Conf-901105--67

THE ROLE OF LABORATORY ANALOG EXPERIMENTS IN ASSESSING THE PERFORMANCE OF WASTE PACKAGE MATERIALS

JAMES C. CUNNANE AND JOHN K. BATES
Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4837

CONF-901105--67

DE91 006503

JAN 22 1991

ABSTRACT

There is an immediate need to begin to validate models that can be used for assessing the performance of waste package materials in an unsaturated repository environment. This paper examines available testing information and testing approaches that could support validation of models for engineering barrier system (EBS) radionuclide release. The content is presented in the context of the general methodology that has been proposed for validating performance assessment models [1]. Available experimental observations are used to test some of the EBS release rate modeling premises. These observations include evidence of fluid film formation on waste glass surfaces in isothermal humid environments, accelerated waste glass reaction rates under repository service conditions of large glass surface area to water volume ratio, and mobilization of radionuclides as solutes and colloids. It is concluded that some important modeling premises may not be consistent with available experimental information. However, it is also concluded that future laboratory testing, which simulates the integrated waste package system (i.e., laboratory analog testing), is needed to evaluate the significance of these inconsistencies and to test the system level models. A small-scale apparatus which was developed and tested to examine the feasibility of laboratory analog testing for the unsaturated Yucca Mountain repository environment is described.

INTRODUCTION

Credible information concerning the long-term radionuclide release performance of high-level nuclear waste packages and their component waste forms is desirable to support major DOE programmatic decisions such as the decision to proceed with hot startup of vitrification plants at Savannah River and West Valley. At issue, for example, in this decision is whether the vitrified glass product will have satisfactory long-term performance in the candidate Yucca Mountain repository. Because resolution of this issue will be based, at least in part, on performance assessments of radionuclide release from the EBS, it is important to begin to validate the models involved. This paper is based on a study [2], that was supported by the DOE Repository Technology Program, to examine available testing information and current and future testing methods that could support validation of EBS radionuclide release models. The content is presented in the context of the general methodology that has been proposed for validating performance assessment (PA) models [1]. This methodology includes the following elements:

- identifying and critically evaluating modeling premises and
- testing the submodels and the system model.

The paper is intended to highlight experimental results, testing methods, and future experimental needs for implementation of each of these elements.

DISCLAIMER

BACKGROUND

Because this paper deals with validation of EBS radionuclide release rate models, it is useful to recall the types of models involved and to identify the subset that are of interest here.

Figure 1 shows a top level hierarchical input-process-output (HIPO) chart, of the type often used in systems analysis, which illustrates the general structure of the modeling hierarchy for the EBS release rate modeling. It illustrates the point that the models involved are organized into a three-tiered hierarchical structure; the boxes represent categories of models and the circles represent input and output parameters. The EBS release rate is obtained from the individual waste package release rate which, in turn, is obtained from the waste form release rate. The focus of this paper is on the models in the two lower tiers of this hierarchical structure. This paper considers only models that support determination of the radionuclide release rate given the state of the waste package and its near-field environment. The plausible states for the waste packages and their near-field environments under which radionuclide release will occur are specified in a number of "release modes" [3,4]. These are:

- A "dry release" mode wherein the breached waste package is in a humid air environment with no water flow in the waste package near-field. Radionuclide release from the waste forms and from the breached waste package is simulated by assuming that only gaseous radionuclide release can occur.
- A "wet drip" mode which envisions water dripping on a breached waste package container and entering the package through the breach opening(s). Depending on the configuration of the breach openings, the dripping water may either accumulate in the bottom of the container leading to a "bathtub" condition, or "trickle through" holes in the bottom of the container.

