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POLYETHYLENE ENCAPSULATION OF NITRATE SALT WASTES: WASTE FORM STABILITY, PROCESS SCALE-UP, AND ECONOMICS

TECHNOLOGY STATUS TOPICAL REPORT

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ABSTRACT

A polyethylene encapsulation system for treatment of low-level radioactive, hazardous, and mixed wastes has been developed at Brookhaven National Laboratory. Polyethylene has several advantages compared with conventional solidification/stabilization materials such as hydraulic cements. Waste can be encapsulated with greater efficiency (i.e., more waste encapsulated per drum) and with better waste form performance than is possible with hydraulic cement. The properties of polyethylene relevant to its long-term durability in storage and disposal environments are reviewed. Response to specific potential failure mechanisms including biodegradation, radiation, chemical attack, flammability, environmental stress cracking, and photodegradation are examined. These data are supported by results from extensive waste form performance testing including compressive yield strength, water immersion, thermal cycling, leachability of radioactive and hazardous species, irradiation, biodegradation, and flammability. The bench-scale process has been successfully tested for application with a number of specific "problem" waste streams including nitrate salts, sludges, incinerator ash, reactor-generated evaporator concentrates (sodium sulfate and boric acid), and ion exchange resins. A production-scale technology demonstration of polyethylene encapsulation of nitrate salt waste, sponsored by the Department of Energy (DOE), Office of Technology Development (OTD), Division of Demonstration, Testing and Evaluation (DT&E) is planned in conjunction with Rocky Flats Plant. In support of the technology demonstration, a scale-up feasibility test was conducted by processing simulated nitrate salt waste with a production-scale extrusion system. Output rates in excess of 454 kg/hr (1000 lb/hr) were achieved, and process data were in close agreement with bench-scale parameters. Quality assurance and performance testing of the resulting waste form confirmed scale-up feasibility. Use of this system at Rocky Flats Plant can result in over 70% fewer drums processed and shipped for disposal, compared with optimal cement formulations. Based on the current Rocky Flats production of about 1×10^6 kg (2.2×10^6 lbs) of nitrate salt per year, polyethylene encapsulation can yield an estimated annual savings between $1.5 million and $2.7 million, compared with conventional hydraulic cement systems.

Table of Contents

Page

ABSTRACT iii

1. INTRODUCTION 1

2. BACKGROUND 3

3. MECHANICAL PROPERTIES 5

3.1 Overview 5

3.2 Properties That Can Potentially Impact Waste Form Stability 5

3.2.1 Biodegradation 8
3.2.2 Radiation Effects 14

3.2.2.1 Mechanisms 14
3.2.2.2 Physical Effects and Changes in Material Properties 20

3.2.3 Resistance to Chemical Attack 24
3.2.4 Flammability 35
3.2.5 Environmental Stress Cracking 36
3.2.6 Photodegradation/UV Effects 37

4. WASTE FORM PERFORMANCE 39

4.1 Waste-Binder Compatibility 40

4.2 Compressive Strength 40

4.3 Water Immersion Testing 44

4.4 Thermal Cycling 44

4.5 Biodegradation 44

4.6 Radiation Stability 45

4.7 Leachability of Radioactive Constituents 46

4.8 Leachability of Hazardous Constituents 47

4.9 Flammability Testing 49

5. PROCESSING AND SCALE-UP 51

6. ECONOMIC FEASIBILITY 63

REFERENCES 69

List of Figures

Page

Figure 3.1 Schematic representation of various types of crosslinking configurations 15

Figure 3.2 Effect of radiation dose on crystallinity of low density polyethylene. 17

Figure 3.3 Thermograms of irradiated low density polyethylene samples at doses of 0, 175 and 200 Mrad 18

Figure 3.4 Radiation effects (total dose and dose rate) on the tensile strength of polyethylene. 19

Figure 3.5 Conservative estimates of hydrogen gas evolution and resultant gas pressure (as per assumptions outlined in the text) for self-irradiated polyethylene waste forms. 23

Figure 3.6 Creep properties of low density polyethylene irradiated to total doses of 50 kGy (5 x 10^6 rad), 100 kGy (10^7 rad), and 200 kGy (2 x 10^7 rad) 24

Figure 3.7 Polyethylene's low permeability as shown by water absorption rate data. 26

Figure 3.8 Schematic diagram illustrating the effects of ultraviolet radiation and mechanical stress on low density polyethylene to form microcracks that can lead to premature failure. 38

Figure 4.1 Differential scanning calorimetry thermogram for polyethylene containing 50% sodium nitrate ($NaNO_3$) or sodium nitrite ($NaNO_2$). 42

Figure 4.2 Differential scanning calorimetry thermogram for polyethylene containing 50% actual or simulated nitrate salt waste. 42

Figure 4.3 Compressive yield strength of polyethylene waste forms containing sodium nitrate salt, untreated and after 90 days in water immersion. 43

Figure 4.4 Comparison of compressive yield strength vs. waste form density for waste forms undergoing ASTM G-21 and G-22 biodegradation testing and control (untreated) samples. 46

Figure 4.5 Leaching index determined according to the ANS 16.1 Leach Test as a function of sodium nitrate waste loading for polyethylene waste forms. 48

Figure 5.1 Sectional view of a simplified screw extruder. The sketch depicts flow of material from the hopper to the output die, where it is extruded in a molten state. 51

Figure 5.2 Photograph of laboratory-scale extruder with separate dynamic feeders for waste and binder. 53

Figure 5.3 Comparison of Rocky Flats Plant (RFP) sodium nitrate encapsulation in polyethylene and cement. 55

List of Figures Continued

		Page
Figure 5.4	Comparison of number of 208 liter (55 gal.) drums required for encapsulation of RFP sodium nitrate salt waste using polyethylene and cement	55
Figure 5.5	Calibration curve for the production-scale polyethylene feeder.	57
Figure 5.6	Calibration curve for the production-scale nitrate salt waste feeder.	57
Figure 5.7	Process flow diagram for full-scale polyethylene encapsulation system.	59
Figure 5.8	Photographs of the polyethylene/sodium nitrate waste form produced during the production-scale feasibility test, showing the outer surface (left) and cross-sectional view (right).	60
Figure 6.1	Results for economic analysis comparing costs to encapsulate 1 x 10^6 kg (2.2 x 10^6 lbs) nitrate salt per year at Rocky Flats Plant using polyethylene and cement formulations from Savannah River Plant and West Valley.	64
Figure 6.2	Summary of cost breakdown for economic analysis of nitrate salt waste encapsulation at Rocky Flats Plant using polyethylene and Savannah River Plant Saltstone cement formulations.	65

List of Tables

		Page
Table 3.1	Properties of Low Density Polyethylene	6
Table 3.2	Change in Polyethylene Properties with Density, Melt Index, and Molecular-Weight Distribution	7
Table 3.3	Biodegradability of Straight Chain Hydrocarbons	12
Table 3.4	Effect of Branching on Hydrocarbon Biodegradability	13
Table 3.5	Environmental Stress Cracking (ESC) of Irradiated Polyethylene	23
Table 3.6	The Application of Polyethylene Resins in Various Chemical Environments	27
Table 3.7	Effect of Various Chemicals on Polyethylene after 3-Month Contact	33
Table 3.8	Explosion Characteristics of Polyethylene Dust	36
Table 4.1	Waste Form Test Methods	41
Table 4.2	Compressive Yield Strength of Cored Pilot-Scale Polyethylene Waste Forms Containing 60 wt% Sodium Nitrate	43
Table 4.3	ANS 16.1 Leach Test Data for Sodium Nitrate in Polyethylene Waste Forms	47
Table 4.4	Results from Extraction Procedure Toxicity Test (EP Tox) and Toxicity Characterization Leaching Procedure (TCLP) for Rocky Flats Plant Nitrate Salt Encapsulated in Polyethylene	49
Table 5.1	Parameter Settings and Test Data for Polyethylene Encapsulation Production-Scale Feasibility	59
Table 6.1	Assumptions Used in the Economic Analysis of Nitrate Salt Encapsulation for Rocky Flats Plant	66
Table 6.2	Economic Analysis for Nitrate Salt Encapsulation at Rocky Flats Plant	67
Table 6.3	Cost Breakdown	68

1. INTRODUCTION

This report describes activities conducted at Brookhaven National Laboratory (BNL) as part of the Encapsulation Development Technology Demonstration Program, sponsored by the U.S. Department of Energy (DOE), Office of Technology Development (OTD), Division of Demonstration, Testing, and Evaluation (DT&E). The overall objective of this program is to demonstrate new and innovative processes for the improved encapsulation of hazardous and mixed wastes at pilot- or production-scale. Bench-scale systems shown to have potential benefits in both performance and cost-effectiveness when compared with conventional technologies are candidates for technology demonstration.

The polyethylene encapsulation system described in this report was developed several years ago at BNL for solidification of low-level radioactive wastes, including reactor-generated evaporator concentrate salts (sodium sulfate and boric acid), incinerator ash, and ion exchange resins [1,2]. In general, polyethylene encapsulation of these wastes was accomplished with greater efficiency (i.e., more waste encapsulated per drum) and with better waste form performance than is possible using conventional hydraulic cement processes. More recently, the polyethylene process was successfully applied to both hazardous and mixed wastes. Based on results from bench-scale processing and waste form property evaluation testing, the process for polyethylene encapsulation of nitrate salt waste was selected for production-scale technology demonstration.

Nitrate wastes result from the neutralization of nitric acids used in a variety of DOE operations, such as spent fuel reprocessing, uranium purification/enrichment, ion exchange resin regeneration, and high-level waste treatment. They are generated in large volumes at several DOE facilities including Rocky Flats Plant (RFP), Savannah River Plant (SRP), Oak Ridge National Laboratory (ORNL), Hanford, and West Valley. Recent estimates put the volume of nitrate wastes being stored at more than 250 million kilograms (551 million pounds) [3]. At RFP alone, about one million kilograms (2.2 million pounds) of dry nitrate salts are produced annually. The oxidizing potential of RFP nitrate salts, along with the presence of chromium (a toxic metal) define this waste as hazardous, under criteria established by the Environmental Protection Agency (EPA) in 40 CFR 261 [4]. Because of the presence of radionuclides contained in the salts, the waste is considered a mixed waste.

Currently, nitrate salts at RFP and other DOE facilities are being encapsulated by conventional hydraulic cement processes. Chemical interactions between the waste and binder limit the quantity of nitrate waste that can be successfully incorporated in cement to between 13 and 20 wt%. Incorporation of higher waste loadings has led to difficulties in maintaining quality assurance of waste forms including: (i) failure to

set, (ii) presence of free-standing water, and (iii) degradation of the mechanical integrity of the waste form under storage and/or disposal conditions. Polyethylene is a thermoplastic material, and thus, can be heated to its melting point (120 °C), combined with waste to form a homogenous mixture, and cooled to form a monolithic solid waste form. As such, it does not react with the waste and solidification is ensured.

Since polyethylene has not been used on a production-scale for waste encapsulation, little is known about its long-term durability for this purpose. Therefore, an extensive literature review was conducted to gather and assess information on the properties of polyethylene relevant to its stability and performance under anticipated storage and disposal conditions. Section 3 includes data on polyethylene's physical and mechanical properties and response to potential failure mechanisms including biodegradation, radiation, chemical attack, flammability, environmental stress cracking, and photodegradation. These data are supported and supplemented by waste form performance testing conducted at BNL, presented in Section 4. After successful laboratory-scale development and testing of the polyethylene encapsulation system, scale-up activities were initiated for a full-scale technology demonstration of this process, scheduled to be held at RFP in FY 1991. A production-scale feasibility test was conducted, and a series of quality assurance and waste form performance tests were performed. These efforts are described in Section 5. An annualized cost economic analysis was prepared to estimate potential cost savings associated with polyethylene encapsulation of nitrate wastes at RFP and is reported in Section 6.

2. BACKGROUND

Polyethylene was first developed in 1933 by Imperial Chemical Industries, Ltd., as a result of research on the high-pressure chemistry of organic compounds. Their first industrial-scale process was on-line in 1939. Use of polyethylene for cable insulation during World War II created an immediate demand for this product and led to the establishment of production facilities by Union Carbide and DuPont. Over the next 45 years, materials and processing refinements expanded the potential applications of this product to such an extent that today it is the most widely used of all plastics. Current production capacity (1989) for the ten domestic producers of low density polyethylene is about 7 x 10^9 pounds per year. The market price for liner grade polyethylene is about $0.38 per pound [5].

Polyethylene is an organic polymer material of crystalline-amorphous structure, formed through the polymerization of ethylene gas. Hundreds of compound variations with differing properties are attainable by the control and design of its molecular structure. Such structural variations are produced by manipulating process parameters and selecting particular additives.

The degree of crystallinity determines density, which, in turn, affects a range of material properties. Two basic processes are employed in the production of polyethylene. Low density polyethylene (LDPE) is produced by a process which uses high reaction pressures (103 to 310 MPa; 15,000 to 45,000 psi) and results in the formation of large numbers of polymer branches. These branches occur at a frequency of 10-20 per 1,000 carbon atoms, creating a relatively open structure. Typically, low density polyethylenes have densities ranging between 0.910 and 0.925 g/cm^3 [6]. High density polyethylene (HDPE) is manufactured by a low pressure process (< 10 MPa; <1,500 psi) in the presence of special catalysts which allow the formation of long, linear chains of polymerized ethylene. Very few side chain branches in the HDPE molecule result in a close packed or dense structure, with densities ranging between 0.941 and 0.959 g/cm^3. Medium density polyethylenes (0.926 - 0.940 g/cm^3) can be formulated by either high or low pressure methods, or by combining LDPE and HDPE materials. Low density polyethylene is being used for the waste encapsulation process developed at BNL because it can be processed at lower temperatures and pressures, and is more cost-effective than high density polyethylene.

Other structural phenomena that affect the properties of polyethylene include molecular weight, molecular weight distribution, and melt index. The molecular weight is the average of all sizes of polymer chains produced during polymerization [7]. Low-density polyethylenes are available in a wide range of molecular weights. Those with high molecular weights tend to be tougher, and have better resistance to harsh chemical environments and stress cracking. However, these materials are more difficult to process. Typically,

the molecular weight distribution for LDPEs ranges between 2.5:1 to 18:1. This parameter has a less dramatic effect on polyethylene properties than the molecular weight itself, but, in general, a narrow molecular weight distribution provides an optimal balance between mechanical properties and ease of fabrication.

The melt index is a measure of the viscosity of the melt (the ease with which it flows) at 190°C and has units of grams/10 minutes. These units originate from the ASTM Test Method D-1238 which measures the rate of extrusion of thermoplastics through an orifice under prescribed temperature and pressure conditions. Melt index may also be used to describe molecular weight because the two parameters are inversely proportional. Values for the melt index can range from < 1g/10 minutes for high molecular weight polyethylene, to > 4,000 g/10 minutes for some low molecular weight polyolefins. For typical applications, however, polyethylenes have melt index values ranging between 1 and 60 g/10 minutes.

3. MECHANICAL PROPERTIES

3.1 Overview

Mechanical and physical properties of low density polyethylene are listed in Table 3.1, along with the test methods used to determine them. These data provide an overview of the strength and durability of this material and background information concerning potential performance for encapsulation of radioactive and mixed wastes. Many of polyethylene's properties are related to material-specific characteristics such as density, melt index, and molecular weight distribution, and Table 3.2 provides qualitative information on the impact of these characteristics for selected properties. More specific data on properties that can impact long-term stability of polyethylene waste forms are presented in Section 3.2.

3.2 Properties That Can Potentially Impact Waste Form Stability

Prediction of long-term durability for any material is a difficult task. Assessment models that estimate potential material performance over long periods of time require a combination of historical analog data and short-term performance tests that provide information on structural characteristics and response to environmental conditions. Uncertainties inherent in application of historical analogs, standard test procedures, and prediction of environmental conditions, as well as the modeling process itself, limit the ability to accurately predict performance.

Since polymers in general, and polyethylene in particular, are relatively recent engineering materials there are little historical data available for predicting performance. Thus, the assessment of long-term durability of polyethylene is further limited to application of short-term property evaluation testing. Selection of appropriate potential failure mechanisms that can affect polyethylene waste form stability is another important consideration. For completeness, mechanisms examined in this section (including exposure to radiation, biodegradation, chemical attack, flammability, environmental stress cracking, and photodegradation) represent a comprehensive set of failure modes known to affect polymers. They are not prioritized according to likelihood of occurrence, and in some cases, may not impact waste form durability at all. For example, photodegradation of polyethylene exposed to the ultraviolet radiation of the sun can cause deterioration of structural integrity, but since waste forms are contained within steel packages during storage, transport and disposal, scenarios involving this failure mechanism are extremely unlikely. Information presented in Section 3.2 was gathered from the literature. BNL test data on polyethylene waste form performance are given in Section 4.

Table 3.1 Properties of Low Density Polyethylene[a]

Property	ASTM Test Method	Results
Brittleness temperature, °C	D 746	-80 to -55
Burning rate	D 635	very slow
Crystalline melting point, °C		108-126
Deflection temperature, at 66 psi, °C	D 648	65-80
Density, g/cm^2	D 792	0.910-0.925
Elongation, %	D 638	100-650
Extrusion process temperature, °C		121-232
Flexural modulus, at 23°C, 10^3 psi	D 790	35-48
Hardness, Shore	D 2240	Shore D 44-50
Heat capacity, cal/°C/g		0.55
Heat resistance, continuous, °C		82-100
Impact strength, ft lb/in of notch	D 256	>16 (No break)
Melt index, g/10 min	D 1238	0.2-55
Mold (linear)shrinkage, in/in		0.015-0.050
Molecular weight, weight average		10^4 - 10^5
Organic solvents, effect of		resistant below 60°C
Tensile impact strength, ft lb/in^2	D 1822	180
Tensile modulus, 10^3 psi	D 638	25-41
Tensile strength, at break, psi	D 638	1,200-4,550
Tensile yield strength, psi	D 638	1,300-2,100
Thermal conductivity, 10^{-4} cal cm/sec cm^2 °C	C 177	8
Thermal expansion, 10^{-6} in/in/°C	D 696	100-220
Water absorption, (1/8 in specimen), 24 hr., %	D 790	<0.01

[a] Adapted from References [5,8]

Table 3.2 Change in Polyethylene Properties with Density, Melt Index, and Molecular-Weight Distribution[a,b]

Property	As density increases	As melt index increases	As molecular weight distribution increases
Abrasion resistance	+	-	
Blocking resistance	+	-	
Brittleness resistance	-	-	-
Brittleness temperature	-	+	-
Chemical resistance	+	-	
Cold flow resistance	+	-	+
Hardness	+	-(sl)	
Impact strength	-	-	-
Load-bearing properties, long-term	+	-	+
Melt elasticity		-	+
Melt viscosity		-	
Mold shrinkage	-	-	
Permeability	-	+(sl)	
Softening point	+		+
Specific heat	-(sl)		
Stiffness	+	-(sl)	
Stress-cracking resistance	-	-	-
Tensile elongation at break	-	-	
Tensile modulus	+	-(sl)	
Tensile strength at break	+	-	
Tensile yield stress	+	-(sl)	
Thermal conductivity	+		
Thermal expansion	-		

(a) + denotes increase; - denotes decrease; sl denotes slight change.
(b) Adapted from Reference [8]

3.2.1 Biodegradation

The consensus of many studies on biodegradation of plastics is that the majority of synthetic polymers, including polyethylene, are highly resistant to microbial attack [9]. With municipal landfill capacity quickly dwindling, the ability of plastics to resist microbial degradation is a major ecological concern and has precipitated several studies on the biodegradability of plastics and how it might be enhanced. However, from the standpoint of its use as an encapsulation material for radioactive, hazardous, and mixed waste, polyethylene's ability to resist microbial attack is an asset rather than a liability. The findings from such studies provide valuable information regarding anticipated long-term behavior of waste forms under disposal conditions.

