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THE NNWSI WASTE FORM TESTING PROGRAM

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ABSTRACT

A waste form testing program has been developed to ensure that the release rate of radionuclides from the engineered barrier system will meet NRC and EPA regulatory requirements. Waste form performance testing will be done under unsaturated, low water availability conditions which represent the expected repository conditions. Testing will also be done under conditions of total immersion of the waste form in repository-type water to cover the possibility that localized portions of the repository might contain standing water. Testing of reprocessed waste forms for CHLW and DHLW will use reaction vessels fabricated from Topopah Spring tuff. Chemical elements which are expected to show the highest release rates in the mildly oxidizing environment of the Topopah Spring tuff horizon at Yucca Mountain are Np and Tc. To determine the effect of residual canister material and of corrosion products from the canister/overpack, waste form testing will be done in the presence of these materials. The release rate of all radionuclides which are subject to NRC and EPA regulations will be measured, and the interactive effects of the released radionuclides and the rock reaction vessels will be determined. The testing program for spent fuel will determine the release rate from bare spent fuel pellets and from Zircaloy clad spent fuel where the cladding contains minor defects. A metal testing program for Zircaloy will establish the expected lifetime of the cladding material. Estimation of the state of cladding for fuel presently in reactor pool storage will provide baseline data for Zircaloy containment credit.

INTRODUCTION

The design and execution of a testing program for waste form materials which is intended to predict the release rate of radionuclides from the waste form in the repository environment must consider the detailed nature of the waste package environment and the interactive effects of other waste package components with the waste form. In order to ensure containment of the radioactivity for the first 300 to 1000 years after disposal, the waste form will be protected by a 304L stainless steel container. Estimates of the corrosion rates for 304L in the Yucca Mountain environment give a conservative upper limit of 0.1 cm per 1000 years for metal loss due to uniform corrosion (1). Thus for the first 10,000 years the environment of the waste form will contain 304L stainless steel. The most likely mechanism to cause breach of the container in the tuff environment is some form of stress corrosion (1). This assessment, combined with the low rate of uniform corrosion, suggests that the waste form will be held in the 304L container for 10,000 years but that the container will eventually develop some cracks which allow water to gain access to the waste form.

Precise determination of the release rate of radionuclides from the container after breach occurs will require the following information:

- (1) Amount of water which will contact the waste container;
- (2) How much of that water will gain access to the waste form;
- (3) How much waste form material will dissolve in the water which contacts the waste form;

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- (4) How much of the water containing radionuclides will escape from the container.

This information requires a thorough understanding of the hydrology at the repository and the corrosion behavior of the container in addition to the need for data on the dissolution rate of the waste form in aqueous solutions of the appropriate chemical composition.

It will be many years before we have sufficient information to give a good picture of the actual rate of release of radionuclides from a waste form held in a breached 304L container. However, we can make some simplifying assumptions which will allow us to determine the upper bound on the rate of release. The first assumption concerns the amount of water which is available to contact each container. In the unsaturated zone, the rate of flow of water is limited by the downward infiltration rate of water. Sass and Lachenbruch (2) estimated that the average infiltration rate is 8 mm/yr through the unsaturated zone at Yucca Mountain. Using that infiltration rate, we can calculate the amount of water which will flow through the repository each year. The result is 8 liters of water per square meter of surface area per year. For a vertical emplacement hole with a 100 cm diameter the volume of water would be 6.3 l/yr if only the downward flux is considered and no concentrating mechanism is invoked.

To obtain a reasonable upper bound on the water availability we have calculated the amount of water encountering areas of rock which would be disturbed by repository construction. We have then assumed that any water which encounters a disturbed area is evenly distributed among the waste packages. For the purposes of this calculation, we have assumed that 15% of the total repository area is disturbed and that the package density is 120 per acre for DHLW and 23 per acre for CHLW. The results of the calculation give 40 l/yr per DHLW package and 208 l/yr per CHLW package as a reasonable upper limit for water availability. For spent fuel packages the result is approximately 300 l/yr per reference 3.3 kW package, which corresponds to approximately 250 ml per fuel pin. Waste form testing will be conducted to cover the range of water availability estimates.

