BNL-NUREG-35283

PROPERTIES OF RADIOACTIVE WASTES AND WASTE CONTAINERS*

H. S. Arora and R. Dayal
Department of Nuclear Energy
Brookhaven National Laboratory
Upton, New York 11973

BNL-NUREG--35283

TI85 000891

ABSTRACT

Major tasks in this NRC sponsored program include (1) an evaluation of the acceptability of low-level solidified wastes with respect to minimizing radionuclide releases after burial, and (2) an assessment of the influence of pertinent environmental stresses on the performance of high-integrity radwaste container (HIC) materials.

The waste form performance task involves studies on small-scale laboratory specimens to predict and extrapolate: (1) leachability for extended time periods; (2) leach behavior of full-size forms; (3) performance of waste forms under realistic leaching conditions; and (4) leachability of solidified reactor wastes. The results show that leach data derived from testing of small-scale specimens can be extrapolated to estimate leachability of a full-scale specimen and that radionuclide release data derived from testing of simulants can be employed to predict the release behavior of reactor wastes. Leaching under partially saturated conditions exhibits lower releases of radionuclides than those observed under the conventional IAEA-type or ANS 16.1 leach tests.

The HIC assessment task includes the characterization of mechanical properties of Marlex CL-100, a candidate radwaste high density polyethylene material. Tensile strength and creep rupture tests have been carried out to determine the influence of specific waste constituents as well as gamma irradiation on material performance. Emphasis in ongoing tests is being placed on studying creep rupture while the specimens are in contact with a variety of chemicals including radiolytic by-products of irradiated resin wastes.

---

*Work carried out under the auspices of the U.S. Nuclear Regulatory Commission.

MASTER

DISCLAIMER

INTRODUCTION

The recently promulgated 10 CFR Part 61 regulation by the U.S. Nuclear Regulatory Commission requires either solidification or the use of high-integrity containers for the disposal of several classes of low-level radioactive waste. Primary concerns in licensing radioactive waste forms and containers are the potential for release of radionuclides and their dimensional stability. The objectives of the present investigation are to assess the radionuclide release and container stability concerns by establishing a data base for evaluating the acceptability of solidified low-level radioactive waste packages for disposal, and to develop test procedures and methodologies which enable the prediction of long-term performance of waste forms and containers on the basis of short-term laboratory tests. This paper summarizes the current status of the program in terms of: (1) waste form evaluation and (2) radwaste container evaluation. Major tasks in these areas are described and experimental results obtained to date are presented and discussed.

WASTE FORM EVALUATION

Major tasks in assessing the performance of solidified wastes consist of a scale-up leach study to estimate Cs-137 release from large-scale cement forms, the solidification and leaching of actual reactor wastes, and wet-dry cycling leach tests in inert media. The status of these experiments is described below.

Scale-up Leach Study

The scale-up leach study was initiated to establish whether laboratory-derived leach data, based on small test specimens, could be extrapolated to full-scale field samples (Dayal et al., 1983; Morcos et al.,1982). For this purpose, simulants of two contrasting waste types (a) organic cation exchange resin and (b) boric acid concentrate waste, incorporated in Portland Type cements were considered. The leachability of Cs-137 from composites of varying surface area (S) to volume (V) ratios (specimen dimensions varied from 5x5 to 55x55, diameter x height, cm) were investigated by employing a modified IAEA leach method.

Using leach data in the region representing diffusion-controlled release, effective diffusivities of $\approx 2\times10^{-8}$ cm^2/s have been calculated for Cs-137 in both waste/cement matrices. A comparison of the observed and predicted cesium release values indicates that on a laboratory time scale leach data derived from testing of small-scale specimens can be extrapolated, using a planar semi-infinite medium approximation, to estimate leachability of a full-scale specimen (Dayal et al., 1983).

The scope of the scale-up study under saturated conditions is being expanded in investigations currently under way to determine if the relationship between CFR and surface area-to-volume ratio (S/V) also holds under cyclic wet-dry leach conditions (Arora and Dayal, 1984a).

