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Keywords: glass, DWPF, glass durability measurement

# DEVELOPMENT OF AN ASTM STANDARD GLASS DURABILITY TEST, THE PRODUCT CONSISTENCY TEST (PCT), FOR HIGH LEVEL RADIOACTIVE WASTE GLASS (U)

by

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An extended abstract proposed for **presentation and publication** at Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, August 14-18, 1994 in Atlanta, GA

Authorized Derivative Classifier

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This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy. 

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# DEVELOPMENT OF AN ASTM STANDARD GLASS DURABILITY TEST, THE PRODUCT CONSISTENCY TEST (PCT), FOR HIGH LEVEL RADIOACTIVE WASTE GLASS

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ABSTRACT

The nation's first, and the world's largest, facility to immobilize high-level nuclear waste in durable borosilicate glass has started operation at the Savannah River Site (SRS) in Aiken, South Carolina. The product specifications on the glass wasteform produced in the Defense Waste Processing Facility (DWPF) required extensive characterization of the glass product before actual production began and for continued characterization during production. To aid in this characterization, a glass durability (leach) test was needed that was easily reproducible, could be performed remotely on highly radioactive samples, and could yield results rapidly. Several standard leach tests were examined with a variety of test configurations. Using existing tests as a starting point, the DWPF Product Consistency Test (PCT) was developed in which crushed glass samples are exposed to 90±2°C deionized water for seven days. Based on extensive testing, including a seven-laboratory round robin and confirmatory testing with radioactive samples, the PCT is very reproducible, yields reliable results rapidly, and can be performed in shielded cell facilities with radioactive samples.

## I. INTRODUCTION

Waste resulting from over thirty years of reprocessing of nuclear fuels for national defense purposes will be immobilized in the DWPF. Waste Acceptance Product Specifications (WAPS)[1] on the wasteform requires extensive characterization of the borosilicate glass product both before and after production begins. To satisfy the WAPS requirements, a leach test was needed which could reliably and easily provide rapid confirmation of the consistency of DWPF glass.

The initial basis for the DWPF Product Consistency Test (PCT) was derived from an intercomparison of crushed glass durability tests from the Materials Characterization Center (MCC), from the American Society for Testing Materials (ASTM), and from Corning Glass Works (CGW). The features of each test which optimized the following criteria were considered during PCT development:

- sensitivity of the test method to glass composition and homogeneity
- minimum 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

In this paper, the vitrified product specifications are discussed, to provide a background for the usage of the PCT. Test development, and the results of confirmatory testing are then presented. Based on extensive testing, including a seven-laboratory round robin, and confirmatory testing with radioactive samples, the PCT has demonstrated that it is reproducible, yields reliable results rapidly, and can be performed in shielded cell facilities with radioactive samples.

## II. WASTE ACCEPTANCE PROCESS

Production of canistered waste forms by the DWPF is scheduled to begin well before submission of the license application for the first repository. Further, it is likely that DWPF glass waste forms will not be shipped to a repository

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until after the year 2008. At this time, the DWPF will have produced approximately 7000 canisters, and processed all of the high-level waste currently at SRS. Thus, to ensure that the DWPF product will be acceptable at a federal repository and to allow production to begin, the Department of Energy, has defined a Waste Acceptance Process for DWPF canistered waste forms.

As part of the Waste Acceptance Process, the repository program developed Waste Acceptance Preliminary Specifications (WAPS) for the DWPF product. The WAPS identify the characteristics that the DWPF wasteforms must have in order to be compatible with the first repository. DWPF compliance with the specifications will ensure that canistered wasteforms produced in the DWPF will be acceptable for disposal.

## III. RADIONUCLIDE RELEASE SPECIFICATIONS

The WAPS specifications most relevant to public health and safety are those relating to release of radionuclides. The three relevant specifications are as follows:

- The DWPF must control its process so that the product has lower releases than the releases measured for the benchmark Environmental Assessment (EA)glass,[2] e.g. the glass qualified in the DWPF Environmental Assessment
- During production, the DWPF must verify that the product conforms to the specification, with a high degree (95%) of confidence
- The DWPF must provide radionuclide release data for glasses covering the expected range of compositions and a wider range of time and temperature treatments so that the response of crystallized glasses are included

These specifications require extensive characterization of the glass product both before and after production begins. Before production, the DWPF had to extensively characterize the chemical durability of simulated and actual waste glasses to demonstrate that the DWPF could produce an acceptable product. After production begins, the DWPF must confirm that the glass produced does, in fact, satisfy the specifications for radionuclide release.