The second assumption which can be made concerns how much of the total water which contacts a breached container will also contact the waste form. For most of the period from 1000 to 10,000 years after disposal only a small fraction of the water which contacts a container will actually enter the container through a breach. The majority of the water should encounter intact steel and not contact the waste form. Thus, it will be a conservative upper limit, if we assume that all water which contacts the waste packages also is able to contact the waste form and to escape from the container after interacting with the waste form. In order to include this assumption in our testing program, we will include 304L stainless steel as a component of the waste form tests but will not allow the steel to impede significantly the contact of water with the waste form.

REPROCESSED WASTE FORM TESTING

NNWSI waste form testing for reprocessed waste is conducted using PNL 76-68 borosilicate glass formulation as the reference CHLW form. Three versions of this glass are being used:

- (1) Simulated fission products + uranium;
- (2) Simulated fission products + all actinides + technetium;
- (3) "Aged glass" - formulated to represent the actual waste form at 300 years after disposal.

The reference waste form for DMLW is based on the Savannah River Laboratory borosilicate glass using 165 frit. Two versions of this glass are tested:

- (1) Simulated fission products + uranium;
- (2) Fully loaded glass using actual SRP waste.

Detailed descriptions of these waste forms are given in reference (3).

Three types of testing will be done to determine the behavior of these reprocessed waste forms under repository conditions. First, parametric testing will be used to determine release rate from the waste form as a function of system components and variables. The parameters which will be investigated include waste form composition, waste form surface area to water volume ratio (SA/V), temperature, presence and nature of corrosion products, water chemistry, and radiation. To date, the effects of SA/V, temperature and metal components have been investigated using U-doped simulated 76-68 glass (4).

Fig. 1 Boron concentrations as a function of reaction time for parametric testing of PNL 76-68 glass in J-13 water. Curve labeled + Tpt M is data for glass + J-13 + tuff monolith; + Tpt M + 304L is data for glass + J-13 + tuff monolith + 304L stainless steel; + Tpt P is data for glass + J-13 + crushed tuff. Reaction temperature was 90°C. Glass SA/solution V = 0.1 cm⁻¹.

Figure 1 shows results for boron release from PNL 76-68 glass at 90°C with glass surface area to solution volume ratio of 0.1 cm⁻¹. This SA/V is far lower than that expected for the repository conditions; it was chosen to allow comparison of the parametric results to existing MCC-1 distilled water leaching data for 76-68 glass. Boron represents 2.7% of the glass by weight, and since it has a high solubility in aqueous solutions, should be a good measure of glass matrix dissolution rate. The largest release of boron occurs for glass reacted with J-13 water without rock present. When a rock "monolith" (Tpt M) is added to the system, release of boron is less. This is because the rock now contributes Si to the solution which reduces the dissolution rate of the glass. Addition of 304L stainless steel to the system lowers the release rate of boron even further. This is in contrast to the behavior of glass

in the presence of carbon steel where leaching of glass is increased due to metal corrosion products reacting with Si and lowering solution Si concentrations (4).

The curve labeled 76-68 + J-13 + Tpt P represents data for the glass in the presence of crushed tuff. The crushed tuff increased solution Si more rapidly than the tuff monolith, and consequently less glass was able to dissolve. Since water which contacts the waste form in the repository environment will have Si concentrations which were increased due to passage through heated rock, this curve is probably more representative of the release rate of boron (and glass dissolution rate) to be expected in the repository environment than the Tpt M curve.

