STANDARDIZED TEST METHODS FOR USE IN WASTE COMPLIANCE TESTING IN THE DEPARTMENT OF ENERGY'S WASTE ACCEPTANCE PROCESS[a]

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ABSTRACT

High-level waste form producers will be required to demonstrate compliance with a number of acceptance specifications prior to disposal of their waste forms at a geologic repository. These specifications are briefly discussed, and standardized tests that appear to be suitable for use in the compliance process are identified. The specifications deal with a number of waste form properties, including radionuclide release, composition, thermally-induced changes, canister properties, proscribed substances (e.g., organics and free liquids), heat generation, radiation dose at the canister's surface, internal canister corrosion, and accident performance. Testing may not be needed for demonstrating compliance with all of the specifications. A standardized test (or tests) should, however, be identified as applicable for demonstrating compliance with each of the specifications for which testing is needed.

The proposed standardized tests identified in the paper are, or will be, available from the Materials Characterization Center (MCC) or other organizations such as the American Society for Testing and Materials (ASTM). These tests include radionuclide release acceptance tests, recommended practices for chemical, radiochemical, and microstructural analyses, a method for determining waste form thermal expansion, a test for determining internal canister corrosion, and a canister drop test. A potential need is identified for standardized tests dealing with waste form volatilization, canister closure leak tightness, and the measurement of removable contamination on the canister's external surface.

INTRODUCTION

Producers of high-level waste forms will be required to demonstrate compliance with a number of acceptance specifications prior to disposal of their waste forms at a geologic repository. The Waste Acceptance Process was developed by the U.S. Department of Energy (DOE) in 1985 to outline the documentation and activities required to ensure that waste forms used for the immobilization of high-level wastes from the reprocessing of spent nuclear fuel will be acceptable at any of the potential repositories. As part of this process, Waste Acceptance Preliminary Specifications (WAPS) have been developed for the borosilicate glass waste forms to be produced by the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project. The West Valley WAPS (1) and the DWPF WAPS are essentially identical. These WAPS specify requirements that these waste forms must meet and documentation that must be supplied to the repository to which the waste will be sent. A number of WAPS requirements, such as those dealing with canister labeling and free-liquid within the canister, can probably be met through the use of administrative controls or literature data. For other requirements, testing will be needed.

The purpose of this paper is to propose a set of tests for use in demonstrating compliance with the existing WAPS (both of which deal with glass waste forms). Some of these tests have been standardized. Others are undergoing standardization or are under development and may ultimately require standardization. The final decision about which tests will be appropriate for waste compliance testing will be made by the repository projects and the DOE Office of Civilian Radioactive Waste Management. Input from the waste form producers and the Nuclear Regulatory Commission (NRC) will be considered during this decision making process.

This paper does not discuss the materials upon which these tests are to be performed, nor does it address the confidence limits that are to be associated with the test data. These are issues that are to be dealt with in the Waste Compliance Plan (WCP) that each waste form producer is required to develop. The WCP is essentially the producer's statement of how he intends to demonstrate compliance with each of the specifications of the WAPS. The producer's compliance strategy will dictate the materials that he intends to test. Different specifications might appropriately be met through the testing of either nonradioactive or radioactively doped simulated waste glass, or testing involving actual production glass. The producer is also to state the confidence limits that are anticipated to be associated with the compliance data that will be generated. The adequacy of each producer's WCP will be determined based on reviews by the repository projects.

The WAPS require the producer to use repository-specified (i.e., standard) tests only for the Radionuclide Release Specification. Although the producer is not required to use standardized tests for the other specifications, it is to his advantage to do so. The producer who uses available methods eliminates the need for developing his own tests. In the process of standardization, a test method is exposed to wide peer review, and a consensus about the utility of the method is developed. Both of these attributes are highly

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valued by the NRC. An additional goal of the standardization process should be that when standardization has been completed, researchers will have sufficient experience with a test that reliable estimates can be made of the precision and accuracy attainable with the method. This will allow the user of such tests to better quantify the statistical confidence associated with his data.

The WAPS requirements that will probably involve compliance testing are summarized in Table I. In most cases where a testing need is noted, a proposed test procedure is also identified. Each of these tests is briefly described in this paper in the section entitled "Proposed Test Methods for Compliance Testing." The majority of these proposed tests are, or will be, available from the Materials Characterization Center (MCC), an organization that was created by the DOE for the purpose of developing key test methods and data related to the disposal of nuclear waste. An ASTM test is also identified in the table.