## IV. DEVELOPMENT OF THE DWPF PCT

In 1987 the Savannah River Technology Center (SRTC) undertook the development of a leach test specifically designed to establish conformance with the WAPS. The primary objective of the test would be to confirm that the DWPF glass product was consistently acceptable. Such a leach test would be easily reproducible, capable of being performed remotely on highly radioactive samples of glass, and able to yield reliable results rapidly. Several standard leach tests were examined, with a wide variety of test configurations. Tests examined included those used widely in the nuclear industry for a variety of waste forms, such as the Materials Characterization Center (MCC-1 and MCC-3)[3] protocols, as well as ASTM tests for commercial glass (ASTM C-225)[4] and container glass classified as municipal waste (ASTM D3987).[5] The tests were screened based on the following criteria:

- Sensitivity of the test to glass quality parameters, such as composition and homogeneity. The response of the test must be dominated by the glass. Tests which are not glass dominated are not adequate measures of glass product quality. For example, tests have been designed to measure glass performance under repository conditions. The responses of these tests are dominated by repository parameters such as groundwater chemistry.[6-7]
- Minimum test duration necessary to demonstrate product quality with a high degree of precision. Use of a short test during production provides rapid confirmation of glass product quality. The extensive characterization of the product before radioactive operations begin will require testing of thousands of samples. Long-term tests make it difficult to get the information needed in a timely manner, and are more susceptible to the effects of inadvertent errors, such as power losses.
- Feasibility of remote performance of the test. Once radioactive operations begin, the test must be performed on highly radioactive samples. These will necessitate performance of the test in shielded cells, with manipulators. Thus, the sample preparation and the test procedure must be mechanically simple to perform.

- Precision of the test. The test must be precise enough so that during production the possibility of obtaining incorrect indications of glass quality is minimized.

- Acceptance of test results by the Federal repository. Ultimately, the DWPF product will go to a Federal repository. The repository must accept the test results as accurate indicators of the consistency of product quality.

Based on the preliminary screening, none of the existing glass leach tests completely fulfilled these objectives. However, the MCC-3 test protocol came closest to satisfying most of the criteria. Thus, a limited test matrix variant of the MCC-3 test method using the shorter test durations and static conditions characteristic of the ASTM and glass industry tests was used as a starting point for development of the PCT (Version 1.0).

A. SRS Internal Round Robin[8]

An internal SRS round robin was held in 1987 using the initial (Version 1.0) test protocol. The round robin had three primary objectives:

- To determine the effects of various test parameters (duration, agitation, radiation, vessel material, and filtration) on the test results.

- To select a set of test responses which were both reliable and sensitive to glass quality parameters (composition and homogeneity).

- To provide initial estimates of the achievable within-laboratory precision of the test.

The PCT was found to be sensitive to both glass composition and homogeneity. Consistent relative glass durabilities could be achieved in only one day. However, optimum precision was achieved at seven days. The 7 day precision (for triplicate tests) for any one investigator was 2-3%. Variations between investigators were 5-7%. The PCT could be performed remotely, with the same precision. The results showed no significant effect of radiation on glass durability and demonstrated that similar results were obtained whether Teflon® or stainless steel vessels were used for non-radioactive glasses. The most sensitive and precise indicators of glass quality were found to be B, Li, Na, and Si. If K was present at greater than 2 wt% in the glass, it was also a good indicator of glass quality. Filtration of leachate samples improved precision and was found to be necessary. Agitation was found to be unnecessary for the seven day test duration.

Based on the results of the internal round robin and technical reviews of the test protocol by experts in other laboratories, the PCT protocol was modified (Version 2.0). The parameters necessary for determining glass quality with a high degree of precision were optimized.

B. Multi-Laboratory External Round Robin[9]

From 1988 to 1989 a seven laboratory round robin was performed using Version 2.0 of the PCT procedure. The purpose of the round.robin was to better determine the inter- and intra-laboratory precision and accuracy of the PCT protocol, for use in establishing product compliance. The participants were selected based on their experience in glass testing, and included:

- Materials Characterization Center (MCC) which is operated by Battelle-Pacific Northwest Laboratory
- Argonne National Laboratory (ANL)
- Catholic University of America (CUA)
- Corning Engineering Laboratory Services (CELS)
- Battelle-Pacific Northwest Laboratory
- Savannah River Technology Center (SRTC)
- University of Florida (UF)

Four glasses were used in the multi-laboratory round robin. These included a National Institute of Science and Technology reference material (SRM-623), an MCC standard reference material (ARM-1), and two glasses which were based on possible compositions to be produced in the DWPF.

The MCC prepared test kits for each of the participants, which included crushed and sieved samples of glass, cleaned leach vessels, filters, sample handling equipment, and the test protocol. In addition to the test materials, 100 mL of a multi-element standard solution for chemical analysis was also supplied. This allowed estimation of the effect of lab-to-lab variability in chemical analysis.