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. It should not be confused with other types of environmental degradation, such as photodegradation caused by exposure to sunlight and oxygen (see discussion in Section 3.2.6). Many environmental variables can affect the growth of microorganisms including [10]:

- Temperature - In general, microbial activity increases with temperature, but since moisture is required for growth, the effective temperature range is -2°C (high salinity water) to about 100°C. The optimal temperature for growth of most microorganisms is < 50°C.

- pH - Strong acids and bases inhibit growth; the majority of microorganisms thrive best in pH range of 4 - 9 (bacteria prefer pH ≈7, fungi and yeast prefer slightly more acidic conditions).

- Water and salinity - Moisture is required for all microbial growth; salinity inhibits growth for most microbes.

- Nutrients - Trace amount of many minerals and higher concentrations of phosphorus, sulfur and magnesium are needed to support growth.

- Dissolved oxygen - Both aerobic and anaerobic decomposition processes (i.e., with or without oxygen) are common in nature, but aerobic decomposition is much more rapid than anaerobic.

- Concentration and species of viable microorganisms - The rate and extent of degradation are related to microbial population density and species.

When appraising potential biodegradability of polyethylene waste forms, it is important to consider these environmental factors in relation to the anticipated conditions of disposal. Most advanced disposal designs minimize water intrusion by use of caps and/or engineered structures so that saturation is avoided. In addition, constituents in the waste can provide localized pH conditions outside the optimal range (the pH of Rocky Flats nitrate salt waste in distilled water is 12.9). In contrast, studies that examine microbial degradation of materials are conducted under ideal growth conditions, so that results represent a conservative estimate of growth under actual conditions.

Some plastics contain additives such as antioxidants, slip or anti-block agents, UV absorbers, plasticizers, and heat stabilizers which may or may not support microbial growth. Thus, some non-biodegradable plastics have mistakenly been thought to support microbial growth when the plastic matrix itself has not been assimilated. This is an important consideration when examining data from studies in this area. In some cases, variations in the ability to support growth differs among particular types of additives. For example, one study indicated that a certain type of polyethylene antioxidant (phenols) exhibited no growth while another type (thioesters) supported heavy growth [11]. Since additives are normally used in very small quantities, (often < 1 wt%) their net effect on biodegradation of polyethylene waste forms would be almost negligible. Specific additives known to be biodegradable can be avoided when choosing appropriate polyethylene binders for waste encapsulation.

While polymeric materials are generally thought to be highly resistant to microbial attack, Potts et al. [12] studied the effects of molecular weight on biodegradation by examining simple straight chain hydrocarbons of increasing molecular weight. Tests were conducted using ASTM Methods D-1924-63 and ASTM D-2676 which have since been superseded by the current ASTM Methods G-21 and G-22, respectively. These procedures require specimens to be placed in or on a solid agar growth medium that is deficient in carbon. The medium and test specimens are inoculated with the microorganisms (fungi or bacteria) and incubated for 3 weeks. If growth occurs, it is directly related to the ability of the organism to metabolize carbon within the specimen. Results are quantified in terms of the following growth ratings:

0 = No growth
1 = Traces (< 10% of surface covered)
2 = Light growth (10 - 30% of surface covered)
3 = Medium growth (30 - 60% of surface covered)
4 = Heavy growth (60 - 100% of surface covered)

Potts, et al. found that very low molecular weight linear hydrocarbon molecules (those with molecular weights below about 450) are susceptible to microbial growth. However, there is a distinct drop in biodegradability for hydrocarbons with molecular weights in excess of about 500, as indicated in Table 3.3. Polymers such as polyethylene are made up of molecules of varying chain lengths. Consequently, molecular weight for polymers is an expression of the average value; the distribution of varying polymer chains approximates a Gaussian distribution around the average value. In other words, regardless of the average molecular weight of a polymer, there is a finite probability that some low molecular weight chains will be present. As the average molecular weight increases, the proportion of low molecular weight components decreases. The average molecular weight of low density polyethylene ranges between about 10^4 and 10^5, well above the range where growth is supported. Under ordinary test conditions (e.g., ASTM Methods G-21 and G-22), the percentage of very low molecular weight chains that are susceptible to biodegradation is so low that microbial growth is not detected. For low density polyethylene specimens with average molecular weights of 56,000 a growth rate = 0 was determined [12].

Some researchers, using linear, low molecular-weight hydrocarbons, have shown that microbial decomposition occurs only at the ends of polymer chains [13]. This phenomenon has led to the theory that higher molecular weight polyethylenes are resistant to microbial attack because they have more chains in a folded orientation, so that fewer chain ends are near the surface, exposed to attack [14].

Polymer molecules may be present as either linear, branched, or cross-linked chains (see description of polymer structures in Section 2). Other researchers [15] have found that even low molecular weight hydrocarbons are no longer susceptible to microbial growth when either branched or cross-linked. The biodegradability of several branched hydrocarbons was measured and compared to hydrocarbons of similar molecular weight but with straight chain orientation, all of which had molecular weights below the cut-off of about 500 where growth is supported. Their results, summarized in Table 3.4, clearly demonstrate that once a hydrocarbon chain is branched, its ability to support the growth of microorganisms decreases dramatically. This phenomenon has a positive impact on low density polyethylene's ability to resist biodegradation. As the amount of branching in polyethylene is increased, crystallinity and density decrease because the polymer chains don't fit together as neatly in a crystalline lattice structure. Low density polyethylene contains many more branched chains than does high density polyethylene, an advantage with respect to biodegradability that offsets the fact that its molecular weight is lower.

As discussed in Section 3.2.6, weathering or ageing of polymeric materials exposed to sunlight is caused by oxidative attack that generally leads to a decrease in molecular weight. Although the average molecular weight of the polymer is still relatively high when it crumbles to powder, continued oxidation over a longer

period could sufficiently reduce molecular weight to allow assimilation by soil microorganisms. Growth on the degraded polyethylene would occur before all the molecules in an object were reduced to the 500 molecular weight level because of the existing distribution of molecular sizes. Swedish researchers measured the evolution of $^{14}CO_2$ from ^{14}C labelled polyethylene to more accurately investigate low growth rates in plastics. Samples exposed to UV irradiation released higher levels of $^{14}CO_2$ than those that were not photochemically degraded [16]. As discussed in Section 3.2.6, photodegradation is limited to thin surface layers and is not expected to impact waste forms. Exposure of uncontainerized waste forms to sunlight during storage, transport, and disposal should be avoided to eliminate photodegradation that can lead to potential biodegradation in polyethylene waste forms. Since polyethylene waste forms are packaged in steel drums, photodegradation before disposal is unlikely.

Attempts at enhancing biodegradation of LDPE by treatment with ionizing radiation, corona discharge, and ozone failed to measurably accelerate growth [12]. The radiation source was a Van de Graaff electron accelerator and samples of LDPE film were exposed to 5, 10, and 20 megareps total dose[1]. Corona discharge exposure was at 120 volts, 2.3 amps, for 15 seconds. Ozone exposure consisted of a flow system at 50°C, containing 2% ozone, for 6 hours, or a total of 54 g ozone.

Based on many studies on biodegradation of plastics, one can reasonably conclude that low density polyethylene is extremely resistant to microbial attack. Lack of appropriate growing conditions makes polyethylene more resistant to attack. For example, polyethylene's hydrophobicity (low permeability) limits any microbial growth that does occur to a thin surface layer. Under ordinary conditions (i.e., waste forms are not subject to extreme photodegradation) the small fraction of low molecular weight polymers susceptible to microbial action is so small that biodegradation rates can be considered negligible. In addition, the conditions at typical disposal facilities discourage growth. Well-designed disposal sites are equipped with caps and other barriers to reduce water intrusion and contaminant leachability. Resulting dry conditions also reduce susceptibility to microbial degradation. Photodegradation (a precursor to microbial degradation in plastics) is minimized by maintaining plastics under low oxygen conditions, away from sunlight.

[1]One rep is the amount of ionizing radiation that causes absorption of 93 ergs per gram of soft tissue.

Table 3.3 Biodegradability of Straight Chain Hydrocarbons [a]

Compound	Formula	Molecular Weight	Growth Rating[b]
Dodecane	$C_{12}H_{26}$	170	4
Hexadecane	$C_{16}H_{34}$	226	4
Octadecane	$C_{18}H_{38}$	255	4
Docosane	$C_{22}H_{46}$	311	4
Tetracosane	$C_{24}H_{50}$	339	4
Octacosane	$C_{28}H_{58}$	395	4
Dotriacontane	$C_{32}H_{66}$	451	4
Hexatriacontane	$C_{36}H_{74}$	507	0
Tetracontane	$C_{40}H_{82}$	563	0
Tetratetracontane	$C_{44}H_{90}$	620	0

[a] Adapted from Reference [12].

[b] Growth rating: 0 = no growth; 1 = traces (< 10% of surface covered); 2 = light growth (10-30% of surface covered); 3 = medium growth (30-60% of surface covered); 4 = heavy growth (60-100% of surface covered).

Table 3.4 Effect of Branching on Hydrocarbon Biodegradability[a]

Compound and Structure	Molecular Weight	Branched	Growth Rating
Dodecane $C_{12}H_{26}$ $(CH_3CH_2CH_2CH_2CH_2CH_2)_2$	170	no	4
2,6,11-Trimethyldodecane $C_{15}H_{32}$ $CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH(CH_3)CH_3$	212	yes	0
Hexadecane $C_{16}H_{34}$ $(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2$	226	no	4
2,6,11,15-Tetramethylhexadecane $C_{20}H_{42}$ $(CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2)_2$	283	yes	0
Tetracosane $C_{24}H_{50}$ $(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2$	339	no	4
Squalane $C_{30}H_{62}$ $(CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2)_2$	423	yes	0
Dotriacontane $C_{32}H_{66}$ $CH_3(CH_2CH_2CH_2CH_2CH_2CH_2)_5CH_3$	451	no	4

[a] Adapted from Reference [12]. For explanation of growth rating see Table 3.3

3.2.2 Radiation Effects

Interactions between the energy from ionizing radiation and the chemical and molecular structure of polymers can cause structural changes in the material that, in turn, can affect their physical properties. When some polymers, such as polyethylene, are exposed to ionizing radiation, many of the resulting changes in physical properties represent improvements over those of the unirradiated material. The potential for improved performance provided the impetus for numerous studies over the past 40 years on radiation effects in polymers, especially for polyethylene, because it is widely used and has a relatively simple chemical structure. Consequently, the behavior of polyethylene exposed to various forms of radiation is better characterized than that of any other polymer [17]. Nevertheless, there is still considerable debate about specific mechanisms for the physical changes measured on a macro scale. Some of these theories, summarized in Section 3.2.2.1, provide insight into how radiation induced changes occur. Radiation effects on the physical properties of polyethylene are discussed in Section 3.2.2.2. Results from radiation stability testing of polyethylene waste forms are presented in Section 4.6.

3.2.2.1 Mechanisms

The effects of exposure to radiation on polymers can be broadly grouped into two categories: (i) the formation of crosslinks, or lateral intermolecular and intramolecular chemical bonds, and (ii) degradation from the breaking of carbon - carbon bonds in the main chains of the polymer, yielding smaller fragments. These competing processes occur simultaneously at varying rates, but based on the molecular structure of the polymer and the conditions of irradiation, one or the other predominates [18]. Polyethylene, polystyrene, polypropylene, and polyesters are among Group I polymers in which crosslinking dominates, whereas polymethacrylates, polyisobutylene, and cellulose are in Group II, where bond scissions predominate. For polyethylene irradiated in the absence of air, the ratio of the number of bond scissions in the main chain to the formation of lateral crosslinks does not exceed 0.1 [19], i.e., about 10 lateral crosslinks are formed for every bond scission that occurs.

Both crosslinking and bond scission act upon primary bonds. Thus, the energy required to break these bonds are high (200 to 600 kJ/mol), [20] and the effects are irreversible. Such changes can profoundly impact the physical properties of the polymers including thermal stability, permeability, creep, stress cracking, resistance to solvents, and impact resistance [21]. In contrast, melting of thermoplastics only requires overcoming the energy associated with van der Waals' forces and hydrogen bonds (secondary bonds), about 2 to 20 kJ/mol, and these effects are reversible.

Various types of crosslinking configurations are possible (Figure 3.1). The initial polymer structure prior to irradiation is shown in 3.1.a. Intermolecular bonds formed between two neighboring molecules are illustrated in 3.1.b (away from chain ends), and 3.1.e (bond between an active terminal end for one molecule and mid-section of a neighboring molecule). Intramolecular bonds formed between neighboring portions of a single folded molecule are represented in 3.1.c. Crosslinking can also occur between parts of a polymer chain and aggregate filler material (waste constituents in polymer waste forms), as shown in 3.1.f. During irradiation of polymers, each of these bond types are formed concurrently, but their distribution depends on the chemical and physical structure of the material and specific conditions of irradiation. As crosslinking continues, the number of isolated polymer molecules rapidly decreases until a discrete point is reached where enough of the macromolecules are joined that the lattice becomes insoluble (3.1.d). This point corresponds to the formation of an average of one intermolecular crosslink per polymer molecule, also referred to as the gel point.

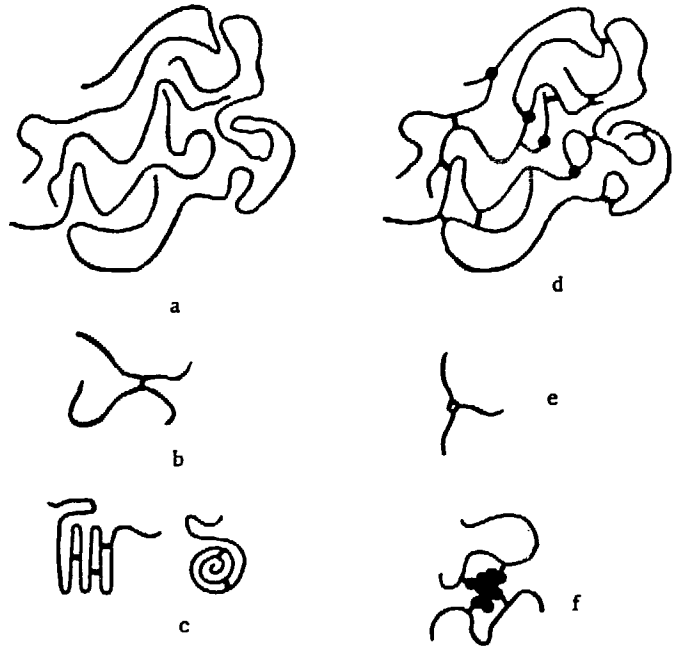

Figure 3.1 Schematic representation of various types of crosslinking configurations [19]. See the text for details.

The extent of crosslinking in polyethylene depends on several factors including the total absorbed dose, availability of oxygen, and type of radiation source. Based on changes in molecular weight, solubility, swelling and elastic properties, Charlesby [22] defines four distinct ranges of dose-dependent property changes:

1) At low radiation doses (less than 2 Mrad or 2 x 10^6 rad), the major effect of crosslinking is an increase in the degree of branching and in the average molecular weight, often leading to an increase in tensile strength. Crystallinity is generally unaffected.

2) On exposure to doses from several megarad to hundreds of megarad, two phases become apparent - a sol and a gel. The gel forms a three-dimensional network which is insoluble and infusible. Mechanical properties are modified by a reduced degree of crystallinity and by the presence of a network. Above the melt temperature, radiation-induced crosslinks in the gel (crosslinking density ranging between 0.1 and 5%) hold the molecules together, and the material has an elastic, rubber-like consistency.

3) A transition region occurs when crystallinity has been virtually eliminated and mechanical properties are dictated by the extent of crosslinking (crosslinking densities from 5 to 10%). The properties corresponding to this phase have been described as "cheese-like," because the material tends to crumble under stress.

4) At very high radiation doses corresponding to high crosslinking densities (>10%), polyethylene develops a brittle glass-like structure. It is characterized by a high elastic modulus and low deformation at break.

More recently, several researchers presented data indicating that under exposure to relatively low doses in air the degree of crystallinity of polyethylene increases [23,24]. Aslanian et al., [23] irradiated polyethylene film samples to doses ranging from 10 to 300 Mrad and the degree of crystallinity was determined by x-ray diffraction. As seen in Figure 3.2, crystallinity gradually increased from 38% for non-irradiated samples to a maximum of 59% at a dose of 275 Mrad. These data are further corroborated by the differential scanning calorimeter thermograms presented in Figure 3.3, which indicate that irradiation produces additional low temperature (~55 - 60°C) and high temperature (~82 - 85°C) endothermal peaks, characteristic of changes in crystalline structure.

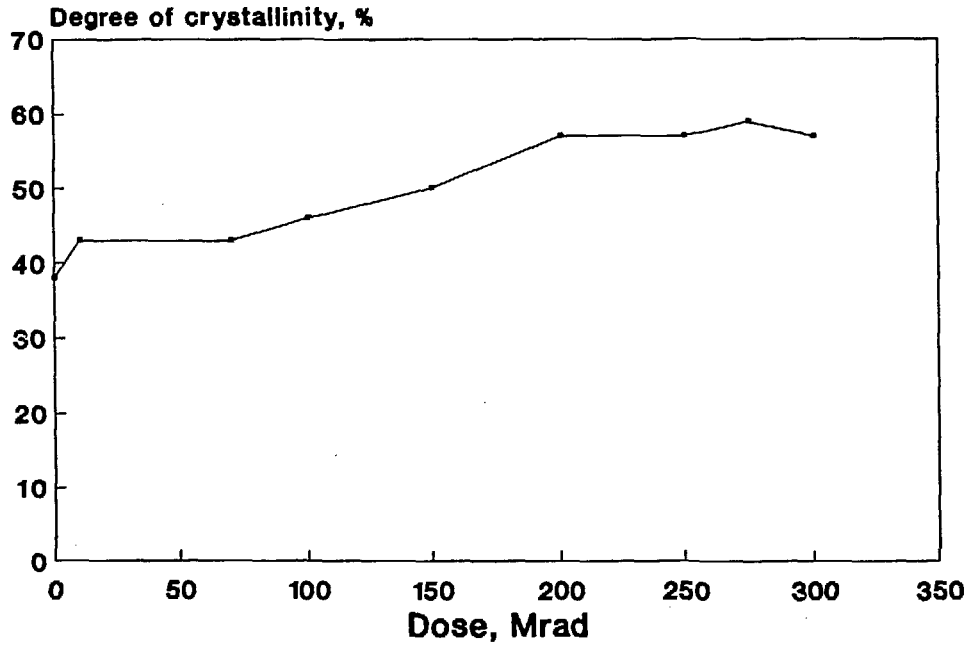

Figure 3.2 Effect of radiation dose on crystallinity of low density polyethylene. Adapted from data in Ref. [23].