TABLE I

Listing of Waste Acceptance Preliminary Specifications
for Which Testing may be Required and the Applicable Test Methods

WAPS Specification	Testing Requirements	Applicable Test Methods
Waste Form Specifications		
1.1 Chemical Specification	composition, microstructure	MCC-7,[a] MCC-13,[b] MCC-17[b]
1.2 Radionuclide Inventory Specification	radiochemical composition	MCC-17[b]
1.3 Specification for Radionuclide Release Properties	waste form chemical durability	MCC-1,[a] MCC-3,[a] MCC-14.4[c]
1.4 Specification for Chemical and Phase Stability	glass transition temperature, TTT diagram	ASTM E 228,[a] MCC-7,[a] MCC-13[b]
Canister Specifications		
2.2 Fabrication and Closure Specification	canister closure leak tightness	no standard test identified
Canistered Waste form Specifications		
3.2 Gas Specification	gasses released as a result of heating of waste form	no standard test identified
3.6 Specification for Removable radioactive on External Surfaces	determination of amount of removable contamination	no standard test identified
3.8 Specification for Maximum Dose rates	maximum canister-surface dose rate	MCC-17[b]
3.9 Chemical Compatibility Specification	corrosion of canister interior	MCC-105.5[c]
3.10 Subcriticality Specification	assure that waste form will remain subcritical	MCC-17[b]
3.12 Drop Test Specification	assure that canister will not breach or deform excessively if dropped	MCC-15[a]

(a) Method is available for use (includes MCC-1, -3, -7, -15, and ASTM E 831).
(b) Proposed scope of method has been defined but only minimal development has occurred (includes MCC-13 and MCC-17).
(c) Method is under development (includes MCC-14.4 and MCC-105.5).

PROPOSED TEST METHODS FOR COMPLIANCE TESTING

In the following sections, acceptance specifications for which testing appears to be necessary are discussed. A proposed test method (or methods) for use in developing compliance data for each of these specifications is identified, and the method is briefly described.

Radionuclide Release

The Specification for Radionuclide Release Properties (Specification 1.3 of the Waste Acceptance Preliminary Specifications) states that the producer must test his waste form using repository specified methods. Each of the repository projects will specify, in the WAPS, a separate test method and the acceptance criteria for the test that it has identified. In order to ensure that the producer's glass will be acceptable at any of the candidate repositories, the producer will be required to demonstrate compliance with each of the radionuclide release tests specified in the WAPS. The April 1986 Draft for Concurrence of the WAPS (1) does not specify these tests but states that they will be identified at a later time. Tests that potentially satisfy this WAPS specification include the MCC-1 Static Leach Test Method, the MCC-3 Agitated Powder Leach Test Method, and the MCC-14.4 Waste Form Compliance Test Method.

In MCC-1, monolithic samples of waste form material are leached for varying periods of time in various leachants (deionized water is most often used). This test method has been published in the Nuclear Waste Materials Handbook (2). A typical glass leach specimen is approximately cubic and has a surface area of approximately 4 cm^2. The specimen is supported within an inert container (typically Teflon®) that contains an amount of leachant such that the ratio of sample surface area to leachant volume is 0.1 cm^{-1}. At the termination of a test period, the test vessel is quenched and the leachate is analyzed. The data that have been proposed for use in waste compliance testing are those obtained in a 28-day test performed at 90°C using deionized water as a leachant. For a waste form to be acceptable, the normalized elemental leach rate for specific waste form constituents, averaged over the 28-day period, must be less than a stated value. The specified constituents include elements contributed by both the waste and the glass matrix.

MCC-14.4 is a test method being developed by the MCC for the Basalt Waste Isolation Project (BWIP). The test will be used to determine steady-state concentrations of certain waste radionuclides in the leachate. The maximum allowable concentrations of these radionuclides will be specified by BWIP; these maximum concentrations will constitute the test's acceptance criteria. In MCC-14.4, samples of crushed waste form and basalt will be combined with synthetic basalt ground water in a titanium reaction vessel. The test will be conducted at a temperature between 150 and 200°C and the test duration will be three months (the specific temperature and sampling times have not yet been chosen. Leachate samples will be obtained and analyzed periodically during the test. During the test the vessel will be slowly agitated. Dip tube sampling will be used to obtain the leachate samples. This process will allow the samples to be taken while the reaction vessel is at temperature and will reduce leachate quenching effects.

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In the MCC-3 test method, which has been published in the Handbook (2), crushed waste form is placed in various leachants for varying periods of time. At the termination of a test period, the test vessel is quenched and the leachate is analyzed. Different waste form size fractions have been employed in MCC-3. A 180- to 425-micrometer particle-size range (-40, +80 mesh, old U.S. sieve designation) is specified in the latest version of the method. The acceptance procedure would probably be conducted in Teflon leach containers at a temperature of 90°C using a synthetic repository-specific groundwater. Crushed repository media would also be present, and the test would be conducted for periods of up to 91 days. As currently envisioned, the acceptance criteria would be based on achieving a final waste form reaction rate that is less than a specified value. This reaction rate would be based on the release of an element, such as boron, that interacts minimally with other leachate components.

