2 *Multi-element Solution Standard* - A reference solution of choice, similar in composition to the leachate being tested, is to be submitted in triplicate along with each batch of leachates for multi-element analysis. The reference solution standard should be traceable to NIST, or a comparable source and have a certified shelf life.

8.3 *pH Buffers* - commercial pH buffers or pH buffers made to the specifications given in ASTM D1293 that bracket the measured pH range of the leachant and leachate. All commercial buffer solutions should be traceable to NIST, or a comparable source, and have a certified shelf life. Keep all the reference buffer solutions well sealed and replace at the expiration of shelf life, or sooner if a visible change is observed (see ASTM D 1293).

8.4 Analytic *Standard Solutions* - The reference solutions should be traceable to NIST, or a comparable source used. All standard solutions must have a certified shelf life.

9. Reagents and Standards

9.1 *ACS*[30] *Reagent Grade Acids* - Reagent grade nitric acid (HNO_3) and hydrofluoric acid(HF) for cleaning leach vessels.

9.2 *ACS*[30]*High Purity Acid* - Ultra high purity concentrated nitric acid(HNO_3) for acidification of leachates.

9.3 *Reageant Grade NaOH* - Reageant grade NaOH for cleaning of new PFA Teflon® vessels.

9.4 *Solvents* - Ethanol 95% pure and reagent grade acetone.

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[29] *for example Approved Reference Material (ARM-1) see G.B. Mellinger and J.L. Daniel, "Approved Reference Materials for Use in Nuclear Waste Management Research and Development Programs," DOE Report PNL-4955-2, Battelle Pacific Northwest Laboratories, Richland, WA (December, 1984), Standard Reference Material SRM-623 (NIST), etc.*

[30] *American Chemical Society*

9.5 *ASTM Type I Water* -Type I water shall have a minimal electrical resistivity of 16.67 MΩ•cm at 25° C (see ASTM D1193).

9.5.1 The source water shall be purified, then passed through a deionizer cartridge packed with a mixed bed of nuclear-grade resin,[31] then through a cellulose ester membrane having openings not exceeding 0.45μm.[32]

9.5.2 Pass the purified water through an in-line conductivity cell to verify its purity. Alternatively, the water can be measured for all anions and cations to verify that there is less than a total dissolved solid content including soluble silica of 0.1 g/m^3 and (see ASTM D 1193 and D 1129).

9.6 Other Leachants - Test Method B allows for the use of other leachants such as simulated or real groundwaters, brine, seawater, pH buffers, and others. The simulated solutions should be made from ACS[30] Reagent grade chemicals. All leachants should be chemically analyzed to verify their composition before durability testing begins. All leachants should have a specified shelf life.

10. Choice of Test Vessel

10.1 *Stainless Steel Vessels* - Unsensitized Type 304L stainless steel vessels must be used in Test Method A and may be used in Test Method B. The user should ensure that the vessels are free from chloride. The user is also cautioned about the attraction of steel for certain radionuclides such as Am, Pu, and other redox sensitive species.[33]

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[31] *A nuclear-grade resin mixture of the strong acid cation exchanger in the hydrogen form and the strong base anion exchanger in the hydroxide form with a one-to-one cation to anion equivalence ratio, such as that available from the Millipore Corp, Bedford, Ma 01730; Barnstead Co., 225 Rivermoor St., Boston, MA 02131; Illinois Water Treatment Co., 854 Cedar St., Rockford, IL 61105; or Vaponics, Inc., 200 Cordage Park, Plymouth, MA 02360, is suitable.*

[32] *An in-line filter such as those made by the Millipore Corp., Bedford, MA 01730; Gelman Instrument Co., 600 S. Wagner Road, Ann Arbor, MI 48106; and Schleicher and Schuell, Inc., 540 Washington St., Keene, NH 10003, has been found satisfactory.*

[33] *W.J. Gray, "Effects of Radiation on the Oxidation Potential of Salt Brine, Scientific Basis for Nuclear Waste Management, XI, Materials Research Society Symposium Volume 112, p. 405 (1987).*

Steel vessels represent "closed system" applications where the influx of CO_2 or O_2 into the leachate is not desired. The user is cautioned that the leachate concentrations and leachate pH in Teflon® and steel vessels may be different due to differences in the leachate equilibration with CO_2 and O_2, i.e. the differences in "open" and "closed" system conditions.

It is recommended that 22mL Parr[34] type vessels be used for the radioactive production application in Test Method A to minimize the amount of radioactive sample being handled.

10.2 *PFA Teflon® Vessels* - PFA Teflon® vessels may be used in Test Method B. PFA Teflon® vessels can be used for Test Method B for short-term durability testing with mixed or simulated nuclear waste glasses. The use of Teflon® vessels is acceptable for test durations of $\leq$ 28 days. Longer test durations are also acceptable only if it can be demonstrated that the vessel interactions do not affect the glass reactivity. The user should ensure that new Teflon® vessels are free from fluoride which is present as a free surface fluoride from vessel fabrication (see Section 16).

PFA Teflon® vessels are "open system" applications where the influx of CO_2 or O_2 into the leachant is either desirable or not of concern. The user is cautioned that the leachate concentrations and leachate pH in Teflon® and steel vessels may be different due to differences in the leachate equilibration with CO_2 and O_2, i.e. the differences in "open" and "closed" system conditions.

PFA Teflon® vessels cannot be used in Test Method A and it is recommended that PFA Teflon® vessels not be used in Test Method B for glasses with radiation doses above 1×10^5 rads beta or gamma.[21] The use of PFA Teflon® vessels for radiation doses $>10^5$ rads causes degradation of the Teflon®, and subsequent uptake of F- and HF by the test solution. The presence of HF in the solution may change the rate of degradation of the glass due to the acidic conditions and F- ions that attack the glass. [24,25]

11. Identification of Vessels and Vessel Cleaning History

11.1 *Identification of Vessels* - A unique identifying number should be permanently marked on each leach vessel. The same number should be permanently marked on the companion lid.

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[34] *Vessels from Parr Instrument Company, 211 Fifty-third Street, Moline, Illinois 61265 have been found satisfactory.*

11.2 *Identification of Vessel Cleaning History* - Each batch of cleaned leach vessels will be labeled with a unique batch number. A log book of the leach vessel number and date the cleaning is completed shall 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 in the log book. In this manner, any inconsistent test responses might be traced to insufficient or improper cleaning of a batch of vessels or to a problem vessel.

The batch number of the test vessel used for each sample and blank while conducting PCT Test Method A or B will be entered on a model data sheet like the one in Appendix II. These data will be maintained in a laboratory notebook for control purposes.

12. Cleaning of New Stainless Steel Vessels for PCT Test Methods A and B

New 304L stainless steel vessels shall be cleaned by the following procedure:

12.1 Remove any gaskets before cleaning new stainless steel vessels. Degrease the vessels and lids in acetone. Check the integrity of the gasket and discard if visibly damaged. Clean new undamaged Teflon® gaskets according to Section 13. Clean new undamaged metallic gaskets according to Steps 12.2 through 12.5.

12.2 Clean the vessels and lids ultrasonically in 95% ethanol for ~ 5 minutes.

12.3 Rinse the vessels and lids 3 times with ASTM Type I water.

12.4 Submerge the vessels and lids in 0.16M HNO_3 (1 wt% HNO_3) and heat on a hotplate to 90±10°C for a minimum of 1 hour. The gasket should not be in the lid during the HNO_3 cleaning step because of the

possibility that small amounts of HNO_3 may be trapped between the gasket and the lid.

12.5 Rinse the vessels 3 times with ambient temperature ASTM Type I water.

12.6 Submerge the vessels and lids in fresh ASTM Type I water for 1 hour at 90±10°C.

12.7 Rinse with fresh ASTM Type I water at ambient temperature.

12.8 Carefully place a cleaned gasket in the lid. Fill the vessel 80-90% full of ASTM Type I water. Close the lid and leave in a 90±10°C oven for a minimum of 16 hours.

12.9 Remove the vessels from the oven, cool to ambient temperature, take a cooled aliquot of the water and measure the pH (see ASTM D1293).

12.10 If the pH is not in the range 5.0-7.0, repeat steps 12.6 through 12.8.

12.11 If the 5.0-7.0 pH range cannot be achieved by 3 repetitions of steps 12.6 through 12.8, then repeat the cleaning and testing method starting at Step 12.6.

12.12 Dry vessels and lids at 90±10°C for a minimum of 16 hours. Cool. If the vessels are not used immediately close the vessels and store in a clean environment until needed.

13. Cleaning of New Teflon® Gaskets for Stainless Steel Vessels for PCT Test Methods A and B

New gaskets for stainless steel vessels should be cleaned by the following method:

13.1 Remove visible grease or dirt from acceptable gaskets using a clean lint free cloth and ethanol. Recheck the integrity of the gasket and discard if damaged.