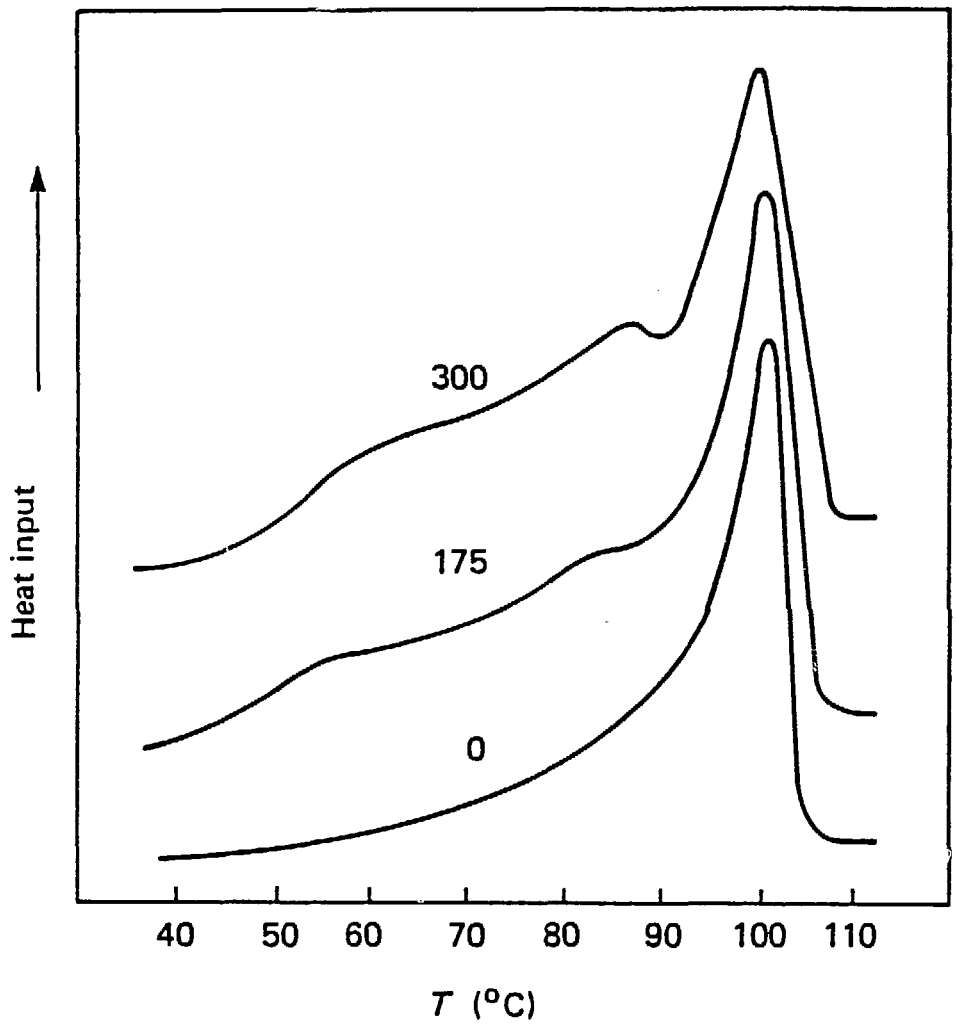

Figure 3.3 Thermograms of irradiated low density polyethylene samples at doses of 0, 175 and 200 Mrad [23].

The effect of dose rate on changes in crosslinking and other physical properties has been extensively investigated. Chapiro presents data from several researchers on the extent of crosslinking for polyethylene samples irradiated under vacuum at dose rates ranging from a few rad/sec for gamma ray sources, to several Mrad/sec for electron accelerators [17]. He concluded that observed changes in melting point and gel content depend only on total dose and are not influenced by the rate at which the dose is delivered to the sample.

These data are corroborated by Makhlis [19], who found that varying the dose rate from 6 to 2,070 Mrad/min did not change the degree of cross-linking for polyethylene samples that were irradiated by accelerated electrons under vacuum. At lower dose rates, in the presence of oxygen, dose rates had a significant effect. Figure 3.4 shows the tensile strength of polyethylene samples irradiated in air decreased for dose rates < 10^8 rad/hr. Similar results were found by Spadaro et al. [18], and Wilski [25], who concluded that for relatively low dose rates in air, increased degradation occurs with decreasing dose rates. This phenomenon is attributed to the destructive action of atmospheric oxygen, and is related to its ability to diffuse through the polymer.

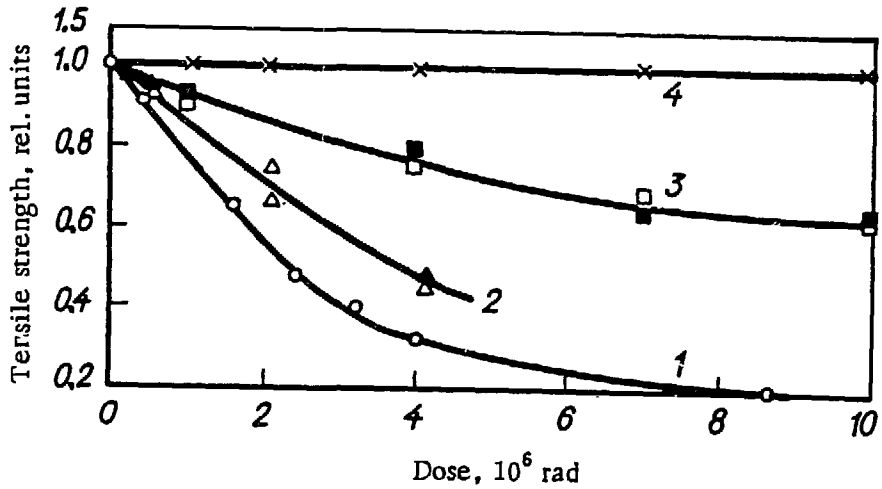

Figure 3.4 Radiation effects (total dose and dose rate) on the tensile strength of polyethylene. Dose rates, rad/hr: 1 = 380; 2 = 4,350; 3 = 3 x 10^5; 4 = 10^8 [19].

Several researchers reported that the irradiation of polyethylene in the presence of air led to marked oxidation of the polymer. Increases in weight due to oxidation were measured for samples irradiated in air, whereas those irradiated under vacuum registered a loss in weight due to gas evolution. Carbonyl groups and other oxygen-related by-products were also detected [26,27]. Almost all the data on this subject are based on examination of thin films. For relatively thick polymer blocks such as polyethylene waste forms, the impacts of radiation-induced oxidation would be considerably reduced or eliminated. Papet et al. [28],

specifically examined the relationship between polymer thickness and radiochemical oxidation of low density polyethylene. They found a distinct reduction in the production of carbonyl groups at sample depths greater than about 150 microns, for doses of 50 and 100 Mrad. Black and Charlesby [29] found similar evidence of reduced carbonyl production as a function of depth which led to their conclusion that "...radio-oxidation of polyethylene is very largely a surface effect, as the rate of oxidation is dependent upon the rate of diffusion of air into the polymer."

3.2.2.2 Physical Effects and Changes in Material Properties

Studies of gas evolution from polyethylene irradiated in the absence of air indicated yields of hydrogen (about 98% of the total gas) with smaller amounts of methane, ethane, propane, butane and other hydrocarbon gases. The chemical yield from radiation reactions, commonly referred to as the "G value," is defined as the number of chemical events occurring per 100 eV of absorbed energy. In the case of hydrogen evolution, $G(H_2)$ is the absolute number of hydrogen molecules produced per 100 eV. This number is equivalent to G micromoles produced per gram of material subjected to 1 megarad. Based on experimental results from several researchers, the average value for $G(H_2)$ of polyethylene at room temperature is 4.1 [17].

To estimate the potential impact of H_2 generation on polyethylene waste forms, some simple calculations were performed. The range of absorbed dose rates to which a waste form would be exposed was derived from data curves of absorbed dose vs. time for waste forms generated at typical boiling water reactors, with activity concentrations ranging from 1.0×10^7 Bq/m^3 to 1.0×10^{11} Bq/m^3 (0.01 Ci/ft^3 to 100 Ci/ft^3) [30]. These data assume a waste form density of 2.0 g/cm^3, so that actual absorbed doses for polyethylene waste forms (with a density of 1.35 g/cm^3) would be lower. Dose rates were calculated conservatively at the steepest portion of the curves (time = 10 years), before radioactive decay significantly reduces the rate. The following assumptions were used:

- waste loading = 60 wt% sodium nitrate ($NaNO_3$)
- waste form density = 1.35 g/cm^3 (84.3 lb/ft^3)
- waste form volume = 198 L (7 ft^3)
- waste form weight = 268 kg (590 lbs)

Based on these assumptions, H_2 gas evolution from 55-gallon polyethylene waste forms, containing 60 wt% sodium nitrate waste, ranges from about 4×10^{-6} liters/day to 4×10^{-2} liters/day, as shown in Figure 3.5. Typical mild steel drums used for waste disposal are not gas-tight (especially to H_2), so this gas generation is not expected to cause any measurable increase in pressure within waste drums. To quantify differences

in pressure, empirical data would be needed on the diffusion rate of H_2 from the waste container and the effective volume of gas generated. Estimating the effective volume available to H_2 within the waste drum is particularly complicated because one must account for: (i) the porosity of polyethylene to H_2 gas, (ii) the void volume associated with the waste, and (iii) the fraction of H_2 gas that is reabsorbed to the solid phase. Nevertheless, a conservative bounding estimate of pressure buildup can be made by assuming an H_2 gas-tight container and an effective volume of 25% of the total waste form volume. Such calculations yield pressure increases ranging from 8.27×10^{-9} MPa/day (1.2×10^{-6} psi/day) to 8.27×10^{-5} MPa/day (1.2×10^{-2} psi/day), for dose rates of 2.7 rad/day to 2.7×10^{4} rad/day, respectively. This conservative estimate confirms the hypothesis that H_2 gas generation due to radiolysis of polyethylene would have a negligible impact.

As mentioned earlier, crosslinking and bond scission by irradiation of polyethylene can change its physical properties as summarized below:

Thermal stability - Crosslinking of polyethylene modifies the thermal resistance of the material so that it resembles a thermosetting polymer. At temperatures of 95 - 105°C, normal polyethylene softens and flows readily, but crosslinked polyethylene can be used for extended periods at temperatures up to 135°C without flowing.

Solvent resistance - Resistance to organic solvents is improved dramatically. When immersed in benzene, ordinary polyethylene dissolves in days, but polyethylene crosslinked by radiation can withstand up to 30 days in solvent immersion, with no loss in tensile strength or percent elongation at break [21].

Environmental stress cracking - (mechanical failure due to exposure to weathering, organic liquids, or surface-active agents as described in Section 3.2.5). As shown in Table 3.5, increased dose reduces environmental stress cracking by increasing the time to failure for half of the specimens tested (F-50 value).

Impact strength - Changes in impact strength appear to be dose-rate dependent. For low density polyethylene films irradiated to 1×10^{7} rad at high dose rates using an electron accelerator, dart-drop impact strength improved by 85%. When irradiated to the same total dose, but at a considerably lower dose rate by a cobalt-60 gamma source, Izod impact strength of high density polyethylene decreased by 25% [31].

Creep resistance - Creep is the time-dependent deformation under a constant stress. Most thermoplastic polymers, including polyethylene, tend to flow slowly when subjected to loads. As demonstrated in Figure 3.6, the cold flow of polyethylene is reduced significantly when irradiated at doses of 50 kGy (5×10^6 rad), 100 kGy (1×10^7 rad), and 200 kGy (2×10^7 rad) [21].

Permeability - Permeability and diffusion through polyethylene is not significantly affected for doses up to 10^7 rad. At higher doses, the permeability of polyethylene films to nitrogen, oxygen, carbon dioxide, and methyl bromide decreases due to a reduction in the diffusion coefficient [32]. From the standpoint of polyethylene waste forms, this phenomenon may result in reduced leachability of contaminants at higher absorbed doses.

Tensile strength - Because crosslinking tends to make polyethylene more brittle, the tensile strength of specimens irradiated in air can be reduced by as much as a factor of 2. In contrast, samples irradiated under vacuum showed very little change in tensile strength [33].

Table 3.5 Environmental Stress Cracking (ESC) of Irradiated Polyethylene [a]		
Dose, kGy	Dose, rad	ESC Resistance F-50 value, hours [b]
0	0	0.3
5	5.0×10^5	0.3
20	2.0×10^6	26
80	8.0×10^6	504
320	3.2×10^7	> 3 months
640	6.4×10^7	> 3 months

[a] Based on Reference [21].
[b] F-50 value: time for one half of the specimens tested to fail.

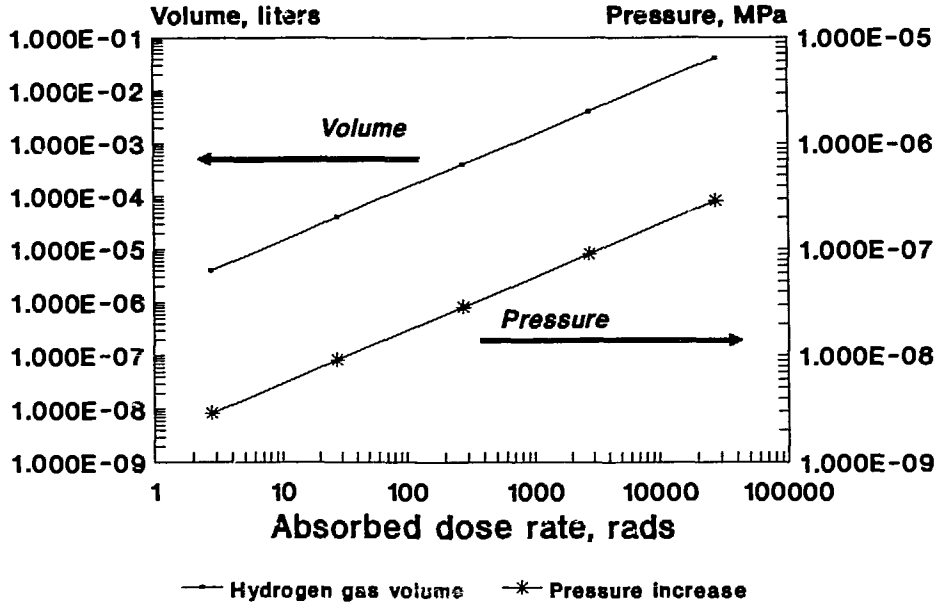

Figure 3.5 Conservative estimates of hydrogen gas evolution and resultant gas pressure (as per assumptions outlined in the text) for self-irradiated polyethylene waste forms.

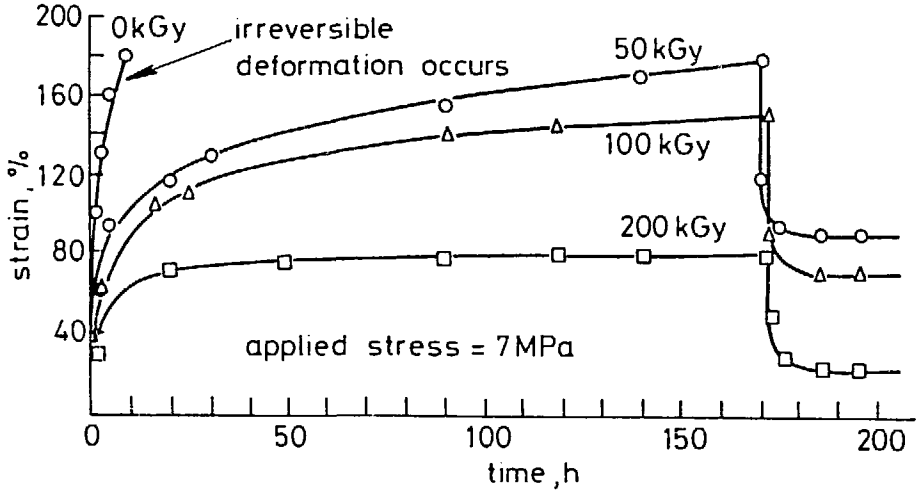

Figure 3.6 Creep properties of low density polyethylene irradiated to total doses of 50 kGy (5×10^6 rad), 100 kGy (10^7 rad), and 200 kGy (2×10^7 rad) [21].

In conclusion, the predominant effect of ionizing radiation on polyethylene is an increase in bonding between and within polymer chains, known as crosslinking. Increased crosslinking has a large impact on the mechanical properties of the polymer that, in most cases, represent improvements over non-irradiated polyethylene. Radiation-induced oxidation has been shown to be a surface phenomena, and therefore would be insignificant for large-scale waste forms. Some bond scission does occur, resulting in liberation of hydrogen gas, but the anticipated effects from this phenomenon on polyethylene waste forms were calculated to be negligible.

3.2.3 Resistance to Chemical Attack

Polyethylene's resistance to aggressive chemicals is a primary reason for its widespread use in many diverse applications. The key to ensuring long-term stability of waste forms is the ability of the binder to withstand the chemical environment, internally from the waste materials and externally from the disposal site. Protection from a broad range of chemical reagents is essential because it is difficult to accurately predict the chemical composition of leachates resulting from varied waste forms in disposal.

At ambient temperatures, polyethylene is insoluble in virtually all organic solvents and is resistant to many acids and alkaline solutions [33]. Polyethylene is resistant to any concentration of hydrochloric, hydrofluoric, phosphoric, and formic acids, ammonia, potassium hydroxide, sodium hydroxide, potassium permanganate, and hydrogen peroxide. In dilute concentrations (up to 50 wt%), polyethylene is resistant to sulfuric and nitric acids. Exposure to some aliphatic, aromatic, and chlorinated hydrocarbons can cause swelling, but will not permanently change mechanical properties (e.g., loss in strength), because the original properties reappear upon evaporation of the swelling media [34]. In general, low density polyethylene is relatively unaffected by polar solvents including alcohols, phenols, esters, and keytones. Table 3.6 is an overview of polyethylene's compatibility with many chemicals, while the specific effect of selected solutions after three months contact time is given in Table 3.7.

At elevated temperatures, polyethylene is more susceptible to attack by some solvents. For example, at 70°C, it is partially dissolved by toluene, xylene, amyl acetate, trichloroethylene, turpentine, chlorinated hydrocarbons, petroleum ether, and lubricating oil. Above 100°C, it is totally miscible in these solvents [33].

There is also some evidence that the presence of polyethylene can reduce the corrosion rate of some steels. The dissolution rate of SAE 1020 steel in dilute hydrochloric and sulfuric acids was decreased in the presence of polyethylene, and the corrosion of this steel in tap water was decreased by about 30% in short-term (25 day) tests [35].

Polyethylene's excellent resistance to water and aqueous solutions is particularly relevant to its use as a binder for encapsulation of waste. Contaminant mobility from a waste form is determined, to a large extent, on leachability. Permeability (rate at which a liquid or gas passes through a solid) determines how quickly groundwater can permeate both in and out of the waste form, and thus, is a controlling factor for waste form leachability. Permeability of water in polyethylene is low. For thin films (0.001 in. thick), water permeability was measured at 0.16 g/24hr./100 in.^{2} [36]. Through bulk materials, permeability would be even lower. Another method of quantifying resistance to liquid penetration is to measure the quantity of water absorbed by the solid over time. Manufacturer's data for water absorption in a thin polyethylene sheet is shown graphically in Figure 3.7. After 2 years of immersion in water, the polyethylene sheet only absorbed 0.3 mg of water per in.^{2} of surface [37]. Another source gives the water absorption, after one year of immersion at 20°C, as 0.2 percent [34].

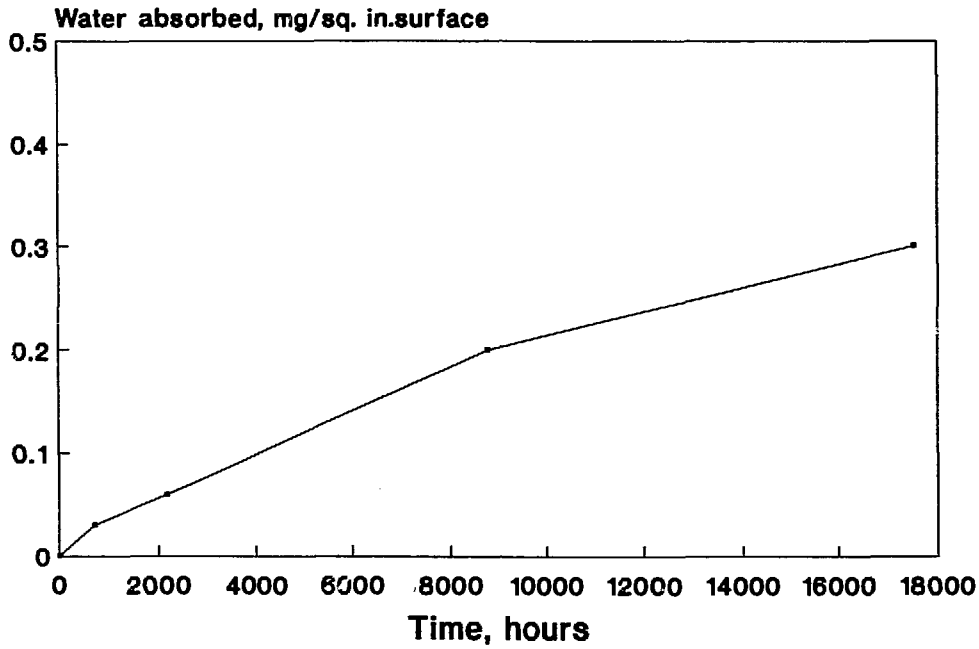

Figure 3.7 Polyethylene's low permeability as shown by water absorption rate data. Based on data from Reference [36].

