QUALIFICATION OF WASTE FORMS TO MEET THE REQUIREMENTS OF 10 CFR 61

J. W. Phillips
Westinghouse Hittman Nuclear Incorporated
9151 Rumsey Road
Columbia, Maryland 21045

ABSTRACT

The purpose of this paper is to provide guidance to waste generators in the development and management of a program to qualify solidified low-level radioactive wastes to the stability requirements of 10 CFR 61. Starting with a review of the implementing regulations and the NRC Branch Technical Position (BTP) the paper discusses various options available in testing methods and procedures. The approach outlined in this paper starts with small scale laboratory testing to select solidification parameters for testing. Suggestions are given on the number and size of samples to use in the various tests. These suggestions are based not only on the technical requirements of the BTP, but also the practical experience of having completed a successful program and the economic considerations needed to run a cost effective program. This paper also discusses how to implement a step by step scale up program when the actual process equipment cannot be used to produce the samples tested. Finally an overview is provided of the resources, from the standpoint of time (schedule), manpower and contractor supplemented testing, necessary to conduct a complete, comprehensive and successful program.

INTRODUCTION

On December 27, 1982, the Nuclear Regulatory Commission (NRC), promulgated a new Part 61 to Title 10, Energy, of the Code of Federal Regulations, entitled Licensing Requirements for Land Disposal of Radioactive Wastes. In the same issue of the Federal Register, a new paragraph 311, Transfer and Disposal Manifests, was added to 10CFR20, Standards for Protection Against Radiation. Although 10CFR61 does not directly apply to existing burial facilities, 10CFR20.311, requires that radioactive wastes shipped by NRC licensed facilities after December 27, 1983, meet certain requirements specified in 10CFR61. These requirements address the classification of wastes and their physical characteristics and are specified in paragraphs 61.55 and 61.56, respectively.

In May of 1983, the NRC published additional guidance for establishing conformance to paragraphs 61.55 and 61.56. This guidance, in the form of two Branch Technical Positions (BTP), is applicable as follows:

- o 10CFR61.55, Waste Classification - Low-Level Waste Licensing Branch Technical Position on Radioactive Waste Classification, Rev. 0, May 1983.
- o 10CFR61.56, Waste Characteristics - Technical Position on Waste Forms, Rev. 0, May 1983.

It is the purpose of this paper to review the NRC position on waste form qualification with specific attention to the Class B and Class C waste forms. As stated in 10CFR61.55, Class B and Class C wastes "must meet both the minimum and stability requirements set forth in Section 61.56." It is to these "stability requirements" that the BTP on Waste Forms is addressed. Table 1 summarizes the various parameters used to evaluate waste form stability and the criteria by which such stability is determined.

Table 1
Waste Form Stability Criteria

Test	Stability Criteria (After Testing)
Initial Sample	Free Standing Monolith Free Liquid ≤ 0.5% of Waste Volume Compressive Strength ≥ 50 psi
Irradiation-10^8 RAD	Compressive Strength ≥ 50 psi
Biodegradation Bacteria Attack Fungus Attack	 Compressive Strength ≥ 50 psi Compressive Strength ≥ 50 psi
Leach Testing	Leachability Index > 6.0 for each Isotope
90-Day Immersion in Water	Compressive Strength ≥ 50 psi
Thermal Cycling	Compressive Strength ≥ 50 psi
Free Liquid	≤ 0.5% of Waste Volume pH - between 4 and 11

The BTP further requires that testing conducted on laboratory sized samples be confirmed by analyzing sections of waste from full size products produced using actual solidification equipment.

DEVELOPING THE TEST PROGRAM

When initiating a Waste Qualification Program, the first step is to determine exactly what testing will be performed on the samples. This will also define the number and sizes needed. The discussion below identifies various factors that should be considered when making these decisions.

INITIAL SAMPLE

The initial samples are used to demonstrate the minimum criteria of a free-standing monolith and no free liquid greater than 0.5% of the waste volume. In addition compression tests are performed to show that the samples meet the minimum compression strength criteria of 50 psi. At least two samples should be used; at least three inches in diameter by six inches high.

This size is recommended for two reasons. First, the molds for this size sample are relatively inexpensive for purchasing in bulk quantity in either coated cardboard or plastic. By comparison, reusable metal molds for two-inch cubes cost several hundred dollars. Second reason is that individual samples can be made up using disposable 1,000 ml plastic beakers. A three-inch by six-inch mold is almost exactly 700 ml.