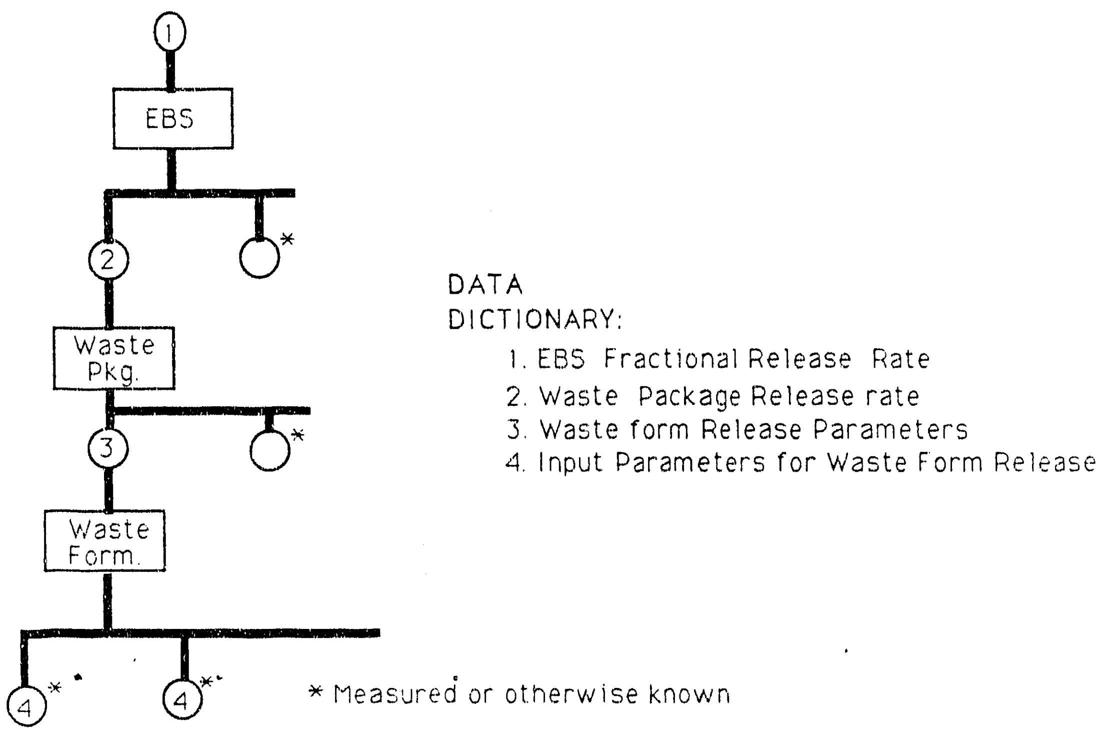

Figure 1. Information Flow (HIPO) Diagram for Assessing the EBS Fractional Release Rate

- A "wet continuous" release mode which envisions water in the partially saturated rock and borehole annulus rubble contacting the waste form and providing continuous connected pathways for water ingress and radionuclide egress.

The application of available information and testing methods for validation of models that describe radionuclide release from borosilicate glass waste and breached waste packages, given these release modes, is discussed below.

LABORATORY TESTING AND VALIDATION OF WASTE FORM RADIONUCLIDE RELEASE MODELS (Tier 1 in Figure 1)

A basic premise that is currently used in waste package PA modeling is that only gaseous radionuclides can be released for the "dry release mode." Experimental information from the open literature that can be used to critically test this premise is discussed below.

Ebert et al. [5] has studied the sorption of water and subsequent hydration of nuclear waste glasses in air atmospheres as a function of relative humidity. It was found that, at relative humidities over ~97%, the observed sorption isotherms are dominated by film formation on the glass surface. Observations that indicate water film growth on glass surfaces exposed in humid atmospheres, even to the point at which the films may flow and drip off, have been reported by other authors [6,7]. These observations can be explained by the fact that the water initially adsorbed on the glass surface can support ion exchange reactions that release sodium and other solutes which then decrease the water vapor pressure at the surface of the glass. Based on the concentration of solutes that have been estimated for these water films [8], the van't Hoff equation indicates that the film osmotic pressure will be about 25 atm. This implies that there is a significant thermodynamic "sink" for water condensation on the glass surface.

The release humidity (p/p_O) of air in equilibrium with a solution that has an osmotic pressure of P_O is given by [9]

$$\ln (p/p_O) = -(M\ P_O)/RT\rho \qquad (1)$$

where

p is the partial water vapor pressure in equilibrium with the solution;

p_O is the water vapor pressure for air saturation;

M and ρ are the molecular weight and density of water, respectively;

T is the prevailing absolute temperature.