Solidification and Leaching of Actual Reactor Wastes

IAEA-type leach testing was also conducted on two types of reactors wastes (resin beads from a BWR and boric acid concentrate from a PWR) solidified in cement. In these wastes, Cs-isotopes were the most mobile constituents followed by Sr-90. Co-60 was found to be the least mobile. Effective diffusivities of these radionuclides were $\approx 10^{-9}$ cm^2/s for Cs-isotopes, $\approx 10^{-11}$ cm^2/s for Sr-90, and $\approx 10^{-13}$ cm^2/s for Co-60 (Arora and Dayal, 1984b). A comparison of the release of Cs-137 from actual reactor wastes and the results of our previous study in which simulants of these reactor wastes were solidified and leached under identical conditions (Dayal et al., 1983) shows a general correspondence in release behavior, indicating that the simulated waste leach data could be employed to evaluate and predict the release behavior for reactor wastes. Leachability Index (LI) values calculated in accordance with the procedure outlined in ANS 16.1 test indicated that the reactor waste composites surpassed the regulatory compliance value of 6.0.

Wet-Dry Cycling Leach Tests in Inert Media

The applicability of leach data based on modified IAEA or ANS 16.1 tests to predict radionuclide releases under field conditions requires a through understanding of the limitations of the model used, as well as the characteristics of the field burial environment. Since the modified IAEA-type testing conducted under fully saturated conditions with frequent leachant renewals represents leaching under "worst conditions", the predicted cesium releases and effective diffusivities calculated from laboratory data are conservatively high. Consequently, leaching experiments which consider more realistic field burial conditions represented by wet-dry cycling were initiated (Morcos and Dayal, 1982).

The simulated waste form for these tests consisted of cation exchange resin (IRN-77), loaded with Cs-137 and Sr-85 as tracers, and solidified in Portland Type I cement. The test specimens were right cylinders with a nominal dimension of 5x10 (diameter x height, cm). Upon curing for a period of 28 days the test specimen was placed in a porous medium contained in a column. To minimize the sorption of leached radionuclides, an inert material [high density polyethylene (HDPE) beads] was selected as a porous medium. The specimen was surrounded on all sides by a 5-cm-thick layer of PE beads. Deionized water or a simulant of Trench sump 6D1 groundwater from Barnwell, SC, site was used as a leachant, with the total volume of leachant being 10 times the exposed surface area of the specimen during the wet period (Morcos and Dayal, 1982). Information on the battery of waste form leaching experiments under cyclic wet/dry conditions is summarized in Figure 1.

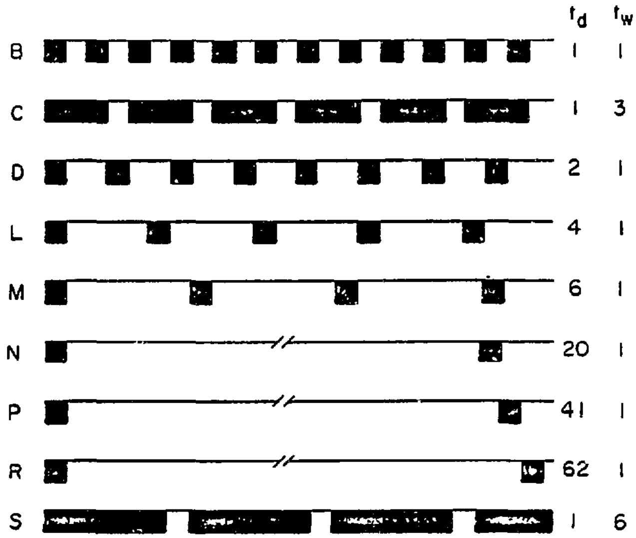

Figure 1. Range of wet (shaded) and dry (unshaded) leach cycle conditions and corresponding leachant contact times for various Experiment Codes. (t_w = immersion time and t_d = dry time, days).

Cs-137 Release

The CFR data of Cs-137 (normalized for V/S) vs total elapsed leach time for cyclic wet-dry experiments using deionized water as a leachant are presented in Figure 2. Elevated releases of Cs-137 and a high degree of scatter were observed for the incremental fractions of first three wetting cycles and may be attributed to a "washing off" effect from the waste form surface. A comparison of Cs release observed as a function of elapsed leach time under unsaturated conditions represented by wet-dry cycles with those observed based on saturated conditions represented by modified IAEA leach test for similar time periods reflects that radionuclide release observed under saturated conditions represents a conservative estimate of release expected in a field situation (Dayal et al., 1984).

Dayal et al. (1984) and Arora et al. (1983) reported that four widely separated release curves (CFR vs elapsed leach time) for Experiment Codes B, D, L, and M converged to a single curve (CFR vs actual immersion time), suggesting that Cs-137 leachability in the predominantly diffusion controlled region of these experiments was primarily governed by actual immersion time rather than the total elapsed leach time.