Each of the laboratories tested all four glasses. Each laboratory tested at least one sample of each glass per week, for three consecutive weeks. Each laboratory tested one of the simulated waste glasses

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in triplicate during the first week. Each laboratory analyzed its own leachate as well as the multi-element chemical standard. Leachate samples and the chemical analysis standard were analyzed for Na, Li, K, Al, Si, Fe, B, F, Cl, $NO_3^-$, and $SO_4^=$. The pH of all solutions were also measured.

The results of this external round robin confirmed the results of the SRS internal round robin. The PCT was determined to be a precise indicator of glass quality. After statistical analysis of the results, the MCC concluded that a laboratory experienced in performing the PCT (i.e., one able to control the test precision) would be able to discriminate between glasses which differed by only 10% (based on B, Na, Si, and Li), to the 95% confidence level. This was approximately four times superior to the results from a round robin of the MCC-1 test also conducted by the MCC. This may be due to either inherently better precision of the PCT, or to a shorter learning curve for performance of the PCT. In either event, the precision which can be realized with production samples (considering multiple test performers, and personnel turnover) should be significantly greater with the PCT.

C. Multi-Laboratory Confirmatory Testing on Radioactive Glasses[10]

The PCT will have to be performed remotely on radioactive samples when DWPF production begins. Hence, additional testing was performed at ANL and SRTC to confirm that the results of the PCT were applicable to radioactive samples as well. Because of the intense radiation from the glass, all of the PCT operations which involved the glass were performed remotely with master slave manipulators. This included grinding, sieving, and washing the glasses, assembling the test apparatus, and leaching in the 90±2°C oven. Because of the small amount of radioactivity released to the leachate during the test, the leachate could be removed from the shielded cells, and sampled in a radioactive hood. The results measured by ANL and SRTC for the non-radioactive elements in the glasses agreed within 10%, providing confirmation that the results of the round robin using non-radioactive samples applied to radioactive samples.

D. ASTM Consensus Process

Based on the results of the SRS internal round robin and technical reviews of the test protocol by experts in other laboratories, the PCT protocol was modified (Version 3.0). Versions 3.0 to 7.0 have been submitted to ASTM subcommittee C26.13 (Repository Waste Package Interactions) for consensus review on the following schedule:

- Version 3.0 in January, 1990
- Version 4.0 in July, 1991
- Version 5.0 in January, 1992
- Version 6.0 in July, 1993
- Version 7.0 in July, 1994

Version 5.0 was balloted at the C26.13 sub-committee with no negatives. Several affirmatives with comments were addressed in Version 6.0. The revised Version 6.0 of the PCT was balloted at the C26 (Nuclear Fuel Cycle) full committee and subcommittee level with no negatives. Additional comments are being addressed in Version 7.0.

## V. PCT SCOPE

- 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. These methods are applicable to radioactive and simulated waste glasses (see Table I).
- Test Method A is a 7 day ± 3.4 hour 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 glasses have been consistently controlled during production.
- 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 durability characteristics of homogeneous and/or devitrified glasses.

## VI. PCT SIGNIFICANCE AND USE

- 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.

- 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).

- 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), 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).[12]

## VII. CONCLUSIONS

A rapid and reproducible glass durability test, the PCT, has been developed to confirm the consistent acceptability of the DWPF glass product. It has been shown that the PCT can be performed remotely with radioactive glass samples and is sensitive to glass quality parameters such as composition and homogeneity, but is not adversely affected by the presence of radiation. These conclusions are based on extensive testing, including inter- and intra-laboratory round robins, and confirmatory testing with radioactive samples.

## ACKNOWLEDGEMENTS

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

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Table I. Summary of PCT Test Methods A and B

| | Test Method A | Test Method B |
|---|---|---|
| Type of Glass | Radioactive<br>Mixed<br>Simulated | Radioactive<br>Mixed<br>Simulated |
| Usage | During production for rapid analysis and for waste compliance[2] | Scoping tests; Crystallization studies;[1] Comparative waste form evaluation |
| Test Vessel | Unsensitized Type 304L stainless steel; vessels rated to > 0.5 Mpascals | Unsensitized Type 304L stainless steel or PFA Teflon® [3] vessels rated to > 0.5 Mpascals |
| Test Duration | 7 days ±3.4 hours | 7 days ±3.4 hours or varying times |
| Leachant | ASTM Type I water | ASTM Type I water or other solutions |
| 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 |
| Temperature | 90 ±2°C | 90 ±2°C or other temperatures provided that any observed changes in reaction mechanism are noted |
| Atmosphere | Air | Air or $CO_2$ free air |
| Type of System | Closed to transport | Open to transport in Teflon; Closed to transport in stainless steel |

1 devitrified glasses containing soluble secondary phases require special handling procedures

2 see Reference 1

3 PFA Teflon® is perfluoralkoxy teflon; labware of PFA Teflon® is manufactured by Savillex® without plasticizers or organic additives

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