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REVIEW OF ENCAPSULATION TECHNOLOGIES

prepared by

Lynn Shaulis

submitted to

Nevada Operations Office
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ABSTRACT

The use of encapsulation technology to produce a compliant waste form is an outgrowth from existing polymer industry technology and applications. During the past 12 years, the Department of Energy (DOE) has been researching the use of this technology to treat mixed wastes (i.e., containing hazardous and radioactive wastes). The two primary encapsulation techniques are microencapsulation and macroencapsulation. Microencapsulation is the thorough mixing of a binding agent with a powdered waste, such as incinerator ash. Macroencapsulation coats the surface of bulk wastes, such as lead debris.

Cement, modified cement, and polyethylene are the binding agents which have been researched the most. Cement and modified cement have been the most commonly used binding agents to date. However, recent research conducted by DOE laboratories have shown that polyethylene is more durable and cost effective than cements. The compressive strength, leachability, resistance to chemical degradation, etc., of polyethylene is significantly greater than that of cement and modified cement. Because higher waste loads can be used with polyethylene encapsulant, the total cost of polyethylene encapsulation is significantly less costly than cement treatment.

The only research lacking in the assessment of polyethylene encapsulation treatment for mixed wastes is pilot and full–scale testing with actual waste materials. To date, only simulated wastes have been tested. The Rocky Flats Environmental Technology Site had planned to conduct pilot studies using actual wastes during 1996. This experiment should provide similar results to the previous tests that used simulated wastes. If this hypothesis is validated as anticipated, it will be clear that polyethylene encapsulation should be pursued by DOE to produce compliant waste forms.

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CONTENTS

FIGURES

TABLES

INTRODUCTION

This report will review micro- and macro-encapsulation technologies and their potential effectiveness to produce storage-compliant wastes. The information in this report was derived from several reports and articles prepared by scientists at the Brookhaven National Laboratory (BNL), Rocky Flats Environmental Technology Site (RFETS), and Idaho National Engineering Laboratory (INEL). The Department of Energy (DOE) is interested in using this technology to store low-level mixed wastes, and over the past 12 years has been supporting the development of encapsulation treatment (Faucette, 1996). Polymer encapsulation has been proposed as the process to produce Resource Conservation and Recovery Act (RCRA)-compliant waste forms for several mixed wastes at RFETS (Armentrout and Faucette, 1996). RFETS has therefore conducted a fair amount of research on encapsulation technology. BNL has also conducted research on encapsulation technology and its application to DOE waste streams. In particular, BNL has examined polyethylene and modified sulfur cement encapsulation while RFETS has focussed on polymer encapsulation.

Encapsulation is a process that coats waste materials in a manner that permits safe storage of the waste. If the waste to be encapsulated contains hazardous or mixed wastes, then the resulting encapsulated product must meet federal (RCRA) and state requirements for storage of these substances. Typically, this means that the encapsulating material must be resistant to leaching and degradation by the contaminants which will be in contact with the encapsulant (40 CFR 268.45). The DOE laboratories that have been testing this technology have not only tested encapsulants for leachability and chemical degradation, they have also tested some encapsulants for: biodegradation; tolerance to irradiation; environmental stress cracking; photodegradation; flammability; compressive strength; and ability to tolerate thermal cycling (Kalb and Colombo, 1984; Kalb *et al.*, 1991b; Kalb *et al.*, 1993). These tests have also shown that encapsulation is an appropriate treatment technology for mixed waste streams including: evaporator concentrate salts, sludges, incinerator ash, ion exchange resins, blowdown solutions, and molten salt oxidation residuals. Additionally macroencapsulation has been proven as an effective treatment of radioactive lead and debris wastes.