Figure 2 shows data for boron release from 76-68 glass reacted with J-13 water at 90°C in the presence of crushed tuff, and in one case with crushed tuff + 304L stainless steel. The surface area of the glass was increased by crushing the glass to produce $(SA/V) = 1 \text{ cm}^{-1}$. Boron concentrations in solution are similar to those in Fig. 1 for glass + crushed tuff, indicating that no further dissolution of glass occurred at the higher SA/V. Also, crushing of the glass does not appear to increase the dissolution rate. If the dissolution rate inferred from this data and the Tpt P curve in Fig. 1 is adjusted for B contributed by J-13 and then scaled to a full size waste package by allowing for the differences in glass surface to glass volume ratio, the calculated annual release rate from the full size waste form is less than 1 part in 100,000 per year. Increasing the amount of rock present in the system from 0.1 g to 1 g produced only a small change in dissolution rate of the glass. The presence of 304L stainless steel in the system did not increase the dissolution rate of the glass, and may actually have caused a slight decrease in the glass dissolution rate.

Fig 2. Boron concentration in solution for the reaction of PNL 76-68 glass with J-13 water + components listed by data symbols at 90°C as a function of reaction time. Tpt is crushed Topopah Spring Member tuff; 304L is 304L stainless steel.

The second type of reprocessed waste form testing will address the events and processes which are anticipated to occur in the repository after disposal occurs. The transport of water in the unsaturated Topopah Spring Member tuff will involve a combination of porous media and

fracture flow. In either case, the likely mechanism for delivery of liquid water to the waste form surface will be by dripping from the borehole surface. Some water may also condense onto the waste form from the vapor phase. To aid in gaining an understanding of the release rates and mechanisms under unsaturated conditions, we have developed a test method to simulate the expected conditions (5).

The unsaturated test method will use a reaction vessel fabricated from 304L stainless steel. The waste form will be cylindrical with perforated end caps of stainless steel to simulate a corroded canister. The waste form will be suspended over a tuff cup which will collect any fluid which drips off the waste form. Water which has been preconditioned by reaction with tuff will be dripped onto the top of the waste form assembly. For DHLW samples with a surface area of 15 cm², the drip rate appropriate to 40 l per DWPF canister per year is approximately one drop (0.1 ml) per 3 days. The test will be run at 90°C for periods of time up to 1 year.

The mechanisms of alteration of the waste form under the conditions of the unsaturated test include dissolution of glass in liquid water as well as alteration of the glass by vapor and liquid films on the glass surface. To monitor the extent of reaction of the glass several types of post-test measurements will be done. These measurements will include solution analyses of any liquids present, rinsing of the tuff to collect any readily soluble material adhering to the rock surface, rinsing of the steel container, analysis of surface alteration products on the waste form, and depth profiling through the tuff cup to determine the extent of penetration of radionuclides.

The unsaturated test method will be refined after preliminary trials now in progress are completed. The test will then be employed using samples of uranium doped simulated DHLW glass and CHLW glass. The results of these tests should provide a reliable estimate for radionuclide release from the waste form under conditions which simulate the repository environment.

The third type of reprocessed waste form testing involves tests under conditions where the glass is submerged in water. This type of testing is appropriate to conditions of full saturation such as exist below the water table. In the unsaturated zone standing water may accumulate if pores and fissures become plugged and allow water to accumulate. Evidence collected to date suggests that development of perched water in the Topopah Spring Member is unlikely (6). Thus, saturated testing of waste forms provides data on release rates under conditions of unanticipated processes and events. These tests should also provide an upper limit on release rates of radionuclides from the glass under all reasonably possible conditions at Yucca Mountain.

Saturated testing will use the estimates of maximum water availability given above, scaled to the specimen size used in the tests. Scaling will presume that both the test specimens and the full size waste forms are uncracked monoliths. (This is essentially true for the test specimens; the full size waste forms will have additional surface area due to cracking. The effect of this additional surface area will be assessed as part of the parametric tests described above.) For testing purposes we will assume that the full annual allowance of water is in contact with the waste form for a full year. Since supersaturation effects are not expected to occur for matrix elements of the glass, this assumption should provide an upper limit to the waste form dissolution

rate. The issue of whether supersaturation can occur will be addressed as part of the parametric testing program.