13.2 Handle the gaskets only with clean tongs or cotton gloves.

13.3 Clean each gasket ultrasonically in 95% ethanol for ~10 minutes.

13.4 Rinse each gasket in ASTM Type I water at ambient temperature for ~3 minutes.

13.5 Bake each gasket in an oven at 200±10°C for a minimum of 4 hours.

13.6 Immerse each cooled gasket in fresh ASTM Type I water in a boiling water bath for a minimum of 2 hours.

13.7 Dry gaskets at 90±10°C for a minimum of 16 hours, and store in a clean environment until needed.

14. Cleaning of Used Stainless Steel Vessels for PCT Test Method A

When stainless steel vessels are reused subsequent to their use with radioactive specimens, residual contamination may be present. The vessels shall be cleaned before reuse by cleaning with HNO_3 and ASTM Type I water until the level of the radioactive element of interest is below the detectable level using the analytical method employed for concentration measurement of the leachate. Stainless steel vessels are also checked for Si contamination before reuse. Used stainless steel containers for radioactive service (PCT Method A) shall be cleaned according to the following method:

14.1 Remove all glass by rinsing the vessel and lid with ASTM Type I water. Fill the vessel 80-90% full with 0.16M HNO_3 (1 wt% HNO_3). Reseal the vessel and place in 90±10°C oven for a minimum of 16 hours to acid strip any radionuclides adhering to the interior of the vessel.

14.2 Check the acid stripped solution for radioactivity. Repeat step 14.1 until the radioactivity of the acid strip solution is less than three times background.

14.3 If possible remove the gasket and discard. Gaskets that have been exposed to HNO_3 during cleaning or acid stripping of the vessel may be compromised because of the possibility that small amounts of HNO_3 may be trapped between the gasket and the lid. Rinse vessels and lids thoroughly with deionized water and then with ASTM Type I water at ambient temperature. Extreme caution should be exercised so that the inside of the vessel is not contaminated with radioactivity that may have contacted the outside of the vessel.

14.4 Fill the vessel 80-90% full of fresh ASTM Type I water. If necessary, put a new gasket in the lid. Close the vessel and leave in a 90±10°C oven for a minimum of 24 hours.

14.5 Remove vessels from oven, take one aliquot of water from each vessel and measure the pH (see ASTM D1293). Take additional aliquots of water from each vessel and measure the radioactivity and the Si content of the solution.

14.6 If the pH is not in the range 5.0-7.0, or the measured radioactivity is greater than three times background, or Si is detected at >0.1 g/m^3 in the solution, repeat steps 14.3 through 14.5.

14.7 If the pH is not in the 5.0-7.0 range, or the measured radioactivity is greater than three times background, and/or the >0.1

g/m^3 Si criteria cannot be achieved by 3 repetitions of steps 14.3 through 14.6, then repeat the cleaning and testing method starting at Step 14.1.

14.8 Dry vessels, lids, and gaskets at 90±10°C for a minimum of 16 hours and store in a clean environment until needed.

15. Cleaning of Used Stainless Steel Vessels for PCT Test Method B

When stainless steel vessels are reused subsequent to their use with radioactive mixed waste specimens, residual contamination may be present. The vessels shall be cleaned before reuse by cleaning with HNO_3 and ASTM Type I water until the level of the radioactive element of interest is below the detectable level using the analytical method employed for concentration measurement of the leachate. Stainless steel vessels are also checked for Si contamination before reuse. Used stainless steel containers for PCT Test Method B shall be cleaned according to the following method:

15.1 For stainless steel vessels that have been used for mixed waste glass follow Sections 14.1 to 14.2. For vessels used for non-radioactive glass testing remove all glass by rinsing the vessel and lid with ASTM Type I water.

15.2 Remove the gasket from the lid and discard. Gaskets that have been exposed to HNO_3 during cleaning or acid stripping of the vessel may be compromised because of the possibility that small amounts of HNO_3 may be trapped between the gasket and the lid.

15.3 Soak the vessels and lids in 0.16M HNO_3 (1 wt% HNO_3) at 90±10°C for 1 hour.

15.4 Rinse vessels and lids thoroughly with ASTM Type I water at ambient temperature.

15.5 Put vessels and lids in ASTM Type I water on a hotplate at 90±10°C for a minimum 1 hour.

15.6 Put a new gasket in the lid. Fill the vessel 80-90% full of fresh ASTM Type I water. Close the lid and leave in a 90±10°C oven for a minimum of 24 hours.

15.7 Remove vessels from oven, take one aliquot of water from each vessel and measure the pH (see ASTM D1293). Take additional aliquots of water from each vessel and measure the Si content of the solution.

15.8 If the pH of the aliquot is not in the range 5.0-7.0 or Si is detected at >0.1 g/m^3 in the solution, repeat steps 15.4 through 15.7.

15.9 If the 5.0-7.0 pH range or the >0.1g/m^3 Si criteria cannot be achieved after 3 repetitions of steps 15.4 through 15.7, then repeat the cleaning and testing method starting at Step 15.2.

15.10 Dry vessels, lids, and gaskets at 90±10°C for a minimum of 16 hours and store in a clean environment until needed.

16. Cleaning of New Teflon® Vessels for PCT Test Method B

New PFA Teflon® vessels are cleaned before use with NaOH and ASTM Type I water to remove any free fluoride from the interior surfaces.[21] New Teflon® leach containers shall be cleaned according to the following method:

16.1 Rinse PFA Teflon® vessels and lids with fresh ASTM Type I water at ambient temperature.

16.2 Fill vessels at least 90% full with 5 wt% NaOH solution.

16.3 Tighten lids and place vessels in a preheated 110±10°C oven for at least 7 days.

16.4 After 12-24 hours remove the vessels from the oven long enough to retighten the lids.

16.5 Remove the vessels from the oven after the 7 days and allow to cool to ambient temperature.

16.6 Open the vessels carefully and dispose of the NaOH solution.

16.7 Rinse the vessel and lid twice with fresh ASTM Type I water at ambient temperature.

16.8 Place the vessels and lids in fresh boiling ASTM Type I water for a minimum of 1 hour.

16.9 Repeat 16.7 and 16.8.

16.10 Dry vessels and lids at 90±10°C for a minimum of 16 hours, and store in a clean environment until needed.

16.11 Fill the Teflon® vessels at least 90% full with fresh ASTM Type I water at ambient temperature. Close the vessels and leave in a 90±10°C oven for a minimum of 16 hours.

16.12 Remove vessels from oven. Allow vessels to cool to ambient temperature. Take an aliquot of water from each vessel and measure the pH (consult ASTM D1293).

16.13 If the pH is in the 5.0 to 7.0 pH range, check the F^- concentration of the water in each vessel by measuring the F^- concentration of another aliquot of the water from each vessel.

16.14If the pH is <5.0 or the F^- content is > 0.5µg/mL, repeat steps 16.1 to 16.13.

16.15 If the pH is above 7.0 repeat steps 16.7 to 16.13.

16.16 Dry vessels and lids at 90±10°C for a minimum of 16 hours, and store in a clean environment until needed.

17. Cleaning of Used Teflon® Vessels for PCT Test Method B

When Teflon® vessels are reused, residual contamination from the glasses tested may be present. The vessels shall be cleaned before reuse by cleaning with HNO_3 and ASTM Type I water. As a precaution fluoride contamination should continue to be checked for the first five uses of a given PFA Teflon® vessel. Used PFA Teflon® containers shall be cleaned according to the following method:

17.1 Remove all glass from the vessels by rinsing both the vessels and lid with ASTM Type I water.

17.2 Soak vessels and lids in 0.16M HNO_3 (1wt% HNO_3) at 90±10°C for ~1 hour on a hotplate.

17.3 Rinse vessels and lids thoroughly with fresh ASTM Type I water at ambient temperature.

17.4 Put vessels and lids on a hotplate in fresh ASTM Type I water at 90±10°C. Remove after ~1 hour.

17.5 Fill each vessel 80-90% full of fresh ASTM Type I water at ambient temperature. Close the lid and leave in a 90±10°C oven for a minimum of 16 hours.

17.6 Remove vessels from oven, take an aliquot of water from each vessel and measure the pH (see ASTM D1293) .

17.7 If the pH is in the 5.0 to 7.0 pH range, check the F^- concentration by measuring the F^- content of another aliquot of the water. If a given vessel has been reused a minimum of 5 times and the vessel cleaning history indicates that the F^- concentration has consistently been <0.5μg/mL when the pH measurement is between 5.0 to 7.0, then the measurement of the solution pH is considered sufficient evidence that the solution is free of F^- contamination.