Bulk diffusion coefficient values calculated on the basis of immersion time rather than the elapsed leach times for these experiments by employing a semi-infinite plane source diffusion model show that D_e value for Cs-137 are on the order of $\approx 10^{-8}$ cm^2/s. These data are in general agreement with those derived on the basis of modified IAEA tests, which represent continuously saturated leach conditions.

Preliminary results of additional experiments involving wet-dry leaching conditions in which one-day immersion periods are followed by dry spans of 20, 41, and 62 days (Experiment Codes N, P, and R) indicate the the CFR data for these widely separated release curves also converge to a single curve for the relationship between CFR and immersion time. These data are being interpreted further.

Significantly higher releases of Cs-137 are observed when synthetic groundwater replaced deionized water as a leachant under the wet-dry conditions of Experiment Codes C and D. Higher releases under the groundwater leachant are related to increased concentrations of competing ions as well as the presence of divalent cations which are expected to more efficiently displace Cs-137.

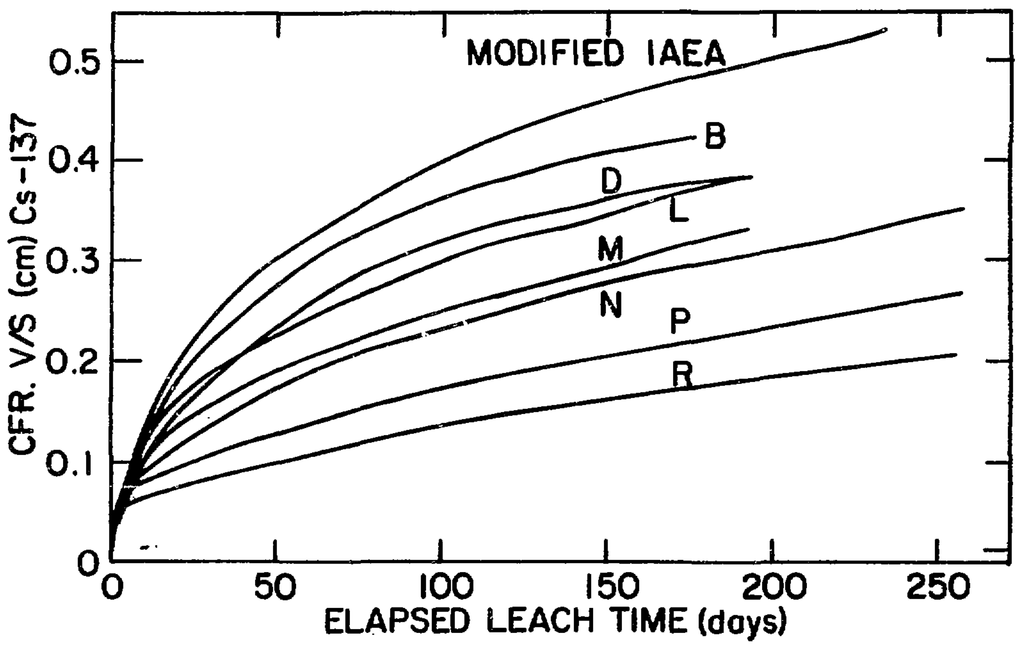

Figure 2. Normalized CFR as a function of elapsed leach time of Cs-137 from resin/cement waste forms subjected to a range of partially saturated leach conditions with deionized water. Three initial immersions for Experiment Codes N, P, and R were performed on the 1st, 3rd, and 5th days but for comparison purposes are shown to occur at prescribed elapsed leach times.

Sr-85 Release

The average CFR vs elapsed leach time plots of Sr-85 for each wet-dry cycle as well as that derived on the basis of modified IAEA method are presented in Figure 3. The CFR plots presented in Figures 2 and 3 indicate significantly lower releases of Sr-85 than that of Cs-137 in a given length of time. Profound differences in the release behavior of these two radionuclides from resin/cement composites are related to their chemical nature and to different mechanisms by which these radionuclides are mobilized and transported from the bulk matrix (Dayal et al., 1984).