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

	Polyethylene can be used at:	
Chemical	25°C	60°C
Acetic acid (10 wt %)	Yes	Yes
Acetic acid (Glacial)	No	No
Acetone	Yes	No
Alcohol, benzyl	No	No
Alcohol, ethyl (35 wt %)	No	No
Alcohol, methyl	No	No
Alcohol, propyl	No	No
Aluminum chloride	Yes	Yes
Aluminum fluoride	Yes	Yes
Aluminum hydroxide	Yes	Yes
Aluminum sulfate	Yes	Yes
Ammonia	Yes	Yes
Ammonium carbonate	Yes	Yes
Ammonium chloride	Yes	Yes
Ammonium hydroxide (28 wt %)	Yes	Yes
Ammonium nitrate	Yes	Yes
Ammonium persulfate	Yes	Yes
Ammonium phosphate (75 wt %)	Yes	Yes
Ammonium sulfate	Yes	Yes
Amyl acetate	No	No
Aqua regia	No	No
Barium carbonate	Yes	Yes
Barium chloride	Yes	Yes
Barium hydroxide	Yes	Yes

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

(Continued)

	Polyethylene can be used at:	
Chemical	25°C	60°C
Barium sulfate	Yes	Yes
Barium sulfide	Yes	Yes
Benzene	No	No
Boric acid	Yes	Yes
Calcium carbonate	Yes	Yes
Calcium chlorate	Yes	Yes
Calcium chloride	Yes	Yes
Calcium hydroxide	Yes	Yes
Calcium hypochlorite	Yes	No
Calcium sulfate	Yes	Yes
Carbon dioxide, dry gas	Yes	Yes
Carbon monoxide	Yes	Yes
Carbon tetrachloride	No	No
Carbonic acid	Yes	Yes
Chlorine gas, dry or wet	No	No
Chromic acid (80 wt %)	Yes	Yes
Citric acid	Yes	Yes
Copper chloride	Yes	Yes
Copper cyanide	Yes	Yes
Copper nitrate	Yes	Yes
Copper sulfate	Yes	Yes
Ethylene glycol	Yes	Yes
Ferric chloride	Yes	Yes

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

(Continued)

	Polyethylene can be used at:	
Chemical	25°C	60°C
Ferric nitrate	Yes	Yes
Ferric sulfate	Yes	Yes
Ferrous chloride	Yes	Yes
Ferrous sulfate	Yes	Yes
Fertilizers	Yes	Yes
Fluorine	No	No
Formaldehyde (40 wt %)	Yes	Yes
Formic acid	Yes	Yes
Gasoline	No	No
Glycerine	Yes	Yes
Hydrochloric acid	Yes	Yes
Hydrofluoric acid (48 wt %)	Yes	Yes
Hydrogen peroxide (3 wt %)	Yes	Yes
Hydrogen peroxide (90 wt %)	Yes	No
Hydrogen sulfide, dry gas	Yes	Yes
Lead acetate	Yes	Yes
Lubricating oil	No	No
Magnesium carbonate	Yes	Yes
Magnesium chloride	Yes	Yes
Magnesium hydroxide	Yes	Yes
Magnesium nitrate	Yes	Yes
Magnesium sulfate	Yes	Yes
Mercuric chloride	Yes	Yes

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

(Continued)

	Polyethylene can be used at:	
Chemical	25°C	60°C
Mercurous nitrate	Yes	Yes
Mercury	Yes	Yes
Methyl chloride	No	No
Methyl ethyl ketone	No	No
Mixed acids	Yes	No
Nickel chloride	Yes	Yes
Nickel nitrate	Yes	Yes
Nickel sulfate	Yes	Yes
Nitric acid (10 wt %)	Yes	Yes
Nitric acid (50 wt %)	Yes	No
Nitric acid (95 wt %)	No	No
Nitric acid vapors	Yes	Yes
Oxidizing gases	Yes	Yes
Ozone	No	No
Perchloric acid	Yes	Yes
Phenol (94 wt %)	Yes	No
Phosphoric acid (30 wt %)	Yes	Yes
Phosphoric acid (85 wt %)	Yes	No
Picric acid	Yes	No
Potassium bicarbonate	Yes	Yes
Potassium borate	Yes	Yes
Potassium bromide	Yes	Yes
Potassium carbonate	Yes	Yes

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

(Continued)

	Polyethylene can be used at:	
Chemical	25°C	60°C
Potassium chlorate	Yes	Yes
Potassium chloride	Yes	Yes
Potassium dichromate (40 wt %)	Yes	Yes
Potassium hydroxide	Yes	Yes
Potassium nitrate	Yes	Yes
Potassium permanganate (95 wt %)	Yes	Yes
Potassium sulfate	Yes	Yes
Silver nitrate	Yes	Yes
Sodium acetate	Yes	Yes
Sodium benzoate	Yes	Yes
Sodium bicarbonate	Yes	Yes
Sodium bisulfate	Yes	Yes
Sodium bisulfite	Yes	Yes
Sodium bromide	Yes	Yes
Sodium carbonate	Yes	Yes
Sodium chloride	Yes	Yes
Sodium cyanide	Yes	Yes
Sodium fluoride	Yes	Yes
Sodium hydroxide	Yes	Yes
Sodium hypochlorite	Yes	No
Sodium nitrate	Yes	Yes
Sodium nitrite	Yes	Yes
Sodium sulfate	Yes	Yes
Sodium sulfide	Yes	Yes

Table 3.6 The Application of Polyethylene Resins in Various Chemical Environments[a]

(Continued)

	Polyethylene can be used at:	
Chemical	25°C	60°C
Sodium sulfite	Yes	Yes
Stannous chloride	Yes	Yes
Stearic acid	Yes	Yes
Sulfur	Yes	Yes
Sulfur dioxide	Yes	Yes
Sulfuric acid (50 wt %)	Yes	Yes
Sulfuric acid (70 wt %)	Yes	No
Sulfuric acid (96 wt %)	No	No
Tannic acid (10 wt %)	Yes	Yes
Toluene	No	No
Transformer oils	No	No
Trichloroethylene	No	No
Trisodium phosphate	Yes	Yes
Vegetable oil	No	No
Water, distilled	Yes	Yes
Xylene	No	No
Zinc chloride	Yes	Yes
Zinc sulfate	Yes	Yes

[a] Adapted from Reference [33]

Table 3.7 Effect of Various Chemicals on Polyethylene after 3-Month Contact [a]

	On Removal from Reagent		After 24 Hr. Conditioning at Room Temp.		
Reagent	Change in Wt, %	Appearance	Tensile Strength, psi	Elonga-tion, %	Resistance Rating [b]
Inorganic Acids and Bases					
H_2SO_4, conc.	+ 0.13	No change	1458	462	E
H_2SO_4, 10%	+ 0.04	No change	1370	483	E
HCl, conc.	+ 0.13	No change	1406	258	G
HCl, 10%	+ 0.20	No change	1442	336	E
HNO_3, conc.	+ 3.02	No change	1093	71	F
HNO_3, 10%	+ 0.22	No change	1387	325	E
NaOH, 50%	+ 0.13	No change	1432	313	E
NH_4OH, conc.	+ 0.31	No change	1378	371	E
Oxygenated Organic Compounds					
Ethanol (denatured)	- 0.02	No change	1550	421	E
Acetone	+ 0.03	No change	1363	379	E
Ethyl acetate	+ 2.76	No change	1295	325	E
Dioxane	+ 0.38	No change	1368	382	E
Butyraldehyde	+ 3.06	No change	1245	417	E
Linseed oil	+ 0.88	No change	1410	483	E
Triethanolamine	+ 0.08	No change	1408	379	E
Camphor oil	+17.42	Swollen	1375	483	G

Table 3.7 Effect of Various Chemicals on Polyethylene after 3-Month Contact [a]

(Continued)

	On Removal from Reagent		After 24 Hr. Conditioning at Room Temp.		
Reagent	Change in Wt, %	Appearance	Tensile Strength, psi	Elonga-tion, %	Resistance Rating [b]
Hydrocarbons					
Ethyl gasoline	+11.75	Swollen	1430	508	G
Benzene	- 0.86	No change	1464	429	E
Xylene	- 0.70	No change	1623	479	E
Lubricating oil	+ 7.54	Swollen slightly	954	167	F
Carbon tetrachloride	+22.35	Swollen	1560	475	E
Ethylene dichloride	+ 0.80	No change	1526	300	E
Tricholorobenzene	+26.33	Swollen	1450	442	G
Aqueous Solutions of Salts					
Na bisulfite, 10%	+ 0.17	No change	1310	483	E
Ca chloride, 15%	+ 0.70	No change	1380	483	E
Ca hypochlorite (bleaching soln.)	+ 0.06	No change	1330	375	E
Duponol ME (fatty alcohol sulfate), 10%	+ 0.04	No change	1225	463	G
Ferric sulfate, 15%	+ 0.02	No change	1307	467	E

[a] Adapted from Reference [33]
[b] E = excellent; G = good; F = fair

3.2.4 Flammability

For existing below-ground disposal facilities and advanced disposal designs that incorporate subterranean disposal, flammability of waste forms is not a concern, since sufficient oxygen to support combustion is unavailable. In the case of above-ground disposal, however, and during processing, temporary storage, and transportation, conditions to sustain combustion may be present.

The flash-ignition temperature of polyethylene (the lowest temperature at which a material will ignite if exposed to a small flame under specified conditions) reported in the literature is 340°C. The self-ignition temperature (the lowest temperature at which a material will ignite without the presence of a flame) is reported to be 349°C [38]. Both of these values are higher than those of cotton, paper, or wood shavings. As discussed in Section 4.9, laboratory testing of low density polyethylene samples resulted in higher ignition temperatures than those reported in the literature (flash-ignition = 409°C; self-ignition = 430°C). Since the extrusion processing temperature of polyethylene is about 120°C, the likelihood of process-related fires, even in the event of a thermal excursion, is slight. If ignited, polyethylene burns slowly in a controlled manner, at about 1.0 in./min. under the conditions specified in ASTM D-635 [39]. When cooled below the flash-ignition temperature, the material is self-extinguishing. The National Fire Protection Association (NFPA) rating for polyethylene flammability, on a scale of 0 (least) to 4 (extreme) is 1 (slight) [40]. Flammability testing for polyethylene and polyethylene/waste combinations is presented in Section 4.9. If additional resistance to fire is needed, many commercially available flame-retardant additives are available. The most successful flame retardants for polyethylene are compounds of antimony.

Data on the explosion characteristics of polyethylene dust are in Table 3.8 for consideration during processing and storing large quantities of polyethylene resin. The ignition temperature for a polyethylene dust cloud consisting of 100 mesh particle size is 450°C.

Table 3.8 Explosion Characteristics of Polyethylene Dust[a,b]	
Ignition temperature of dust cloud, °C	450
Minimum energy required for ignition, joules	0.08
Minimum explosive concentration, oz/cu ft	0.025
Maximum pressure, psi	83[c]
Rate of pressure rise, psi Average Maximum	 410[c] 1240[c]

[a] Particle size: 100 mesh.
[b] Adapted from Reference [8]
[c] Values determined on dust concentrations of 0.500 oz/cu ft for confined explosion in bombs.

3.2.5 Environmental Stress Cracking

Although ductile in air, low density polyethylene can become embrittled if exposed to specific conditions that lead to failure by environmental stress cracking (ESC) [41]. ESC can occur under certain 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. Mechanisms for this phenomenon are not fully understood, but studies conducted to date have examined the influences of material properties and environmental conditions. Material properties that may impact ESC resistance include: molecular weight [42,43], melt index [44], and thermal history of the material during processing and cooling [45,46,47]. Environmental factors that have been examined include: temperature, loading stresses, and the types and viscosities of solvents. [41,48]

ESC is a concern primarily for the use of polymeric containers designed to store specific aggressive liquids, such as soaps, detergents, wetting agents, and oils. This phenomenon should have little or no impact on the long-term stability of polyethylene waste forms in disposal, since the chemical agents required to initiate crack propagation are generally not present in significant concentrations within the waste or disposal environment. In addition, extrusion processing of waste forms does not involve the use of intricately shaped molds that can set up areas of localized stress, conducive to ESC.

3.2.6 Photodegradation/UV Effects

The behavior of plastics, particularly polyethylenes, under exposure to the environment has been studied extensively. Plastics subject to long-term exposure to the atmosphere can degrade due to the influence of solar irradiation and oxygen, causing deterioration of mechanical properties, cracking, and molecular weight loss [49]. The ultraviolet portion of the sun's energy with wavelengths around 300 nm is primarily responsible for degradation of polyethylene since energy in the visible and infrared spectrum is too low to damage the polymer's chemical structure.

The degradation process for polyethylene is similar to other hydrocarbon polymers, whereby carbon bonds are broken, forming free radicals that react with oxygen and result in stable carbonyl groups [50]. It is theorized that the mechanism for degradation begins in a comparatively localized region near the initiation site (such as a photosensitive impurity or structural element in the polymer or additive) which, when stressed, can act as a stress concentrator and crack nuclei [51]. This process is depicted in Figure 3.8. Several researchers have investigated the relationship between photochemical degradation and depth. These studies concluded that the rate of photo-oxidation is more rapid in the outer tens of angstroms of low density polyethylene than in the subsurface [52], and the phenomenon is limited to surface regions of effectively constant thickness [53,54]. The most likely explanation for these results is the reduction in the amount of oxygen present within the polyethylene due to limited diffusion through the solid [55].

Natural weathering of polyethylene is one of the processes that can degrade its structure and mechanical properties. However, this process is a photochemical effect that requires both exposure to specific wavelengths of ultraviolet light and the presence of oxygen. Thus, containerized polyethylene waste forms that are stored or disposed would not be expected to encounter solar irradiation that could lead to photodegradation. Further, since this phenomenon is limited to the surface, its impact on full-scale waste forms with diameters of $\geq$ 45 cm would be insignificant, even if waste forms were exposed to sunlight for prolonged periods.

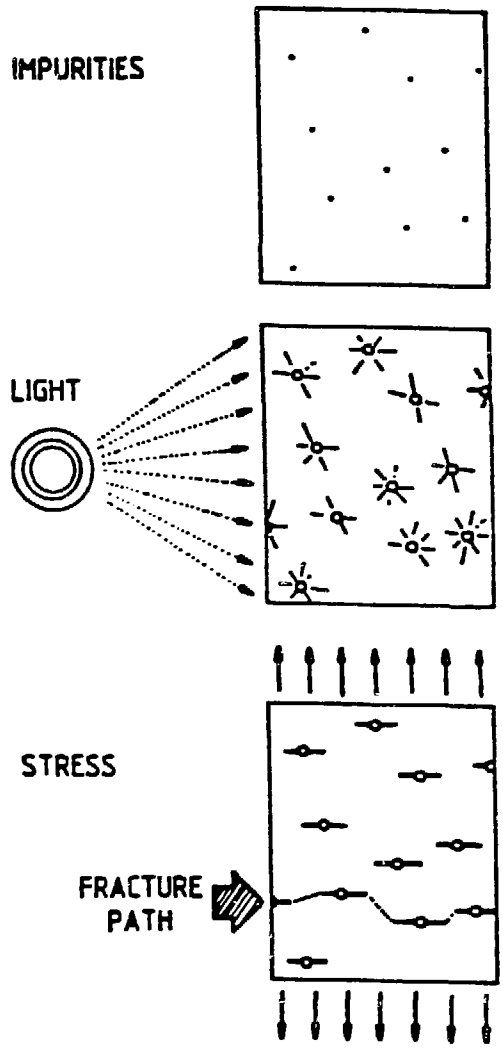

Figure 3.8 Schematic diagram illustrating the effects of ultraviolet radiation and mechanical stress on low density polyethylene to form microcracks that can lead to premature failure [51].

4. WASTE FORM PERFORMANCE

A review of material properties (e.g., Section 3) is helpful in scoping potential performance of binder materials, especially those like polyethylene that have yet to be applied under field conditions. Since the use of polyethylene for waste encapsulation is relatively new, little data are available in the literature on waste form properties or performance. Thus, testing of waste form performance under anticipated disposal conditions has been conducted to:

- provide input data for modeling disposal site performance,
- estimate long-term durability of waste forms,
- demonstrate compliance with existing environmental regulations,
- examine potential synergistic effects of waste-binder interactions on performance and durability, and
- compare performance among potential binder materials.

To this end, polyethylene waste forms containing various forms of radioactive and hazardous wastes have been subjected to a comprehensive set of performance evaluation tests. These include those specified by the U.S. Nuclear Regulatory Commission (NRC) for low-level radioactive waste, the U.S. Environmental Protection Agency (EPA) for hazardous waste, the U.S. Department of Transportation (DOT) for solid oxidizers, and other testing to confirm waste-binder compatibility. Due to the lack of DOE waste form performance criteria, NRC waste form test criteria were applied. The NRC tests are stipulated in the Technical Position on Waste Form [56], developed in support of 10 CFR 61 [57]. EPA testing for characteristic hazardous waste is defined in 40 CFR 261 [58]. The test for transporting solid oxidizer materials is suggested by DOT in support of 49 CFR 173 [59]. Waste form performance evaluation tests that have been conducted are listed in Table 4.1, along with test methods and criteria for evaluation, where applicable. The following sections will review results from these tests, concentrating on data for sodium nitrate waste encapsulated in polyethylene. Additional details on how tests were conducted, as well as performance data for encapsulation of other waste streams in polyethylene (including sodium sulfate, boric acid, incinerator ash, and ion exchange resins) can be found in references [1], [2], [60], and [61].

Tests were conducted using laboratory-scale (51 mm diam x 102 mm ht; 2 in x 4 in) waste form specimens, containing simulated sodium nitrate salt waste, or actual nitrate salt waste from Rocky Flats Plant. In addition, testing was also conducted on sample cores taken from a pilot-scale (30 gal.) waste form. The pilot-scale waste form was produced during a scale-up feasibility test using a production-scale 4.5 in. extruder to encapsulate simulated sodium nitrate salt waste in polyethylene (see description in Section 5).

Examination and testing of the cored specimens were conducted to demonstrate product quality and correlate test results from laboratory and larger-scale waste forms. Cored samples measured 51 mm x 51 mm x 101 mm (2 in x 2 in x 4 in).

4.1 Waste-Binder Compatibility

Before initiating process development efforts, waste-binder compatibility was examined to confirm that no reactions would occur that could adversely affect either the health and safety of workers during processing operations or the long-term durability of waste forms. Differential scanning calorimetry (DSC) was used to investigate the thermal behavior of nitrate waste and waste components in the presence of polyethylene. Waste stream components comprising more than 5% of the nitrate salt waste compositions for both Rocky Flats Plant and Savannah River Plant were analyzed. Testing was performed at temperatures to 400°C, which is above the decomposition temperature of the major nitrate waste components (e.g., sodium nitrate and sodium nitrite.) This temperature is also over 3 times higher than the processing temperature (120°C), providing a margin of safety. Several of the thermograms obtained by DSC are shown in Figures 4.1 and 4.2. The only observable peaks were characteristic endotherms corresponding to melting points or crystal transitions of the materials. The absence of exothermic peaks at temperatures up to 400°C is indicative of the thermal stability of the polyethylene/nitrate salt waste mixtures.

