46 FR 35280
(PR-60)
(WM-2)
Return to WM 623-SS PDR

bnl
aui

105.3.2

BROOKHAVEN NATIONAL LABORATORY

ASSOCIATED UNIVERSITIES, INC.

Upton, Long Island, New York 11973

Department of Nuclear Energy

(516) 282
FTS 666 3510 or 4492

May 13, 1982

Mr. John B. Martin
Director, Division of Waste Management, NMSS
Mail Stop 905 SS
U. S. Nuclear Regulatory Commission
Washington, DC, 20555

Dear Mr. Martin:

As part of our recommendations to the NRC in the DSTP, we have attempted to extract from our task reports a limited number of high priority issues the resolution of which we feel is of major importance if the NRC is to evaluate performance of a DOE high level waste package.

For reasons we hope are evident from the discussions below, we believe that a waste package that can be evaluated with minimal new R&D and with the greatest reliability is one which, along with a waste form, includes a canister system and a discrete backfill. We use the term discrete backfill to denote any backfill other than crushed host rock that is emplaced as part of the waste package so as to contribute directly or indirectly to the performance of the package.

In reviewing the performance of individual components and the package in toto we concluded that restricting water flow around the waste package offers many advantages in favorable performance with no significant disadvantages. In the discussions that follow we have assumed that all packages will be emplaced with some backfill to at least restrict water flow around the canister system and therefore around the waste form when the canister is breached. This, we believe, is compatible with views in the DOE community which would make their solubility limited degradation models and the MCC leach tests more realistic.

A. In the following list of major issues on the waste form, we have taken borosilicate glass as the example for the waste form.

   1. Design temperature of the glass to be as low as possible (preferably below 100°C) at time of contact with water.

XA

8210290014

Reasons:

a. At present the leach rates of the best borosilicate glasses approximate the one part in $10^5$ criterion at around 30°C in pH values between 5 and 8 and at low flow rates.

b. Not only do the leach rates of borosilicate glass increase with increasing temperature, but the uncertainties in the leach rate become greater. The vast majority of existing data on the effects of pH and flow rate on leaching are at temperatures below 100°C. (See references 21, 22, 23, 24, 25, 26, 3, 28 in "Glass Corrosion - A Review" T. M. Ahn and E. Veakis, NUREG/CR-2482, BNL-NUREG-51494, Vol. 1).

In order to evaluate the performance of glass at temperatures above 100°C a great deal more R&D would be required than is necessary to evaluate the performance below 100°C. We believe that at high temperatures the chemical compositions of the groundwaters change in more complex manners. The variations in pH and ionic composition become larger and evaluation of performance becomes more uncertain. For most silicate glasses, the quantity leached in a given time is nearly doubled for every 8°C to 15°C rise in temperature and the reaction rate increases by a factor of 10-100 for every 100°C increase in temperature, depending on the composition of the glass. Below approximately 80°C near pH 7, a siliceous layer forms on a glass which acts to retard further leaching. Metasomatic reactions, in which new crystalline compounds form from some of the glass constituents, can also occur at the glass surface, particularly at elevated temperatures. Such complications make it difficult to theoretically define a single rate-determining step in a given temperature range. In hydrothermal environments, the complexity is more significant since glass is altered rapidly if the temperature is sufficiently high. Under hydrothermal conditions, alteration is a major variable influencing the enhanced leach rate. Since the alteration is accompanied by complications such as stress generation, a delineation of the mechanisms involved in hydrothermal leaching is not easily achieved.

2. Determine matrix dissolution rates of actinide doped glass whose composition represents simulated 1000-year-old glass.

Reasons:

a. Long-term leach behavior of glass is more likely to be determined by matrix dissolution than by the radionuclide specific effects that are observed in short-term experiments. The diffusion of radionuclides in glass is expected to be so slow that after initial surface changes, long-term behavior should be governed by the factors that alter matrix dissolution (i.e., chemical composition, possibl phase separation, homogeneity, etc.) and the factors that change the leaching environment.

b. If the waste form is to be protected from leaching during the containment period, the composition of the glass and the radionuclides of concern are not represented by much of the existing data. Experiments should be initiated on leaching of simulated aged glass, where the aging corresponds to the time at which containment fails.

3. Radiolysis of groundwaters - radiation effects.

Much of the past work on radiation dealt with radiation effects on the glass. Although such effects may alter the leach behavior, existing evidence indicates the effects are small compared to the effects of temperature or pH. We believe the radiolysis of groundwaters which may produce species that could increase leaching rates is of greater concern. Here little work is available. If it is assumed that the repository will be saturated early in its life, then large quantities of water which may be relatively slow moving will be subjected to high radiation fields if the waste packages are unshielded.