17.8 If the pH is <5.0 or the F^- content is > 0.5μg/mL, repeat steps 17.4 to 17.7.

17.9 If the 5.0-7.0 pH range or the F^- content cannot be achieved by 3 repetitions of steps 17.4 to 17.7, then repeat the cleaning and testing method starting at Step 17.2.

17.10 Dry vessels and lids at 90±10°C for a minimum of 16 hours, and store in a clean environment until needed.

PCT Test Method A

18. Sample Preparation for PCT Test Method A

18.1 *Sample Handling* - All glass must be handled with clean equipment and stored in clean containers. For highly radioactive glass, when operations must be performed in a hot cell with manipulators: as much care as possible must be taken during these sample preparation steps.

18.2 *Choice of Appropriate Sample* - Samples of glass may either be fabricated individually or taken from larger samples of glass (see ASTM E456 and E1402). The glass does not have to be annealed. Flush the sample surface with ASTM Type I water to remove potential surface contamination and dry before crushing.

18.3 *Choice of Sample Mass* - The reference ratio of leachant volume to sample mass (V_{soln}/m_{solid}) is 10 ± 0.1 mL/g. The volume of leachant is constrained by the volume of the leach vessel chosen and the need to minimize sample size when dealing with highly radioactive glasses. For example, 1.5 g of sample can be tested in 15 mL of leachant contained in a 22 mL steel vessel. Samples must be ≥ 1 gram.

18.4 *Number of Sample Replicates* - A minimum of three replicate samples shall be used to provide estimates of experimental variability.

18.5 *Crushing and Sieving Glass* - If the glass is not fully oxidized (redox sensitive), the user is cautioned that grinding the glass in advance of the test may cause the glass to oxidize and may alter the leachate results. Redox sensitive glasses should be used within 2 days of grinding (see ASTM C169 and Reference 35). If the sample has dimensions larger than 2 cm, wrap the sample in a clean plastic bag and break it into smaller fragments with a hammer. It may be necessary to use steel crushing devices. Mild steel should be avoided due to the known interactions of mild steel and glass in solution.[27] Crushing devices made of Types 304L and 316L stainless steel should be used to minimize these effects. A representative sample of the material to be tested shall weigh at least twice the required weight of the amount of glass needed to perform the PCT in triplicate in order to have enough glass to test.

18.5.1 Transfer glass fragments into a clean manual or mechanical grinder. Clean the grinder prior to crushing a different type of glass. Do not use mechanical grinders with steel blades unless they are known to be made of Types 304L or 316L stainless steel because of the known interactions of mild steels and glass in solution.[27] If a laboratory size grinding mill is used, ensure that the blade is tungsten carbide and not mild steel. Because of the brittle nature of the tungsten carbide blades, glass samples should be ~1 to 1.5 cm before using the grinding mill. The sample basket of laboratory grinding mills can also be made of stainless steel. If the sample basket appears dull due to erosion of the steel, replace the sample basket as a precaution so that the sample does not contain excess iron.

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[35] *R.M.Torres Sanchez, E.M. Curt, C. Volzone, R.C. Mercader, and A.L. Cavalieri, "Study of Fe(II) Oxidation in Ground Magnetite, Materials Research Bulletin, v.25, 553-561 (1990).*

18.5.2 Clean brass or stainless steel sieves, catch pan and lid before and after every use.[36]

18.5.3 Visually inspect the sieves for holes or tears before every use. If a sieve is torn or deformed, discard the sieve and use a new sieve. Transfer crushed glass to the clean nest of sieves. No more than 100 grams of crushed glass should be placed on an 8 inch diameter sieve (see ASTM C225 and ASTM C371).[37] Scaling the amount of glass to the exposed surface area of the sieve, indicates that no more than 50 grams of crushed glass should be placed on a 5 inch diameter sieve and no more than 25 grams should be placed on a 3 inch diameter sieve. The correct amount of crushed glass should be placed on a 100 mesh (0.149 mm) sieve. A 200 mesh (0.074 mm) sieve should be under the 100 mesh sieve with a catch pan below.

18.5.4 Place the lid on the nest of sieves and sieve mechanically or manually as follows:

Mechanical Sieving - the mechanical shaking device38 shall be such as to produce a lateral and vertical motion of the sieve, accompanied by a jarring action so as to keep the sample moving continuously over the surface of the sieve (see ASTM C371). The mechanical sieving should continue for a minimum of 15 minutes (see ASTM C429).

Hand Sieving - alternately tap and rotate the sieves while holding them in a slightly inclined position so that the test sample will be well distributed over the sieve (see ASTM C92). Sieve for several minutes.

18.5.5 Remove the 100 mesh sieve containing +100 mesh glass fraction. Then remove the 200 mesh sieve containing the -100 to +200 mesh fraction.

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[36] *It is recommended that brass or stainless steel sieves should be cleaned by flushing them with deionized water from all directions. Dry immediately with high pressure air or in an oven at 90-110°C. Do not use solvents and/or high temperatures as the brass mesh has a protective film to inhibit corrosion.*

[37] *The variability of the sample surface area to the solution volume has the largest effect on the precision of the test (Reference 10). Particle size analysis of samples sieved with more than 100 grams of glass on an 8 inch sieve has indicated a wider gaussian particle size distribution than for samples with < 100 grams of glass on an 8 inch sieve.*

[38] *The Ro-Tap Testing Sieve Shaker supplied by W.S. Tyler Co, Mentor, OH 44060 is suitable.*

18.5.6 Tap the 200 mesh sieve forcefully over contrasting colored paper. For example, if the glass is light colored tap the sieve on dark paper. For dark glass, e.g. black nuclear waste glass, tap the sieve on white paper. Tap the sieve in an inclined position on one side, repeat several times tapping the inclined sieve on opposite sides each time. Continue the tapping until less than 0.1g of the glass passes through the sieve onto the paper after 1 minute of continuous tapping (see ASTM C92). If >0.1 g of powder appears on the paper, repeat steps 18.5.4 through 18.5.6 until <0.1 g of glass powder passes through the 200 mesh sieve.

18.5.7 Transfer the -100 to +200 mesh fraction of the sieved glass into a clean container labeled with the sample identification. The date and the name of the person preparing the sample should also appear on the container.

18.5.8 If additional material is needed, recrush the +100 mesh size fragments or repeat step 18.5.1. When new glass fragments have been prepared repeat steps 18.5.3 through 18.5.7.

18.5.9 Enter sample identification, date, and name of the person preparing the sample on a sample log sheet such as that given in Appendix II.

18.6 *Washing the -100 to +200 Mesh Glass -*

18.6.1 Washing of the -100 to +200 mesh glass to remove adhering fines is required for homogeneous glasses (see Figure 2). However, devitrified glasses may contain soluble secondary phases that might be substantially removed from the glass grains during the washing process. This possibility must be addressed when the test is used to determine the effect of devitrification on test leachate concentrations. Secondary phases present should be identified and either their potential dissolution rates relative to the bulk glass considered, or the wash solutions analyzed directly. If preferential extraction is likely in the washing step, then Sections 18.6.2 through 18.6.9 should be omitted from the test procedure and noted on the data sheet such as that given in Appendix II.

18.6.2 Place sieved glass in a clean glass beaker that will hold about 2.5 times the sample volume. For example if 15-20 grams of sieved glass is used, a 50 mL glass beaker should be used.

18.6.3 Forcibly add ambient temperature ASTM Type I water from a squirt bottle to the glass. The volume of water added should be about one and a half times the sample volume estimated from its height in the beaker. During water addition, the squirt bottle should be moved in a circular motion so that the wash stream agitates all the glass.

Figure 2. Adherent fines on -100 to +200 mesh glass particles prior to washing (Top). Glass particles after washing in ASTM Type I water and Ethanol (Bottom).

18.6.4 Allow the glass-water mixture to settle ~15 seconds, then decant off the water.

18.6.5 Repeat steps 18.6.3 to 18.6.4.

18.6.6 Repeat step 18.6.3.

18.6.7 Prepare the ultrasonic cleaner by filling with water to ~1 cm. Place the beaker from step 18.6.6 in the ultrasonic cleaner for 2 minutes. After removing the beaker from the cleaner, decant the water from the beaker and discard.

18.6.8 Repeat 18.6.6 and 18.6.7.

18.6.9 Forcibly add Ethanol from a squirt bottle to the glass. The volume of alcohol added should be about one and a half times the sample volume estimated from its height in the beaker. During this addition, the squirt bottle should be moved in a circular motion so that the wash stream agitates all the glass.

18.6.10 Place the beaker from step 18.6.9 in the ultrasonic cleaner for 2 minutes. After the 2 minutes decant the alcohol from the beaker.