An example of the type of data from which this final reaction rate could be determined is given in the paper by Freunde, et al. (3) and is reproduced in Fig. 1. These data were obtained from experiments with glass chips leached in NaCl solutions at 200°C using different ratios of glass surface area to leachant volume (S/V) (10 to 100 m^{-1}) and times (3 to 120 days). These data are plotted versus equivalent time for an S/V of 10 m^{-1}. In this log-log plot the boron data are linear for times greater than 0.1 year, and the slope of this linear portion of the curve is equal to unity. This indicates that a constant reaction rate has been achieved. The value of this final reaction rate is found by extrapolating the linear portion of the curve back to a time of 1 day.

Composition-Related Specifications

A number of the specifications in the WAPS deal with requirements that are related to the composition of the waste form. Two that deal with this directly are the Chemical Specification and Radionuclide Inventory Specification (Specifications 1.1 and 1.2, respectively). These specifications require the producer to report to the repository the composition of his waste form (including its radionuclide inventory). These composition data (when coupled with a knowledge of the

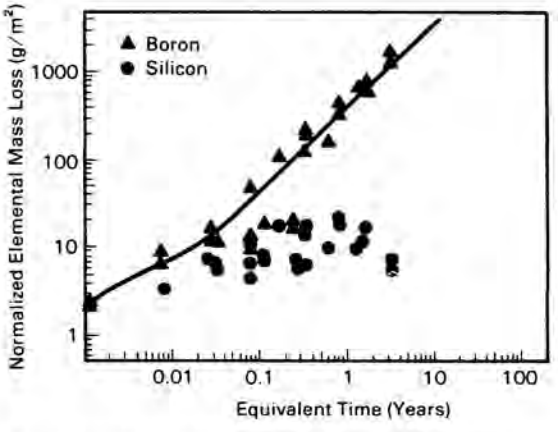

Fig. 1. Normalized Elemental Mass Loss (static test) as a Function of Equivalent Time for C-31-3EC at 200°C in Saturated NaCl Solutions (3).

waste form geometry) could be used for demonstrating compliance with certain other specifications. These are the Heat Generation Specification, Specification for Maximum Dose Rates, and Subcriticality Specification (Specifications 3.7, 3.8, and 3.9, respectively).

Waste form producers may use process data, particularly melter feed chemical analyses, as input to mass balance models that will determine the composition of their waste glass during production. Sampling and chemical analysis of production waste glass will also be done. It will be important that a high level of confidence be associated with these melter feed and product glass analyses. The MCC is currently developing the MCC-17 Method for Chemical and Radiochemical Analyses that recommends practices to be followed that will help to ensure this confidence.

It is perhaps easiest to describe MCC-17 by first stating what it does not include. MCC-17 will not recommend that specific analytical techniques such as inductively coupled plasma spectroscopy (ICP), ion chromatography (IC), or atomic absorption (AA) should be used. A method that made such recommendations would have limited utility for a number of reasons. Such a method would tend to be a "cook book" that would specify particular ways of applying specific techniques and, perhaps, specific instruments. This type of method would not be able to address other equally valid methods and instruments in adequate detail without becoming cumbersome. Also, the capabilities of available analytical techniques have and will continue to improve with time, and new analytical techniques will be developed that may make current analysis methods obsolete. Such a method would need to be continuously updated to incorporate these changes.

Instead of specifying particular analytical techniques, MCC-17 will recommend practices that should be followed to ensure the technical quality of the analyses, regardless of the analytical technique employed. The recommendations made in the method will include such practices as the analysis of standard and blind samples, random sequencing of analyses, and control charting. The method will also recommend specific ways of implementing and documenting these practices.

Much of what will be included in MCC-17 has been developed and documented by organizations such as the Environmental Protection Agency (EPA), National Bureau of Standards, and U.S. Geological Survey. The advantage of combining the applicable portions of this material into MCC-17 is that it would provide a single guideline, with which both the repository projects and producers would concur, that would specify the baseline activities needed for chemical analyses to be acceptable to the repository projects. The EPA material will be especially applicable to the generation of licensing data because many of the EPA recommendations deal with practices that help to assure that analytical data will be defendable in court. Following these practices would help to enhance the defensibility of the data before the NRC.

Microstructure-Related Specifications

Two of the WAPS specifications require heat treatment and/or microstructural characterization of the waste form. These two specifications are the Chemical Specification (which deals with the waste form's as-fabricated microstructure) and the Specification for Chemical and Phase Stability (that deals with thermally induced microstructural changes). These are identified as Specifications 1.1 and 1.4, respectively.

