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STANDARD LEACH TESTS FOR NUCLEAR
WASTE MATERIALS

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INTRODUCTION

In October 1979, the U.S. Department of Energy established the Nuclear Waste Materials Characterization Center at the Pacific Northwest Laboratory. The Center has the charter to develop standard tests for the characterization of the components of the waste package, which include spent fuel, waste forms overpacks, canisters, and barriers, and to publish a Nuclear Materials Handbook. Development of these tests will result in a more fundamental understanding of these materials as well as unifying test procedures. The tests will evaluate chemical and physical properties, including thermal stability, leaching, mechanical strength, radiation stability, corrosion and others. These tests are submitted by the MCC to the Materials Review Board for acceptance. Data generated by the MCC and others using the approved tests are also submitted to the Materials Review Board for acceptance. These data are then published by the MCC in the Materials Handbook.

Five related leach tests have been proposed by the Center to study time dependent leaching of waste forms. The first four tests include temperature as a variable and the use of three standard leachants. Three of the tests are static and two study leaching under dynamic conditions. All tests require multielement analyses and measurement of the pH of the leachate. Bulk chemical analysis before leaching is required and other solid-state analyses are strongly suggested. This suite of tests satisfies the needs for waste form comparison and for comprehensive information about the leaching behavior of waste forms under various conditions.

In this paper, we discuss the waste-form leach tests in some detail and report representative data that have been collected. Systems tests which test the waste package assembly are in the early stages of design and are not discussed in this paper.

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STATIC TESTS

MCC-1 Static Low Temperature Test

Test MCC-1 has, in essence, been used by a number of investigators for some time (Bradley, 1980; Chick, 1980; Rusin, 1979) and as reported by Turcotte and Strachan (1980). In this test a monolithic sample with an approximate surface area of 400 mm^2 is totally immersed in leachant of $4 \times 10^4 \text{ mm}^3$ ($\text{SA/V} = 1 \times 10^{-2} \text{ mm}^{-1}$). The leach container is made from PFA Teflon. Distilled or deionized water, 80% saturated WIPP Brine A (Dosch, 1978) and an abbreviated Tuff ground water (Wolfsberg, 1979) are the standard leachants but the use of other groundwaters is acceptable.

A minimum test matrix is required for all studies to assist in data comparison, for quick comparison of waste forms and to assist the Center and the Materials Review Board in data verification. For MCC-1, this matrix requires 28 days to complete, the use of the three standard leachants, and a test temperature of 90°C . Leachate analyses are required. The minimum test matrix results are shown in Fig. 1, for PNL 76-68 glass.

A round robin is currently underway to verify the practicality and reproducibility of this procedure.

MCC-2 High Temperature Static Test

This test extends the MCC-1 test temperature to above 100°C . Testing can be done in autoclaves or in inexpensive Teflon® lined acid digestion vessels. A monolithic sample is used with the surface area such that the ratio of SA/V is $1 \times 10^{-2} \text{ mm}^{-1}$. A minimum test matrix is required for the same reasons outlined under MCC-1. This matrix is similar to the MCC-1 minimum matrix and is performed at 150°C . Leachate analyses are required. An example of the results for PNL-76-68 glass is shown in Fig. 2. Solid state analyses such as x-ray diffraction, depth profiling, ESCA, and SEM analyses are strongly recommended. These initial data indicate a marked change in the leaching of PNL-76-68 glass between 150°C and 250°C .

MCC-3 Solubility Test

This test is performed on powdered samples to determine the maximum solubility of the waste form in the leachant of interest. In this test the waste-form sample is ground to pass through a 325 mesh screen. The sample is then allowed to react with a volume of leachant equal to ten times the sample mass until no change in the leachate composition is observed. As indicated in Fig. 3 even at 250°C and 14 days with powdered PNL-76-68 glass the leachate composition has not reached steady state. High releases of material after one day of reaction are probably due to the high reaction rate of the ground samples that include many fines. Decreases in concentration indicate alteration to less soluble

FIGURE 1. Normalized Elemental Mass Loss vs Time for PNL-76-68 Glass Leached in Deionized Water at 90°C Using the MCC-1 Test.