18.6.11 Repeat steps 18.6.9 through 18.6.10 two more times.

18.6.12 Put the beaker containing the cleaned glass in a 90±10°C oven overnight to dry. If possible, examine the dried glass under a microscope to ensure that the fines have been removed and that there are no metal filings from the grinding. Use a magnetic tweezer to move the glass around while observing the glass under the microscope. If metal filings from the grinding are present they will stick to the magnetic tweezer making identification easier. If metal filings are present the sample must not be used. If the magnetic and/or metallic species are incorporated in the waste glass do not discard the sample and proceed to Step 18.6.13.

18.6.13 Store dried acceptable glass in a clean, sealed and labeled container in a dessicator until use. Use within 3 months. If the glasses have not been stored in a dessicator or they have been stored in a dessicator for over 3 months they must be redried at 90±10°C overnight. Drying the glass before weighing ensures that the powders do not contain adsorbed water when weighed and therefore ensures mass and surface area uniformity.

18.6.14 Enter sample identification, date, and name of the person performing the sample washing on a sample log sheet like that given in Appendix II.

19. *Preparation of Reference Glass for PCT Test Method A*

The reference glass should be prepared at the same time as the "set" of unknown glasses being tested. The same person should prepare the reference glass using the same equipment that is used for the unknown glasses being tested.

19.1 *Reference Glass Handling* - same as18.1.

19.2 *Reference Glass Sample Size* - same as 18.3.

19.3 *Number of Standard Reference Glass Replicates* - same as 18.4.

19.4 *Crushing, Sieving, and Washing of Reference Glass* - same as Sections 18.5 and 18.6.

20. *Procedure - PCT Test Method A*

20.1 *Number of Sample Replicates* - All tests for each glass should be carried out at least in triplicate (see Section 18.4).

20.2 *Number of Reference Glass Replicates* - A standard glass test shall be run at least in triplicate as part of each "set" of samples.

20.2.1 A "set" of samples is considered to be those that are tested simultaneously in the same oven.

20.3 *Number of Vessel Blanks* - A blank is considered to be a cleaned test vessel that has been filled with the same amount of ASTM Type I water as the sample vessels but contains no glass. For each "set" of samples, two blanks from the same batch of cleaned vessels shall be used. If more than one batch of cleaned vessels is used in a "set" of samples, then two blanks from each batch of vessels will be used.

20.3.1 Enter batch cleaning identifier for the blanks, the blank vessel number, the date of blank cleaning, and the name of the person who cleaned the vessels for each sample on a sample log sheet like that given in Appendix II.

20.4 *Testing Method* - Each sample, standard, and blank shall be tested according to the following method:

20.4.1 Collect a sufficient amount of fresh ASTM Type I water from the Water Purification System to fill all the leach vessels in the "set" of samples, including standards, and blanks being tested. Ensure that the Type I water meets the minimum electrical resistivity of 16.67 MΩ•cm at 25°C. Record the resistivity of the water collected on each log sheet including those for each sample glass, each reference glass, and each blank.

20.4.2 Calibrate the pH meter. Determine the pH of an aliquot of ASTM Type I water collected. Pour the water into a sealed cleaned vessel for transport to the shielded cell. Keep the water container sealed until use. Slow absorption of gaseous species from the air can cause the initial conductivity and pH of Type I water to slowly drift with time (consult ASTM D1125). Record the initial measured pH, the temperature at which the pH was measured, the pH values of the calibration solutions used, and the identification number of the pH meter used on a sample log sheet like that given in Appendix II. Initial all measurement entries on the sheet. Discard the aliquot of ASTM Type I water used for the pH measurement.

20.4.3 Standardize the balance according to Section 7.2.2. It is recommended that a user's log of the balance standardization be kept. Record the balance identification number and the annual calibration date.

20.4.4 Weigh the empty vessel with the lid and gasket. Record the vessel number and the initial weight on a sample log sheet like that given in Appendix II.

20.4.5 Place the desired amount of prepared glass in the clean leach vessel. The glass may be preweighed prior to placing it in the vessel. If the glass is preweighed record the weight of the glass. Replace the lid and reweigh the vessel, lid and sample. Record this composite weight. If the glass has not been preweighed prior to placing it in the vessel then the difference between the two vessel weighings should be recorded as the weight of the glass on a sample log sheet.

20.4.6 Add ASTM Type I water equivalent to 10 times the mass of glass added as calculated in 20.4.5 so that $(V_{soln}/m_{solid}) = 10 \pm 0.1$ mL/g. Swirl to wet the glass. Cap and seal the leach container and reweigh. Record the total weight on a sample log sheet. For blanks add a similar amount of water but no sample.

20.4.7 The "set" of samples including the reference glass vessels, and blanks should be placed immediately into a preheated 90±2°C oven. The 7 day ±3.4 hour test period starts at this time. Record the date and time (d:h:min) on a sample log sheet and on the recording device which monitors the oven temperature.

20.4.8 The testing period shall be controlled to within plus or minus 2% of the total time period of the test. At the conclusion of the test remove the leach container from the oven. Record the date and time (d:h:min) at which the sample is removed from the oven on a sample log sheet and on the recording device which periodically monitors oven temperature. The weighing, leachate pH measurement, and filtration in 20.4.9 to 20.4.12 must be done as soon as the leachate has cooled to ambient temperature.

20.4.9 Check the balance calibration according to Section 7.2.2. Record the balance identification number and the annual calibration date. It is recommended that a user's log of the balance standardization be kept. Weigh the cooled leach container plus contents. Record final weight on the sample log sheet and initial the entry. If the mass loss is calculated to be greater than 5% of the original leachant mass, disregard the results of that test and use the remaining test results (minimum of two). If more than one replicate of the same glass shows a mass loss of greater than 5% of the original leachant mass, disregard the triplicate tests and the test specimens. Repeat the test in triplicate starting with new test specimens.

20.4.10 For remote operation with radioactive glass, the leachate will need to be removed from the radioactive cell to minimize contaminating the solution. Carefully decant the leachate into a clean transport vessel and transfer this vessel to a radiochemical hood. Once this vessel is in the radiochemical hood carefully transfer the solution from the transport vessel to another clean vessel to avoid contamination.

20.4.11 Calibrate the pH meter at the same temperature as the leachate being measured (see Section 7.2.3 for frequency). Pipette an aliquot of leachate into a clean, disposable container. Determine the pH of the aliquot. Record the measured pH as the final test pH on a sample log sheet. Also record the temperature of the aliquot at the time at which the pH was measured, the pH values of the calibration solutions used, and the identification number of the pH meter used on a sample log sheet. Initial all entries. Discard the aliquot used for the pH and temperature measurement.

20.4.12 Draw a sufficient amount of the remaining leachant through a 0.45 μm syringe filter into a clean oil free disposable syringe.[39,9] Note the usage of bidirectional filters allows the leachant to be filtered in either direction. Monodirectional filters are allowed but care must be exercised to filter in one direction only. More than one syringe filter may be necessary per sample. Transfer the filtrate

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[39] *E. Vernaz, T. Advocat, and J.L. Dussossoy, "Effects of the SA/V Ratio on the Long-Term Corrosion Kinetics of R7-T7 Glass," Nuclear Waste Management, III, G.B. Mellinger (Ed.), Ceramic Transactions, v.9, Am. Ceramic Society, Westerville, OH, P. 175-185 (1990).*

into a clean specimen bottle[40] for cation analysis. For leachates with pH values ≥ 11, the solution will need to be diluted before acidification (Section 20.4.13) in order to prevent gellation of the leachate. If optional anion analyses are desired draw another filtered aliquot of the sample and transfer the contents of the syringe into a clean specimen bottle. Samples for anion analysis are not acidified (Section 20.4.14).

20.4.13 The solution must be analyzed for B, Si, and all alkali elements present in the glass at >1 wt%, e.g. Na, Li, and K. Acidify the aliquots drawn for cation analysis with concentrated ultra high purity HNO_3 equal to 1 volume % of the aliquot volume. [41] Perform cation analyses and include acidified multielement solution standards. For radioactive glasses, submit appropriately acidified aliquots for all desired radiochemical analyses. Note the analytic service identification number (if any) on the sample log sheet along with the analysis requested.

20.4.14 Anion analysis is optional but is strongly recommended. Use the non-acifified aliquot (see 20.4.12) for anion analysis. Include an unacidified multielement solution standard. Note the analytic service identification number (if any) on a sample log along with the analysis requested.

20.4.15 Measure cation and anion concentrations of glass leachates, standard glass leachates, blanks, and multielement solution standards (consult ASTM C 1109 and D 4327). The short-term precision of these analytic methods at concentrations at least 100 times the detection limit range from 0.3 to 2% relative standard deviation. Precision degrades with decreasing concentration to approximately 25% relative standard deviation at approximately two times the detection limit. The detection limits for each analysis must accompany the reported results.