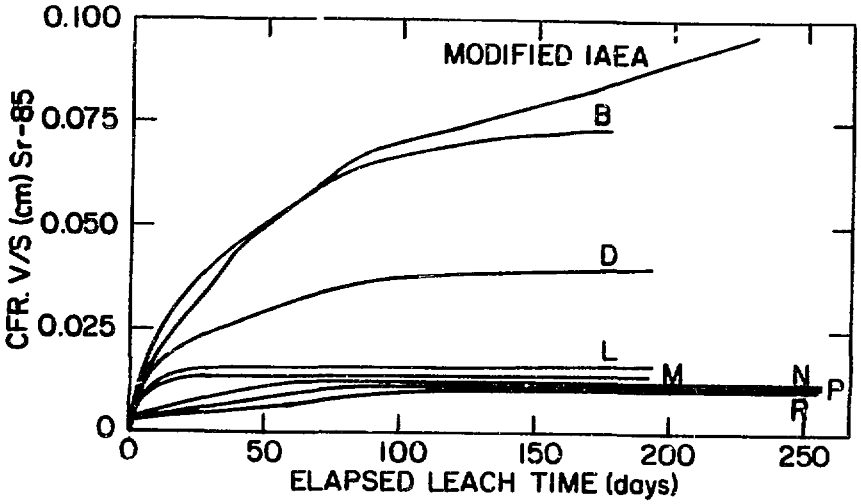

Figure 3. Normalized CFR as a function of elapsed leach time of Sr-85 from resin/cement waste forms subjected to a range of partially saturated leach conditions with deionized water. Three initial immersions for Experiment Codes N, P, and R were performed on the 1st, 3rd, and 5th days but for comparison purposes are shown to occur at prescribed elapsed leach times.

Preliminary examination of Sr-85 release data indicates that total immersion time does not appear to be a dominant factor controlling the release of Sr-85. As discussed by Dayal et al. (1984), the length of the dry period in wet/dry cyclic leach experiment appears to control the overall release of Sr.

RADWASTE CONTAINER EVALUATION

The primary objective of this task is to provide a data base for evaluating the combined influence of burial environments and waste components on the properties of high density polyethylene (HDPE). Our approach consists of characterizing a HIC material in terms of physical, chemical, and mechanical properties to serve as baseline information. In addition, modifications in these properties which result from the solitary and/or combined influence of varying chemical, thermal, and radiation stresses are studied.

Marlex CL-100 - highly cross-linked thermoplastic HDPE, trademark of Phillips Chemical Company of Bartlesville, OK, was selected for the study because it has been licensed for the disposal of dewatered resins at the Barnwell site. Most test specimens were acquired from the side walls of a

General Observations

Visual examination of Marlex CL-100 material indicated that the inner surface of the rotationally molded Poly-Pro container has a glossy texture while the outer surface has a dull and somewhat roughly-textured finish. Microscopic observations of the inner oxidized surface indicated irregular trenches and round-to-oval crater-like pits with a flat bottom but a slightly raised annulus. The diameter of the pits, some of which were interconnected, varied from 12-20 μm (Figure 4). The outer unoxidized surface was devoid of pits and trenches and was largely featureless.

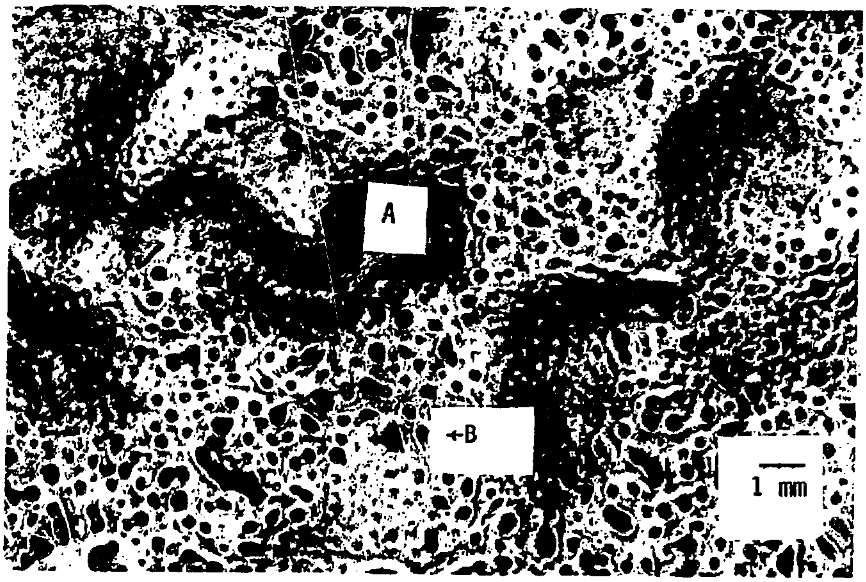

Figure 4. A view of (A) irregular trenches and (B) crater-like pits observed on the glossy inner surface of Marlex CL-100 Poly-Pro container.