4.2 Compressive Strength

Measurement of compressive strength is a general indication of a waste form's mechanical integrity and its ability to withstand loading pressures associated with stacking of waste forms and overburden from soil or engineered barrier materials. Polyethylene itself is a nonrigid plastic with no discrete brittle fracture yield point under compressive load. However, when combined with dry solid wastes (i.e., aggregates), polyethylene waste forms subjected to compressive strength testing do exhibit measurable yield strength behavior. Thus, ASTM D-695, "Standard Method of Test for Compressive Properties of Rigid Plastics" was used. Results presented in Figure 4.3 indicate that waste form compressive yield strength varies with waste loading, from a minimum of 7.03 MPa (1,020 psi) for 70 wt% sodium nitrate, to a maximum of 16.3 MPa (2,360 psi) for 30 wt% sodium nitrate. All samples tested were well above minimum NRC strength criteria of 0.41 MPa (60 psi). Compressive yield strength data for the cored 60 wt% sodium nitrate salt pilot-scale specimen compared favorably (within about 8%) with laboratory-scale data.

Table 4.1 Waste Form Test Methods

Test	Method	Test Criteria[a]
NRC:		
Compressive strength	ASTM D-695	Compressive Strength ≥ 60 psi
90-Day Water Immersion		Compressive Strength ≥ 60 psi
Thermal Cycling	ASTM B-553	Compressive Strength ≥ 60 psi
Leachability (90 days)	ANS 16.1	Leachability Index > 6.0
Irradiation - 10^8 rad	Gamma Irradiator or Equivalent	Compressive Strength ≥ 60 psi
Biodegradation		
Fungus Attack	ASTM G-21	No observed fungal growth Compressive Strength ≥ 60 psi
Bacteria Attack	ASTM G-22	No observed bacterial growth Compressive Strength ≥ 60 psi
EPA:		
Hazardous Constituent Leachability	TCLP EP-Tox	Constituent Dependent Constituent Dependent
DOT:		
Solid Oxidizer	Test for Solid Oxidizing Substances	Comparison with reference oxidizers

[a] The minimum strength for generic waste forms specified by NRC is 60 psi. However, maximum practical compressive strengths for a given solidification agent are required. Minimum compressive strength for hydraulic cement waste forms is 500 psi.

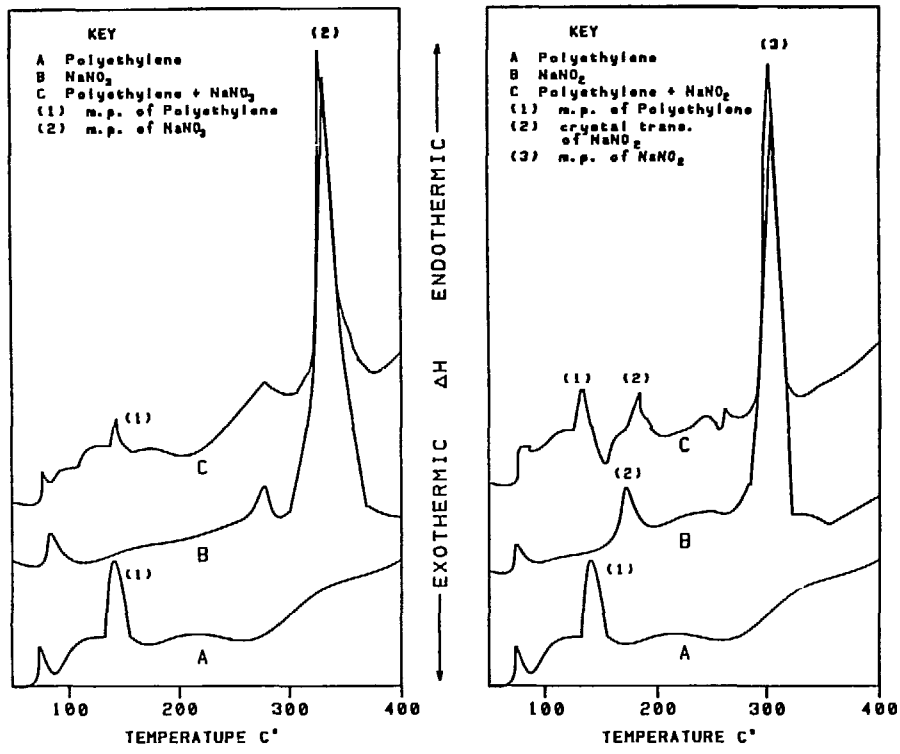

Figure 4.1 Differential scanning calorimetry thermogram for polyethylene containing 50% sodium nitrate ($NaNO_3$) or sodium nitrite ($NaNO_2$).

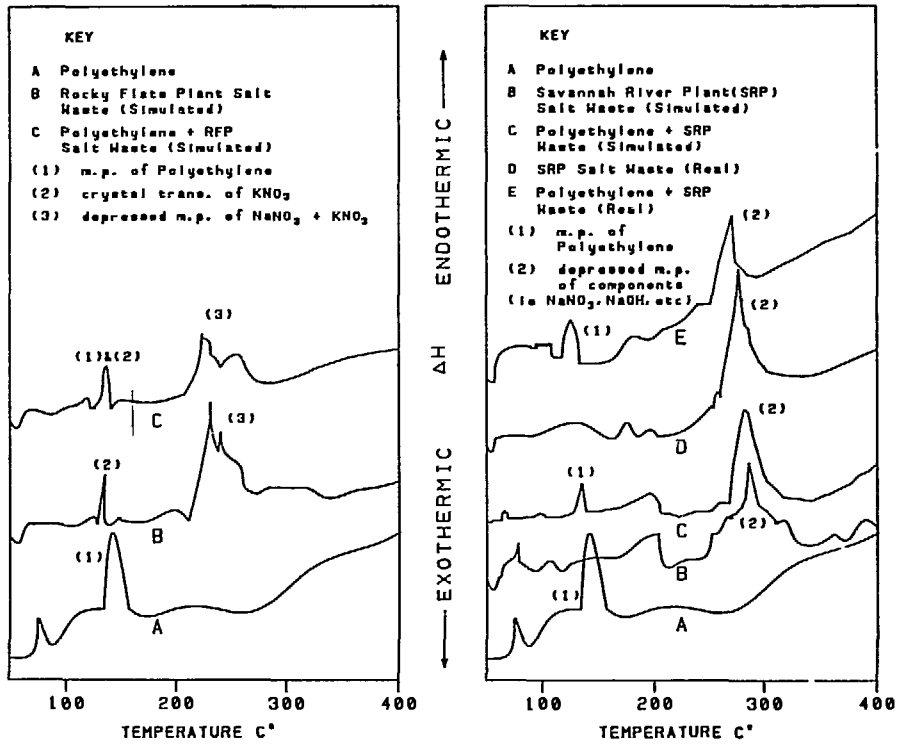

Figure 4.2 Differential scanning calorimetry thermogram for polyethylene containing 50% actual or simulated nitrate salt waste.

Table 4.2 Compressive Yield Strength of Cored Pilot-Scale Polyethylene Waste Forms Containing 60 wt% Sodium Nitrate

Test Description	Compressive Yield Strength, MPa (psi)[a,b]
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.

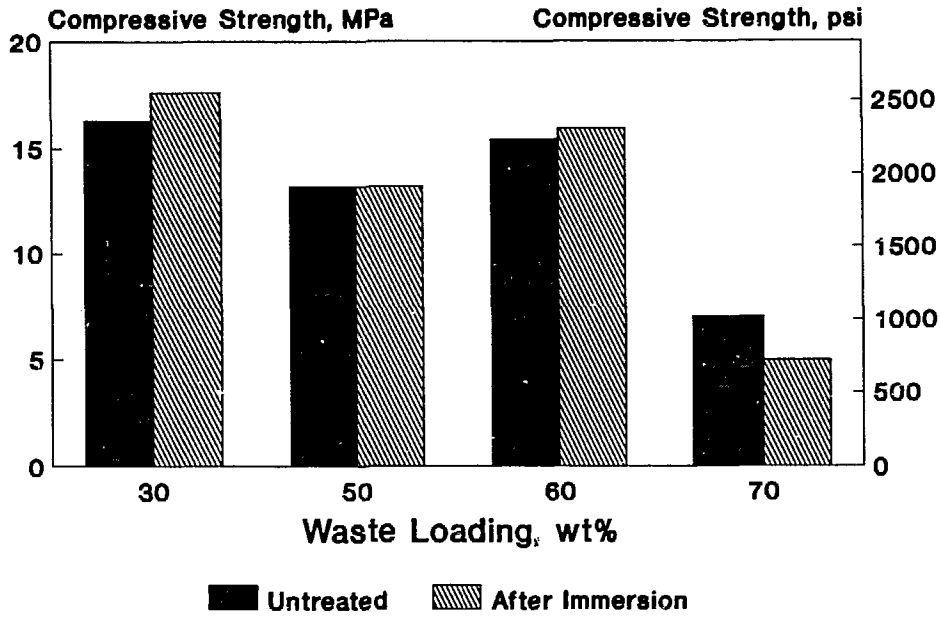

Figure 4.3 Compressive yield strength of polyethylene waste forms containing sodium nitrate salt, untreated and after 90 days in water immersion.

4.3 Water Immersion Testing

Despite efforts to reduce infiltration of water into the disposal environment, waste forms may be subjected to periodic exposure to aqueous conditions in the form of percolation water and/or groundwater. Depending on the composition of contained waste and the physical properties of the waste form, such conditions have been shown to cause swelling, cracking, dissolution, or exfoliation of the waste form structure. For example, severe loss of structural integrity in portland cement-based waste forms containing sodium sulfate [62] and ion exchange resins [63] when exposed to water, has been well documented. Waste form degradation, in turn, can accelerate container failure, increase contaminant migration, and contribute to deterioration of the disposal structure.

Polyethylene waste forms were subjected to water immersion testing for a period of 90 days, followed by repetition of compressive yield strength testing (results contained in Figure 4.3). In general, no loss of compressive yield strength was observed. Waste forms containing 70 wt% sodium nitrate salt exhibited a reduction of about 30% in compressive yield strength to 4.96 MPa (720 psi), but still exceeded minimum strength criteria by at least one order of magnitude. Specimens were also examined for dimensional changes due to swelling. Average change in length was +0.2%, while change in diameters averaged -0.1%. Such slight dimensional changes are not expected to impact stability or long-term durability of polyethylene waste forms under actual conditions.

4.4 Thermal Cycling

Thermal cycle testing was performed to determine the effects of extreme temperature environments that waste forms may experience during storage, transportation, or disposal. Testing was conducted in accordance with the procedures of ASTM B-553, "Standard Method of Test for Thermal Cycling of Electroplated Plastics." Cored specimens from the pilot-scale waste form were cycled between temperature extremes of -40°C and +60°C for a total of 30, five-hour periods. Upon completion of thermal cycling, specimens were subjected to compressive yield strength testing. Results presented in Table 4.2 show that no statistically significant changes in yield strength occurred as a result of thermal cycling.

4.5 Biodegradation

The ability of a waste form to resist microbial degradation is an important consideration for maintaining long-term durability. Review of the literature on biodegradation of plasitics (Section 3.2.1) indicated that polyethylene is not susceptible to biodegradation. Previous biodegradation testing of

polyethylene waste forms (containing sodium sulfate, boric acid, incinerator ash, and ion exchange resins) resulted in zero growth of microorganisms [2]. Nevertheless, testing of polyethylene waste forms containing sodium nitrate and blanks containing no waste was conducted to provide additional documentation on durability. Testing was conducted 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." Six replicate specimens were prepared from the pilot-scale polyethylene/sodium nitrate waste form for each test. Blank control specimens consisting of the same batch of polyethylene were tested concurrently. These tests provide ideal conditions for microbial growth (i.e., proper moisture, temperature, and nutrients), in contrast to actual disposal conditions, so they represent a conservative estimate of potential biodegradation of waste forms. On completion of the 21 days incubation, no fungal or bacterial growth was observed on any of the test specimens. Samples were then tested for compressive yield strength. The mean compressive yield strength of 12 biodegradation specimens with waste (Table 4.2) was 10.1 ± 1.8 MPa (1,460 ± 255 psi.) Mean compressive strength for control specimens was 14.2 ± 0.3 MPa (2,060 ± 45 psi), or about 29% greater than the bio-test waste forms. Apparent loss of strength cannot be attributed to biodegradation, however, since no growth was observed. A re-examination of biodegradation specimens revealed an average weight loss following bio-testing of about 14%, resulting in a similar reduction in density. This was due to solubilization of nitrate salts in cored waste form specimens, in both the nutrient agar and sterilization solvents. Such solubilization is greatly accelerated by the presence of freshly cut surfaces on each face of the cored samples, and does not occur under ordinary processing. Figure 4.4 shows a clear relationship between compressive yield strength and waste form density for both bio-test and untreated specimens.

4.6 Radiation Stability

As discussed in Section 3.2.2, exposure of polyethylene to radiation can cause increased crosslinking, resulting in potential changes in material properties. To determine the impact of irradiation on compressive yield strength, waste form specimens prepared from the pilot-scale sodium nitrate waste form 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. As seen in Table 4.2, average compressive yield strength of irradiated waste forms increased by about 18% over un-irradiated control specimens. These results confirm literature data that predict improvements in polyethylene strength with exposure to radiation doses associated with low-level waste.

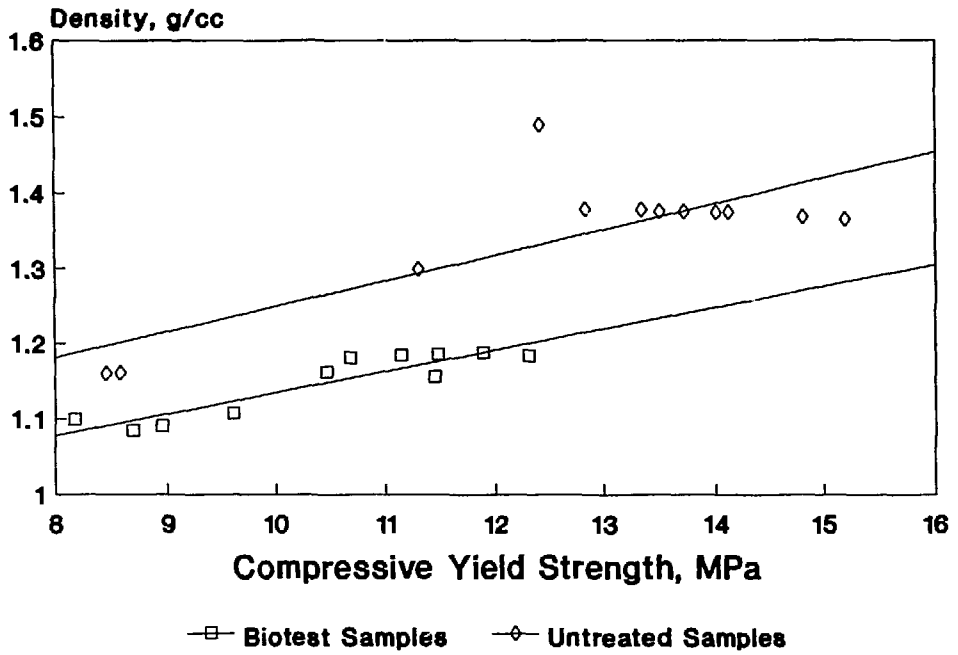

Figure 4.4 Comparison of compressive yield strength vs. waste form density for waste forms undergoing ASTM G-21 and G-22 biodegradation testing and control (untreated) samples. Test specimens consisted of 60 wt% sodium nitrate in polyethylene, and were cored from a pilot-scale (30 gal.) waste form.

4.7 Leachability of Radioactive Constituents

Leachability is a measure of the waste form's ability to retard the release of radioactive and hazardous constituents into the accessible environment. Many types of leaching tests have been devised to simulate different conditions, but because of the large number of variables that must be taken into account, no simple test accurately replicates actual leaching conditions in disposal. As its name implies, the ANS 16.1 Standard, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes" was designed as a standardized laboratory method for characterizing the leaching behavior of low-level waste forms to enable evaluation of independent data on a common basis. These procedures do not simulate waste form leaching under actual conditions, but allow a comparison of the relative leachability of various waste-binder combinations. For these reasons, the ANS 16.1 leach test has been adopted by the NRC in support of 10 CFR 61 disposal regulations.

Leach testing of laboratory-scale polyethylene waste forms containing 30, 50, 60, and 70 weight percent sodium nitrate was conducted for 90 days in accordance with procedures outlined in ANS 16.1. Rather than adding radioactive tracers, release of sodium nitrate, as sodium, was monitored. Results are given in Table 4.3 in terms of average values for cumulative fraction leached, leach rate, and leach index. The leach index is a dimensionless figure-of-merit that quantifies the relative leachability for a given waste type/solidification agent combination. Since 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 (i.e., improved retention) of contaminants. Leach indices, plotted in Figure 4.4, ranged from 11.1 for 30 wt% sodium nitrate loading, to 7.8 for 70 wt% sodium nitrate loading, showing a clear relationship between leachability and waste loading. This behavior is expected for the leaching of highly soluble salts such as sodium nitrate.

Table 4.3 ANS 16.1 Leach Test Data for Sodium Nitrate in Polyethylene Waste Forms

Weight Percent $NaNO_3$	Cumulative Fraction Leached	Leach Rate (s^{-1})	Leach Index
30	0.9	8.4×10^{-10}	11.1
50	6.3	6.0×10^{-9}	9.7
60	15.0	1.1×10^{-8}	9.0
70	73.4	1.5×10^{-7}	7.8

4.8 Leachability of Hazardous Constituents

Sodium nitrate salt from Rocky Flats Plant contains chromium in levels above those established by the EPA defining characteristic hazardous wastes. Thus, this salt 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) [58]. The leaching procedure specified in the original version of this regulation was the Extraction Procedure Toxicity test (EP Tox) [64], but it was recently superseded by the Toxicity Characteristic Leaching Procedure (TCLP) [65]. These tests were designed to approximate leaching conditions at a sanitary landfill, to determine the potential environmental impact of disposal if the waste were

not subject to RCRA control. The primary differences between the two procedures are: (i) the TCLP no longer allows testing of monolithic waste forms, and (ii) the TCLP requires a more vigorous method of agitation, making it a more conservative test. Both procedures specify maximum allowable concentrations for eight metals (including chromium) as well as a number of organic compounds. Results of EP Tox and TCLP tests for polyethylene samples containing nitrate salt waste from Rocky Flats are compared with untreated waste in Table 4.4, where data are given for 4 of the 8 toxic metals established by EPA. Concentrations of chromium in excess of allowable limits for the untreated waste were reduced below the levels defining characteristic wastes when encapsulated in polyethylene.