Based on the above expression, the relative humidity (p/p_O) for a water film with an osmotic pressure of 25 atm at ambient laboratory temperatures is about 98%. This corresponds closely with the conditions under which condensation dominates the sorption isotherms [5] and under which the maximum rates of glass hydration have been observed [14].

Determination of the significance of the experimentally observed water films for radionuclide release under "dry release" repository conditions requires that the following questions be addressed:

1. will water films form on waste glass surfaces in the repository?
2. if such films do form in the repository, what significance will they have for glass reaction and radionuclide release?

The answer to the first question depends on the balance between several competing effects. The matric potential of the host rock as well as residual temperature gradients will tend to inhibit film formation while the colligitive properties of the surface films with solutes supplied both by the glass and radiolysis will tend to support film formation. Laboratory analog experiments that simulate the repository conditions are needed to investigate these competing affects.

The significance of water films in the repository is two-fold:

- They will probably lead to local reaction conditions that may be quite aggressive from the point of view of glass reaction. This expectation is based on the known effects of large surface area to volume ratios on glass reaction rates [8] and the effects of radiolysis product accumulating in the small film volumes involved. To illustrate the latter point, Figure 2 shows a comparison between the observed corrosion behavior of glass under humid air exposure conditions with and without radiation.
- The surface water films may grow either through water vapor condensation or through the effects of the osmotic potential gradient on water flux [10] if the films are connected through wet continuous pathways to water in the host rock. Formation of films in the repository would invalidate the premise that only gaseous radionuclides can be released for the "dry release" mode. This is an important issue because it affects a basic premise in the modeling of radionuclide release for 90% of the waste packages [11].

Another important premise in radionuclide release rate modeling is that radionuclide concentrations in groundwater are solubility limited [4]. Experimental results which examine the formation, the particle size distribution, and the extent to which individual radioelements are associated with colloidal particles, under test conditions that simulate the repository release modes, can be used to test this premise.

A small-scale experimental test procedure has been developed [12,13] to simulate, in the laboratory, glass and spent fuel reactions under the "wet drip" release mode. This involves periodically dripping groundwater onto a waste form assemblage (waste form plus container metal) and monitoring the changes in solution chemistry, the waste and metal reactions, and the formation of secondary reaction phases. Table I presents the results obtained when the solution collected from such a test procedure, applied to West Valley glass, was filtered through a sequence of filters with successively decreasing pore sizes. A transmission electron microscope (TEM) micrograph of particles that formed under these conditions is shown in Figure 3. The data in Table I show that the americium and plutonium are associated with particles greater than 1 μm while only about 20% of the neptunium is filterable with a 1 μm filter. The balance of the neptunium appears to be in solution. The reason for observed decrease in the fraction transmitted between the 0.05 and 0.015 μm filter is not clear. Under these test conditions, most of the Pu and Am in the solution is believed to be associated with the type of particles shown in Figure 3. These data and other reported observations of the formation of colloidal particles [14] under repository-relevant testing conditions indicate that the formation and transport of colloidal particles may be important in the release of some radionuclides.

LABORATORY TESTING AND VALIDATION OF WASTE PACKAGE RADIONUCLIDE RELEASE MODELS (Tier 2 in Figure 1)

Few attempts have been made to experimentally simulate radionuclide release, at an integrated waste package system level, in any repository environment. However, as indicated above such laboratory analog experiments are desirable to test modeling premises. They are also desirable to support the system model testing involved in the second element of the proposed validation methodology [1].

The most complete laboratory analog simulations that have been reported in the literature were conducted for the basalt repository [15,16]. A modular approach was used in simulating the key phenomena and interactions that were believed to be important in groundwater ingress to the waste form, waste form reactions, and groundwater/radionuclide egress.