Mechanical Characteristics

Tensile Strength

The tensile test data for untreated Marlex CL-100 specimens of different thicknesses and for specimens stamped out perpendicular or parallel to the wall of the Poly-Pro container indicated that the effect of specimen thickness or preparation on the tensile properties of Marlex was minimal except for the specimens machined from a Marlex sheet which exhibited lower yield stress. The coupons undergoing tensile strength testing deformed by necking prior to failure. Microscopic examination of the deformed structure of the unoxidized surface indicated that the material is ductile. The oxidized surface, however, exhibits numerous narrow cracks suggesting brittle behavior in the thin surface layer. The exposed matrix exhibits oblong cracks which penetrate deep into the unoxidized bulk material. For specimens immersed in scintillation fluid the yield point is significantly reduced and the elongation at yield increased after a contact time of one rotationally molded ≈5000-L capacity container purchased from Poly-Processing (Poly-Pro), Inc., Monroe, LA. Nominal thickness of the Poly-Pro container varied form 3.4 to 4.4 mm. Although the 5000-L container does not conform to design specification of HICs in terms of its size or wall thickness, the container was fabricated from the basic feed material as used in making approved HIC's. Information on specimen preparation in the configuration of a "dog bone" and mechanical testing in terms of tensile strength and tensile creep is provided elsewhere (Arora and Dayal, 1984c; Swyler and Dayal, 1982).

For chemical compatibility and aging tests, the most probable chemical reagents anticipated in the radwaste or the burial environment were selected (Table 1). The HDPE coupons were immersed in these chemicals in accordance with the procedure outlined in ASTM D-543 (Resistance of Plastics to Chemical Reagents). Since no significant changes were observed in weight, dimension, or appearance even upon extended immersion in most of these chemicals, measurement of these parameters was de-emphasized in later experiments. The tensile strength was also measured upon extended immersion of HDPE coupons in these chemicals. Some of the immersed specimens were aged while under stress (U-bend samples). Stress-rupture resistance of HDPE was determined upon tensile creep testing in air and during or upon contact of the coupons with various chemical reagents and irradiation treatments.

Table 1. List of reagents employed in chemical compatibility testing of Marlex CL-100 (Poly-Pro) HDPE material.

	Fluid	Active Ingredient	Basis for Selection
1.	Scintillation Fluid (INSTA-GEL)	Xylene and a blend of other organics	Typical aromatic solvent representing severe impact for scoping measurements
2.	Oil	Mobil OTE 797/Mobil OTE medium	Simulant of turbine pump oil waste
3.	Hydrogen Peroxide	H_2O_2	Strong oxidant
4.	By-products of resin bead irradiation	Acids, bases, organic decomposition products	HICs are presently licensed for the disposal of dewatered resins
5.	Trimethylamine	Trimethylamine	Decomposition by-product of resin irradiation (Swyler et al., 1983)
6.	Sulfuric Acid	H_2SO_4	Decomposition by-product of resin irradiation (Swyler et al., 1983)
7.	Igepal	Nonylphenoxypoly (ethyleneoxy) ethanol	Surfactant employed in environmental stress cracking resistance test (ASTM D-2552)
8.	Boric Acid Concentrate	H_3BO_3	Simulant of PWR aqueous concentrate waste
9.	Sodium Sulfate Concentrate	Na_2SO_4	Simulant of BWR aqueous concentrate waste
10.	Decontamination Agent	Na_2-EDTA	Simulant of decontamination waste
11.	Oxic and Anoxic Leachates	Organic and inorganic contaminants	Trench leachates collected from Maxey Flats disposal site

week. No effect of sulfuric acid, turbine oil, or other chemicals on tensile behavior of HDPE contacted for a period of up to 120 days is evident.

These short-term tensile strength tests are most indicative of the fundamental performance of thermoplastic polymers (McGraw Hill, 1982) and may be readily employed to determine the sequential or simultaneous effect of different types of stresses. These tests, however, do not lend themselves to evaluating the aging performance of the material in terms of structural integrity.