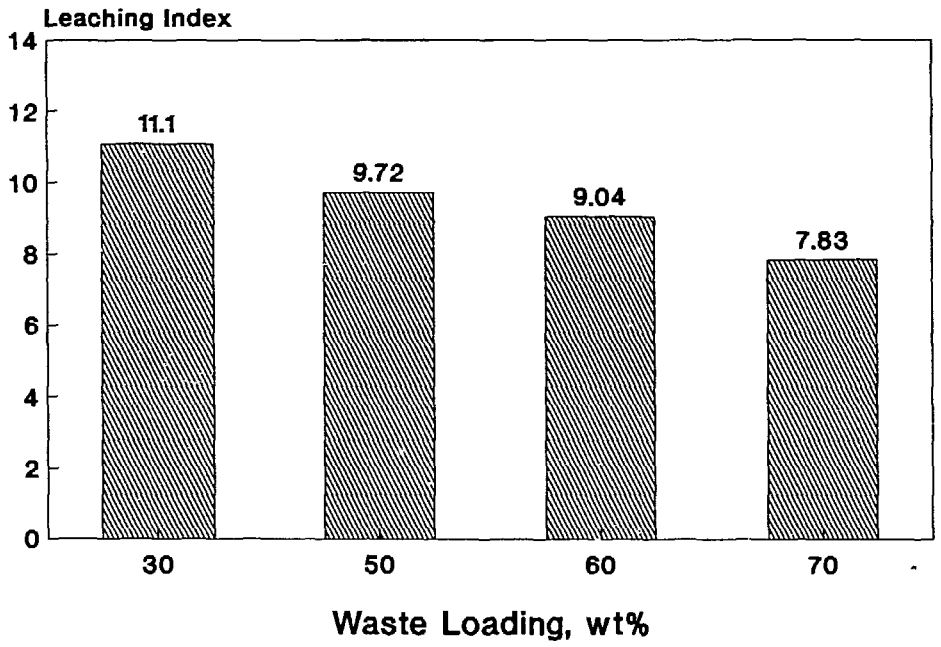

Figure 4.5 Leaching index determined according to the ANS 16.1 Leach Test as a function of sodium nitrate waste loading for polyethylene waste forms.

Table 4.4 Results from Extraction Procedure Toxicity Test (EP Tox) and Toxicity Characterization Leaching Procedure (TCLP) for Rocky Flats Plant Nitrate Salt Encapsulated in Polyethylene[a]

	Concentrations of Criteria Metals, ppm			
Sample Tested	Cr	Cd	Pb	Ba
RFP Nitrate Salt	9.0	0.4	0.5	<0.5
60 wt% RFP Salt in LDPE	3.6	0.2	0.3	<0.5
60 wt% RFP Salt in LDPE[b]	0.8	0.1	0.2	<0.5
EPA Allowable Limit	5.0	1.0	5.0	100

[a] Data for TCLP test, except where noted.
[b] Data for EP Tox test.

4.9 Flammability Testing

Because of its strong oxidizing potential, nitrate salt can be hazardous if involved in an accidental fire during shipping or storage. Several tests were conducted to quantify flammability hazards of nitrate salts encapsulated in polyethylene. These include testing of self-ignition temperature and the U.S. Department of Transportation (DOT) test for solid oxidizing materials.

The self-ignition temperature for combinations of sodium nitrate, sodium nitrite and polyethylene was determined in accordance with ASTM D-1929, "Standard Method of Test for Ignition Property of Plastics." This test is conducted in a hot air furnace under controlled air flow conditions. Results presented in Table 4.5 indicate that the self-ignition temperatures for polyethylene/nitrate mixtures are lowered about 17%, compared with polyethylene alone. The flash-ignition temperature of low density polyethylene was measured at 405°C, and when combined with 60 wt% sodium nitrate, was 380°C.

Table 4.5 Self-Ignition Temperatures of Polyethylene with Nitrate Salt and Salt Waste Components[a]		
Specimen	Specimen Temperature at Ignition Point, °C ± 5 °C	Air Temperature at Ignition Point, °C ± 5°C
Polyethylene	426	430
Polyethylene/50 wt% $NaNO_3$	380	381
Polyethylene/30 wt% $NaNO_3$	362	360
Polyethylene/50 wt% $NaNO_2$	360	358
Polyethylene/70 wt% $NaNO_2$	363	359
Polyethylene/50 wt% SRP Nitrate Salt	365	365

[a] Testing in accordance with ASTM D-1929, "Standard Method of Test for Ignition Property of Plastics."

The U.S. Department of Transportation has recommended a test to quantify hazards associated with solid oxidizing materials such as nitrates. This method, "Test for Solid Oxidizing Substances" was published by the Canadian Department of Transportation [66] and has been approved by the U.N. Group of Rapporteurs on the Transportation of Dangerous Goods (12/86). It supersedes the one previously recommended by DOT, "Methods for Testing for Oxidizers" [67].

The "Test for Solid Oxidizing Substances" was conducted at BNL to determine effects of polyethylene encapsulation on the oxidization potential of Rocky Flats Plant sodium nitrate salt waste. Results indicated that the nitrate salt solidified in polyethylene burned significantly slower (by a factor of 8 to 33 times) and less violently than any of the reference oxidizing materials (ammonium persulfate, potassium perchlorate, and potassium bromate). Compared to unsolidified sodium nitrate salt, the waste form test samples burned about 16 times slower. The solidified waste burned only about 1.3 times faster than plain polyethylene. Based on these results, sodium nitrate solidified in polyethylene is not classified as an oxidizer by the DOT, and thus does not need to meet regulations for shipping of oxidizers.

5. PROCESSING AND SCALE-UP

Several processing techniques were considered for encapsulation of wastes in polyethylene, including batch heating vessels, wiped film evaporators, and screw extruders. Based on consideration of processing ease, quality control, and the use of a proven or available technology, extrusion was selected [1]. This process simultaneously heats, mixes, and conveys the waste and binder, so that a homogeneous, molten mixture is extruded into a container for cooling. Once cooled below the melting temperature of polyethylene (120°C), a monolithic waste form is ensured. A simplified schematic diagram of a single-screw extruder is shown in Figure 5.1.

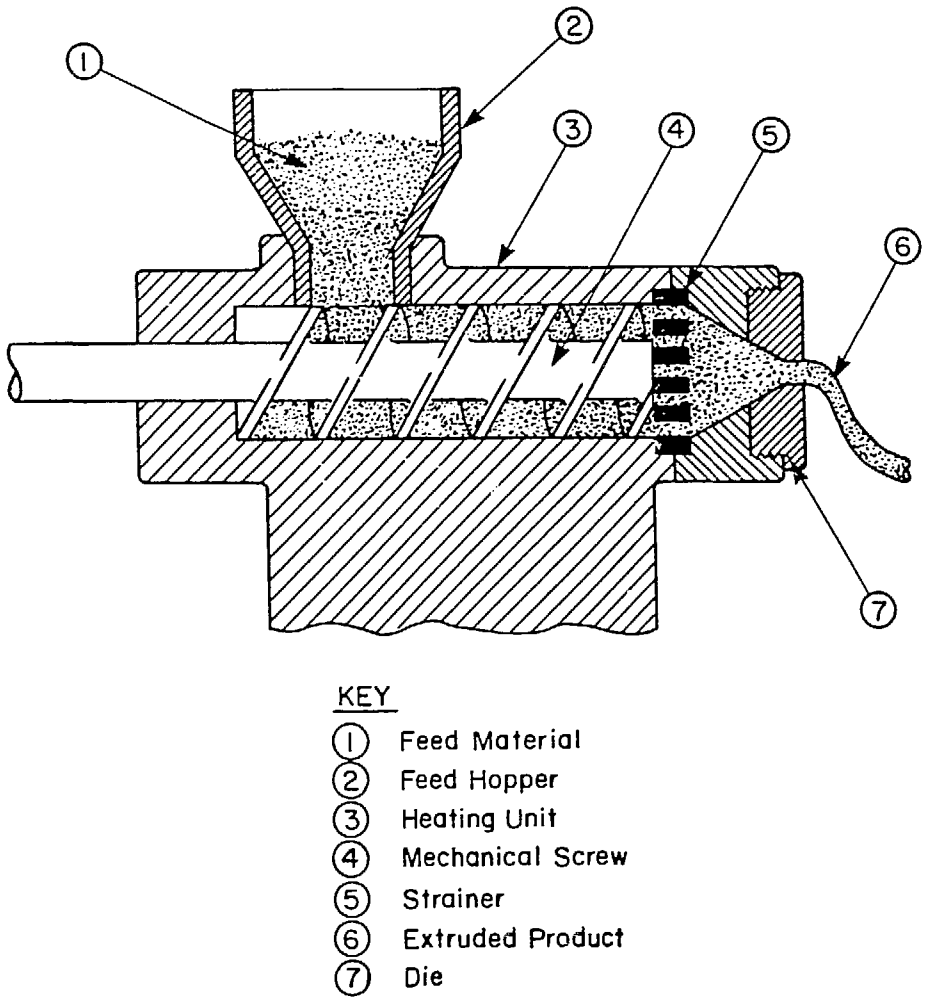

Figure 5.1 Sectional view of a simplified screw extruder. The sketch depicts flow of material from the hopper to the output die, where it is extruded in a molten state.

Process development for encapsulation of nitrate salt waste in polyethylene was performed using a laboratory-scale plastics extruder (32 mm; 1.25 in. diameter screw) as shown in Figure 5.2. [1,2,61]. Envelopes of potential and optimal operating ranges were defined for critical process parameters such as temperature, pressure, feed rate, extrusion rate, and solidification kinetics. The impact of other relevant parameters, including polyethylene flow properties (i.e., melt index), waste-binder mixing techniques, waste pre-treatment requirements, and power needs also were investigated. Some of these parameters are reviewed briefly to provide background to the discussion on scale-up.

Temperature: Temperature is an important parameter in processing polyethylene, because it influences processibility and product quality. For waste encapsulation, minimal temperatures are preferred to reduce potential volatilization of contaminants. Typical process temperatures for waste encapsulation ranged between 125°C and 150°C.

Pressure: Pressure is a function of many factors including the type of polyethylene used, waste characteristics, and extrusion parameters such as screw design, temperature and rate. Moderate pressures in the range of 1 - 20 MPa (up to several thousand psi) are desirable for processing to enhance mixing and delivery of mixture to the mold.

Process Rates: Feed and extrusion rates can vary based on waste loading and characteristics; these must be coordinated to avoid jamming or starving conditions. The lab-scale extruder was operated with an output rate between 1 kg/hr (2.2 lbs/hr) and 9 kg/hr (20 lbs/hr).

Melt Index: As discussed in Section 2, melt index describes a material's ability to flow at 190°C. For optimal processing of laboratory-scale waste forms, a melt index of 55 g/10 min was selected.

Feed Method: When using a stock (static hopper) feed system, density and particle size differences led to segregation of waste and binder, creating a heterogeneous mixture. Separate dynamic feeders for waste and binder were used to overcome these difficulties and provide a means of precise control of waste/binder ratios.

Pre-treatment: For optimal extrusion, waste should be dry; granular particles provide best flow characteristics.

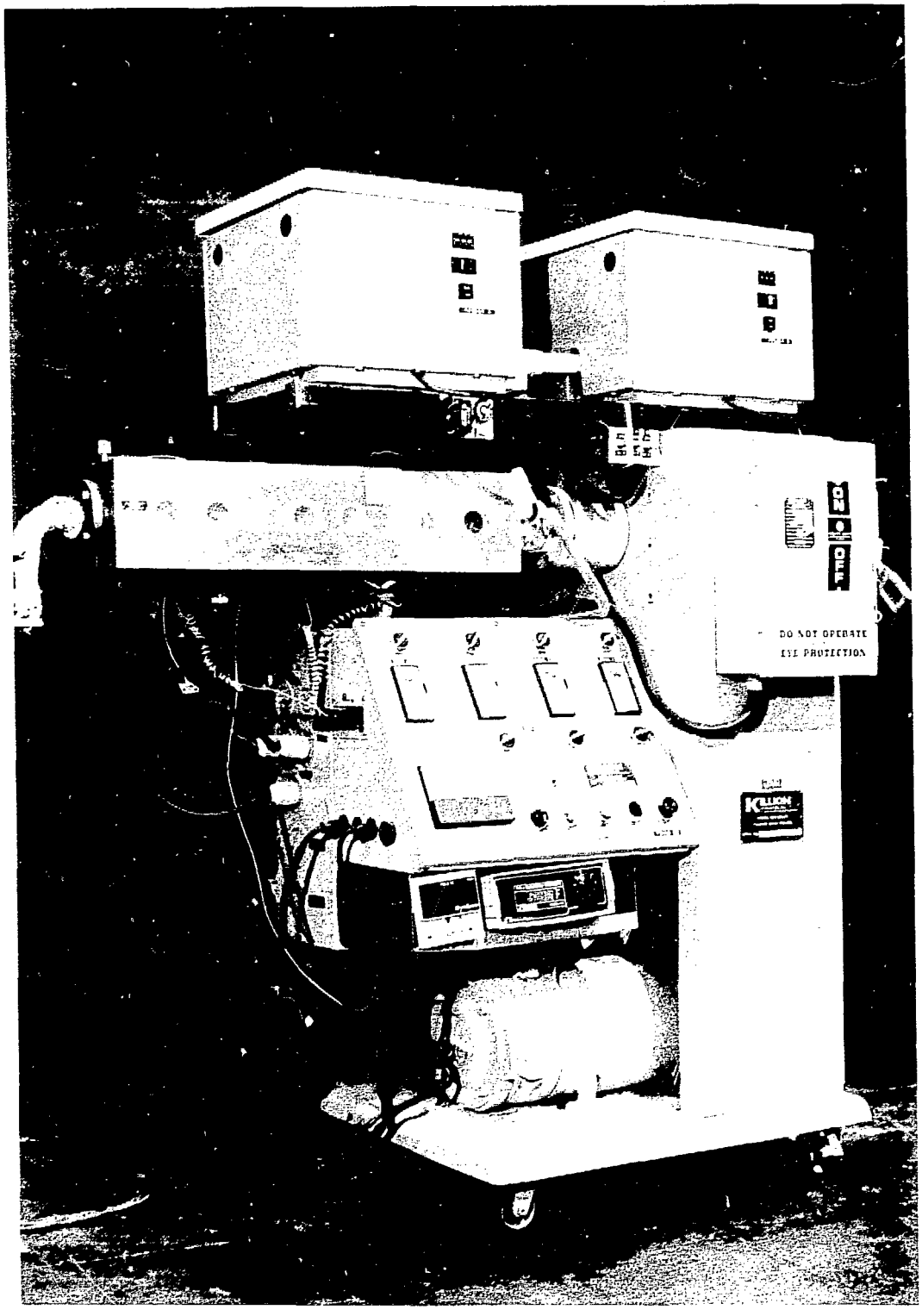

Figure 5.2 Photograph of laboratory-scale extruder with separate dynamic feeders for waste and binder.

Based on consideration of these parameters and overall processibility, maximum waste loading for sodium nitrate salt encapsulation in polyethylene was determined to be 70 wt%. This compares with 13 wt% nitrate salt loading for cement formulations used at Savannah River (i.e. Saltstone) [68], and about 20 wt% nitrate salt in cement formulations developed at West Valley [69], as shown in Figure 5.3. With a nitrate salt/polyethylene product density of 1.67 g/cm^3 (104 lb/ft^3), this equates to about 230 kg (508 lbs) of nitrate waste per 208 liter (55 gal) drum. Assuming an annual production rate of a million kilograms (2.2 million pounds) of nitrate salt waste at Rocky Flats, 4,332 drums per year would be required using polyethylene encapsulation. As shown in Figure 5.4, the equivalent number of drums required would be 22,303 using the Savannah River cement formulations, and 15,611 using the West Valley cement formulation.

When bench-scale formulation and testing for the polyethylene encapsulation of nitrate salt was complete, plans were initiated to demonstrate this system using production-scale equipment in conjunction with Rocky Flats Plant. Estimates of necessary production capacity were made based on data from RFP. Sizing of extruder equipment varies over a wide range, from bench-scale equipment (diameter of screw between 0.75 in. and 1.25 in.; 19 mm and 32 mm) to very large machines with screw diameters up to 6 in. or more. Typically, lab-scale extruders can process around 9 - 14 kg/hr (20 - 30 lbs/hr), while production-scale machines can process hundreds or thousands of kg/hr. For the technology demonstration, a 4.5 in. (114 mm) extruder, with output capacities in the range of 900 kg/hr (2000 lb/hr) was selected. Parameter data generated during bench-scale investigations were reviewed to develop a set of required design specifications. A survey of potential vendors was then conducted. Equipment designs were examined to ensure that processing and monitoring requirements could be met using conventional, "off-the-shelf" equipment.

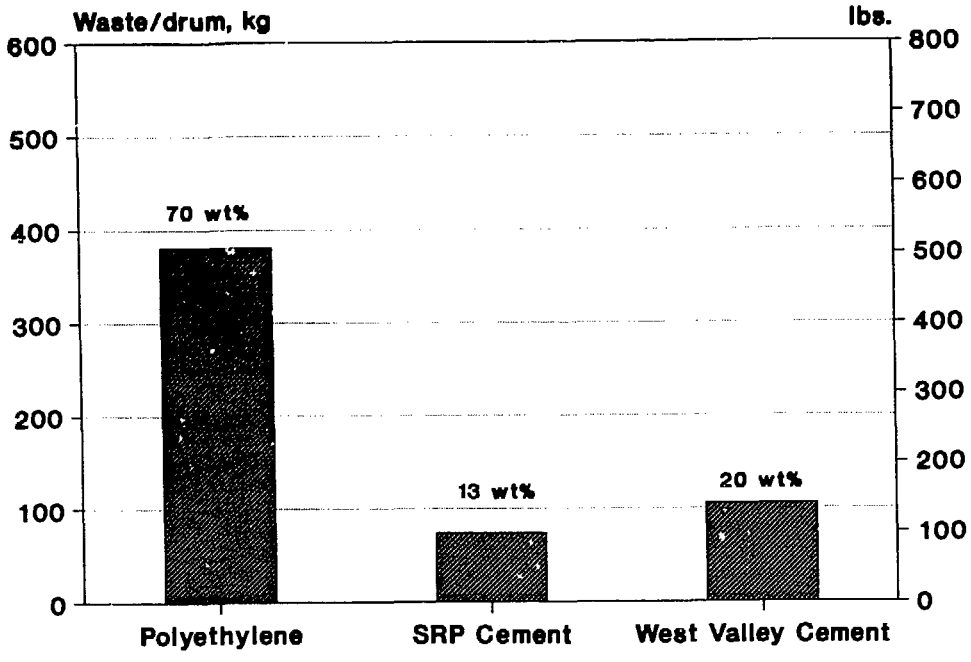

Figure 5.3 Comparison of Rocky Flats Plant (RFP) sodium nitrate encapsulation in polyethylene and cement.

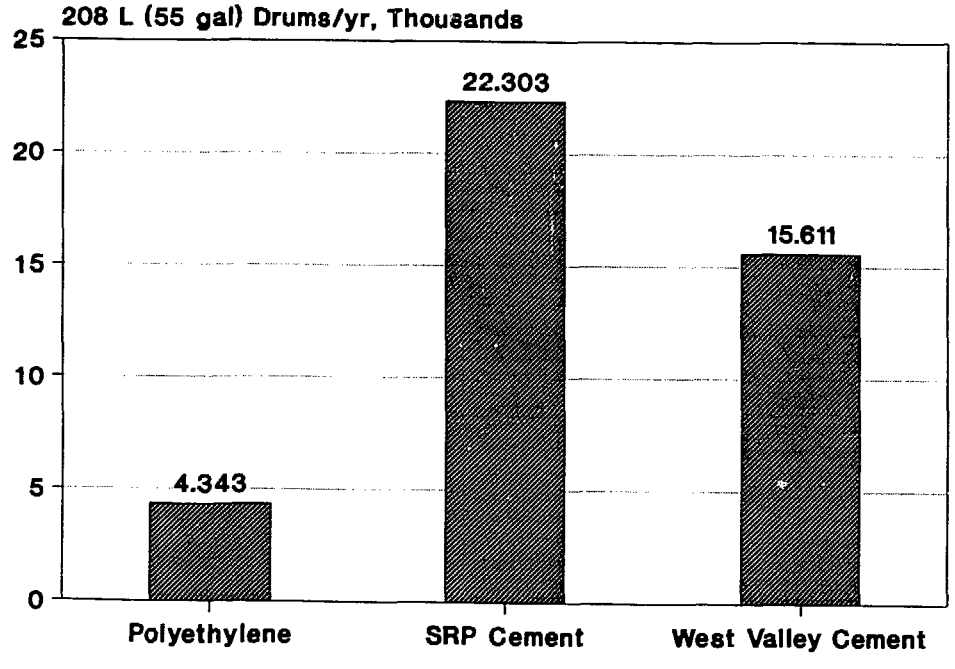

Figure 5.4 Comparison of number of 208 liter (55 gal.) drums required for encapsulation of RFP sodium nitrate salt waste using polyethylene and cement. Based on RFP production of 1 x 10^6 Kg of nitrate salt per year.