20.4.16 Analysis of the solids on the filter or the remaining solid glass sample is optional. If solids analysis is not desired, the filter and solid glass sample may be discarded. If solids analysis is desired, record the appearance of the specimen powder, e.g., visible changes in color, agglomeration, and physical characteristics. Wash the

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[40] *Sample vials can be cleaned by boiling specimen bottles and caps for 1 hour in ASTM Type I water. Allow the specimen bottles to remain in the water overnight but reduce the temperature so that boiling has stopped. Remove the bottles and caps and dry in an oven at 80°C.*

[41] *Other HNO_3 acidification/dilution techniques can be used if necessary: the final diluted sample should be at least 1% HNO_3 to prevent possible hydrolysis of heavy metal cations*

specimen powder from the leach container with pure water onto a clean watch glass and dry at ≤90±2°C. A temperature of 90±2°C will only drive off adsorbed moisture and not water of hydration. After drying, store in a clean container or analyze.

PCT Test Method B

21. Sample Preparation for PCT Test Method B

21.1 *Sample Handling* - All glass must be handled with clean equipment and stored in clean containers.

21.2 *Choice of Appropriate Sample* - Samples of glass may either be fabricated individually or taken from larger samples of glass (see ASTM E456 and E1402). The glass does not have to be annealed. Flush the sample surface with ASTM Type I water to remove potential surface contamination and dry before crushing.

21.3 *Choice of Sample Mass* - The recommended ratio of leachant volume to sample mass (V_{soln}/m_{solid}) is 10 ± 0.1 mL/g. Other V_{soln}/m_{solid} can be used. The volume of leachant is constrained by the volume of the leach vessel chosen. Samples must be ≥ 1 gram.

21.4 *Number of Sample Replicates* - A minimum of three replicate samples shall be used to provide estimates of experimental variability.

21.5 *Crushing and Sieving Glass* - If the glass is not fully oxidized (redox sensitive), the user is cautioned that grinding the glass in advance of the test may cause the glass to oxidize and may alter the leachate results. Redox sensitive glasses should be used within 2 days of grinding (see ASTM C169 and Reference 35). If the sample has dimensions larger than, 2 cm wrap the sample in a clean plastic bag and break it into smaller fragments with a hammer. It may be necessary to use steel crushing devices. Mild steel should be avoided due to the known interactions of mild steel and glass in solution.[27] Crushing devices made of Types 304L and 316L stainless steel should be used to minimize these effects. A representative sample of the material to be tested shall weigh at least twice the required weight of the amount of glass needed to perform the PCT in triplicate.

21.5.1 Transfer glass fragments into a clean manual or mechanical grinder. Clean the grinder prior to crushing a different type of glass. Do not use mechanical grinders with steel blades unless they are known to be Types 304L or 316L stainless steel because of the known interactions of mild steels and glass in solution.[27] If a laboratory size grinding mill is used, ensure that the blade is tungsten carbide and not mild steel. Because of the brittle nature of the tungsten carbide blades glass samples should be ~1 to 1.5 cm before using the grinding mill. The sample basket of laboratory grinding mills can also be made of stainless steel. If the sample basket appears dull due to erosion of the steel, replace the sample basket as a precaution so that the sample does not contain excess iron.

21.5.2 Clean brass or stainless steel sieves, catch pan and lid before and after every use.[42]

21.5.3 Visually inspect the sieves for holes or tears before every use. If a sieve is torn or deformed discard the sieve and use a new sieve. Transfer crushed glass to the a clean nest of sieves. No more than 100 grams of crushed glass should be placed on an 8 inch diameter sieve (see ASTM C225 and ASTM C371). [43] Scaling the amount of glass to the exposed surface area of the sieve, indicates that no more than 50 grams of crushed glass should be placed on a 5 inch diameter sieve and no more than 25 grams should be placed on a 3 inch diameter sieve. The correct amount of crushed glass should be placed on the largest mesh sieve. The smallest mesh chosen should be under the largest mesh sieve with a catch pan below. The recommended mesh sizes are 100 mesh (0.149 mm) and 200 mesh (0.074 mm).

21.5.4 Place the lid on the nest of sieves and sieve mechanically or manually as follows:

Mechanical Sieving - the mechanical shaking device[44] shall be such as to produce a lateral and vertical motion of the sieve,

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[42] *It is recommended that brass or stainless steel sieves should be cleaned by flushing them with deionized water from all directions. Dry immediately with high pressure air or in an oven. Do not use solvents and/or high temperatures as the brass mesh has a protective film to inhibit corrosion.*

[43] *The variability of the sample surface area to the solution volume has the largest effect on the precision of the test (Reference 10). Particle size analysis of samples sieved with more than 100 grams of glass on an 8 inch sieve has indicated a wider Gaussian particle size distribution than for samples with < 100 grams of glass on an 8 inch sieve.*

[44] *The Ro-Tap Testing Sieve Shaker supplied by W.S. Tyler Co, Mentor, OH 44060 is suitable.*

accompanied by a jarring action so as to keep the sample moving continuously over the surface of the sieve (see ASTM C371). The mechanical sieving should continue for a minimum of 15 minutes (see ASTM C429).

Hand Sieving - alternately tap and rotate the sieves while holding them in a slightly inclined position so that the test sample will be well distributed over the sieve (see ASTM C92). Sieve for several minutes.

21.5.5 Remove the largest mesh size glass fraction. Then remove the smallest mesh sieve containing the mesh fraction to be used in the test.

21.5.6 Tap the smallest mesh sieve forcefully over colored paper. For example if the glass is light colored tap the sieve on dark paper. For dark glass, e.g. black simulated nuclear waste glass, tap the sieve on white paper. Tap the sieve in an inclined position on one side, repeat several times tapping the inclined sieve on opposite sides each time. Continue the tapping until less than 0.1g of the glass passes through the sieve onto the paper after 1 minute of continuous tapping (see ASTM C92). If >0.1 g of powder appears on the paper, repeat steps 21.5.4 through 21.5.6 until <0.1g of glass powder passes through the smallest mesh sieve.

21.5.7 Transfer the fraction of the sieved glass to be used for testing into a clean container labeled with the sample identification. The date and the name of the person preparing the sample should also appear on the container.

21.5.8 If additional material is needed, recrush the fragments of glass lying on top of the largest sieve screen or repeat step 21.5.1. When new glass fragments have been prepared repeat steps 21.5.3 through 21.5.7.

21.5.9 Enter sample identification, date, and name of the person preparing the sample on a sample log sheet like that given in Appendix II.

21.6 *Washing the Sized Glass -*

21.6.1 Washing of the -100 to +200 mesh glass to remove adhering fines is required for homogeneous glasses (see Figure 2). However, devitrified glasses may contain soluble secondary phases that might be substantially removed from the glass grains during the washing process. This possibility must be addressed when the test is used to determine the effect of devitrification on test leachate concentrations. Secondary phases present should be identified and either their potential dissolution rates relative to the bulk glass considered, or the wash solutions analyzed directly. If preferential extraction is likely in the washing step, then Sections 21.6.2 through 21.6.8 should be omitted from the test procedure and noted on the data sheet such as that given in Appendix II.

21.6.2 Place sieved glass in a clean glass beaker that will hold about 2.5 times the sample volume. For example if 15-20 grams of sieved glass is used, a 50 mL glass beaker should be used.

21.6.3 Forcibly add of ambient temperature ASTM Type I water from a squirt bottle to the glass. The volume of water added should be about one and a half times the sample volume estimated from its height in the beaker. During water addition, the squirt bottle should be moved in a circular motion so that the wash stream agitates all the glass.

21.6.4 Allow the glass-water mixture to settle ~15 seconds, then decant off the water.

21.6.5 Repeat steps 21.6.3 to 21.6.4.

21.6.6 Repeat step 21.6.3.

21.6.7 Prepare the ultrasonic cleaner by filling with water to ~1 cm. Place the beaker from step 21.6.6 in the ultrasonic cleaner for 2 minutes. After removing the beaker from the cleaner, decant the water from the beaker and discard.

21.6.8 Repeat 21.6.6 and 21.6.7.

21.6.9 Forcibly add Ethanol from a squirt bottle to the glass. The volume of alcohol added should be about one and a half times the sample volume estimated from its height in the beaker. During this addition, the squirt bottle should be moved in a circular motion so that the wash stream agitates all the glass.

21.6.10 Place the beaker from step 21.6.8 in the ultrasonic cleaner for 2 minutes. After the 2 minutes decant the alcohol from the beaker.