Materials that are used as encapsulating agents include cement, modified cement, and two classes of polymers, namely, thermosetting and thermoplastic. Thermosetting polymers, e.g., epoxies, are the product of the chemical reaction between a liquid monomer and a curing agent. They are used to encapsulate powdered waste by mixing the waste with the two thermosetting substances. One of the significant problems with thermosetting encapsulation is the possibility of the waste chemically reacting with the thermosetting agents and thereby preventing solidification (Faucette, 1996). However, thermosetting polymers may successfully be used for macroencapsulation of wastes. Thermoplastic polymers, e.g., polyethylene, are heated above their melting point temperature (110°C) then mixed with powdered waste and poured into a disposal container for cooling and hardening. Because this temperature is sufficiently low, no off-gas treatment is required and no secondary wastes are produced (Faucette, 1996). The following text will discuss microencapsulation and macroencapsulation in more detail. This discussion will describe the processes, types of encapsulants, and the potential durability of the encapsulated products.

DISCUSSION

Microencapsulation

Microencapsulation is a process that thoroughly mixes fine waste particles with an encapsulant prior to or during extrusion (see Figure 1). According to RCRA 40 CFR 268.45, microencapsulation is an alternative treatment standard for hazardous waste, but must produce a final waste that meets the RCRA Toxicity Characteristic Leaching Procedure (TCLP) concentration limits, Method 1311 of EPA Publication SW-846 (Roach, 1996). Microencapsulating materials primarily include cement/grout and polymers. Common cements and grouts, such as Portland cement, are typically considered to be less expensive than polymer encapsulants (at 20 tons/hr, polyethylene would cost \$95 to \$112 per ton of waste ash treated versus \$50 to \$60 per ton for cement; Faucette, 1996). However, if all operation costs are considered, specifically storage, shipping and disposal, then polymer microencapsulation is significantly more cost effective than cement (\$18,744/m^3 for polymer encapsulation versus \$65,707/m^3 for cement; Faucette, 1996). The primary reason that polymer encapsulation is more cost effective when all processes are considered is due to the fact that polymers have a higher waste loading (i.e., more waste per unit encapsulant)