Tensile Creep

Creep rupture tests conducted in the presence of liquids for this study are very similar to environmental stress cracking (ESC) tests described in the literature. The tensile creep vs stress data presented in Figure 5 indicate that the Marlex CL-100 specimens deform at an accelerated rate during initial stages followed by a continuous deformation at a slower rate is observed during later stages and >1000 hours time-to-rupture is required for specimens undergoing creep at a stress level of 1500 psi in air. A spectacular increase in tensile creep rate was observed prior to rupture at stress level of >1600 psi in air. Also presented in Figure 5 are the elongation vs time creep data obtained at a stress level of 1500 psi while the HDPE coupons are in contact with two chemical agents and upon pre-treatment to a gamma irradiation dose of 5×10^7 rad. These data indicate that the Marlex CL-100 specimens ruptured in about 10 h when in contact with scintillation fluid and in ≈250 h when in contact with Igepal. Also, unlike specimens in air which showed necking and extreme ductile elongation in failure, specimens immersed in scintillation fluid rupture abruptly and necking was not evident.

Arora et al. (1983) reported that the effect of prior gamma irradiation on the creep behavior of HDPE was pronounced. Significantly reduced rates of creep were observed upon irradiation to 10^7 rad. The specimen exposed to 10^8 rad exhibited no long-term creep for a test duration of more than 10 weeks. From these data we concluded that pre-irradiation markedly improves tensile creep resistance. In this sense, irradiation might be said to improve material strength properties. As reported previously, however, irradiation reduces ductility in HDPE and tends to embrittle the material. At the same time (at least for irradiation at $\approx 10^8$ rad), the tensile yield point is increased. The increased resistance to creep in irradiated materials is very likely related to the irradiation-induced increase in tensile yield stress.

Microscopic examination of a failed specimen suggests that crack initiation and propagation modes for irradiated and unirradiated specimens are vastly different. While cracks in unirradiated specimens are observed on the oxidized glossy surface, cracks developed only at the unoxidized outer surface for specimens pre-irradiated to a total dose of 10^8 rad.

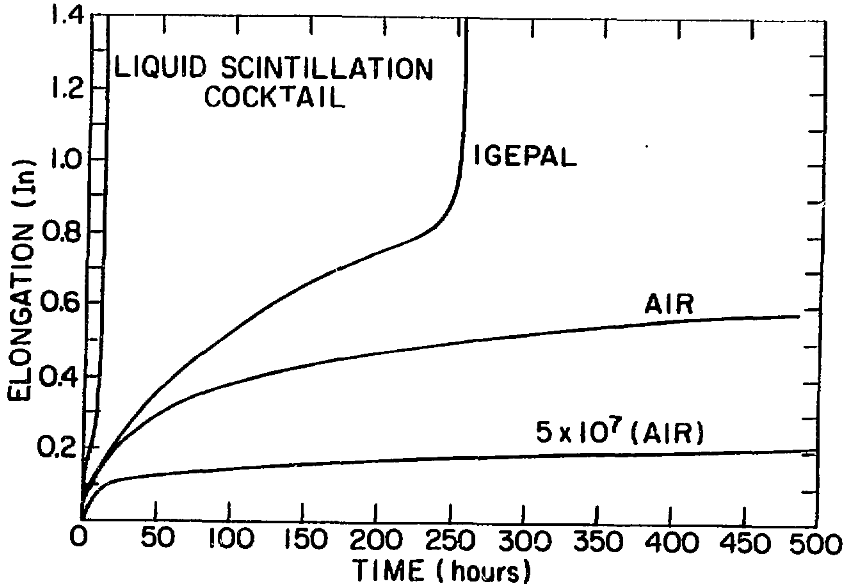

Figure 5. Influence of chemicals and irradiation on elongation of Marlex CL-100 HDPE (Poly-Pro) at 1500 psi.

Influence of an Oxide Layer

Terselius et al. (1982) reported that the thermally oxidized layer of a HDPE pipe exhibited brittle behavior and contained crater-like structures. As described previously, the inner surface of the rotationally molded Marlex CL-100 container exhibits a glossy texture while the outer surface has a dull and somewhat roughly textured finish. The thickness of the glossy layer varied from 40 to 170 µm. As indicated previously, the oxidized layer has pits of varying size as opposed to the unoxidized surface which is completely devoid of pits. We presented preliminary infrared spectroscopic data which indicated the the thin glossy surface was highly oxidized and tended to spall off during solvent extraction (Arora and Dayal, 1984c).