Experiments determining the changes in composition of typical groundwaters and their subsequent effects on leaching (and corrosion) will be required if the DOE does not develop a self shielded package. Again, in the absence of a self shielded package much of the existing work on leaching may need to be repeated in the presence of a radiation field if the DOE claims performance of the glass during the containment period. Such a situation would correspond to a waste package without a canister system where containment could be attempted from combined properties of the glass and backfills. We believe this situation would require a great deal more R&D for performance evaluation than would a package in which a canister system provides reasonable assurance of containment.

4. pH and flow rate effects.

pH

Along with temperature, glass composition and homogeneity, and radiolysis of the leach media, the factors most affecting leaching appear to be pH and flow rates. We believe pH effects may be more readily evaluated in the absence of radiolysis than in a radiation field. For glasses, data indicate that the enhanced leaching is due to radiolysis effects on leachant chemistry. Studies show that nitric acid, formed by water radiolysis in the presence of atmospheric nitrogen, can significantly enhance leach rates by lowering the leachant pH. It does not appear that acid formation in the presence of air can account for all the irradiation enhanced leaching. The importance of factors other than irradiation induced pH changes depends on the radiation dose rate, and possibly depends on sample type. At repository dose rates, these effects could be less significant than pH effects.

The possible effects of leachant radiolysis have received emphasis in leach testing. Studies have been carried out investigating alpha and beta radiolysis effects, as well as the leaching under gamma radiation. Effects of gamma radiolysis products on leachant pH were emphasized. It appears that the major effect on leach rates may be due to an irradiation induced decrease of leachant pH. It is not yet clear whether this mechanism can account for all the observed radiolysis changes.

Flow Rates

Contact time variations will affect the release and subsequent movement of radionuclides from the package. In the repository, groundwaters will contact the package components for varying time depending on a number of conditions, such as permeability of the host rock, temporal variations in the thermal field, etc. The contact time, or flow rate, is the most difficult variable to estimate because it will be controlled by site-specific conditions that are not easily predictable.

It is our view that designing a package which attempts to restrict flow around the canister and waste form is a more reasonable approach than developing a program to try to completely understand the effects of flow.

If a backfill with positional stability is placed around the canister system we believe the uncertainties in leach behavior due to flow effects can be minimized.

In unshielded packages or in packages without discrete backfill a great deal of additional R&D will be required to evaluate both leach performance of the waste form and corrosion performance of the canister system.

B. Issues of major concern for canisters providing containment.

Metallic canister systems can provide long term containment in several ways depending upon the waste package design. These may range from a single, relatively thin corrosion resistant overpack, through can-in-a-can-in-a-can concepts, to thick sacrificial metals that corrode in a predictable manner. In the last case, the major issues of concern would involve determining the corrosion rate in the "worst case" repository environment, providing a rationale and model that the worst case corrosion rate either remains constant or decreases with time and then determining the thickness required for the containment period. The reliability and confidence associated with such a design would be related to the uncertainties in corrosion rate and to the excess thickness used in the design. A major concern with such a design may involve the positional, thermal, and chemical instability of the backfill-container interface after appreciable thicknesses of the container have corroded. The mechanical, chemical and thermal changes resulting from the gap formed may seriously affect performance and will require careful evaluation. In the situation where the corrosion products do not spall and a gap is not formed, the corrosion products may occupy a greater specific volume than the original metal. The consequences of this expansion and the possible pressures applied at the canister-backfill interface will also require evaluation. Since we know of no significant effort on the DOE's part in developing such a design, we have restricted our discussion at this time to the above generic comments.

In the following issues of major concern on the first type of canister system we have chosen TiCode-12 as an example of the component to provide long-term containment.

1. Maintain canister (overpack) surface temperature as low as possible.

   Reasons:

   a. General

      Of all practical kinetic systems we believe corrosion is the most difficult to predict or accelerate by obtaining data at elevated temperatures. Here again, not only do the rates increase but new mechanisms may arise and the uncertainties in the results increase with increasing temperature.

      In order to predict the corrosion rate for times appreciably longer than those studied, the mechanisms of corrosion must be accurately known and it must be assumed that they remain the same over the time required. To predict reactions involving metallic corrosion, it is necessary to prove that neither the metal nor the metal-solution interface undergoes any structural, physical, or chemical change that can alter the corrosion rate over the total time for which the prediction is intended.

      For metals such changes might include:

- isothermal stress annealing in the bulk
- formation and subsequent breakaway of a surface film
- stresses developed or removed by formation or cracking of a corrosion product or film
- diffusion of corrosion products into or out of the metal surface
- diffusion of bulk components into surface depleted zones
- initial selective attack at a site that eventually is depleted
- grain size changes
- grain boundary precipitation, etc.

Any or all of these might lead to a change in the corrosion rate with time. In general, the overall corrosion rate of most metals represents contributions from several different mechanisms with different temperature dependencies.

