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**Long-Term Durability of Polyethylene for Encapsulation of Low-Level Radioactive, Hazardous,
and Mixed Wastes***

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ABSTRACT

The durability of polyethylene waste forms for treatment of low-level radioactive, hazardous, and mixed wastes is examined. Specific potential failure mechanisms investigated include biodegradation, radiation, chemical attack, flammability, environmental stress cracking, and photodegradation. These data are supported by results from waste form performance testing including compressive yield strength, water immersion, thermal cycling, leachability of radioactive and hazardous species, irradiation, biodegradation, and flammability. Polyethylene was found to be extremely resistant to each of these potential failure modes under anticipated storage and disposal conditions.

INTRODUCTION

A polyethylene encapsulation process for treatment of low-level radioactive (LLW), hazardous, and mixed wastes has been developed at Brookhaven National Laboratory. The system has successfully undergone bench-scale development/testing and a production-scale technology demonstration of this system is planned. The process has been applied to a wide range of waste types including evaporator concentrate salts, sludges, incinerator ash, and ion exchange resins [1]. This study contains test data from the encapsulation of nitrate salt wastes generated in large volume

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at several DOE facilities. Polyethylene encapsulation results in higher loading efficiencies (i.e., more waste encapsulated per drum) and better waste form performance, compared with conventional solidification/stabilization materials such as hydraulic cements. For example, up to 70 wt% nitrate salt waste can be encapsulated in polyethylene, compared with a maximum of 13 - 20 wt% using portland cement.

WASTE FORM DURABILITY

Many types of LLW, hazardous, and mixed wastes require continued isolation for long periods of time. The durability of the waste form for encapsulated wastes can directly affect mobility of contaminants in the accessible environment and, ultimately, the health and safety of an exposed population. Polyethylene was first developed in 1933, but was not widely used until World War II. Little is known about the long-term durability of polyethylene for waste encapsulation since it is a relatively new engineering material and has not been used for this purpose on a production-scale. This paper highlights the results of a literature review and testing program on the properties of low density polyethylene relevant to the long-term durability of waste forms in storage and disposal [2].

PROPERTIES THAT IMPACT WASTE FORM DURABILITY

Compressive Strength:

Compressive strength is a measure of a waste form's mechanical integrity and its ability to withstand pressures resulting from stacking or overburden of soil and barrier materials. Polyethylene is a nonrigid plastic with no discrete brittle fracture yield point under compressive load. However, polyethylene waste forms containing dry solid wastes (i.e., aggregates), do exhibit a discernible yield strength when tested for compressive strength. Compressive strength testing of polyethylene waste forms containing sodium nitrate at several waste loadings was conducted in accordance with ASTM D-695, "Standard Method of Test for Compressive Properties of Rigid Plastics." Waste form strength (Figure 1) ranged from a minimum of 7.03 MPa (1,020 psi) for those containing 70 wt% sodium nitrate, to a maximum of 16.3 MPa (2,360 psi) for those containing 30 wt% sodium nitrate. All samples tested had compressive strengths well above Nuclear Regulatory Commission (NRC) minimum criteria of 60 psi (500 psi for cement waste forms) for licensing of commercial low-level radioactive waste forms [3].

Resistance to Saturated Conditions:

Water immersion testing was conducted for 90 days to determine waste form stability under saturated disposal conditions. Compressive strength measured following immersion revealed no statistically significant changes in waste form strength, as shown in Figure 1.

Resistance to Thermal Cycling:

Thermal cycling was performed in accordance with ASTM B-553, "Thermal Cycling of Electroplated Plastics," to determine the effects of extreme temperature variations that waste forms may encounter during storage, transportation, or disposal. Waste form specimens containing 60 wt% sodium nitrate were cycled between temperatures of -40°C and +60°C for a total of thirty, 5-hr periods. Samples were tested for compressive strength on completion of the thermal conditioning. Results given in Table 1 show that no statistically significant changes in yield strength occurred as a result of thermal cycling.

Resistance to Microbial Degradation:

Biodegradation is the process by which organic substances are broken down into carbon dioxide, water, and other simple molecules by microorganisms such as molds, fungi, and bacteria when exposed under conditions conducive to their growth. The overwhelming consensus of studies on biodegradation of plastics indicates that the majority of synthetic polymers, including polyethylene, are highly resistant to microbial degradation [4]. In fact, studies conducted to enhance biodegradation of plastics and, thereby, relieve overburdened municipal waste landfills have largely proven unsuccessful [5,6]. Potts, et al., found that only polymers with very low molecular weight linear chains (molecular weights below about 450) were susceptible to microbial degradation. [5] The average molecular weight of low density polyethylene is between 10^4 and 10^5 , well above the range where growth is supported. Barua, et al., found that even low molecular weight hydrocarbons are not biodegradable when they are branched or cross-linked [7]. Compared to other polymers, low density polyethylene contains many branched chains, further reducing susceptibility to microbes.