21.6.11 Repeat steps 21.6.8 through 21.6.9 two more times.

21.6.12 Put the beaker containing the cleaned glass in a 90±10°C oven overnight to dry. If possible, examine the dried glass under a microscope to ensure that the fines have been removed and that there are no metal filings from the grinding. Use a magnetic tweezer to move the glass around while observing the glass under the microscope. If metal filings from the grinding are present they will stick to the magnetic tweezer making identification easier. If metal filings are present the sample must not be used. If the magnetic and/or metallic species are incorporated in the waste glass do not discard the sample and proceed to Step 21.6.13.

21.6.13 Store dried acceptable glass in a clean, sealed and labeled container in a dessicator until use. Use within 3 months. If the glasses have not been stored in a dessicator or they have been stored in a dessicator for over 3 months they must be redried at 90±10°C overnight. Drying the glass before weighing ensures that the powders do not contain adsorbed water when weighed and therefore ensures mass and surface area uniformity.

21.6.14 Enter sample identification, date, and name of the person performing the sample washing on a sample log sheet like that given in Appendix II.

22. *Preparation of Reference Glass for PCT Test Method B*

The reference glass should be prepared at the same time as the "set" of unknown glasses being tested. The same sample mesh size, V_{soln}/m_{solid}, type of vessel, test duration, test temperature as the samples being tested should be used.The same person should prepare the reference glass using the same equipment that is used for the unknown glasses being tested.

22.1 *Reference Glass Handling* - same as 21.1.

22.2 *Reference Glass Sample Size* - same as 21.3.

22.3 *Number of Reference Glass Replicates* - same as 21.4.

22.4 *Crushing, Sieving, and Washing of Reference Glass* - same as Sections 21.5 and 21.6.

23. *Procedure - PCT Test Method B*

23.1 *Number of Sample Replicates* - All tests for each glass should be carried out at least in triplicate (see Section 21.4).

23.2 *Number of Reference Glass Replicates* - A standard glass test shall be run at least in triplicate as part of each "set" of samples.

23.2.1 A "set" of samples is considered to be those which are tested simultaneously in the same oven for the same test duration.

23.3 *Number of Vessel Blanks* - A blank is considered to be a cleaned test vessel that has been filled with the same amount of ASTM Type I water as the sample vessels but contains no glass. For each "set" of samples, two blanks from the same batch of cleaned vessels shall be used. If more than one batch of cleaned vessels is used in a "set" of samples, then two blanks from each batch of vessels will be used.

23.3.1 Enter batch cleaning identifier for the blanks, the blank vessel number, the date of blank cleaning, and the name of the person who cleaned the vessels for each sample on a sample log sheet like that given in Appendix II.

23.4 *Testing Method* - Each sample, standard, and blank shall be tested according to the following method:

23.4.1 Collect a sufficient amount of fresh ASTM Type I water from the Water Purification System to fill all the leach vessels in the "set" of samples, including standards, and blanks being tested. Ensure that the Type I water meets the minimum electrical resistivity of 16.67 MΩ•cm at 25°C. If ASTM Type I water is used record the resistivity of the water collected on each log sheet including those for each sample glass, each reference glass, and each blank.
Other leachants can be used, including but not limited to simulated groundwater, actual groundwater, seawater, brine, pH buffers. Add pertinent shelf life information on a log sheet like that given in Appendix II.

23.4.2 Calibrate the pH meter. Determine the pH of an aliquot of the leachant. Pour the water into a sealed cleaned vessel for transport. Keep the water sealed until use. If ASTM Type I water is used note that slow absorption of gaseous species from the air can cause the initial conductivity and pH of Type I water to slowly drift with time (consult ASTM D1125). Record the initial measured pH, the temperature at which the pH was measured, the pH values of the calibration solutions used, and the identification number of the pH meter used on a sample log sheet like that given in Appendix II. Initial all measurement entries on the sheet. Discard the aliquot of leachant used for the pH measurement.

23.4.3 Standardize the balance according to Section 7.2.2. It is recommended that a user's log of the balance standardization be kept. Record the balance identification number and the annual calibration date.

23.4.4 Weigh the empty vessel with the lid and gasket. Record the vessel number and the initial weight on a sample log sheet like that given in Appendix II.

23.4.5 Place the desired amount of prepared glass in the clean leach vessel. The glass may be preweighed prior to placing it in the vessel. If the glass is preweighed record the weight of the glass. Replace the lid and reweigh the vessel, lid and sample. Record this composite weight. If the glass has not been preweighed prior to placing it in the vessel then the difference between the two vessel weighings should be recorded as the weight of the glass on a sample log sheet.

23.4.6 Add leachant equivalent to the $V_{soln}/m_{solid})$ chosen. A V_{soln}/m_{solid} of 10±0.1 mL/g is recommended. Swirl to wet the glass. Cap and seal the leach container and reweigh. Record the total weight on a sample log sheet. For blanks add a similar amount of leachant but no sample.

23.4.7 The "set" of samples including the reference glass vessels, and blanks should be placed immediately into the oven preheated to the desired temperature. The recommended temperature is 90±2°C. The desired test period starts at this time. The recommended test duration is 7 days ±3.4 hours. Record the date and time (d:h:min) on a sample log sheet and on the recording device that monitors the oven temperature.

23.4.8 Leave sample vessels in oven at test temperature between 4-16 hour before testing the tightness of the lids. Quickly remove samples from the oven and retighten loose lids while the vessels are hot and return immediately to oven for the remainder of the test duration. This is especially important when using PFA Teflon® vessels. Note which lids required additional tightening on a sample log sheet.

23.4.9 The testing period shall be controlled to within plus or minus 2% of the total time period of the test. At the conclusion of the test remove the leach container from the oven. Record the date and time (d:h:min) at which the sample is removed from the oven on a sample log sheet and on the recording device which continuously monitors oven temperature. The weighing, leachate pH measurement, and filtration in 23.4.11 to 23.4.14 must be done as soon as the leachate has cooled to ambient temperature. Alternatively, a vessel with a septum can be used for periodic sampling of the leachate while at the test temperature. For each aliquot of leachate removed record the date and time (d:h:min) at which the sample is removed from the oven on a sample log sheet and on the recording device that periodically monitors oven temperature.

23.4.10 Check the balance calibration according to Section 7.2.2. Record the balance identification number and the annual calibration date. It is recommended that a user's log of the balance standardization be kept. Weigh the cooled leach container plus contents. Record final weight on the sample log sheet and initial the entry. If the mass loss is calculated to be greater than 5% of the original leachant mass, diregard the results of that test and use the remaining test results (minimum of two). If more than one replicate of the same glass shows a mass loss of greater than 5% of the original leachant mass, disregard the triplicate tests and the test specimens. Repeat the test in triplicate starting with new test specimens.

23.4.11 Calibrate the pH meter at the same temperature as the leachate being measured (see Section 7.2.3 for frequency). Pipette an aliquot of leachate into a clean, disposable container. Determine the pH of the aliquot. Record the measured pH as the final test pH on a sample log sheet. Also record the temperature of the aliquot at the time at which the pH was measured, the pH values of the calibration solutions used, and the identification number of the pH meter used on a sample log sheet. Initial all entries. Discard the aliquot used for the pH and temperature measurement.

23.4.12 Draw a sufficient amount of the remaining leachant through a 0.45 μm syringe filter into a clean oil free disposable syringe.[45,9] Note the usage of bidirectional filters allows the leachant to be filtered in either direction. Monodirectional filters are allowed but care must be exercised to filter in one direction only. More than one syringe filter may be necessary per sample. Transfer the filtrate into a clean specimen bottle[46] for cation analysis. For leachates with pH values ≥11, the solution will need to be diluted with ASTM Type I water before acidification (Section 23.4.13) in order to prevent gellation of the leachate when acidified. Leachates with pH values above 11 should be diluted with ASTM Type I water as a precaution. If optional anion analyses are desired draw another filtered aliquot of the sample and transfer the contents of the syringe into a clean specimen bottle. Samples for anion analysis are not acidified (Section 23.4.14).

23.4.13 The solution must be analyzed for B, Si, and all alkali elements present in the glass at >1 wt%, e.g. Na, Li, and K. Acidify the aliquots drawn for cation analysis with concentrated ultra high

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[45] *E. Vernaz, T. Advocat, and J.L. Dussossoy, "Effects of the SA/V Ratio on the Long-Term Corrosion Kinetics of R7-T7 Glass," Nuclear Waste Management, III, G.B. Mellinger (Ed.), Ceramic Transactions, v.9, Am. Ceramic Society, Westerville, OH, P. 175-185 (1990).*

[46] *Sample vials can be cleaned by boiling specimen bottles and caps for 1 hour in ASTM Type I water. Allow the specimen bottles to remain in the water overnight but reduce the temperature so that boiling has stopped. Remove the bottles and caps and dry in an oven at 80°C.*

purity HNO_3 equal to 1 volume % of the aliquot volume. [47] Perform cation analyses and include acidified multielement solution standards. Note the analytic service identification number (if any) on the sample log sheet along with the analysis requested.

