CONF-820854--8

BNL-NUREG--31833

DE82 022051

BNL-NUREG-31833

PROPERTIES OF RADIOACTIVE WASTES AND WASTE CONTAINERS*

Nabil Morcos and Ramesh Dayal
Brookhaven National Laboratory
Department of Nuclear Energy
Upton, NY 11973

ABSTRACT

This program is sponsored by the Nuclear Regulatory Commission to address basic concerns in assessing the performance of solidified radwaste. Experiments were initiated to address these concerns. In particular, leachability of solidified radwastes and the physical stability of the ensuing waste forms were evaluated. In addition, leaching experiments designed to address the effects of alternating wet/dry cycles and of varying the length of these cycles on the leach behavior of waste forms were initiated.

OBJECTIVES OF PROGRAM

The objectives of this program, sponsored by the Nuclear Regulatory Commission (NRC), are to provide a data base which will assist the NRC in evaluating the acceptability of solidified low level waste packages for disposal with regards to minimizing radionuclide migration after burial. The program will establish tests for the physical and chemical properties to evaluate the performance of solidified wastes in long-term storage or disposal and will establish procedures for testing containers with respect to conforming with regulatory guidelines. Test procedures and methodology are being evaluated to study: (1) long-term performance of waste forms based on short-term laboratory test results; (2) behavior of full size forms from tests on several size forms, (3) in situ leach behavior from laboratory tests; and (4) properties of actual reactor waste. The information generated in this program should be a useful source term for modeling of radionuclide migration in radwaste burial sites.

*Work performed under the auspices of the United States Nuclear Regulatory Commission.

PROPERTIES OF SOLIDIFIED WASTE

Basic concerns in assessing the performance of solidified wastes (waste forms) are dimensional stability and radionuclide release in shallow land burial (SLB) or disposal environments.

The following parameters were addressed:

Waste types: 1. Simulated waste - evaporator concentrate (boric acid wastes) and organic ion exchange resins (cation and anion resins).

2. Actual waste - Acquired from a LWR (Prairie Island) in conjunction with NRC project FIN A-6359.

Solidification agents: Portland (I,II and III) and high alumina (Lumnite) cements and bitumen.

Radiotracers: ^{137}Cs, ^{85}Sr and ^{60}Co.

Tests used: Modified IAEA leach test[1] and ASTM-C 39-72 standard compressive strength test.

BORIC ACID WASTE IN PORTLAND III CEMENT

A study designed to evaluate the leachability of ^{137}Cs, ^{85}Sr, and ^{60}Co from simulated boric acid waste in Portland III cement and to measure the compressive strength of the ensuing waste forms was performed.[2] The simulated waste forms were leached using a modified IAEA leaching procedure for periods extending to 229 days. The compressive strength of specimens was measured before and after immersion in the leachant for 352 days. The waste forms were made with 3%, 6%, and 12% boric acid solutions; the waste-to-cement ratios studied were 0.5 and 0.7.

Increasing the waste-to-cement ratio from 0.5 to 0.7 caused an increase in the leachability of ^{137}Cs from the three boric acid/ cement composite formulations. This effect is not noticeable for the leachability of ^{85}Sr. The extent of ^{85}Sr release in a given time was approximately one-twentieth that of ^{137}Cs from these composites. Cobalt-60, on the other hand, was below the detection limit in the leachate for all the composites (3.0×10^{-2} μCi per 1.5 L samples).

For a waste/cement ratio of 0.5, 352 days of immersion caused a substantial decrease (approx. 50%) in the compressive strength of specimens. For a waste/cement ratio of 0.7, although initially the compressive strength of these specimens was approximately 40 to 50% lower than those for w/c ratio of 0.5, it did not decrease further after 352 days of leaching. The compressive strength of specimens for waste/cement ratios of both 0.5 and 0.7 was approximately 20 to 38 times higher than the minimum acceptable limit (50psi) set forth in the proposed Code of Federal Regulations, 10 CFR Part 61.56.

ORGANIC ION EXCHANGE RESINS IN PORTLAND AND LUMNITE CEMENTS

An experiment was performed to determine the leachability of ^{137}Cs, ^{85}Sr, and ^{60}Co from organic ion exchange resin/cement composites.(2) Portland II and Lumnite (high alumina) cements were used as binders, with waste-to-cement ratios of 1.0 and 1.8 for both cements. In addition, the displacement of the three radiotracers from the ion exchange resins upon mixing the loaded resins with the two cements (before solidification) was measured.

Lumnite cement showed a lower leachability of ^{137}Cs and ^{85}Sr than Portland II cement. Cobalt-60 was below the detection limit in leachates for both types of cement. Strontium-85 was observed only in leachates for Portland II cement. These observations may be due to either an isotopic dilution of radiotracers with the cement components or to an actual chemical interaction of the radiotracers with the cement matrices.

The amounts of ^{137}Cs, ^{85}Sr, and ^{60}Co displaced from the ion exchange resins during the paste phase of the solidification process were comparable when mixed with Portland II cement (waste-to-cement ratio of 1.0 and 1.8), but not with Lumnite cement.