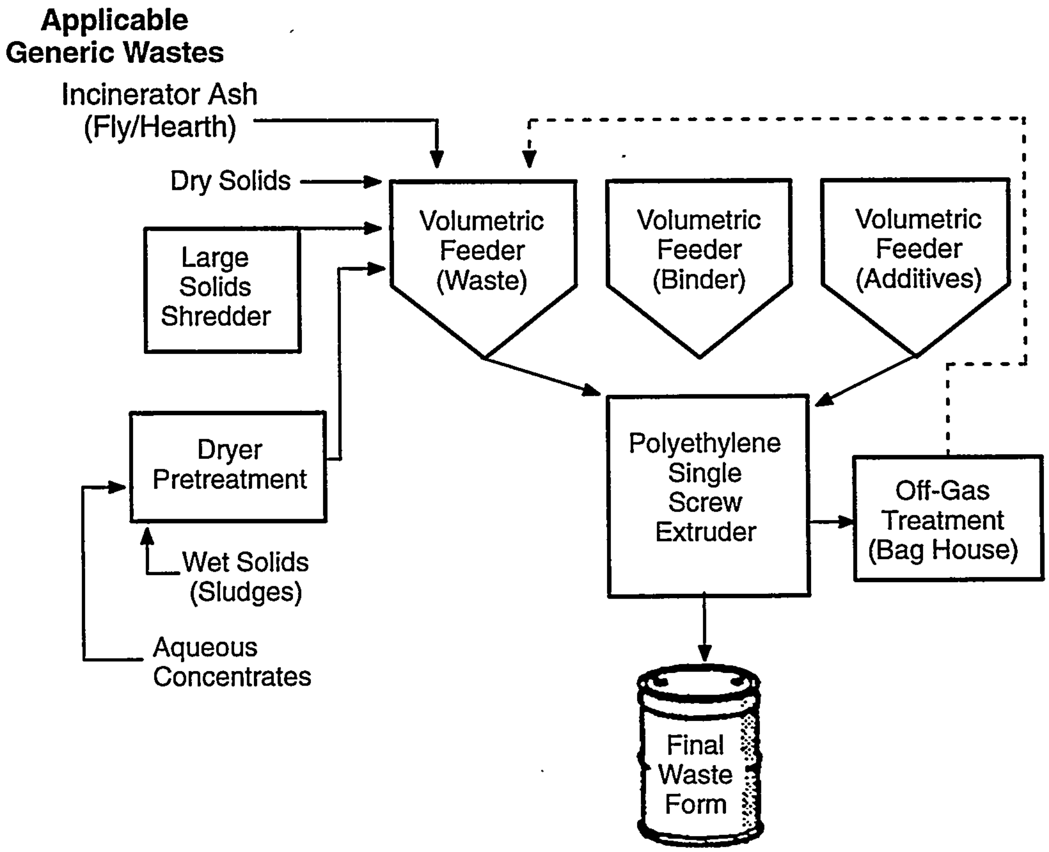

Figure 1. A flow diagram of the microencapsulation process (from Kalb, 1993).

than cement which results in a significantly reduced waste product volume. Figure 2a depicts a cost breakdown and comparison for polyethylene and concrete encapsulation. Figure 2b depicts the maximum waste loadings for the two different encapsulants. However, polymer encapsulation is not amenable to wastes which contain greater than 2% by weight moisture or volatile organic content. This is due to the fact that the heat generated during waste/polymer mixing can produce

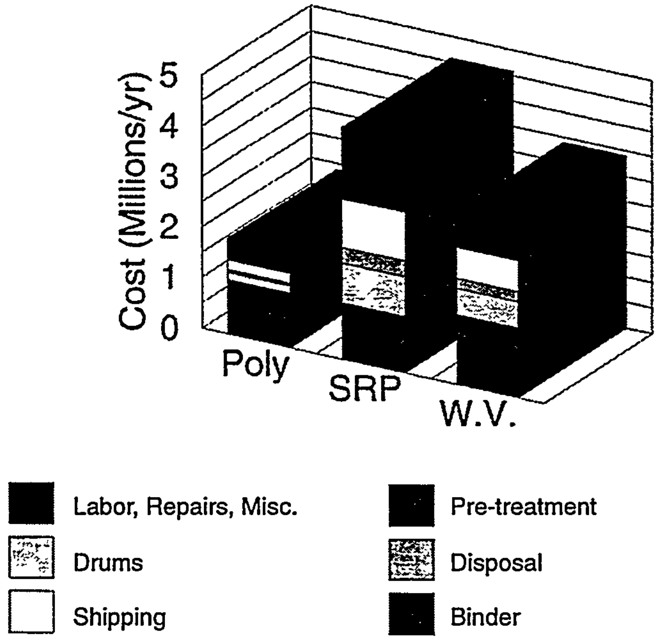

Figure 2a. A comparative cost breakdown to encapsulate 1 x 10^6 kg (2.2 x 10^6 lbs) of nitrate salt per year at Rocky Flats Plant using polyethylene and cement formulations from Savannah River Plant (S.P.) and West Valley (W.V.) (from Kalb *et al.*, 1991b).