23.4.14 Anion analysis is optional but is strongly recommended. Use the non-acifified aliquot (see 23.4.12) for anion analysis. Include an unacidified multielement solution standard. Note the analytic service identification number (if any) on a sample log along with the analysis requested.

23.4.15 Measure cation and anion concentrations of glass leachates, standard glass leachates, blanks, and multielement solution standards (consult ASTM C 1109 and D 4327). The short-term precision of these analytic methods at concentrations at least 100 times the detection limit range from 0.3 to 2% relative standard deviation. Precision degrades with decreasing concentration to approximately 25% relative standard deviation at approximately two times the detection limit. The detection limits for each analysis must accompany the reported results.

23.4.16 Analysis of the solids on the filter or the remaining solid glass sample is optional. If solids analysis are not desired, the filter and solid glass sample may be discarded. If solids analysis is desired, record the appearance of the specimen powder, e.g., visible changes in color, agglomeration, and physical characteristics. Wash the specimen powder from the leach container with pure water onto a clean watch glass and dry at ≤90±2°C. A temperature of 90±2°C will only drive off adsorbed moisture and not water of hydration. After drying, store in a clean container or analyze.

24. Calculation and Reporting for PCT Test Methods A and B

24.1 *Use of Multielement Standard* - Calculate the mean of the triplicate analyses and standard deviation of the analytic results of the multielement standard. If the mean values agree within 10% of the standard values and the relative standard deviation is <10%, then the analytic results of the study are considered acceptable.

24.2 *Use of Blanks* - Blanks are used to determine if significant amounts of those elements which are in the glass leach from the vessels themselves (probably due to improper cleaning) or are present in the original leachant itself (whether leachant is ASTM Type I water or a groundwater). A blank concentration is considered significant if

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[47] *Other HNO_3 acidification/dilution techniques can be used if necessary: the final diluted sample should be at least 1% HNO_3 to prevent possible hydrolysis of heavy metal cations*

it is >10% of the concentration of that respective element in the leachate when the glass was present in the test. Leachate concentrations, especially those for the major soluble elements in the glass (Li, B, Na, K, and Si) are measured for the replicate blanks. The mean concentration of the replicate blanks is used to correct all the sample leachate analyses. If corrections of >10% of any contaminant element occur, data for that element are invalid.

24.3 *Calculations of Leachate Concentrations* - Leachate concentrations, especially those for the major soluble elements in the glass (Li, B, Na, K, and Si) are calculated for the test glasses and the standard glass. Standard glass leachate concentrations and pH values should be control charted. Concentrations from each new set of standard glass analyses should be compared to previous standard glass test responses. If the current standard glass data set is within the control chart range then all of the leachate test data can be compared to previous data sets. If the data is outside the normal control chart range for this glass, then the data for all the samples must be bias corrected before it can be used. Use of a standard glass allows the inter-laboratory long term and short term variables to be bias corrected. Use of the standard glass also allows data from different laboratories to be compared on an equivalent basis by bias correction of the intra-laboratory variables (ASTM Manual on Presentation of Data and Control Chart Analysis[6]).

24.3.1 Calculate the final leachate volume for for each test including blanks. The amount of water loss is equal to the weight loss that occurred during heating. Leachate losses of greater than 5% of the initial volume invalidate Test Method A data, while leachate loses of greater than 5% of the initial volume invalidate Test Method B data (see Sections 20.4.9 and 23.4.10). All weight losses should be reported with the leachate data.

24.3.2 Calculate the average blank concentration in appropriate units for each element, by dividing the sum of the concentrations for the valid tests by the number of valid blank tests.

24.3.3 Calculate the corrected leachate concentration for each sample by subtracting the average blank concentration from the measured concentration. Note that for a valid test, the blank concentrations are to be <10% of the leachant concentrations.

24.3.4 Calculate the mean concentration for each valid element by dividing the sum of the corrected concentrations by the number of tests performed.

24.3.5 Calculate the standard deviation for the corrected leachate concentrations for valid element concentrations.

24.4 *Reporting and Deviations*

24.4.1 Report all results as the concentration of the elements in solution and as the concentration of the elements in solution normalized by the weight fraction of that element present in the glass.

24.4.2 All data should be recorded in a retrievable manner.

24.4.3 Deviations from the test method and the expected effect on the results should be discussed.

25. Precision and Bias for PCT Test Methods A and B

25.1 *Precision:*[48]

25.1.1 The data used to generate the measures of precision for PCT Test Method B in Teflon® are the result of intra- and inter-laboratory round robins.[8,9] These measures are typical of the methods as applied to the glasses and standards used in the round robins, and are not all inclusive with respect to other types of glasses. The measures of precision were determined in accordance with procedures in ASTM Practice E691 and E177. These measures are designated as follows:

Repeatability: the standard deviation for within-laboratory determinations.

Reproducibility: the standard deviation for between-laboratory determinations.

25.1.2 *PCT Method A Within - Laboratory Precision:* There is no round robin data involving three or more laboratories to support a statement concerning repeatability and reproducibility for PCT Test Method A in stainless steel vessels. However, Data from two separate laboratories have been used to determine the within laboratory precision for remote radioactive operation (Sections 25.1.2.1 through 25.1.2.2). Within laboratory precision has also been determined for "hands on" operation with a non-radioactive glass (Section 25.1.2.3).

25.1.2.1 *Radioactive Glass 200R* (a radioactive borosilicate glass containing U-235 neutron fission and activation products). Within-lab standard deviations for B were 2.2 and 5.3% using washed -100 to

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[48] *Precision and cited from references 8 and 9 are for Version 1.0 and 2. 0 of the PCT which did not require sample washing. Better precision has been observed when samples are washed Reference 10)*

+200 mesh glass in ASTM Type I water for 7 days (Data in Reference 49 Table III). For Si the within lab standard deviations were 0.7 and 1.1%.

25.1.2.2 *Radioactive Glass 165/42* (a radioactive borosilicate waste glass containing U-235 neutron fission and activation products). Within-lab standard deviations for B were 2.9 and 3.5% using washed -100 to +200 mesh glass in ASTM Type I water for 7 days (Data in Reference 49 Table IV). For Si the standard deviation for both laboratories was 3.2%.

25.1.2.3 *Nonradioactive Glasses SRL 202-P, 202-G* (borosilicate glasses containing simulated nonradioactive nuclear waste) and ARM-1, and SRM-623 (approved reference materials). Within laboratory relative standard deviations for B for the four glasses were 3.0, 2.1, 8.1 and 2.0% respectively. (Data in Reference 50, Table II.) Note that the precision of PCT-A performed remotely with radioactive glass is comparable to the precision presented above where the glass is handled directly.

25.1.3 *PCT Method A Between - Laboratory Precision:* There is no round robin data from three or more laboratories to support a statement concerning between laboratory precision for PCT Test Method A in stainless steel vessels using radioactive glass. Data from two separate laboratories have been used to determine the between laboratory precision for remote radioactive operation (Sections 25.1.3.1 through 25.1.3.2).

25.1.3.1 *Radioactive Glass 200R* (a radioactive borosilicate glass containing U-235 neutron fission and activation products). Between-lab relative standard deviations for B and Si were 13% and 11%, respectively, using ~~un~~washed -100 to +200 mesh glass in ASTM Type I water for 7 days (Data in Reference 49 Table III).

25.1.3.2 *Radioactive Glass 165/42* (a radioactive borosilicate waste glass containing U-235 neutron fission and activation products). Between-lab relative standard deviation for B and Si was 14% using washed -100 to +200 mesh glass in ASTM Type I water for 7 days

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[49] *N.E. Bibler and J.K. Bates, "Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glasses, "Scientific Basis for Nuclear Waste Management , XIII," V.M. Oversby and P.W. Brown (Eds.), Materials Research Society, Pittsburgh, PA, 327-338 (1990),*

[50] *H.K. Manaktala, "Leaching of Borosilicate Glass using Draft ASTM Procedure for High-Level Waste," U.S. Report CNWRA 92-018, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX (August, 1992).*

±3.4 hours (Data in Reference 49 Table IV).

25.1.4 *PCT Method B Within-Laboratory Precision for Teflon® Vessels:*

25.1.4.1 *Approved Reference Material (ARM-1*, a simulated borosilicate nuclear waste glass). Within-lab relative standard deviation for B was 2.3% and for Si was 1.8% using unwashed -100 to +200 mesh glass in ASTM Type I water for 7 days (Data in Reference 9).