IRRADIATION

This test is quite straightforward and there isn't much room for variation. The 10^8 Rad dose is easily achieved in a gamma field using a Co-60 source. The total exposure time for a 1 MRad source is 100 hours and can be achieved in less than a week. Two samples should be sufficient, and in fact for many wastes, only one sample may be necessary.

BIODEGRADATION

The ASTMG-21[1] test for Fungi and the ASTMG-22[2] test for bacteria are common test methods for plastics. Each test takes three weeks although an additional two to three weeks must be allotted for the testing lab to procure the cultures and incubate sufficient material to conduct the testing. The more samples to be tested the longer an incubation period required.

For waste solidified in cement only one sample per test should be required as the high pH levels that normally occur in the agar are not conducive to growth of either the fungi or bacteria. Additional samples may be necessary when testing solidification media where growth is expected.

One note of caution. One of the fungi, penicillium funiculosum is a plant pathogen. As such, anything that comes in contact with it must be sterilized. Methods of sterilization are available that will not effect the samples. However, some labs may not have the facilities available to perform the sterilization procedure best suited to your waste type. In this case a substitute fungus may be in order. Penicillium jenseni is a similar fungus, both being common soil fungi, and is not a plant pathogen.

LEACH TEST

The BTP specifies that leach testing should be performed in accordance with ANS 16.1[3] for a period of ninety (90) days. ANS 16.1 is a five-day leach test, and the expansion of the test to ninety (90) days is currently left open. Since leach testing using radioactive tracers is expensive, it is recommended that the additional leach intervals be minimal without totally ignoring the interval between the fifth day and the ninetieth day. One such testing cycle would be: 2 hours, 7 hours, 1, 2, 3, 4, 5, 19, 46, 90 days, for a total of ten leach intervals.

If the leach tests are to be conducted using radioactive tracers, the following four isotopes have been commonly used in most recent test programs: Co-60, Cs-137, Sr-85 and Ce-144. Concentrations should be kept relatively low to minimize exposure to the personnel performing the testing, usually 1 to 10 μCi/cc will be acceptable.

The BTP does not address the number of samples to be leached for each type of waste to be tested. Based upon Hittman's experience, two samples are both necessary and sufficient. They are necessary from the standpoint of confirming unexpected spikes in the leachate if the same spikes are seen in both samples; sufficient in that additional samples would not provide enough additional data to warrant their cost.

The last major issue is what to use as the leachate. The BTP states that "In addition to the demineralized water test specified in ANS 16.1, additional testing using other leachants specified in ANS 16.1 should also be performed . . . It is preferred that the synthesized sea water leachant also be tested." While there may be some academic interest in how certain solidified wastes react to various leachants the economic concerns in running such a program are not conducive to such multiple testing. Data is available on how various wastes behave in certain leachates. Selecting a leachate that represents the worst case leachate for a specific waste type and using only that leachant, is from the authors standpoint the most practical approach.

One last comment. The BTP states that "Speciman sizes should be consistent with the samples prepared for the ASTM C-39 or ASTM D1074 compressive strength tests." To do so would result in significant quantities of liquid waste that are not warranted. Using three-inch diameter by six-inch high samples, and a leachate volume to sample surface area ratio of 10 cm, would require a leachate volume of over 4½ liters. A commonly used leach test specimen size of one-inch diameter by two-inches high requires a leachate volume of 506 ml. Considering two specimens and ten leachate changes the difference is between disposing of ten liters of contaminated liquid and 91 liters of liquid.

90-DAY IMMERSION IN WATER

In most of the wastes tested by Hittman, the 90-day immersion test was the most critical to the success of the program. With only one exception solidified products that passed the immersion test also passed all the other tests. Because of the sensitive nature of the test, it is recommended that at least two samples be put through the full 90-day program. Additional samples should also be tested at shorter immersion periods, say 2, 4, 6, and 10 weeks. This will also allow the identification of mixes that are destined to fail the full 90-day test without waiting for full 90 days. Depending on the specifics of the test program anywhere from 2 to 10 samples may be required. For the purpose of this discussion, we will assume eight.

THERMAL CYCLING

The thermal cycling test specified in the BTP ASTM-B553-79, requires cycling samples between +60°C and -30°C. Samples are exposed to each temperature extreme for one hour. Between the extremes, the samples are air cooled, or air warmed, to a temperature of 20+3°C and maintained at that temperature for one hour. Thirty such cycles are recommended.(4) Assuming the air cooling and air warming each take one hour, then a full cycle takes six hours, and thirty cycles takes about a week of day and night testing.

The ability of a laboratory to conduct this test is obviously dependent on the availability of equipment that is capable of achieving both temperature extremes, automatically cycling between the extremes, and holding the temperature at 20° between extremes.