Two MCC test methods could be used for demonstrating compliance with Specifications 1.1 and 1.4. These are MCC-7 Method for Isothermal Heat Treatment of Waste Forms and MCC-13 Method for Microstructural Characterization. MCC-7 is an existing method [published in the Handbook (2)] that specifies experimental techniques and required documentation that will allow the researcher to reproducibly heat treat samples, such as the samples that are characterized in developing the time-temperature-transformation diagram that Specification 1.4 requires. MCC-13 is a proposed method that will recommend practices to be followed during microstructure analyses. The intent of these practices will be to ensure a high confidence level in the resulting data. The format and types of recommendations made in MCC-13 will be similar to those that will be found in MCC-17.

Impact Resistance

Specification 3.12, Drop Test Specification, is intended to ensure that filled waste canisters will be able to withstand potential facility related handling accidents without breaching or undergoing excessive deformation. The producer is required to document the canister deformation caused by a design basis fall and the leak tightness of the canister subsequent to the fall.

The MCC-15 Waste/Canister Accident Analysis Test Method could be used for supplying the compliance related information required by Specification 3.12. In MCC-15, full-scale canisters of simulated waste glass are impact tested. Prior to being impacted, a canister's weight and center of gravity are determined, and strain circles are applied to the area of the canister to be impacted. The canister is then lifted to the height required for the particular test, and positioned so that the correct impact orientation (e.g., vertical, horizontal, or corner drop) is obtained. The canister drop and its impact is recorded on high speed film. Subsequent to the impact, the strain of the canister material in the area of the impact is determined from an analysis of the changes of dimensions of the strain circles. A dye penetrant examination is done to determine whether cracks have developed, and the canister's leak tightness is measured using a helium leak test. The canister is then cut into sections, the glass is removed, and the particle size distribution of the glass is determined. MCC-15 and its development are described in detail in a paper by Slate et al. (4).

Other Specifications

There are two other specifications for which testing may be required and for which standardized tests exist. The first is the Specification for Chemical and Phase Stability (Specification 1.4), which requires that the waste form's glass transition temperature be determined. The glass transition temperature (T_g) is the temperature at which the high and low temperature thermal expansion curves for a glass intersect. The T_g occurs because glasses have greater coefficients of thermal expansion when they are at higher temperatures (above and somewhat below the melting point) than they have when they are at lower temperatures (5). A test method that would probably be appropriate for making T_g determinations is ASTM E 228, which specifies a method for determining the linear thermal expansion coefficient of solid materials using dilatometry.

The second of these specifications is the Chemical Compatibility Specification (Specification 3.9). Specification 3.9 requires the producer to assure that

internal corrosion of the canister will not cause adverse effects on normal handling during storage, transportation, and repository operation. Corrosion of the canister by the solidified waste glass will be negligible (6,7,8). Therefore, the only corrosion of concern is the corrosion by the internal canister atmosphere, of that portion of the canister that encloses the void space above the glass. A modified version of the MCC-105.5 Air-Steam Corrosion Test Method might be used for this testing. In this test, samples of canister material, representative of the material present in production canisters, are exposed to an air-steam atmosphere. The corrosive effect of this exposure on the canister material is determined.

There are also a number of specifications for which testing may be required, but for which appropriate standardized tests are not available. These include the Fabrication and Closure Specification, Gas Specification, and Specification for Removable Contamination on External Surfaces (Specifications 2.2, 3.2, and 3.6, respectively). Techniques are available for performing these measurements, but they have not been codified and subjected to peer review as standard test methods. Standardization of appropriate methods should be pursued if a need for standardized test methods is established.

SUMMARY

Standardized test methods that are currently in use or under development appear to adequately cover most of the testing that may be required to demonstrate compliance with the WAPS. It may be important to complete standardization of those tests that are under development, and to develop additional standardized tests for those specifications for which no standardized tests exist. A significant amount of work would be involved in this effort. Therefore, before this effort is undertaken, DOE must decide whether there is a need for a set of standardized test methods that would receive an "official approval" for use in waste compliance testing. If a set of approved tests is needed, DOE would need to determine what types of tests to include in the "approved list," who should develop these tests, and which organizations should review and approve the test methods. Test method review and approval might be accomplished through the use of the Materials Review Board (MRB), an organization that was created by DOE for the purpose of reviewing and approving key test methods and data related to the repository licensing process. Alternatively, other means of standardizing these tests might be considered, such as processing the tests through the American Society for Testing and Materials for publication as ASTM standards.

If a set of approved tests is adopted, producers would not be required to use these tests; however, if a producer wished to propose other tests for compliance testing, it would be reasonable to require that such test procedures undergo a review/approval process similar to that which the officially approved tests had undergone. Once approved, these alternate procedures could be used for compliance testing.

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