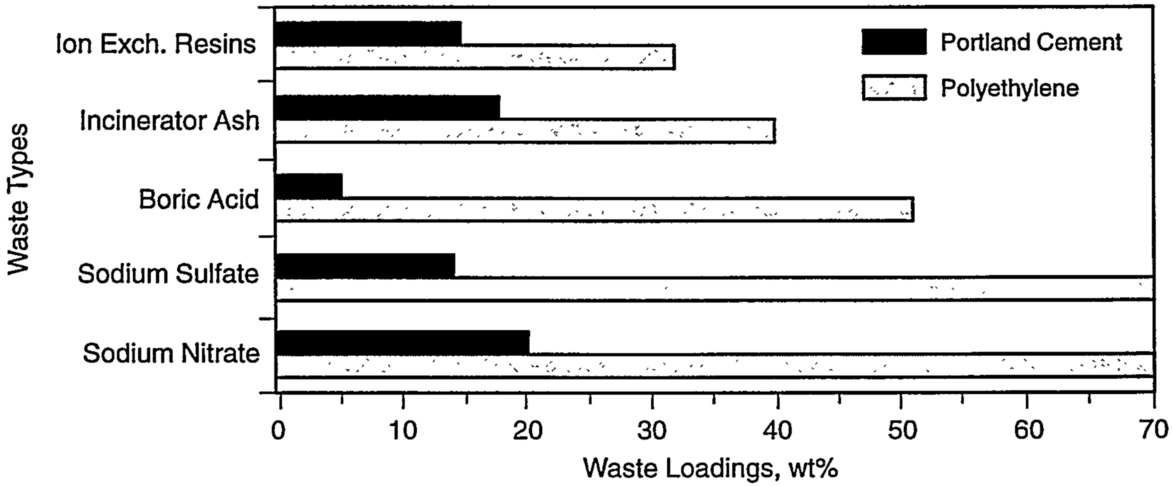

Figure 2b. The maximum waste loadings of various wastes encapsulated in cement and polyethylene (from Kalb, 1993).

vaporization/volatilization of the water/organic in the waste. Pre-encapsulation treatments, such as drying, can yield waste streams that are amenable to encapsulation.

Modified Cement Encapsulation

Some waste streams contain soluble metal salts which form acids when exposed to moisture. An acidic environment can prevent solidification of cements leading to a reduction in mechanical strength and increased mobility of contaminants. Kalb *et al.* (1991a) investigated the efficacy of a modified sulfur cement as an encapsulant for INEL mixed-waste-contaminated incinerator ash that contained metal chloride salts, primarily zinc chloride. "Modified sulfur cement is a thermoplastic material that can be easily melted, combined with waste components in a homogeneous mixture, and cooled to form a solid monolithic waste form" (Kalb *et al.*, 1991a). Sulfur cements have several advantages over common hydraulic cements (e.g., portland cement), namely: solidification does not require any chemical reaction; compressive and tensile strengths are twice those of portland cements; and sulfur cements are resistant to degradation by most acids and salts (Kalb *et al.*, 1991a).

The U.S. Bureau of Mines developed modified sulfur cement in 1972 to utilize the sulfur by-product from flue gas and petroleum distillation processes. Elemental sulfur is reacted with hydrocarbon polymers that yield a product that suppresses solid-phase transformation and therefore improves material stability (Kalb *et al.*, 1991a).

Kalb *et al.* (1991a) tested the leachability of the sulfur cement/waste product using the TCLP. The results of this test showed that the leachate contained cadmium (Cd) and lead (Pb) contents well above the 1.0 mg/L Cd and 5.0 mg/L Pb allowed by EPA (i.e., leachate Cd and Pb contents were 85 mg/L and 46 mg/L, respectively). Therefore, Kalb *et al.* investigated several potential additives that would reduce the mobility of heavy metals in the incinerator ash waste. Sodium sulfide (Na_2S) was selected for use as an additive because it reacts with metal salts to form metal sulfides which have an extremely low solubility. TCLP tests were conducted on the modified sulfur cement plus additive waste product and the metal content of the leachates were well below EPA allowable contents. Table 1 lists the results of the TCLP test. Figure 3 depicts how use of modified sulfur cement and Na_2S results in a higher waste loading than common cement.

Polymer Encapsulation

There are two general groups of polymers, thermoplastic and thermosetting. Because thermoset polymers require reaction between a liquid monomer and curing agent, some waste components react with the monomer and curing agent thus interfering with solidification (Faucette, 1996). Therefore, thermoset polymers are better suited to macroencapsulation. Another consideration is the relatively high cost of thermoset resins. Thermoplastic polymers (such as polyethylene) are heated above their melting point (110°C) and mixed with powdered wastes. The molten mixture is poured into disposal containers (e.g., 55-gallon drums) where solidification occurs as the mixture cools (Faucette, 1996). Most chemicals do not react with polyethylene and therefore polyethylene is well suited for microencapsulation. In addition, polyethylene may be derived from recycled plastics, a cost-effective and environmentally efficient approach to encapsulation.