Tensile strength data of six replicate specimens, for which the glossy layer was polished off with a fine sandpaper prior to testing, are presented in Table 2. These data indicate that although the yield stress is similar to that observed for unpolished specimens, a dramatic increase in elongation at break is observed suggesting that the low extensibility of the oxidized surface significantly contributes to the brittle behavior of untreated HDPE specimens.

During tensile creep testing, a consistent pattern of the initiation of transverse cracks on the inner surface (oxide layer) was observed. A comparison of the elongation vs time data for untreated and upon the removal of inside oxide layer determined in the presence of scintillation fluid indicated that time-to-rupture at a stress level of 1400 psi was lower for the unpolished specimens (≈150 vs 124 hours). It is important to note that scintillation fluid is an aggressive chemical mixture and chemically attacks the HDPE. A similar comparison of the elongation vs time data for specimens immersed in Igepal, a surfactant, indicated a significant increase in time-to-rupture for specimens with their oxide layer removed. These data tend to suggest that the presence of a thin oxide-rich layer exerts a significant influence on the mechanical behavior of HDPE in terms of crack initiation and propagation.

Table 2. Tensile strength of Marlex CL-100 (Poly-Pro) coupons with and without the inside oxide layer.

Specimen	Yield Stress (psi)	Break Stress (psi)	Elongation at Yield (%)	Elongation at Break (%)
Without the oxide layer	3115± 36	3560±508	17.4±1.3	908±116
With oxide layer	3060±160	----	18.2±1.0	220±180

Low-level wastes emplaced in HIC containers may promote oxidative attack on the polymer by two possible ways: first, the passive role of depleting the antioxidant, and second, a more active role of promoting oxidation through irradiation and the physical action of chemical on the polymer itself. Such oxidation, however, will necessarily be largely confined to a thin zone near the surface in contact with the waste. At the dose rates and cumulative doses employed in our experiments (>1.0 x 10^5 rad/h, 10^5 to 2 x 10^8rad), discernible evidence of any environmental effects (oxidation, etc.) on the bulk properties of Marlex was not observed.

Environmental Stress Rupture Tests

Long-term performance evaluation of polymeric materials has largely been carried out to estimate the service life-time of plastic pipes. The general method consists in subjecting the material to internal pressure stresses which cause failure and measure the time-to-failure as a function of applied stress. Data for time-to-rupture vs applied stress have also been employed to generate environmental stress rupture curves for extrapolating the aging performance of plastics (McGraw Hill, 1982). A family of environmental stress rupture curves as a function of various environmental stresses is presented in Figure 6. Preliminary analysis of these data indicate that stress levels required for time-to-rupture are greater for pre-irradiated specimens and that a threshold applied stress appear to exist for Marlex CL-100 below which rupture is not observed under short-term laboratory tests. Practical implication of the threshold stress is that the stress experienced by an HIC in the burial environment should be kept below this limit. Although a 100-fold extrapolation of test data is required for low-level burial applications, it is important to note that a general consensus is that data on creep and creep rupture should not be extrapolated by more than one decade of time.

Since the HIC's are primarily licensed for the disposal of dewatered demineralizer resin waste by the State of South Carolina. Emphasis in on-going tests in being placed on studying creep rupture while the specimens are in contact with radiolytic by-products of irradiated resin wastes.