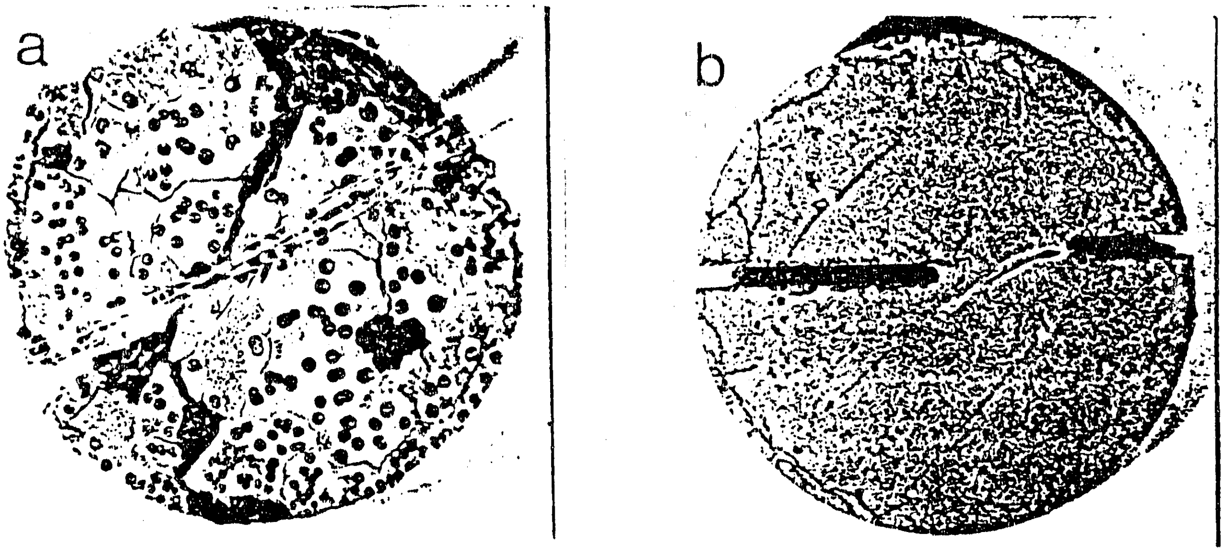

Figure 2. Micrograph of (a) the Surface of 202A Glass Hydrated at 200°C in a Gamma Radiation Field of ~5000 R/hr, (b) 202U Glass Hydrated at 200°C Without Radiation. The experimental duration of both samples was 56 days. The magnification is 8X. Note the 202A glass has reacted completely through the 2 mm thick sample while the 202U glass has not yet formed secondary phases on the surface.

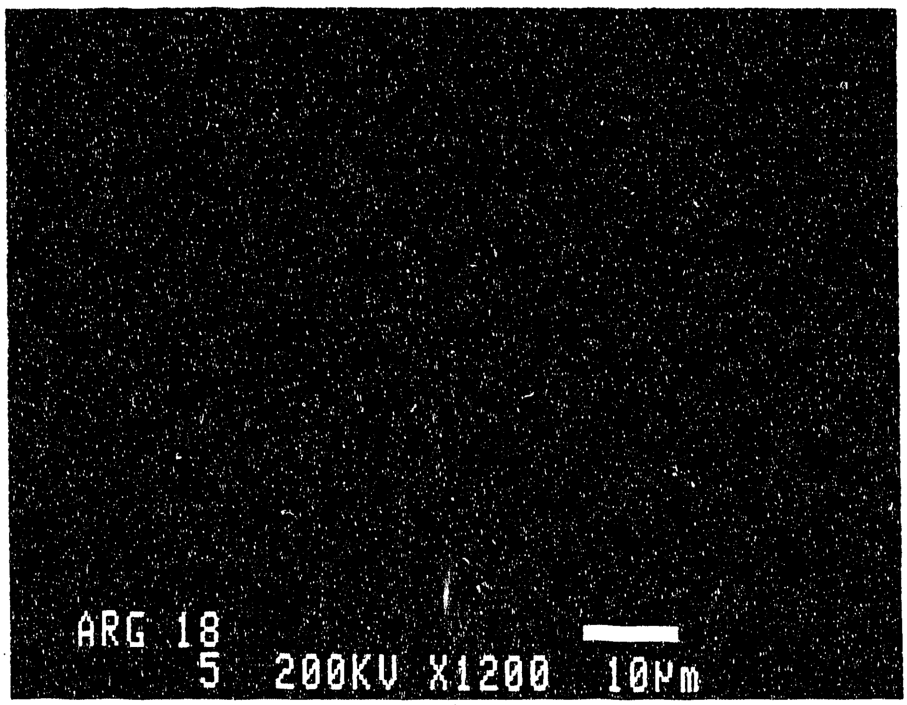

Figure 3. TEM Picture of Particles Collected from the Wet Drip Test Procedure.