It is our concern that the use of elevated temperatures to increase corrosion rates for the purpose of predicting long-term corrosion behavior at the lower temperature can be theoretically unjustified and technically unsound and that the R&D needed to evaluate the performance of a canister system at high temperatures is much more extensive and complicated than the R&D required for evaluation at a lower temperature.

If the surface temperature of the canister system is designed to be low, then a minimal R&D effort at higher temperatures will suffice to determine over what temperature range the corrosion mechanisms may remain the same. Similarly, the corrosion tests at elevated temperatures used to obtain information on failure modes should be fewer and simpler if the design favors a low canister temperature.

The point we wish to stress is that the mechanisms of corrosion at high temperatures are very likely to be different from those at low temperatures. Any design which has the canister initially at a high temperature will require corrosion data over a range of temperatures covering the thermal changes during the containment period. The level of the required R&D for such a design will be much more extensive than that required if the surface temperature is low at emplacement.

In addition to changing mechanisms at higher temperatures, there are a large number of theoretical and practical reasons why the scatter and uncertainties of kinetic reactions such as corrosion and leaching increase as the temperature increases. At higher temperatures the Maxwell distribution of energies (velocities) of both reactants and products widens so that a wider range of different close energy states exists. The consequences of these effects in corrosion and leach measurements result in a bigger spread in final values. In practice, high temperature experiments are more difficult and more expensive.

b. Specific

Based on data on titanium and TiCode-12, temperature is likely to be one of the most important variables in the corrosion of HLW containers. The following evidence may be cited to support this:

- For titanium, exposed to 20% NaCl solution at 105°C, uniform corrosion, pitting corrosion and crevice corrosion occur. If the temperature is decreased to 80°C then pitting and crevice corrosion failure mechanisms are absent. Therefore, decreasing the temperature greatly reduces the number of possible failure mechanisms.

- The above statement is intimately connected with the widespread observation that in chloride containing solutions temperature changes from approximately 100°C to 200°C can change titanium based materials from the passive (very low corroding) state to the active state.

- In brine at 200°C, measurements show that very high acidity levels may be present (pH = 2). At room temperature the pH ranges between 4.0 to 6.5. Thus, by keeping the temperature low in a brine environment, accelerated corrosion from low pH values is minimized.

- Decreasing temperatures will reduce the rate of hydrogen diffusion into a TiCode-12 container, thereby reducing the potential for hydrogen embrittlement.

- Low temperature will greatly minimize the rate of plastic deformation in a container and reduce the possibility of failure associated with creep and stress-corrosion cracking.

- Oxide scales formed at low temperature will be thinner. This will reduce the buildup of stresses at the scale/metal interface and minimize scale spallation. Spallation, if it occurs, would lead to accelerated corrosion which would be extremely difficult to quantify over periods of hundreds of years.

- Because of the fewer failure mechanisms and slower kinetics at lower temperatures it would be expected that scatter in the experimental data would be reduced. This would allow more accurate extrapolation of behavior of container materials to very long times.

In summary, it is advisable to minimize the design temperature of a TiCode-12 container. Low temperatures will greatly reduce the number of possible corrosion and mechanical failure modes, especially in brine. Reaction kinetics will be far slower and data scatter minimized. This will allow a more accurate estimate to be made of long term corrosion behavior.

2. Radiation effects and radiolysis of groundwaters.

An unshielded commercial high level waste package may subject the adjacent host rock to a total dose of $10^{10}$ to $5 \times 10^{10}$ rads during decay of the fission products. When salt at 115 to 170°C experiences a radiation dose of $2 \times 10^{10}$ rads the amount of colloidal sodium formed may be between 3 and 50%. For very large variations in the brine content of the salt, this amount of colloidal sodium in contact with the brine will result in a solution with a pH of about 14. There is essentially no work available on the performance of backfill material, metallic container material or waste forms in solutions with a high pH. The information that does exist indicates that:

- The backfill materials such as bentonite may dissolve.
- For materials such as Ti alloys, hydrogen pickup is accelerated in a basic medium.
- The rate of matrix dissolution in glass can increase by as much as three orders of magnitude.
- There is no data base for corrosion of metals considered for waste canisters in strong NaOH solutions.

In other repositories the major failure modes of TiCode-12 are associated with hydrogen pickup. In order to evaluate long-term performance of TiCode-12 in an unshielded package a great deal of R&D on radiolysis of typical groundwaters and threshold effects on detrimental hydrogen absorption will be required that would not be necessary for a shielded package.

3. Evaluate potential for crevice corrosion in repository environments.

Recent evidence shows that TiCode-12 may undergo crevice corrosion under certain conditions. Since the conditions for crevice corrosion are waste package design dependent, proper evaluation of the performance would be facilitated by an early DOE waste package design.