FIGURE 2. Normalized Elemental Mass Loss vs Time for PNL-76-68 Glass Leached in Deionized Water at 150°C and 250°C Using the Proposed MCC-2 Test.

phases. Stirring of the sample may also be very important. The data summarized in Fig. 3 were obtained under basically static conditions but the sample was stirred four times daily. The ovens are being modified so that the vessels can be continuously stirred.

Some materials will require lengthy times to equilibrate with the leachate and laboratory studies are continuing. However, the minimum test matrix at 150°C may require testing of samples at 3, 7, and 14 days in water and triplicate data obtained in the standard leachants at 14 days. Constant stirring of the sample may also be required. Data obtained using the Teflon®-lined, acid digestion vessels will be corroborated using an autoclave from which leachate samples at temperature and pressure can be extracted.

FLOW TESTS

MCC-4 Low Flow Test

In principle, this test will most closely simulate repository conditions. It is similar to that developed by Coles et al., 1978, but uses the same leach container as MCC-1. In this test the leachant is pumped past a monolithic sample. Data are collected from the leachate after a single pass through the leach container. The minimum test matrix at 90°C extends to 28 days with flow rates of 0.1, 0.01 and 0.001 mL·min⁻¹. Using the minimum test matrix, analyzable quantities of material were found in the unconcentrated leachate from 76-68 glass. However, at flow rates > 0.1 mL·min⁻¹ or with more durable waste forms, techniques for concentrating the leachate or samples with radioactive tracers may be needed.

Data are plotted as normalized cumulative amount of element "i" leached per unit area versus time. This plot is then differentiated either mathematically or graphically to obtain the slope of the curve at any time. The slope is the normalized instantaneous leach rate which can be plotted versus time as shown in Fig. 4. The conditions for the experiment shown in Fig. 4 were 90°C and 0.10 mL·min⁻¹ using water as a leachant. Under these conditions a combination of ion exchange and corrosion mechanisms exist at the beginning of the leaching experiment. At about 10 days the dominant mechanism appears to be corrosion since such dissimilar elements as Cs, Si and Sr leach at equivalent rates. The 28d average leach rates obtained using MCC-1 are also shown in Fig. 4. The static conditions of MCC-1 yield leach rates which are lower by a factor of two for Si and 200 for Sr.

MCC-5 Soxhlet Test

This test was adopted because it provides a convenient method of assessing waste-form leach rates under conditions of infinite dilution. It has been in use for a long time by the waste form developers and is currently in popular use in Europe. Three features of the test as used in the past have been changed. A monolithic sample replaces the powdered sample. Solution analyses and an all Teflon® apparatus are required.

FIGURE 3. Leachate Solution Concentration vs Time for Powdered PNL-76-68 Glass at 250°C Using the Proposed MCC-3 Test.

FIGURE 4. Normalized Instantaneous Leach Rate vs Time for PNL-76-68 Glass at 90°C and Flow Rate of $0.10 \pm 0.01 \text{ mL min}^{-1}$ Using the Proposed MCC-4 Test

In the past the soxhlet apparatus was constructed of Pyrex®. However, solution analyses are now required and Pyrex® contributes to and interferes with the leachate concentrations. For instance, when a synthetic leachate is allowed to reflux for 14 days in the Pyrex® soxhlet apparatus, elements such as Cs, Ca, Sr, and Mo decreased in concentration by up to a factor of 100. Elements such as B, Si, and Na were found to increase in concentration by up to a factor of 10. These problems should be alleviated by using an all-Teflon® apparatus and by adding acid to the leachate, which then remains in the apparatus for 12 hours before sampling. Results from experiments using MCC-5 are not yet available.

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