Polyethylene waste forms were tested for resistance to microbial degradation to substantiate durability under long-term disposal conditions. Samples containing 60 wt% sodium nitrate and blanks containing no waste were tested in accordance with ASTM G-21, "Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi," and ASTM G-22, "Standard

Practice for Determining Resistance of Plastics to Bacteria." No fungal or bacterial growth was observed on any of the test specimens. Mean compressive strength following bio-testing (Table 1) was 10.1 Mpa (1,460 psi), which is well above the minimum NRC standards. Loss in strength for bio-test specimens was an artifact of sample preparation (i.e., coring from a large sample and dissolution of salt in sterilization media) and is not related to microbial degradation.

Resistance to Ionizing Radiation:

Numerous studies indicate that the predominant effect of ionizing radiation on polyethylene is an increase in bonding between and within polymer chains, known as crosslinking. About 10 lateral crosslinks are formed in the main chain for every bond scission that occurs in polyethylene irradiated in the absence of air [8]. Crosslinking affects primary bonds that require large amounts of energy to disturb (200 to 600 kJ/mol). Thus, the impacts of crosslinking are irreversible and can have a positive effect on many mechanical properties of interest including compressive strength, thermal stability, solvent resistance, environmental stress cracking, creep, and permeability [9,10].

The effects of gamma irradiation on the compressive strength of polyethylene waste forms containing 60 wt% sodium nitrate were examined. Waste form test specimens were exposed to a ^{60}Co gamma source at a dose rate of 3.6×10^6 rad/hr, for a total dose of 10^8 rad. Compressive strength of irradiated waste forms (Table 1) increased about 18%, thus confirming the effects of crosslinking.

Evolution of hydrogen gas from irradiated polyethylene is low due to the small number of bond scissions that occur. The potential impact of hydrogen gas generation on polyethylene waste forms was estimated based on its "G value" (number of H_2 molecules produced per 100 eV) of $4.1 \mu\text{moles/g/Mrad}$. Typical boiling water reactor waste forms with absorbed dose rates ranging from 10^7 Bq/m³ to 10^{11} Bq/m³ (0.01 Ci/ft³ to 100 Ci/ft³) were assumed. Estimated hydrogen gas evolution from 208-liter (55-gallon) polyethylene waste forms containing 60 wt% sodium nitrate ranges from about 4×10^{-6} l/day to 4×10^{-2} l/day, corresponding to dose rates of 0.03 - 300 gray/day ($3 - 3 \times 10^4$ rad/day), as shown in Figure 2. Typical mild steel drums used for waste disposal are not gas-tight (especially to hydrogen). Therefore, this gas generation is not expected to cause any measurable pressure increase within the drum. Quantification of a pressure increase would require empirical data on the diffusion rate of hydrogen from the waste container and the effective volume of gas generated (based on the porosity of polyethylene to hydrogen, void volume within the waste form,

and the fraction of hydrogen reabsorbed to the solid phase). Assuming a gas-tight container and an effective volume of 25% of the total volume, however, yields a conservative bounding estimate for pressure increases between 8×10^{-9} and 8×10^{-5} MPa (10^{-6} to 10^{-2} psi/day). This conservative estimate confirms the negligible impact of hydrogen gas generation due to radiolysis of polyethylene.

Leachability of Radioactive and Hazardous Constituents:

Leachability is a measure of the waste form's ability to retard the release of radioactive and hazardous constituents into the accessible environment. Leach testing of polyethylene waste forms containing 30 to 70 wt% sodium nitrate was conducted according to the ANS 16.1 Standard [11]. Results are expressed in terms of a leach index, a dimensionless figure-of-merit that quantifies the relative leachability for a given waste type-solidification agent combination. Since the leach index is inversely proportional to the log of effective diffusivity, an incremental increase in leach index represents an order of magnitude reduction in leachability. Leach index values (Figure 3) ranged from a minimum of 7.8 (70 wt% sodium nitrate loading) to a maximum of 11.1 (30 wt% sodium nitrate). The minimum leach index specified by NRC is 6.0.

Sodium nitrate salt from Rocky Flats Plant contains both chromium (in levels above those established by the EPA defining characteristic hazardous wastes) and radioactive contaminants. Thus, this waste is classified as a mixed waste and is subject to regulations promulgated by EPA contained in 40 CFR 261 in support of the Resource Conservation and Recovery Act (RCRA) [12]. Leaching of hazardous constituents (e.g., chromium) was conducted for waste forms containing 60 wt% sodium nitrate, in accordance with the Toxicity Characteristic Leaching Procedure (TCLP). Leachate concentrations of the encapsulated waste contained 3.6 mg/l chromium, compared with 9.0 mg/l for the unencapsulated waste. The EPA maximum allowable concentration for chromium in TCLP leachates is ≤ 5.0 ppm.