Saturated tests will be conducted in tuff reaction vessels. The tuff will be pre-saturated with J-13 water, placed in an inert container, and J-13 water will be added to both the outer container and inside the tuff vessel. Glass samples, or glass + 304L stainless steel, will be suspended in the liquid phase. The tuff vessel will be covered with a loose fitting lid of tuff and the outer inert container will be closed. Testing will be conducted at 90°C for periods of time up to one year.

Testing of DHLW forms under saturated conditions is currently in progress using both simulated and fully active waste forms (7). Testing of actinide doped PNL 76-68 glass will begin in the near future. Post-test analyses will include samples of solutions taken from inside and outside the saturated tuff vessel. This will allow an assessment of the extent of migration of radionuclides through the tuff. The waste form will be examined for surface alteration and development of chemical composition gradients. The effects of canister corrosion products will be assessed by running tests both with and without canister materials. Radiolysis effects will be estimated through comparison of results from simulated and fully active glasses. Radionuclide migration will be estimated by examination of tuff reaction vessels after completion of the tests.

SPENT FUEL TESTING

The NNWSI testing program for spent fuel has been designed to evaluate the performance of Zircaloy clad UO_2 in the Topopah Spring tuff environment. The Zircaloy cladding on spent fuel provides a containment barrier against release of radionuclides for as long as the cladding remains intact. The population of fuel which will be delivered to the repository should contain less than 0.1% of fuel pins which have breached cladding (8). Breach typically occurs as a pin-hole defect or a stress corrosion crack. Our spent fuel testing program will evaluate the release rate of radionuclides from fuel pins which contain defects in the Zircaloy cladding relative to the release rate from bare UO_2 fuel pellets. The experimental work is being conducted by the Westinghouse Hanford Company.

Initial testing of spent fuel is being conducted in deionized water at ambient hot cell temperature. Test specimens are 5 inch long segments of PWR fuel with burnup of approximately 26,000 MWD/MTHM. The specimens are fitted with water tight end caps. The test matrix includes three control specimens of fuel without induced cladding defects, one control specimen consisting of the fuel removed from the cladding, a pin segment into which a 200 micron diameter hole was burned with a laser, a pin segment containing two laser punctures, and a pin segment into which a slit 150 microns wide by 2.5 cm long was machined.

Pin segments fitted with end caps are placed in a vertical orientation in a fused quartz reaction vessel. The upper end cap is vented to allow easier access of water through defects in the cladding. Fused quartz rods are placed in the container; they are used to monitor plate-out of radionuclides during the test. Water is added to the quartz vessel up to the level of the top end cap. The solution volume is approximately 200 ml. A loose fitting quartz lid is placed over the quartz vessel. The bare fuel control sample uses the fuel placed on the bottom of the quartz vessel with an amount of water equal to that used in

the other tests. The cladding material from which the fuel was removed is placed in the quartz vessel with the bare fuel.

Solution samples are removed for radiochemical analysis after 1, 5, 15, and 30 days and every 30 days thereafter until termination of the test. After sampling, deionized water is added to replace the solution volume removed. Fused quartz rods are pulled periodically and any plated out material stripped from them using acid. Upon completion of the tests the quartz vessel will be analysed for plated out radioactivity.

Figure 3 shows data for uranium in solution as a function of reaction time. The line labeled "hole" is for the two puncture specimen. For reference, the solution concentration equivalent to one part in 10^5 of the fuel inside the pin segment is shown. Solution concentrations appear to have reached steady state in all cases, with the laser puncture specimen showing concentrations which are only slightly higher than the intact control specimen.

Fig. 3 Uranium concentration in solution for spent fuel segments submerged in 200 ml deionized water. The undeformed sample is a control specimen of Zircaloy clad fuel. The hole sample contains two laser puncture defects (9).

Fig. 4 Total uranium deposited on one quartz rod which had remained in the test solutions for the total time shown on the horizontal axis. See Fig. 3 for solution concentration.