TABLE I
Fraction* of Np, Pu, and Am Transmitted through Filters with Successively Decreasing Pore Sizes

Filter Pore Size	Fraction Transmitted		
	Np	Pu	Am
1 μm	0.78	0.02	0.04
0.4 μm	0.87	0.01	0.01
0.1 μm	0.75	-	-
0.05 μm	0.78	-	-
0.015 μm	0.56	-	-
4.8 nm	0.58	-	-
3.8 nm	0.57	-	-
2.8 nm	0.53	-	-

*Note: The transmitted fractions represent the ratio of the amount measured in the filtrate, after each filtration stage, to the original amount in the test solution.

Although tuff analog laboratory experiments, that simulate waste package release, have not been conducted, the experience with the basalt analog experiments indicate that key aspects of the waste package radionuclide release performance may be amenable to laboratory simulation. On this basis, several approaches for laboratory simulations applicable to the Yucca Mountain waste package environment have been investigated [2]. Following the basalt laboratory analog testing precedence, the initial investigations have examined the feasibility of a coupled laboratory simulation of the water ingress, waste form reaction, and water and radionuclide egress sequence.

A schematic representation of the experimental apparatus used to evaluate the coupled experimental analog approach is shown in Figure 4. The initial system design consisted of a tuff core with a diameter of ~4" and a length of ~8". The core was cut diametrically into two unequal sections and the mating faces of the core sections were polished to an optical finish. A one-step cavity was machined into the bottom section.

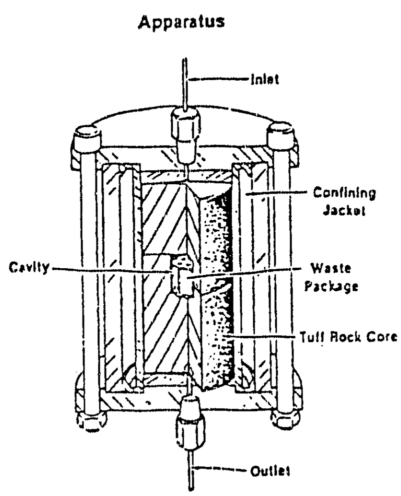

Figure 4. Representation of the Initial Laboratory Analog Test Apparatus.

This cavity was used to contain the waste form (Figure 4) which was held between two sections of perforated metal making up the waste package assembly (WPA). The WPA rested on the cavity step making contact with the tuff at four points where the support pins rested on the tuff.

During normal operation, the two sections of tuff fit together within a flexible confining sleeve that was in turn held in place by an outer metal shell. A tight fit was maintained between the tuff and the flexible sleeve by pressurizing the space between the metal shell and the sleeve.

Water flow was imparted to the system through the inlet opening. The source of water was a water reservoir (not shown) that was connected to the inlet via a narrow ID metal tube. The pressure gradient for driving water through the tuff was generated by heating the water reservoir.

Preliminary testing with this apparatus indicated that meaningful analog simulations are feasible. However, further development and testing are needed, at both the bench scale and pilot engineering scale, before laboratory analog experiments can be conducted for examining waste package radionuclide release under each of the release modes mentioned earlier.

CONCLUSIONS

The following general conclusions can be drawn concerning the use of available experimental information and the role of laboratory analog testing in supporting implementation of the proposed validation methodology for EBS radionuclide release modes.

- Available information from experimental investigations of radionuclide release from waste glass, under repository-relevant conditions, raises several issues concerning the validity of some of the basic premises that are currently used in radionuclide release modeling. However, better laboratory experimental simulations, at an integrated waste package system level, are needed to resolve these issues.
- Although initial small-scale testing indicates that key aspects of the radionuclide release from breached waste packages are amenable to experimental simulation in the laboratory, very little work has been done in this area. The results obtained from the simulations done at lower levels of integration suggest that larger scale laboratory analog experiments are needed to support validation of performance assessment models used to calculate release from an individual waste package.
- Analog laboratory experiments can support development of credible performance assessment models by (1) ensuring that all important processes are modeled and (2) providing data to support model validation. A rational testing sequence to support performance assessment modeling would include the following general sequence:
  (1) analog screening experiment to identify important effects and processes and test basic modeling premises,
  (2) separate effects experiments (not the subject of this paper) to support development and validation of submodels for the processes identified in the laboratory analog screening experiments, and
  (3) analog experiments to support model validation at the waste package system level.