Prior to final selection of equipment, a production-scale feasibility test was conducted in order to:

- demonstrate system feasibility using simulated waste,
- examine correlation of processing parameters needed for scale-up with those generated during bench-scale studies,
- confirm rated production capacities for waste-binder combinations,
- investigate effects of screw design on production capacity and product quality,
- perform quality assurance testing on scale-up waste forms,
- conduct waste form performance tests for cored specimens taken from the scale-up specimen and compare results with lab-scale test data.

The production-scale feasibility test was conducted using a 4.5 in. (114 mm) extruder, at laboratory facilities provided by Davis-Standard (Pawcatuck, CT), a manufacturer of extruder equipment. Their facility was designed for feasibility testing; it was equipped with state-of-the-art monitoring and control systems for data collection and process control, as well as a wide selection of extruder and screw designs to accommodate diverse user needs. Personnel from Brookhaven National Laboratory and Rocky Flats Plant attended the demonstration, and the staff at Davis-Standard provided technical assistance.

Two Accu-Rate (Whitewater, WI) Model 610 dry material feeders were purchased and calibrated prior to the demonstration so that an accurate waste loading of 60 wt% sodium nitrate salt could be maintained. Because of the many variables under consideration, a slightly more conservative waste loading was selected (compared with the maximum loading of 70 wt%); optimization of waste loading under full-scale conditions will be performed as part of the Technology Demonstration at RFP. Calibration curves for the polyethylene and sodium nitrate feeders are shown in Figures 5.5 and 5.6, respectively. These feeders are larger versions of the feeders used in bench-scale studies. They were installed above the extruder feed throat in place of a standard static feed hopper.

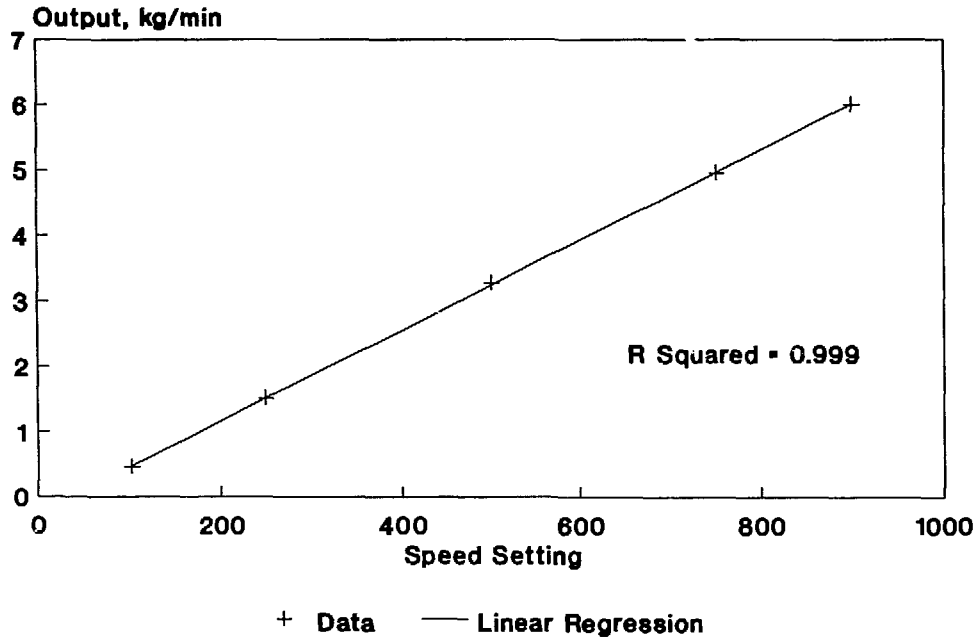

Figure 5.5 Calibration curve for the production-scale polyethylene feeder.

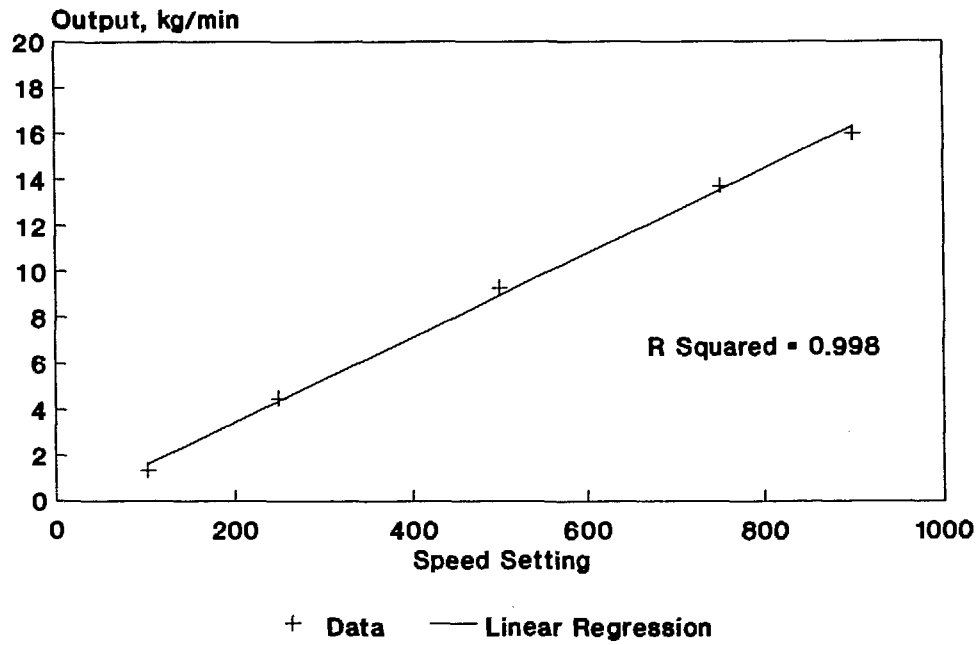

Figure 5.6 Calibration curve for the production-scale nitrate salt waste feeder.

Initial trials resulted in excessive foaming due to air entrainment, an artifact of the physical properties of the simulated granular salt waste and length of the extruder barrel. This problem was quickly remedied by removing the extruder screw and replacing it with one designed to vent gases midstream. As shown in Table 5.1, process settings similar to those developed at BNL were successfully duplicated. Maximum output rates were not attempted, but an output peak of 1,577 kg/hr (3,477 lb/hr) was attained at 65 RPM and steady-state rates in excess of 454 kg/hr (1000 lbs/hr) were easily achieved. A 114 liter drum (30 gal.) of encapsulated sodium nitrate was filled in about 25 minutes. Upon cooling, only minimal shrinkage was observed, indicating a lack of significant voids in the waste form. Figure 5.7 is a simplified process flow diagram of the full-scale polyethylene encapsulation system.

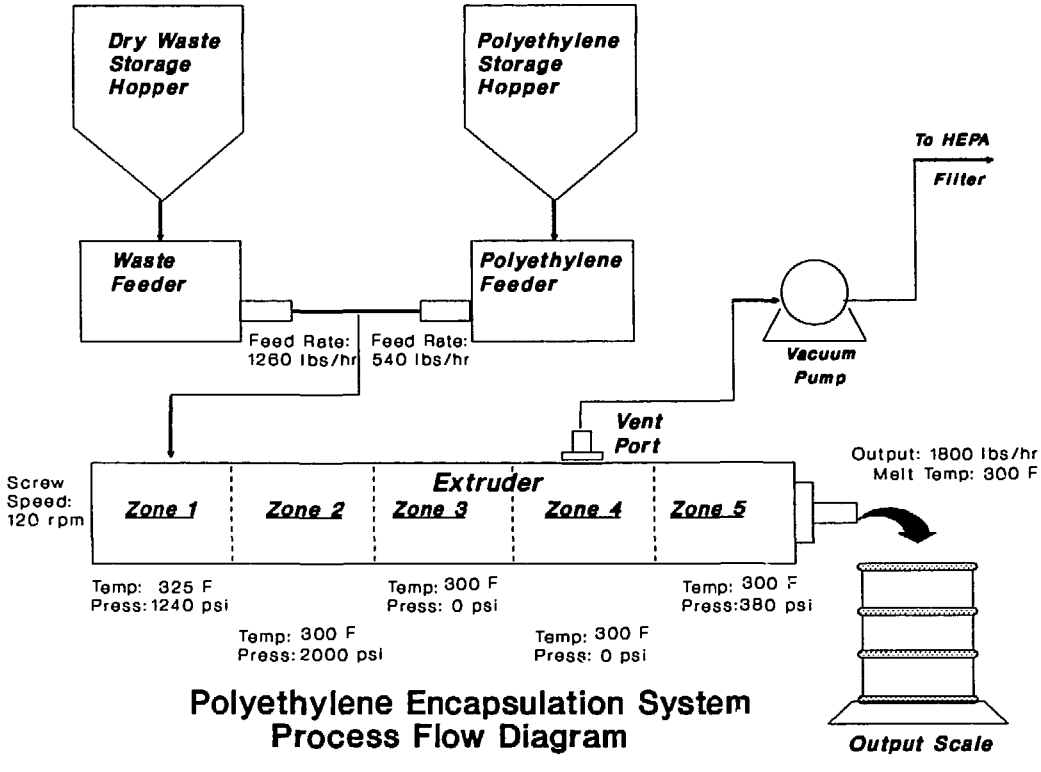

Figure 5.7 Process flow diagram for full-scale polyethylene encapsulation system.

Table 5.1 Parameter Settings and Test Data for Polyethylene Encapsulation Production-Scale Feasibility	
Melt Temperature, °C (°F)	149 (300)
Melt Pressure, MPa (psi)	2.6 (380)
Max. Screw Speed, RPM	65
Steady-state Output, kg/hr (lb/hr)	>454 (1,000)
Max. Output, kg/hr (lb/hr)	1,577 (3,477)
Horsepower at Max Output	354

Testing of the 114 liter (30 gal.) waste form began by cutting the sample in an axial plane to check for void formation, and physical examination of homogeneity. Several small voids are present (the largest measures about 25 mm x 6 mm x 6 mm deep), but no major voids were observed, as seen in the photograph of the cut specimen (Figure 5.8). The interior of the waste form appears well-mixed with salt granules uniformly distributed throughout. It has an even, opaque white color from the nitrate salt. In contrast, polyethylene with no waste has a distinctive translucent color. No sections are visible in which the salt appears highly concentrated or absent.

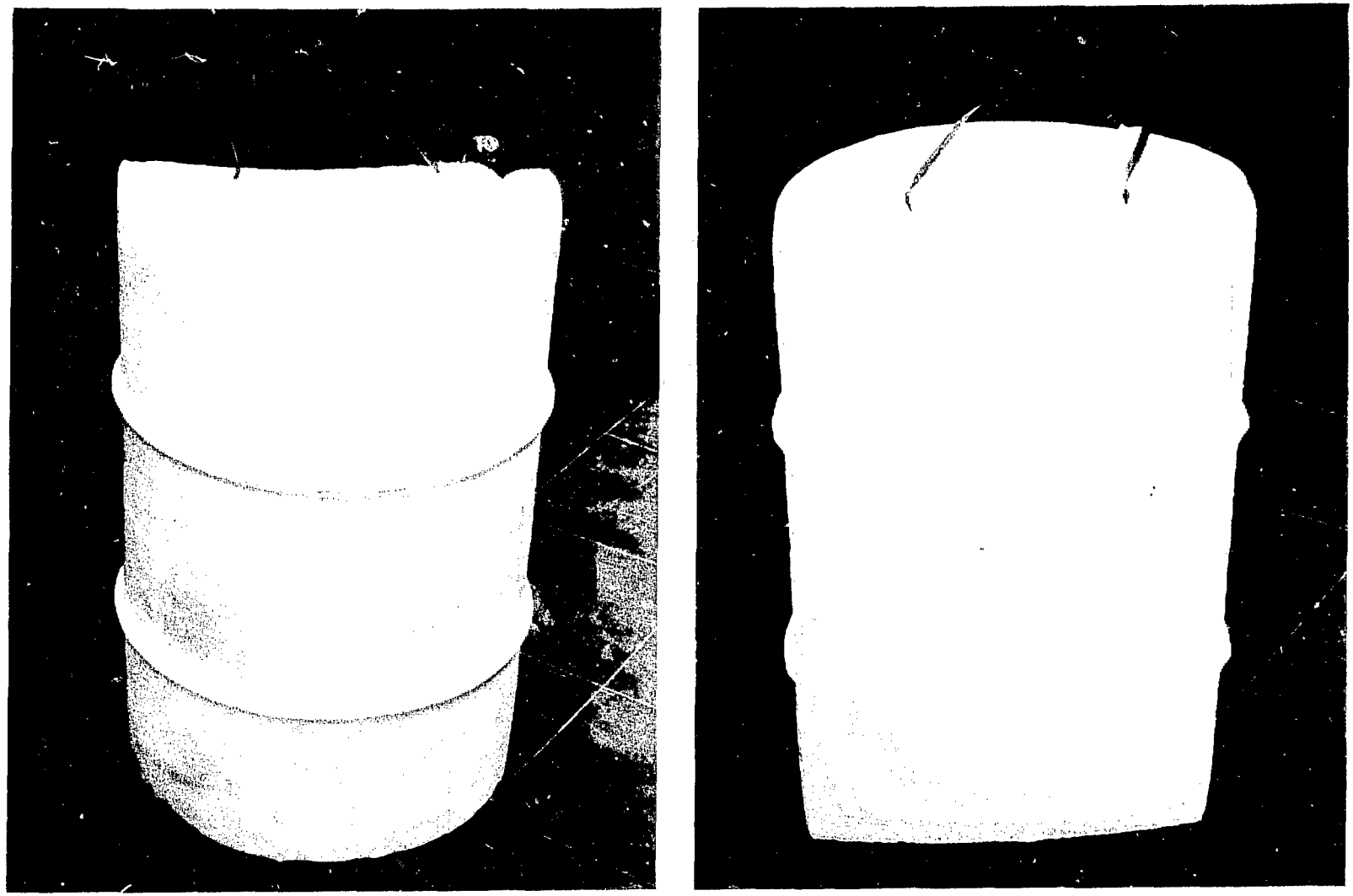

Figure 5.8 Photographs of the polyethylene/sodium nitrate waste form produced during the production-scale feasibility test, showing the outer surface (left) and cross-sectional view (right).

One half of the waste form section was cut further, into a total of 81 rectangular core specimens nominally measuring 51 mm x 51 mm x 101 mm (2 in x 2 in x 4 in). All specimens were weighed and measured and apparent densities calculated. Overall average density was 1.345 ± 0.014 g/cm^3. The small variability in density of cored specimens (< 1%) indicates a homogenous waste form product, feed and mixing processes functioned properly, and product segregation did not occur during cooling/solidification.

In addition to the inspection and density measurements, cored specimens were subjected to several waste form performance tests to provide further quality assurance data for the full-scale system and to compare with similar data generated from tests of waste form specimens produced with laboratory-scale process equipment. Testing of cored specimens included compressive yield strength, thermal cycling, radiation stability, and biodegradation. Results are presented in Table 4.2. These tests were performed using 6 replicate specimens chosen from various sections throughout the waste form. In each case, variation among compressive yield strength replicates was low (± 2.0% for control samples, ± 3.6% for thermal cycled samples, and ± 4.0% for irradiated samples, ± 11.1% for biodegradation samples; errors were calculated at the 95% confidence level) indicating that mechanical properties are uniform throughout the scale-up waste form. Results for the compressive yield strength are in close agreement (within 8 percent) with data from lab-scale samples.

Results of the production-scale feasibility test for the polyethylene encapsulation of nitrate salt wastes can be summarized in the following points:

- Polyethylene encapsulation of at least 60 wt% nitrate salt wastes can successfully be accomplished using a production-scale 4.5 in. (114 mm) extruder, at steady-state rates of at least 454 kg/hr (1000 lb/hr).

- Comparison of bench- and production-scale process data confirm that process scale-up is feasible and that information generated during research and development phases of this project can be applied during the Technology Demonstration phase.

- Quality assurance testing of the 114 liter (30 gal.) waste form produced during the full-scale feasibility test demonstrates that a homogenous waste form with excellent properties can be produced using off-the-shelf production equipment.

- Close agreement of results from waste form performance tests of specimens produced using bench-scale and full-scale systems, indicate the validity and importance of bench-scale R & D, prior to scale-up and demonstration of new technologies.

Based on the results of the R & D activities, together with the information gathered as a result of the full-scale feasibility test, the technology demonstration of polyethylene encapsulation of nitrate salt wastes is scheduled to be held at Rocky Flats Plant during FY 1991.

6. ECONOMIC FEASIBILITY

Section 5 discusses the advantages of polyethylene encapsulation of Rocky Flats nitrate salt waste from the standpoint of increased waste loading per drum, leading to a reduction in the number of processed drums required for storage, transport, and disposal. To determine net economic feasibility, savings resulting from this reduction must be balanced with overall costs including such factors as differences in the cost of binder materials. A simple economic analysis was performed to estimate potential cost savings from polyethylene encapsulation of nitrate salt waste at Rocky Flats. A more rigorous economic analysis of polyethylene solidification of commercial reactor waste reported earlier concluded that significant cost savings could be achieved using this technology [70].

The analysis compares three alternatives for encapsulation of nitrate salt waste at Rocky Flats Plant (RFP): (i) polyethylene, (ii) Saltstone, (portland cement formulation using a concentrated aqueous salt solution) developed at Savannah River Plant (SRP) [68], and (iii) West Valley formulation for concentrated nitrate salt encapsulation in cement [69]. RFP has also used a portland cement-based formulation incorporating higher salt loadings (Saltcrete) developed there, but due to catastrophic failures of these waste forms in storage, this formulation was not considered [71]. Maximum nitrate salt waste loadings of 13 wt% and 20 wt% in the SRP and West Valley formulations, respectively, were taken from published literature [68,69]. Data for polyethylene waste forms were based on R & D work performed at BNL [61].

To simplify economic calculations, an annualized cost economic analysis (which considers present costs and benefits and neglects potential future variations) was performed. Some of the economic data were adapted from previous RFP analyses [71,72] with allowances made for escalation. In addition, RFP data were based on an annual nitrate salt waste production of 1.78 million pounds (800,000 kg) per year, and these calculations were updated to reflect the current RFP production rate of 2.2 million pounds (1.0 million kg) per year. Transportation and disposal costs assume shipment of waste packages to the Nevada Test Site for disposal and are based on RFP data. Equipment costs for all systems were neglected based on the assumption that these costs are roughly equivalent. Operating costs were assumed to be negligible compared to other costs and were therefore excluded. Assumptions used in the calculations are summarized in Table 6.1.

Technical data used in the analysis are summarized in Table 6.2, and cost breakdowns and results are included in Table 6.3. Component and total costs are presented graphically in Figure 6.1, and the percentages of the total cost for the BNL and SRP formulations are presented in Figure 6.2. Taking into account the increased waste loading capacity and lower transport and disposal costs due to fewer and lighter

packages, polyethylene represents a potential cost savings of about $2.7 million per year over the SRP cement formulation, and $1.5 million over the West Valley cement formulation. Although these results are approximate and do not reflect rigorous economic analysis, they should provide a first order estimation of potential savings.