ORGANIC ION EXCHANGE RESINS/BITUMEN COMPOSITES

H^+, Na^+, Cs^+, and Sr^{+2} form cationic resins, loaded with ^{137}Cs and ^{85}Sr, were mixed in varying ratios with anionic resins in SO_4^{-2} form, and subsequently solidified in bitumen. The leachability and physical integrity of the resulting composites were evaluated.(2)

The presence of anionic resins in the sulfate form (50% by weight of resins) increased the leachability of ^{137}Cs from the waste forms by approximately two orders of magnitude and by approximately an order of magnitude for ^{85}Sr. The physical integrity of the forms deteriorated during leaching, as the amount of SO_4^{-2} resin increased.

REACTOR WASTE

A sample of actual reactor waste from the Prairie Island reactor was acquired in conjunction with NRC Project A-6359. The waste was solidified according to optimized process parameters. After curing, the waste forms will be leached using the modified IAEA leaching procedure. Data from this study will be used in conjunction with data generated from NRC project A-6359 to correlate the leach behavior of simulated waste with that of real waste.

ANALYSIS OF IRRADIATED ION EXCHANGE MATERIALS

Under a subcontract from BNL, a study was undertaken at the Georgia Institute of Technology to investigate the effects of radiation on the physical and chemical properties of organic ion exchange resins, and corrosion effects on the walls of the irradiation containers in contact with the resins and their radiolytic byproducts. Organic ion exchange resins were irradiated up to a dose of 5 x 10^9 rad. The irradiation containers were fabricated from stainless steel type 304.

Gases detected following irradiation of resins were: H_2, O_2, N_2, CO_2, CO, CH_4, C_2H_6, C_3H_8, C_4H_{10}, and sulfur gas (SO_2, SO_3). Radiolytic by-products resulting from irradiating cationic resins did not significantly attack Type 304 stainless steel, whereas those from anionic resins caused significant localized corrosion. The attack was in the form of etching under surface deposits and pitting. This type of localized corrosion might cause perforation of the container walls for longer exposures.

TEST DEVELOPMENT, EXTRAPOLATION AND CORRELATION

CORRELATION OF ^{137}Cs LEACHABILITY FROM SMALL-SCALE SAMPLES TO LARGE-SCALE WASTE FORMS

A study correlating the leachability of ^{137}Cs from small-scale to large-scale cement forms was performed.(3) The waste forms consisted of organic ion exchange resins incorporated in Portland I cement, with a waste-to-cement ratio of 0.6 and a water-to-cement ratio of 0.4 (as free water) and boric acid waste (12% solution), incorporated in Portland III cement, with a waste-to-cement ratio of 0.7. ^{137}Cs was added to both waste types prior to solidification. The samples' dimensions varied from 1 in. x 1 in. to 22 in. x 22 in. (diameter x height) in size. Leach data extending over a period of 260 days were obtained. The observed ^{137}Cs leach data for resin/cement and boric acid/cement can be represented by a diffusional mass transport relationship. This semiempirical relationship has been used to estimate the cumulative fractional releases from forms varying in size from 2 x 2 to 22 x 22 for a given leaching period. The following observations were made from the ^{137}Cs release curves.

The initial ^{137}Cs release was primarily surface controlled, with the bulk of the release reaction being diffusion-controlled. The effective bulk diffusion coefficients (D_e) for ^{137}Cs in the waste form matrices were calculated from the slopes of the linear regions of the ^{137}Cs release curves vs $t^{1/2}$. D_e values were on the order of

$10^{-8} cm^2/s$, and increased with increasing waste form size for both matrices. The observed increase in D_e with waste form size may be attributed to variations in the degree of curing of the waste forms.

WASTE FORM LEACHING IN AN INERT ENVIRONMENT

In most of the leaching studies performed to date, a modified IAEA test procedure was used. Considering the nature of the IAEA leach test, the results generated to date provide information on the leaching behavior under "conservative conditions," that is, continuous leaching under water saturation conditions, with periodic leachant renewal. Since these conditions are far removed from those in an actual burial site, we have developed experiments which approximate more realistic burial conditions. The data from these experiments may help establish the degree of conservatism in leach behavior relative to the laboratory test referred to above.

Specifically, the effects of alternating wet/dry cycles and of varying the length of these cycles on the leach behavior of a given waste form will be investigated. Radionuclide release rates calculated from leach data resulting from such experiments will be a useful source term parameter for modeling of radionuclide migration at burial sites. Further, this study will provide information on the effects of varying the periods of water saturation and the frequency of leaching on leach rates. A scoping study has been initiated. Leach data from this study will be compared with data for similar forms without the inert medium. This comparison will provide information on the effect of partial saturation and drying cycles on the waste form leachability. In turn, this information will provide a more realisitic predictive data basis for the leach behavior of waste forms in shallow-land burial sites.

REFERENCES

1. P. Colombo et al., Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, First Topical Report," Appendix C, NUREG/CR-0619, BNL-NUREG-50957, August 1979.

2. N. Morcos, R. Dayal, and A. J. Weiss, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Status Report, October 1980-September 1981," NUREG/CR-2617, BNL-NUREG-51515, April 1982.

3. N. Morcos and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, October-December 1981," NUREG/CR-2193, BNL-NUREG-51410, Vol. 1, Nos. 3-4, May 1982.