If such equipment is not available, or if such extremes are not realistic, say for a generator in southern California shipping to a California site, then alternate testing should be proposed. One such alternate test accepted by the NRC is eight hours at 120°F and eight hours at 0°F with four hour transition times between extremes. One full cycle is completed each twenty-four hour period with the test running a total of 50 days.

Any such alternate testing should take into account the actual extremes to be encountered between the generators facility and the potential burial sites. Again, two samples should be used for the thermal cycling tests.

With the program now well defined, the next step is to ensure yourself that the testing is acceptable to the NRC. Depending on how many variations there are between the proposed test program and the BTP will determine what type of concurrence may be needed. If it is intended to follow the BTP to the letter, then very little interaction may be required with the NRC prior to using the solidification parameters verified by the test program as meeting the Class B or C criteria. If on the other hand, significant differences are planned, it is recommended that these differences be put in writing to the NRC. This submittal should be in the form of a request to the NRC for concurrence that the proposed test program is an acceptable alternate to the program outlined in the BTP.

SAMPLE TESTING

All of the testing discussed so far is testing to be performed on solidified samples for which there is reasonable assurance that the samples will pass. That level of assurance is obtained by performing an initial screening program using several variations of waste to solidification media and evaluating each recipe for the parameters listed in Table 2.

Table 2
Screening Test Parameters

- Set time
- Free standing monolith
- Less than 0.5% free water
- Initial strength
- Ability to withstand immersion in water

The first three items in Table 2 should be evaluated at some predetermined time after solidification, nominally between 4 and 24 hours. Also, while the regulations allow for 0.5% of free water, this should be taken as condensation inside a sealed container and not liquid that failed to be absorbed by the solidification process. Initial product strengths should be obtained through compression tests of samples at some consistent time period after the samples are made. The BTP does not specify a minimum or maximum age for the samples.

For cement solidified samples, experience has shown that immersion in water is the most critical test in verifying waste form stability. It is also the easiest to run requiring only the ability to submerge the sample in water. By immersing more than one sample for a period of time less than ninety (90) days, it is usually possible to predict which recipes will withstand the 90-day immersion and those that will not.

With the evaluation of the screening samples completed and one, or possibly two, recipes selected for complete testing, it is necessary to prepare a sufficient number of samples for all of the tests. Table 3 reviews the number of samples previously identified for each test. As identified, a total of 15 to 16 samples will be required, and in fact a few extra should be prepared in the event that one is dropped or should a test require repeating. Depending on the magnitude of the program being conducted, it may or may not be reasonable to produce up to 20 samples individually. If several recipes or different waste types are to be tested, it is recommended that a single mix be prepared large enough to fill the necessary number of molds. Not only is this easier on those preparing the mixes, it also removes one variable from the program - were all the samples prepared in the same manner. These samples when properly cured can be delivered to the appropriate test laboratories for testing.

Table 3
Number of Required Samples

Test	No. of Samples
Initial Strength	2
Irradiation	1 or 2
Biodegradation	2
Leach Test	N.A.
Immersion Test	8
Thermal Cycling	2
Total:	15-16

SCHEDULE OF TESTING

Unless you have extreme confidence that the samples will pass all of the tests, based upon previous testing of similar materials, it is recommended that testing be performed in three stages:

First - Start the long term immersion test and process samples through at least six weeks of immersion before starting stage two. If the test schedule permits, complete the whole 90-day test.

Second - Test samples for resistance to biodegradation, thermal cycling and irradiation. Compression test one, or two, of the extra samples for comparison to the compression strength after these samples complete testing.

Third - Perform leach testing after successfully completing the previous tests.

CURING OF SAMPLES

Exactly how the samples are treated from the time they are molded until they are put into testing is, to a degree, dependent on the type of solidification agent under examination. While curing at elevated temperatures (100^{o}F to 120^{o}F for cement) is presently an accepted practice, the same may not be true for other solidification media. The use of a laboratory oven for heating cement samples is used to simulate the temperature buildup in drums and large liners due to the heat of hydration as cement cures. Equivalent temperatures are not seen in small laboratory size samples due to the small thickness of the samples and the high surface to volume ratio.

Once the samples are molded, they should be tightly sealed to prevent moisture loss due to evaporation and should remain sealed until ready to be put into testing, including through transportation, if necessary.

SCALE UP TESTING

If the samples tested are prepared using actual full scale equipment, additional testing may not be required other than to show the waste form produced is homogeneous throughout the package. One example of full scale equipment would be an in-drum mixer where samples are taken after mixing and cured in the sealed drum. Another example would be where samples are taken directly from the output of an in-plant solidification system, or a full scale demonstration system. A full-size container may also be necessary to demonstrate homogeneity of the mix throughout the container.