4. Weld evaluation and stress evaluation.

The prime failure modes in TiCode-12 involve hydrogen induced-stress induced failure. Threshold levels will be required for both the body and welds in order to evaluate long-term performance. Crevice corrosion studies will be required.

C. Issues of major concern with backfills.

1. Positional stability and water permeability with wet and dry cycling.

Backfills can be used to prevent water from reaching the waste package, control the water flow to and from the package and retard radionuclides during and after containment.

In all cases the positional stability and the stability with time of water flow properties are of prime concern under expected events of wet and dry cycling.

2. Radionuclide retardation.

a. Temperature and radiation.

If the backfill is to perform by controlling radionuclide migration during containment, the retardation properties over the expected temperatures and in the expected radiation fields will require evaluation.

In an unshielded package, backfill performance after being soaked in irradiated groundwaters will require evaluation.

D. Issues of major concern with groundwaters/repository waters.

It is our view that a major factor in determining how the waste form, the canister system, the backfill(s) and the total package will perform is proper characterization of the water environment.

1. Groundwater

a. Composition (temperature, chemical species, pH, and Eh).
b. Variation of above with radiation.

2. Repository water (groundwater altered by engineered components such as backfill, corrosion products, etc.

a. Composition (temperature, chemical species, pH, and Eh).
b. Variation of above with radiation.

Reasons:

The complexity of the mechanisms of leaching and corrosion indicate that complete understanding of the factors involved probably will not be achievable in the times necessary to license a repository. A more reasonable approach to understanding and predicting the performance of a waste package is to limit the R&D to the range of variables that will occur in a given situation. This limited range of variables can be determined by adequate characterization of the groundwater and by beginning an R&D program on how the waste package will alter the groundwater.

In our efforts to summarize the major issues of the task reports we have found that there are very significant differences in the level and complexity of the R&D that will be required to evaluate different types of waste packages. The attached tables attempt to illustrate the differences for waste packages that use borosilicate glass as the waste form and TiCode-12 as the overpack material.

Sincerely yours,

Donald G. Schweitzer, Associate Chairman
Head, Nuclear Waste Management Division

M. Sue Davis, Deputy Division Head
Nuclear Waste Management Division

DGS:MSD:gfs
Attachments (Tables)
cc: W. Y. Kato
H. J. C. Kouts
A. J. Romano
C. Sastre
P. Soo

NRC: R. Browning
F. R. Cook
Document Control Center
E. Wick

The tables are based on what is known of the performance of the materials chosen as examples and are meant to illustate some of the major issues which should be addressed in order to evaluate the performance of the design options listed. The following assumptions were used to develop these tables:

(1) The package materials were assumed to be borosilicate glass (BSG), TiCode-12, and sand-bentonite or zeolite backfills.

(2) The repository considered was a hard rock repository.

(3) The optimum containment time has been defined as the time required for the waste form to return to ambient temperatures.

(4) It should be noted that the addition of a new parameter (e.g., radiation) to a test program or the extension of the range on a parameter (e.g., temperature) increases the quantity of work required to address an issue.

(5) Any test program which uses accelerated test methods to address an issue should be accompanied by a rationale justifying the use of the accelerated test procedure.

(6) These tables also assume that a statistical approach to testing is used, the average behavior and uncertainty in the average are determined from a statistically significant number of samples.

(7) In comparing Cases 2 and 3 to Case 1, the estimates on how much more extensive the required R&D would be were based on two major factors:

    (a) estimates of new types of experiments that were not needed for Case 1, and
    (b) estimates of how much more replication might be required to reduce the greater uncertainties in performance due to radiation (Case 2) and/or reduced performance by canister during containment (Case 3).

## TABLE LEGEND

The Δ in parentheses next to each table refers to changes relative to Table 1:

| | | |
|---|---|---|
| Δ:NS | = | no shielding |
| Δ:T↑ | = | higher temperature |
| Δ:CWB | = | containment also achieved by properties of waste form and backfill |
| Δ:SC | = | sacrificial container |

Example: Δ: NS, T↑, CWB indicates a package with no shielding, higher temperature, container fails before waste form reaches ambient and waste form and backfill provide for containment until waste form returns to ambient.

# DOCUMENT/ PAGE PULLED

# ANO. 8210290014

NO. OF PAGES 7

REASON

☐ PAGE ILLEGIBLE

☐ HARD COPY FILED AT. PDR CF

OTHER ____________

☐ BETTER COPY REQUESTED ON ___/___/___

☒ PAGE TOO LARGE TO FILM

☒ HARD COPY FILED AT. PDR (CF)

OTHER ____________

☒ FILMED ON APERTURE CARD NO 8210290014-01

thru

8210290014-07