It appears that laboratory analog testing is feasible and can provide important support for the development of PA models at various stages in their development and validation. More development of laboratory analog testing and integration of the results of such testing into PA modeling would support the credibility of long-term performance predictions for the waste package.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Repository Technology Program, under Contract W-31-109-Eng-38.

REFERENCES

1. C. F. Voss, "A Proposed Methodology for Validating Performance Assessment Models for the DOE Office of Civilian Radioactive Waste Management Program," Proc. of Internat. Topical Mtg. on High-Level Radioact. Waste Mgmt., Las Vegas, NV, April 8-12, 1990.
2. J. K. Bates, T. A. Abrajano, D. J. Wronkiewicz, T. J. Gerding, and C. A. Seils, "Strategy for Experimental Validation of Waste Package Performance Assessment," Argonne National Laboratory report ANL-90/21 (1990).
3. W. J. O'Connell, "Status of Integrated Performance Assessment of the Waste Packages and Engineered Barrier System," Proc. of Internat. Topical Mtg. on High-Level Radioact. Waste Mgmt., Las Vegas, NV, April 8-12, 1990.
4. M. J. Apted and D. W. Engel, "Mass-Transfer Analysis of Waste Packages Containing Defense Waste Processing Facility Glass as a Waste Form," Proc. of Internat. Topical Mtg. on High-Level Radioact. Waste Mgmt., Las Vegas, NV, April 8-12, 1990.
5. W. L. Ebert, R. F. Hoburg, and J. K. Bates, "The Sorption of Water on Obsidian and a Nuclear Waste Glass," submitted for publication in Physics and Chemistry of Glasses (1990).
6. T. A. Abrajano, Jr., J. K. Bates, and J. J. Mazer, "Aqueous Corrosion of Natural and Nuclear Waste Glasses. II. Mechanisms of Vapor Hydration of Nuclear Waste Glasses," J. Non-Cryst. Sol. 108, 269-288 (1989).
7. W. L. Ebert and J. K. Bates, "The Reaction of Synthetic Nuclear Waste Glass in Steam and Hydrothermal Solution," Mat. Res. Soc. Symp. Proc. Vol. 176, 339-346 (1990).
8. W. L. Ebert and J. K. Bates, "The Importance of Secondary Phases in Glass Corrosion," paper presented at this symposium.
9. E. C. Childs, An Introduction to the Physical Basis for Soil Water Phenomena, J. Wiley and Sons, Ltd. (1969).
10. D. Hillel, Fundamentals of Soil Physics, Academic Press (1980).
11. Site Characterization Plan, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, DOE Report DOE/RW-0199 (1988).
12. J. K. Bates and T. J. Gerding, "NNWSI Phase II Materials Interaction Test Procedures and Preliminary Results," Argonne National Laboratory report ANL-84-81 (1985).
13. J. K. Bates and T. J. Gerding, "Application of the NNWSI Unsaturated Test Method to Actinide Doped SRL 165 Type Glass," Argonne National Laboratory report ANL-89/24 (1990).
14. J. K. Bates, W. L. Ebert, and T. J. Gerding, "Vapor Hydration and Subsequent Leaching of Transuranic-Containing SRL and WV Glasses," Proc. of Internat. Topical Mtg. on High-Level Radioact. Waste Mgmt., Las Vegas, NV, April 8-12, 1990.
15. M. G. Seitz, D. L. Bowers, T. J. Gerding, and G. F. Vandegrift, "Laboratory Studies of a Breached Nuclear Waste Repository in Basalt," Argonne National Laboratory report ANL-84-16; NUREG/CR-3710 (1984).
16. M. G. Seitz, "Repository-Analog Experiments of Nuclear Waste Leaching and Migration," Proc. of Internat. Atomic Energy Symp. on Migration in the Terrestrial Environ. of Long-Lived Radionuclides from the Nuclear Fuel Cycle, IAEA-SM-257, July 27-31, 1981.

END

DATE FILMED

02 / 08 / 91