25.1.5 *PCT Method B Between - Laboratory Precision:*

25.1.5.1 *Approved Reference Material (ARM-1*, a simulated borosilicate nuclear waste glass). Between-laboratory relative standard deviation (including within laboratory and between laboratory %RSD) for B was 12% and for Si was 10.2% for laboratories with varying analytic capabilities. Unwashed -100 to +200 mesh glass in ASTM Type I water for 7 days was used in the intra-laboratory comparison (Data in Reference 8 Table C.2).

25.1.5.2 *-NIST Reference Glass SRM 623* (a borosilicate glass). Between-laboratory standard deviation (including within laboratory and between laboratory %RSD) for B was 19.8% and for Si was 18.3% for laboratories with varying analytic capabilities. Unwashed -100 to +200 mesh glass in ASTM Type I water for 7 days was used in the intra-laboratory comparison (Data in Reference 8 Table C.2).

25.2 *Bias:*

25.2.1 For both PCT Method A and B the average corrected leachate concentrations for the standard glass allow assessment of long term bias or variability of the test, e.g. how reproducible the experimental variables such as oven temperature, sieving, leachate analyses, etc. are over time. Use of a standard glass allows the inter-laboratory long term and short term nuisance variables to be bias corrected. Use of the standard glass also allows data from different laboratories to be compared on an equivalent basis by bias correction of the intra-laboratory variables (ASTM Manual on Presentation of Data and Control Chart Analysis[6]).

Appendix I Calculation of the Exposed Glass Surface Area

Glass particles are neither spherical, tabular, nor square (see Figure 2). In order to calculate exposed glass surface area from the mass of glass used, one must assume a given geometric shape. If the glass is assumed to be spherical and the particle size distribution between the -100 (0.149 mm) to +200 (0.074 mm) mesh is assumed to be Gaussian the following calculation allows an estimated glass surface area to be calculated. Recent particle size analyses of well sieved samples has confirmed the Gaussian particle size distribution (see Figure 3). Based on this, the average diameter is 1.12×10^{-4} m.

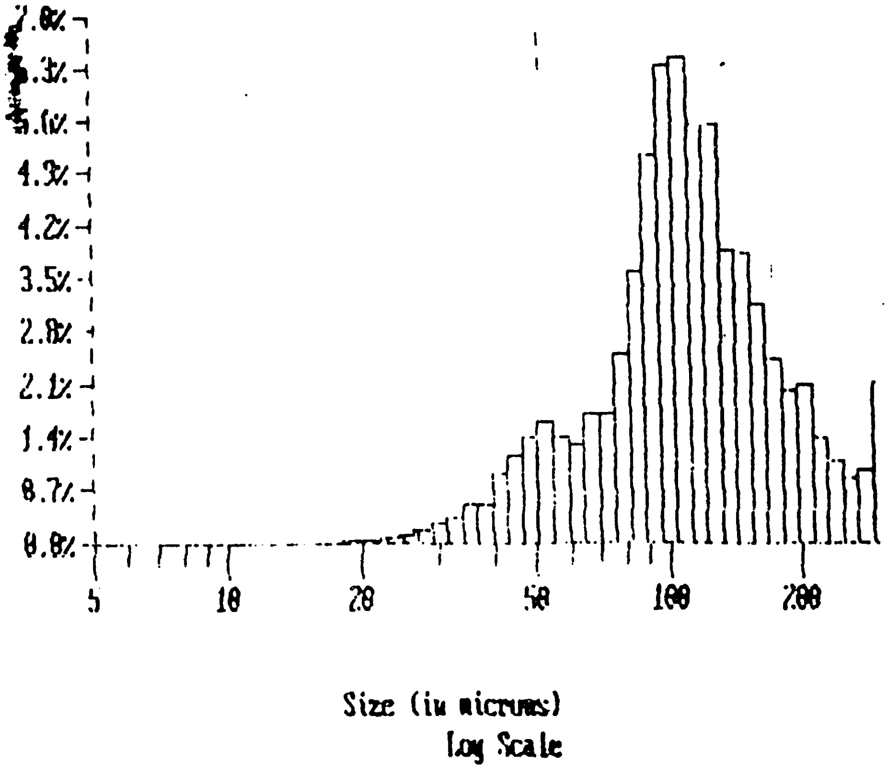

Figure 3. Example of the Gaussian particle size distribution on the 100 to +200 mesh sieve.

For this example the glass density is assumed to be 2.7 g/cc and it is assumed that the researcher has used a m_{solid} to volume ratio of 4 grams of glass to 40 cc of water. The area (A) and volume (V) of a spherical particle are given by

$$A = \Pi d^2 \quad \text{and} \quad V = (1/6)\,\Pi d^3$$

where d is the average particle diameter, 1.12×10^{-4} m for -100+200 mesh and Π is 3.14. The area and volume of an average spherical -100+200 mesh size particle is, therefore, 3.90×10^{-8} m^2 and 7.25×10^{-13} m^3, respectively. Since the assumed glass density is 2.7 g/cc or $2.7\ g/1 \times 10^{-6}\ m^3$ and density is mass/unit volume, the mass of an average size particle can be determined as

average particle mass = mass/volume
average particle mass = $(2.7\ g/1 \times 10^{-6}\ m^3)/(7.25 \times 10^{-13}\ m^3)$ =
average particle mass = 1.96×10^{-6} g

This enables the calculation of the number of particles per gram of crushed glass, e.g. there is $1 gram/1.96 \times 10^{-6}$ grams = 5.11×10^5 particles in 1 gram of -100 to + 200 mesh glass. Each particle has a surface area of 3.90×10^{-8} m^2 as given above. The total calculated surface area in 1 gram of -100 to + 200 mesh glass (A per gram) is A per gram = $(5.11 \times 10^5$ particles$)(3.90 \times 10^{-8}$ m2) = 1.99×10^{-2} m^2. The calculated surface area in 4 grams is 8×10^{-2} m^2. As long as the glass density and glass particle size remain comparable between leach tests, this parameter will remain a constant and need not be calculated every time.

Assuming cubic[51] or tabular[52] shapes imparts only a ~1% difference in the surface area calculation compared to assuming spherical shapes.

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[51] *J.W. Shade and D.M. Strachan, "Effect of High Surface Area to Solution Volume Ratios on Waste Glass Leaching," Am. Ceram. Soc. Bull., 65[12], 1568-1573 (1986).*

[52] *G.L. Pine and C.M. Jantzen, "Implications of a One-Year Basalt Weathering/Reactivity Study for a Basalt Repository Environment," U.S., DOE Report Dp-1742, E.I. duPont deNemours & Co., Savannah River Laboratory, Aiken, SC (March, 1987).*

Appendix II MODEL PCT DATA SHEET

Sample ID __________

Sample Preparation

1. Ground/Sieved on __________ by ______
2. Sample Washed on __________ by ______
3. Sample Dried on __________ by ______

Vessel Preparation

1. Sample Vessel ID # __________ Batch Cleaning #__________
2. Vessel Cleaned on __________ by ______
3. 1st Vessel Blank # __________ Batch Cleaning #__________
4. 2nd Vessel Blank # __________ Batch Cleaning #__________
5. Blanks Cleaned on __________ by ______

Run Data

	Initial Conditions	Initials	Final Conditions	Initials	Change
1. Type of solution			N/A	N/A	N/A
2. Resistivity if ASTM Type I water			N/A	N/A	N/A
3. pH/temp (°C) of leachant					
4. pH/temp (°C) of buffer solutions					N/A
5. pH meter ID #					N/A
6. wt of empty vessel (g)			N/A	N/A	N/A
7. wt of vessel + lid +sample(g)			N/A	N/A	N/A
8. wt of sample (Item 7-6 g)			N/A	N/A	N/A
9. mL of solution (Item 8 x10)			N/A	N/A	N/A
10. wt of vessel + sample + lid + solution					*
11. test and temp	PCT Version 7.0 @ 90°C				
12. date, hour, min test started and ended					**
13. vessel lid re-tightened (Y/N)			N/A	N/A	N/A

* if greater than 5% of initial value for PCT Test Method A and B the data is not usable:

** If greater than 2% of total time period then data is not usable

Leachate Analyses

Acidified with ______________ on ________ by ______
Diluted with ______________ on ________ by ______
Dilution factor ______________ on ________ by ______

Analytic Service ID's

Undiluted Cation Analysis # ____________ for ____________
Diluted Cation Analysis # ____________ for ____________
Corresponding Blank ID # ____________ for ____________
(Optional)
Undiluted Anion Analysis # ____________ for ____________
Diluted Anion Analysis # ____________ for ____________
Solids Analysis # ____________ for ____________

REMARKS/DEVIATIONS/COMMENTS:

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