Resistance to Chemical Attack:

The ability of a waste form to resist attack from aggressive chemical environments, internally from the waste itself and externally from the disposal site, is a key factor in maintaining long-term durability. Polyethylene's ability to resist chemical attack is a primary reason for its widespread use in diverse applications. It is insoluble in virtually all organic solvents (at ambient temperature) and is resistant to many acids and alkaline solutions [13]. A summary of polyethylene suitability for

use in specific chemical environments is given in Reference [2].

Flammability:

Flammability of waste forms is not a concern for existing shallow land disposal facilities and advanced designs that incorporate subterranean disposal, since oxygen to support combustion is unavailable. However, for above-ground disposal and during processing, temporary storage, and transportation, conditions to sustain combustion may be present. The flash ignition temperature is the lowest temperature at which a material will ignite if exposed to a small flame under specified conditions. The self-ignition temperature is the lowest temperature at which a material will ignite without the presence of a flame. Samples of low density polyethylene used for waste encapsulation were tested in accordance with ASTM D-1929, "Standard Method of Test for Ignition Property of Plastics." Flash ignition temperature was 409°C and self-ignition temperature was 430°C. The extrusion processing temperature of polyethylene is about 120°C, so process-related fires are unlikely. If ignited, polyethylene burns slowly in a controlled manner, at about 1.0 in/min under conditions specified in ASTM D-635. When cooled below the flash-ignition temperature, the material is self-extinguishing. The National Fire Protection Association (NFPA) has given polyethylene a flammability rating of 1 (slight), on a scale of 0 (least) to 4 (extreme) [14].

Environmental Stress Cracking and Photodegradation:

Low density polyethylene can become embrittled if exposed to conditions that lead to environmental stress cracking (ESC). ESC can occur under conditions of stress, in the presence of chemical agents such as soaps, detergents, wetting agents, or oils and results in mechanical failure by cracking at stresses below those that would cause cracking in the absence of these agents. This phenomenon should have little or no impact on the long-term durability of polyethylene waste forms, since they are generally not exposed to significant concentrations of chemical agents required to initiate crack propagation and extruded waste forms would not be under high stresses that result from complex molds shapes.

Polyethylene exposed to sunlight (ultraviolet radiation) and oxygen for extended periods is subject to deterioration of mechanical properties, cracking, and molecular weight loss by a process known as photodegradation. Several researchers have found that these effects are limited to outer surface regions (on the order of tens of angstroms) since insufficient oxygen is available in deeper layers [15,16]. Containerized polyethylene waste forms that are stored or disposed will not

likely encounter solar irradiation that could lead to photodegradation. Even if waste forms were exposed to sunlight and oxygen for prolonged periods, photodegradation impacts would be minimal since the phenomenon is limited to surface effects.

SUMMARY/CONCLUSIONS

Review of existing property data and studies of material behavior, supplemented by the results of waste form performance testing, confirm the long-term durability of polyethylene for encapsulation of low-level radioactive, hazardous, and mixed wastes. Polyethylene is highly resistant to microbial degradation and attack by aggressive chemicals. Radiation doses through 10^8 rad increase crosslinking and improve strength and other physical properties. Flash- and self-ignition points are relatively high, and NFPA has rated polyethylene flammability as "slight". Other failure mechanisms including environmental stress cracking and photodegradation should have little effect on long-term durability. Polyethylene waste forms exceed minimum performance standards established by NRC and EPA for commercial LLW and hazardous wastes, respectively.

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Table 1. Compressive Yield Strength of Cored Pilot-Scale Polyethylene Waste Forms Containing 60 wt% Sodium Nitrate

<u>Test Description</u>	<u>Compressive Yield Strength, MPa (psi)^(a,b)</u>
Initial	14.2 ± 0.3 (2,060 ± 45)
Post Thermal Cycling	13.3 ± 0.5 (1,930 ± 70)
Post Irradiation	16.7 ± 0.7 (2,420 ± 100)
Post. Biodegradation ^(c)	10.1 ± 1.8 (1,460 ± 255)

(a) Based on 6 replicate specimens.

(b) Error expressed as ± one standard deviation.

(c) Based on 12 replicate specimens.

Figure 1. Compressive yield strength of polyethylene waste forms containing sodium nitrate salt, untreated and after 90 days in water immersion.

Figure 2. Conservative estimates of hydrogen gas evolution and resultant gas pressure for self-irradiated polyethylene waste forms containing 60 wt% sodium nitrate.

Figure 3. Leaching index determined according to the ANS 16.1 Leach Test as a function of sodium nitrate waste loading for polyethylene waste forms.

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