TABLE 1. RESULTS FROM TCLP TESTS ON INEL INCINERATOR FLY ASH ENCAPSULATED IN MODIFIED SULFUR CEMENT (from Kalb *et al.*, 1991).

Sample Tested	Concentrations of Criteria Metals, mg/L[a] Cd	 Pb
INEL Fly Ash	46.0	85.0
55 wt% Ash 45 wt% MSC[b]	27.5 (50.0)	17.6 (32.0)
40 wt% Ash 60 wt% MSC	13.6 (34.0)	12.0 (30.0)
40 wt% Ash 53 wt% MSC 7 wt% Na_2S	0.1 (0.3)	1.0 (2.5)
43 wt% Ash 50 wt% MSC 7 wt% Na_2S	0.2 (0.5)	1.5 (3.5)
EPA Allowable Limit	1.0	5.0

[a] Data in parentheses represent concentrations normalized to account for reduced mass of fly ash in sample tested.

[b] MSC = modified sulfur cement

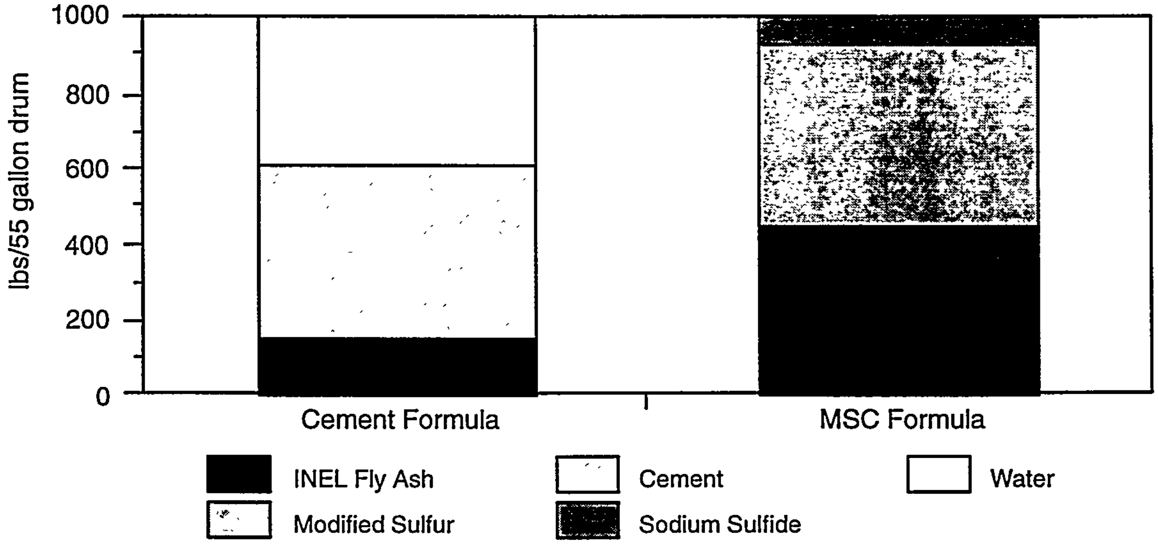

Figure 3. Waste loadings comparison of incinerator ash encapsulated in modified sulfur cement (MSC) and portland cement (from Kalb *et al.*, 1991a).

Studies completed to date indicate that waste loadings of 30 to 80 wt% are possible with polyethylene extrusion. Waste loadings of 50 wt% are typical for most mixed wastes that have been tested (Faucette, 1996). Kalb *et al.* (1993) state that polyethylene encapsulation can accommodate up to 70 wt% nitrate salt waste compared to 13 to 20 wt% when portland cement is used as the encapsulant. Faucette (1996) states that polymer encapsulation provides increased waste loadings, i.e., more waste by wt% can be encapsulated with polyethylene than cement, increased encapsulation product durability, and is rather insensitive to variations in waste stream chemistry in comparison to common cement. While the polyethylene microencapsulation process is resistant to most chemicals, it is sensitive to moisture content. If wastes contain more than 3 to 10% moisture, a drying procedure must be performed prior to polyethylene extrusion.