Data for uranium plated out onto quartz rods is given in Fig. 4. After 30 days the quantity of uranium on a single rod had essentially stabilized at 60 to 80 µg for the bare fuel, 0.5 µg for the slit defect, and less than 0.1 µg for both the hole defect and the control specimen. This corresponds in the case of bare fuel to an amount of U equivalent to or greater than that in the solution being plated out onto each rod. Clearly the solution became supersaturated early in the test (Fig. 3) and then precipitated U to reach solution concentrations controlled by solubility. The amount of plate-out in the case of the slit defect is approximately 1/10 of the solution total U per rod. For the hole defect, the plate-out is also about 1/10 of the solution total U

but is an order of magnitude lower in absolute abundance than the slit defect case. Data for other radionuclides are available and will be presented in a more detailed technical publication (9).

The deionized water experiment will be continued for long enough to confirm that steady state conditions have been achieved. At the conclusion of the test the specimens will be examined to determine the extent of alteration of the induced defects in the cladding and the fuel inside the defected cladding.

A new series of tests will be conducted this year using J-13 well water. A parallel series of tests will analyze the effect of adding Topopah Spring tuff to the system. Testing at elevated temperatures will also be done.

In order to show that cladding will provide a barrier to radionuclide release from spent fuel it is also necessary to investigate the corrosion rates and mechanisms of Zircaloy in the repository environment. An experimental program will begin this year to investigate the following topics: (1) what is the rate of production of defects in cladding during the containment period; (2) what alteration occurs to existing and newly produced defects during the containment period; (3) what is the production rate of defects after water gains access to the cladding; (4) what is the alteration which occurs to defects in an aqueous corrosion environment?

The data obtained from the corrosion experiments will be combined with that from the relative release rate testing to determine the time dependent release rate of radionuclides from the spent fuel population. This will be accomplished by

- (1) Estimation of the population of fuel pins which will be delivered to the repository with defects in the cladding;
- (2) Estimation of how many new defects will be formed during repository handling operations and by Zircaloy failure during the containment period;
- (3) Determination of the expected change in defect character during the containment period;
- (4) Calculation of release rate by assuming that rods with no defects produce no release and using the experimental results to provide release rates for other cases;
- (5) Adjust the defect population as a function of time to allow for production of new defects and enlargement of existing defects;
- (6) Recalculate the release rate for new conditions.

Preliminary results indicate that release rates calculated on this basis will be lower than 1 part in 10^5 per year of the 1000 year inventory in the fuel. Should results from the Zircaloy corrosion testing show that the increase in defect numbers or size is too great to limit release rates to acceptable levels, a tailored packing material may be used to further reduce release rates.

CONCLUSIONS

The NNWSI waste form testing program has provided preliminary results related to the release rate of radionuclides from the waste package. Those results indicate that release rates from both spent fuel and borosilicate glass should be below 1 part in 10^5 per year. Future testing will be directed toward making release rate testing more closely relevant to site specific conditions.

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REFERENCES

1. R. D. McCright, H. Weiss, M. C. Juhas and R. W. Logan, Lawrence Livermore National Laboratory Report UCRL-89988, 1983.
2. J. H. Sass and A. H. Lachenbruch, U.S. Geological Survey Open File Report-82, 1982.
3. V. M. Oversby, Lawrence Livermore National Laboratory Report, in preparation, 1984.
4. G. L. McVay and G. R. Robinson, Battelle Pacific Northwest Laboratories Report PNL-4897, 1983.
5. The unsaturated test method is being developed by John Bates of Argonne National Laboratory. This method will be documented during 1984.
6. C. A. Morrow, D. E. Moore and J. D. Byerlee, paper in this volume, 1984.
7. This work is being done as part of a cooperative testing program involving NNWSI and Savannah River Laboratory.
8. R. E. Woodley, Hanford Engineering Development Laboratory Report HEDL-TME 83-28, 1983.
9. This work is being conducted by C. N. Wilson at the Hanford Engineering Development Laboratory. The work will be documented in a HEDL-TME report during 1984.