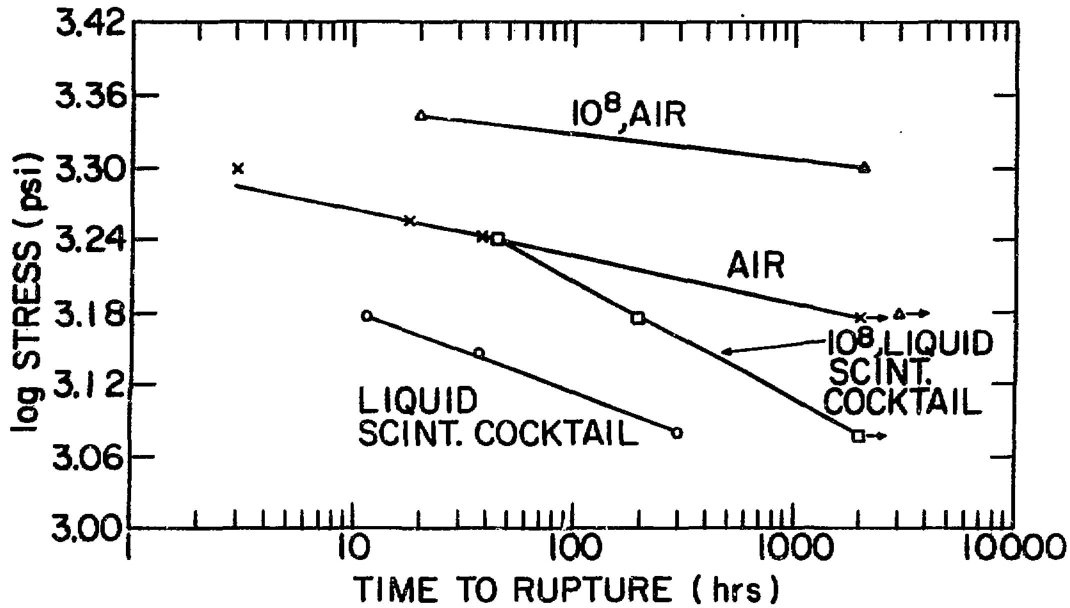

Figure 6. A family of environmental stress rupture curves of Marlex CL-100 as a function of various stresses.

SUMMARY AND CONCLUSIONS

Conclusions on the basis of experimental results obtained to date are as follows:

- The results of laboratory tests show that leach data derived from testing of small-scale specimens can be extrapolated to estimate leachability of full-scale specimens and that radionuclide release data derived from testing of simulants can be employed to predict the release behavior of reactor wastes. Leaching under partially-saturated conditions exhibits lower releases of radionuclides than those observed under the conventional IAEA-type or ANS 16.1 leach tests.

- The inner surface of Marlex CL-100 is glossy, smooth textured, and highly oxidized. Preliminary data indicate that the thin layer exerts a significant influence on the mechanical behavior of HDPE in terms of crack initiation and propagation.

- Gamma irradiation causes the HDPE materials to become brittle. Tensile creep is significantly less in irradiated samples as compared with unirradiated samples. For the unirradiated samples, once the stress is removed the samples largely recover to their initial dimensions for the test conditions used in this work.

- A family of environmental stress rupture curves as a function of chemical and irradiation levels has been developed to establish threshold stresses below which rupture is not observed and may be used to estimate long-term performance of the material under study.

References

1. Arora, H. and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, April-June 1984," BNL-NUREG-34331, 1984a.

2. Arora, H. S. and R. Dayal, Brookhaven National Laboratory, "Solidification and Leaching of Boric Acid and Resin LWR Wastes," BNL-NUREG-51805, 1984b.

3. Arora, H. and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, October-December 1983," BNL-NUREG-34331, 1984c.

4. Arora, H., K. J. Swyler, and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers," Fifth Annual Participants Information Meeting, Denver, Colorado, BNL-NUREG-33626, 1983.

5. Dayal, R. , H. Arora, and N. Morcos, Brookhaven National Laboratory, "Estimation of Cesium-137 Release From Waste/Cement Composites Using Data From Small-Scale Specimens," BNL-NUREG-51690, 1983.

6. Dayal, R., D. R. Schweitzer, and R. E. Davis, Brookhaven National Laboratory, "Wet/Dry Cycle Leaching: Aspects of Release in the Unsaturated Zone," BNL-NUREG-33580, 1984.

7. McGraw Hill Book Company, Modern Plastic Encyclopedia, 426-519, 1982-1983.

8. Morcos, N. and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, April-June 1982, BNL-NUREG-31566, 1982.

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

10. Swyler, K. J., C. J. Dodge, and R. Dayal, Brookhaven National Laboratory, "Irradiation Effects on the Storage and Disposal of Radwaste Containing Organic Ion-Exchange Media," BNL-NUREG-51691, 1983.

11. Swyler, K. J. and R. Dayal, Brookhaven National Laboratory, "Properties of Radioactive Wastes and Waste Containers, Quarterly Progress Report, July-September 1982," BNL-NUREG-32069, 1982.

12. Terselius, B., U. W. Gedde, and J. R. Jansson, "Structure and Morphology of Thermally Oxidized High Density Polyethylene Pipes," Polymer Engineering and Science 22, 422-431, 1982.