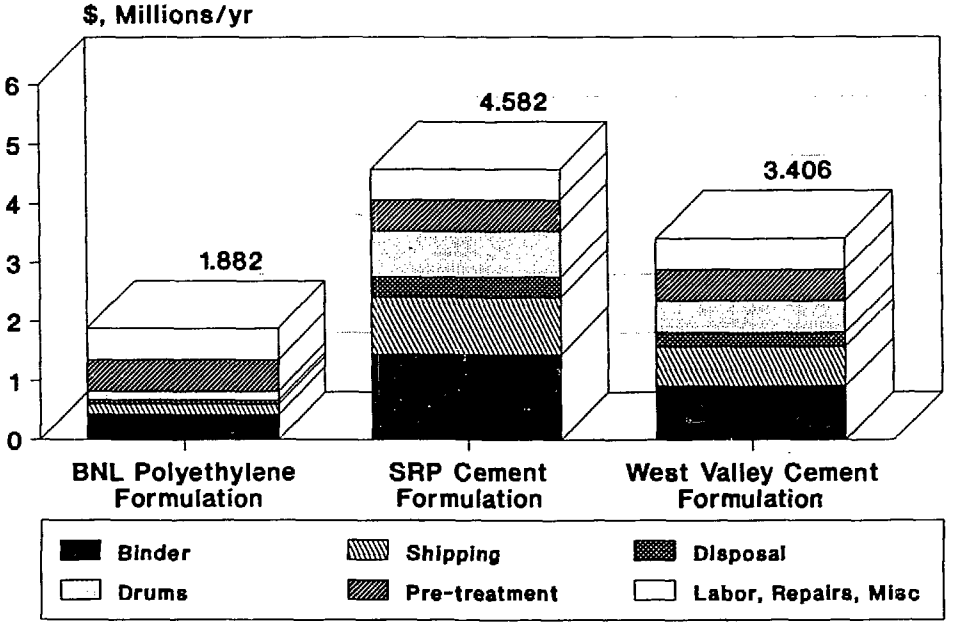

Figure 6.1 Results for economic analysis comparing costs to encapsulate 1 x 10^6 kg (2.2 x 10^6 lbs) nitrate salt per year at Rocky Flats Plant using polyethylene and cement formulations from Savannah River Plant and West Valley.

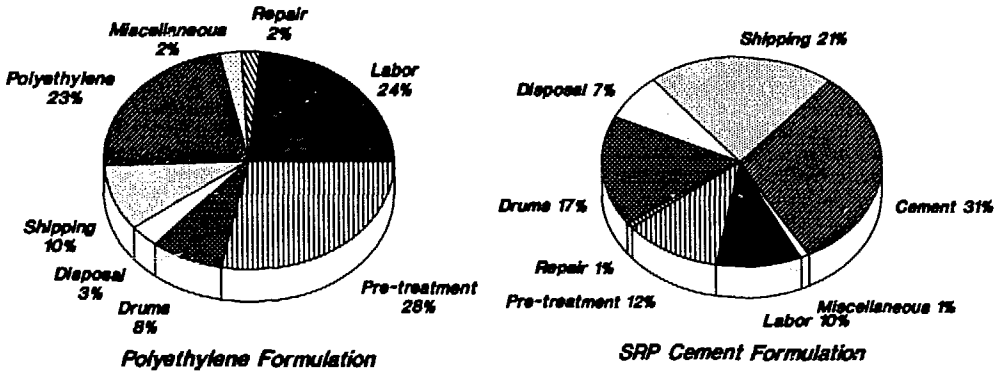

Figure 6.2 Summary of cost breakdown for economic analysis of nitrate salt waste encapsulation at Rocky Flats Plant using polyethylene and Savannah River Plant Saltstone cement formulations.

Table 6.1 Assumptions Used in the Economic Analysis of Nitrate Salt Encapsulation for Rocky Flats Plant

RFP Nitrate Salt Production:	kg/yr	1,000,000	
	(lbs/yr)	(2,204,000)	
Materials Costs: $/kg ($/lb)			
Cement		0.22 (0.10)	
Polyethylene		0.99 (0.45)	
1986 Cost Data:[a]			
		8.07×10^5 kg/yr (1.78×10^6 lbs/yr)	1.0×10^6 kg/yr (2.2×10^6 lbs/yr)
Labor		295,500	365,784
Repair		25,150	31,132
Miscellaneous		30,210	37,395
Waste Pre-treatment		350,860	434,311
Shipping ($/lb)		0.047	
Disposal ($/lb)		0.016	
Drums ($/drum)		28.700	
Escalation @ 5%/yr:		1990$ = 1986$ $(1 + 0.05)^4$	

Equipment and operating costs not included based on the assumption that:
- equipment costs for all systems are roughly equivalent
- operating costs are negligible compared to other costs

[a] Adjusted from data in Ref. [71,72], to reflect increased salt production

Table 6.2 Economic Analysis for Nitrate Salt Encapsulation at Rocky Flats Plant

	Polyethylene	RFP Cement	West Valley Cement
Waste Loading (wt% dry salt)	70	13	20
Product Density, g/cm^3 (lb/ft^3)	1.67 (104)	1.70 (106)	1.65 (103)
Waste & Binder, kg/drum (lbs/drum)	329 (725)	337 (743)	328 (724)
Waste/drum, kg (lbs)	230 (508)	45 (99)	64 (141)
Binder/drum, kg (lbs)	99 (218)	292 (644)	264 (583)
Total binder, kg/yr (lbs/yr)	428,377 (944,571)	6,515,841 (14,367,429)	4,126,333 (9,098,564)
Drums/yr	4,343	22,303	15,611
Drum wt, kg/yr (lbs/yr)	49,238 (108,571)	7,768,260 (557,585)	176,999 (390,282)
Total Shipping Wt., kg/yr (lbs/yr)	1,477,162 (3,257,143)	7,768,260 (17,129,014)	5,302,878 (11,692,846)

Table 6.3 Cost Breakdown[a]

	Polyethylene	RFP Cement	West Valley Cement
Labor	444,612	444,612	444,612
Repair	37,841	37,841	37,841
Miscellaneous	45,454	45,454	45,454
Portland Cement	---	1,436,743	909,856
Polyethylene	425,057	---	---
Shipping	186,077	333,127	227,404
Disposal	63,345	333,127	227,404
Drums	151,501	778,055	544,600
Waste Pre-treatment	527,907	527,907	527,907
Total	1,881,795	4,582,299	3,405,673
Unit Cost, $/kg salt ($/lb salt)	1.88 (0.85)	4.58 (2.08)	3.41 (1.55)

[a] Cost data given in 1990$.

REFERENCES

1. Kalb, P.D., and P. Colombo, "Polyethylene Solidification of Low-Level Wastes," BNL-51867, Brookhaven National Laboratory, Upton, NY, October 1984.

2. Franz, E.M., and P. Colombo, "Waste Form Evaluation Program, Final Report," BNL-51954, Brookhaven National Laboratory, Upton, N.Y. September 1984.

3. Johnson, A.J., and P.M. Arnold, "Waste Generation Reduction - Nitrates, Comprehensive Report of Denitrification Technologies," RFP-3899, Rockwell International, March 15, 1986.

4. U.S. Environmental Protection Agency, Identification and Listing of Hazardous Waste, 40 CFR 261, Fed. Reg. 45, 33119, May 19, 1980.

5. Theis, E.N., "Low-density Polyethylene," *Modern Plastics Encyclopedia*, R. Juran, ed., McGraw-Hill, New York, (1989).

6. Henkel, R.N., "Polyethylene and Ethylene Copolymers," *Modern Plastics Encyclopedia*, Vol. 61, No. 10A, J. Agranoff, ed., McGraw-Hill Publications Co., New York, (October 1984).

7. Barnhard, W.S., "Polymer Structure and Properties," *Polymer Processing, Chemical Engineering Process Symposium Series*, No. 49, Vol. 60, American Institute of Chemical Engineers, New York, (1964).

8. "Ethylene Polymers", *Encyclopedia of Polymer Science and Technology,* Vol. 6, P. 275, N.M. Bikales, ed., Interscience Publishers, New York, (1967).

9. Albertsson, A., S.O. Andersson, and S. Karlsson, "The Mechanism of Biodegradation of Polyethylene," *Polymer Degradation and Stability,* 18, pp. 73-87, (1987).

10. Brink, R.H., "Biodegradation of Organic Chemicals in the Environment," *Environmental Health Chemistry,* Ann Arbor Science Publishers, Ann Arbor MI, (1981).

11. Potts, J.E., R.A. Clendinning, and W.B. Ackart, "The Effect of Chemical Structure on the Biodegradability of Plastics," *Proceedings of Institute of Electrical Engineers, Degradability of Polymers and Plastics,* London, (1973).

12. Potts, J.E., R.A. Clendinning, and W.B. Ackart, "An Investigation of the Biodegradability of Packaging Plastics," EPA-R2-72-046, U.S. Environmental Protection Agency, Washington, D.C., August 1972.

13. Schnabel, W., *Polymer Degradation, Principles and Practical Applications,* Macmillan Publishing Co., New York, (1981).

14. Rodriguez, F., "The Prospects for Biodegradable Plastics," *Chemical Technology,* p.409, July 1971.

15. Barua, P.K., et al, "Comparative Utilization of Paraffins by a Trichosporon Species," *Applied Microbiology*, pp. 657-661, November 1970.

16. Nykvist, N.B., *Plastic Polymers* 42, p. 195 (1974).

17. Chapiro, A., *Radiation Chemistry of Polymeric Systems,* Interscience Publishers, New York, (1962).

18. Spadaro, B., E. Calderaro, and G. Rizzo, "Radiation Induced Degradation and Crosslinking of Low Density Polyethylene," *Acta Polymerica,* 40, No.11, pp. 702-705, (1989).

19. Makhlis, F.A., *Radiation Physics and Chemistry of Polymers,* John Wiley and Sons, New York, (1975).

20. Engel, L., H. Klingele, G.W. Ehrenstein, and H. Schaper, *An Atlas of Polymer Damage, Surface Examination by Scanning Electron Microscope,* Prentice-Hall Inc., Englewood Cliffs, NJ, (1981).

21. de Hollain, G., "Physical Properties of Irradiated Polymers," *Plastics and Rubber: Materials and Applications,* Vol. 5, (3) August 1980.

22. Charlesby, A. *Atomic Radiation and Polymers,* Pergamon Press, London, (1960).

23. Aslanian, V.M., V.I. Vardanian, M.H. Avetisian, S.S. Felekian, and S.R. Ayvasian, "Effect of Radiation on the Crystallinity of Low-Density Polyethylene," *Polymer,* Vol. 28, April, pp. 755-757, (1987).

24. Bhateja, S.K., "Changes in the Crystalline Content of Irradiated Linear Polyethylene Upon Ageing," *Polymer,* Vol. 23, No.5, pp. 654-655, (1982).

25. Wilski, H., "The Radiation Induced Degradation of Polymers," *Radiat. Phys. Chem.,* Vol. 29, No. 1, pp. 1-14, (1987).

26. Dole, M., Report of Symposium IX "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Maryland, p. 120, (1950).

27. Charlesby, A., *Proc. Roy. Soc. (London),* A215, 187 (1952).

28. Papet, G., L. Jirackova-Audouin, and J. Verdu, "Diffusion Controlled Radiochemical Oxidation of Low Density Polyethylene, Depth Dependence and Morphological Changes," *Radiat. Phys. Chem.,* Vol. 29, No. 1, pp. 65-69, (1987).

29. Black, R.M., and A. Charlesby, "The Oxidation of Irradiated Polyethylene: Radio-Oxidation," *International Journal of Applied Radiation and Isotopes,* Vol. 7, pp. 126-133, (1959).

30. Colombo, P., and R.M. Neilson, Jr., "Properties of Radioactive Wastes and Waste Containers, First Topical Report," BNL-NUREG-50957 prepared for the Nuclear Regulatory Commission by Brookhaven National Laboratory, Upton, NY, January 1979.

31. Barlow, A., J. Biggs, and M. Maringer, "Radiation Processing of Polyolefins and Compounds," *Radiat. Phys. Chem.,* Vol. 9, pp. 685-699, (1977).

32. Sobolev, I., J.A. Meyer, V. Stannett, and M. Szwarc, *J. Polymer Sci.,* 17, p. 417 (1955).

33. Raff, R.A.V., and J.B. Allison, *Polyethylene,* Interscience Publishers, New York, (1956).

34. Whelan, T., and J. Goff, "Low Density Polyethylene - Material Properties," *British Plastics and Rubber,* pp. 41-43, (1988).

35. Gatos, H.C., *J. Chem. Education,* Vol. 31, p.533, (1954).

36. "Bakelite Polyethylene for Paper Coatings," Bakelite Co., p. 8, (1951).

37. "Bakelite Polyethylene for Polyethylene Coatings", Bakelite Co. p. 6, (1951).

38. Hilado, Carlos, J., *Fiammability Handbook for Plastics,* Third Edition, Technomic Publishing Co., Westport CT, (1982).

39. Fenner, O.H., "Chemical and Environmental Properties of Plastics and Elastomers," *Handbook of Plastics and Elastomers,* C.A. Harper, ed., McGraw-Hill, New York, (1975).

40. "Material Safety Data Sheet, Gulf Polyethylene (All Grades)," MSDS Number: PL0001, Chevron Chemical Company, Houston, TX, (1989).

41. Ogata, N., T. Yanagwa, and K. Yoshida, "Effects of Loading Conditions and Temperature on Environmental Stress Cracking of Low-Density Polyethylene," *Journal of Polymer Science: Part B: Polymer Physics,* Vol. 24, pp. 1917-1929, 1986.

42. E.J. Kramer, "Environmental Cracking of Polymers," *Developments in Polymer Fracture - 1,* E.H. Andrews, ed., Applied Science Publishers, London, (1979).

43. R.H. Carey, "Stress Cracking of Polyethylene," ASTM Bulletin No. 167, July 1950.

44. Bikales, N.M., ed., *Mechanical Properties of Polymers,* Wiley-Interscience, NY,

45. Shanahan, M.E.R., C. Chen-Fargheon, and J. Schultz, "The Influence of Spherulitic Size on the Environmental Stress Cracking of Low Density Polyethylene," *Makromol. Chem.* 181, pp.1121-1126, (1980).

46. B. Maxwell, "Modifying Polymer Properties Mechanically," *Chemical Engineering Progress Symposium Series,* No. 49, Vol. 60, American Institute of Chemical Engineers, New York, (1964).

47. Howard, J.B., and W.M. Martin, "Effects of Thermal History on Some Properties of Polyethylene," SPE Journal, pp. 407-412, April 1960.

48. Rogers, C.E., "Stress Cracking of Polyethylene in Organic Liquids," ARO 19329.3MS, U.S. Army Research Office, Research Triangle Park, NC, February 1986.

49. Raab, M., L. Dotulak, J. Kolarik, and J. Pospish, "The Effect of Ultraviolet Light on the Mechanical Properties of Polyethylene and Polypropylene Films," *Journal of Applied Polymer Science,* Vol. 27, 2457-2466, 1982.

50. Giesse, R., and M.A. DePaoli, "Surface and Bulk Oxidation of Low-density Polyethylene Under UV-Irradiation," *Polymer Degradation and Stability,* 21 pp. 181-187, (1988) .

51. Qureshi, F.S., M.B. Amin, A.G. Maadhah, and S.H. Hamid, "Weather-Induced Degradation of Linear Low-Density Polyethylene: Mechanical Properties," *Polym. Plast. Technol.* Eng., 28(7&8), pp. 649-662 (1989)

52. Munro, H.S., "ESCA Studies of the Photo-oxidation and the Gamma Radiation Induced Oxidation of Low Density Polyethylene," *Polymer Degradation and Stability,* 12, pp. 249-259, (1985).

53. La Mantia, F.P., "Natural Weathering of Low Density Polyethylene - Mechanical Properties," *Eur. Polym. J.,* Vol. 20, No. 10, pp 993-995, 1984.

54. Benachour, D. and C.E. Rogers, "Strain-Enhanced Photodegradation of Polyethylene," American Chemical Society, Division of Organic Coating and Plastics Chemistry, Preprints, Vol. 42, pp. 767-769, (1980).

55. Furneaux, G.C., K.J. Ledbury, and A. Davis, "Photo-oxidation of Thick Polymer Samples: The Variation of Photo-oxidation with Depth in Naturally and Artificially Weathered Low Density Polyethylene," *Polymer Degradation and Stability,* 3, pp. 431-442, (1980-81).

56. U.S. NRC, "Technical Position on Waste Form, Revision 1" Final Waste Classification and Waste Form Technical Position Papers, U.S. Nuclear Regulatory Commission, Washington, DC, January 1991.

57. U.S. Nuclear Regulatory Commission, "Licensing Requirements for Land Disposal of Radioactive Waste," Title 10 of the Code of Federal Regulations, Part 61, US NRC, Washington, DC, May 1983.

58. U.S. Environmental Protection Agency, "Identification and Listing of Hazardous Waste," 40 CFR 261, Fed. Reg. 45, 33119, May 19,1980.

59. U.S. Department of Transportation, "Definition of Oxidizer," 49 CFR 173, Fed. Reg. 46, 31294, June 15, 1981.

60. Franz, E.M., J.H. Heiser, and P. Colombo, "Solidification of Problem Wastes Annual Progress Report, BNL-52078, Brookhaven National Laboratory, Upton, NY, February 1987.

61. Heiser, J.H., E.M.Franz, and P. Colombo, "A Process for Solidifying Sodium Nitrate Waste in Polyethylene," *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes, ASTM STP 1033,* P. Cote and M. Gilliam, eds., American Society for Testing and Materials, Philadelphia, 1989.

62. Zhou, H. and P. Colombo, "Solidification of Radioactive Waste in a Cement Lime Mixture," *Proceedings of Waste Management '84, Vol. 2,* Tucson, AZ, (March 1984).

63. Neilson, R.M., Jr., P.D. Kalb, M. Fuhrmann, and P. Colombo, "Solidification of Ion Exchange Resin Waste in Hydraulic Cement," *The Treatment and Handling of Radioactive Wastes,* A.G. Blasewitz et al., eds., Springer-Verlag, New York, (1983).

64. U.S. Environmental Protection Agency, EP Toxicity Test Procedures, 40 CFR 261, Appendix II, Fed. Reg. 45, 33119, May 19, 1980, as amended by Fed. Reg. 48, 14293, April 1, 1983, and Fed. Reg. 50, 663, January 4, 1985.

65. U.S. Environmental Protection Agency, Toxicity Characteristic Leaching Procedure, 40 CFR 261, Appendix II, Fed. Reg. 55, 11863, March 29, 1990.

66. "Test for Solid Oxidizing Substances," Canadian Department of Transportation, TP 2711E, ISSN 0710-0914, 4/87.

67. U.S. Department of Transportation, 49 CFR 173, Appendix C, Fed. Reg. 46, 31294, June 15, 1981.

68. Wilhite, E.L., "Concept Development for Saltstone and Low Level Waste Disposal," DP-MS-86-110, Savannah River Laboratory, Aiken, SC, March 1987.

69. McVay, C.W., J.R. Stimmel, and S. Marchetti, "Cement Waste Form Qualification Report - WVDP Purex Decontaminated Supernatant, Topical Report," DOE/NE/44139-49, West Valley Nuclear Services Co., West Valley, NY, August 1988.

70. Kalb, P.D., and P. Colombo, "An Economic Analysis of a Volume Reduction/Polyethylene Solidification System for Low-Level Radioactive Wastes," BNL-51866, Brookhaven National Laboratory, Upton, NY, January 1985.

71. Petersen, R.D., A.J. Johnson, and K.G. Peter, "Nitrate Salt Immobilization Process Development and Implementation," RFP-3919, Rockwell International, Rocky Flats Plant, Golden, CO, November 1986.

72. Petersen, R.D., A.J. Johnson, and S.D. Swanson, "Application of Microwave Energy for In-Drum Solidification of Simulated Precipitation Sludge," RFP-4148, Rockwell International, Rocky Flats Plant, Golden, CO, August 1987.