In the event full scale equipment is not used to produce the samples, then a program should be conducted to show that the samples tested are in fact representative of the product produced by the full scale equipment. Obviously, the need to address this issue should be inherent throughout the program. The best starting point is with the full scale equipment, working back to the lab scale equipment. Depending on the specific hardware used in a full scale system, several parameters should be quantified and then scaled down to the lab equipment. The factors to be considered include, mixing times - both to add the solidification agents and after all the components are added, mixing speeds and mixing blade tip speeds, physical configuration of the mixing blades, and energy input in terms of BTU's per unit volume of final product. Evaluating each of these parameters, or as many as are applicable to a given system, will help in selecting the appropriate lab scale mixing systems.

However, once the lab samples are produced, it's a long way back to the full scale system, especially if one is going from one liter beakers in the lab to the large disposable liners used in nuclear power plants, which can run to 170 ft^3 or larger. A convenient intermediate size is a 55-gallon drum. This size container, again using properly scaled mixing equipment is easily handled, affords an intermediate evaluation of the scale up without the larger expense of actual full scale tests.

RESOURCES

As was previously identified, the time frame to conduct a complete program can easily extend from nine months to a year when starting from scratch. This estimate is based on one to two months to complete a screening program and prepare samples for testing, and three months to conduct the long term immersion tests. Biodegradation, irradiation and thermal cycling tests can be conducted simultaneous at the conclusion of the immersion tests, or during the last months of the immersion test if the intermediate data is satisfactory. Upon completion of these tests, the three month leach tests can be initiated. Scale up testing, if required, can start during the final phases of the leach testing and again may add from two to five months depending on whether or not any testing needs to be performed on any of these samples.

Finally, one or two months should be alloted to pull all of this information into a report for use in satisfying the NRC criteria that the test data be available for review. If the waste is to be shipped to the burial site in Barnwell, South Carolina, the test results must be formally submitted to the NRC for review as a Topical Report.

If, on the other hand, one is absolutely confident that a particular waste form will pass all of the tests such that all of the tests are conducted simultaneously, a complete program will still take up to six months. Again, this may be extended by the necessity of performing scale up testing.

In terms of man hours of effort to perform a full program, the effort is not insignificant. Beginning from scratch, a safe estimate would be one to two man months for a single waste type, depending on the scope of the screening program. This estimate includes all long-term immersion testing but does not include preparation of any reports, implementing procedures or process control programs. The thermal cycling tests are relatively inexpensive since this test is not labor intensive. If several samples, a dozen or more, are tested at the same time, the test can probably be performed for about a hundred to two hundred dollars per sample. The fewer samples tested, the higher the unit cost. The biodegradation tests will cost between $400 and $500 per sample with little cost reduction for multiple samples. Irradiation testing, with ten or more samples will run about $150 per sample. The leach testing cost will vary not only with the number of samples tested (the more samples tested the lower the unit cost) but with the number of leachates taken (the more leachate sample analyzed the higher the cost). For one single waste type, in duplicate with ten leachates, the cost would be about $4,000 to $5,000. Table 4 summarizes these items assuming a program covering four waste types.

Table 4
Estimated Costs for Four Waste Types

Screening Tests, Initial Strength Immersion Tests	6 man-months
Irradiation Tests	$ 1,200
Biodegradation Tests	$ 3,600
Thermal Cycling	$ 1,200
Leach Testing	$18,000
Scale-Up Tests Intermediate and Full Scale	2 man-months
Preparation of Report, Procedures, Process Control Programs	1 man-month
Topical Report Submittal	Free - up to 6/30/84 ~$25,000 after 6/30/84

Total Cost: $24,000 plus 9 man-month labor plus ~$25,000 Topical Report Fee after 6/30/84.

SUMMARY

The program required to demonstrate compliance with the Class B or C stability criteria must be well-thought out and planned in advance. Any alternate testing to that recommended in the BTP should be reviewed with the NRC to ensure they are in agreement with the alternatives considered. Before starting and laboratory preparation of samples, consider exactly how the actual solidification process is conducted. Evaluate the parameter of that process to ensure that the lab samples are representative of the full scale process.

Most important of all is - don't rush through a program that can't achieve acceptance. Plan well in advance and give yourself sufficient leeway for a limited number of failures. If the resources to perform your own program are not available, there are organizations that can be contracted with to perform the testing for you. These organizations, using previously generated proprietary data, can in many cases perform the testing in a shorter time frame, and with less expense, than you can do it yourself.