Polyethylene is a thermoplastic polymer that has been researched more extensively than any other thermoplastic polymer by DOE laboratories. Therefore, this discussion is limited to polyethylene. "Polyethylene is an organic polymer material of crystalline-amorphous structure, formed through the polymerization of ethylene gas" (Kalb *et al.*, 1991b). By controlling the design of polyethylene's molecular structure, hundreds of compound variations with differing properties may be produced. These variations are produced by manipulating process parameters and selecting particular additives, and are characterized by the degree of crystallinity (Kalb *et al.*, 1991b). The degree of crystallinity determines the density of a particular polyethylene, which affects a number of material properties, as listed in Table 2. In addition, the melt index (a measure of viscosity or the ease with which molten polyethylene flows) and molecular weight (an average of all polymer chains produced during polymerization) affect the properties of polyethylene. Polyethylenes with high molecular weights tend to be tougher and are more resistant to stress cracking and harsh chemicals than low molecular weight polyethylene. However, they are more difficult to process; therefore, a narrow molecular weight distribution (2.5:1 to 18:1) provides a balance between process ease and optimal mechanical properties (Kalb *et al.*, 1991b).

TABLE 2. CHANGES IN POLYETHYLENE PROPERTIES WITH DENSITY, MELT INDEX, AND MOLECULAR-WEIGHT DISTRIBUTION[a,b] (from Kalb *et al.*, 1991b).

Property	As Density Increases	As Melt Index Increases	As Molecular Weight Distribution Increases
Abrasion resistance	+	-	
Blocking resistance	+	-	
Brittleness resistance	-	-	-
Brittleness temp	-	+	-
Chemical resistance	+	-	
Cold flow resistance	+	-	+
Hardness	+	-(sl)	
Impact strength	-	-	-
Load-bearing properties, long-term	+	-	+
Melt elasticity		-	+
Melt viscosity		-	

TABLE 2. CHANGES IN POLYETHYLENE PROPERTIES WITH DENSITY, MELT INDEX, AND MOLECULAR-WEIGHT DISTRIBUTION[a,b] (from Kalb *et al.*, 1991b) (Continued).

Property	As Density Increases	As Melt Index Increases	As Molecular Weight Distribution Increases
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 a slight change

[b] Adapted from Bikales, ed., 1967

By controlling the polymerization process pressure, low-density polyethylene (LDPE) or high-density polyethylene (HDPE) may be produced. LDPEs (densities ranging from 0.910 - 0.925 g/cm^3) result from high-process pressures which produce a large number of polymer branches. HDPEs (densities ranging from 0.941 - 0.959 g/cm^3) are formed under low-process pressures that give rise to long linear chains of polymerized ethylene. Medium-density polyethylenes (0.926 - 0.940 g/cm^3) can be produced either by adjusting process pressures or mixing LDPE and HDPE materials. Although Table 2 indicates that higher-density polyethylenes have greater mechanical strengths and are more resistant to harsh chemicals, LDPE is more favorable because its increased branching results in a greater resistance to biodegradation (Kalb *et al.*, 1991b). BNL uses LDPE for its encapsulation process because it does not require high temperatures and pressures and it is therefore more cost effective than HDPE (Kalb *et al.*, 1991b).

As stated previously, various waste streams have been used to test encapsulation processes. In particular, polyethylene microencapsulation has been shown to be an effective treatment approach for evaporator concentrate salts, sludges, incinerator ash, and ion exchange resins, all of which may contain mixed wastes (i.e., radiation and toxic heavy metals). Table A-1 in Appendix A lists the various chemicals for which polyethylene may be used. This list clearly shows that there are very few chemicals for which polyethylene would be an inappropriate encapsulating material with a major exception of various oils and gasoline.

Several studies have been performed by DOE laboratories to evaluate encapsulated waste form performances. The primary goals of these studies were 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
- compare performance among potential binder materials" (from Kalb *et al.*, 1991)

The tests performed by Kalb *et al.* (1991) used laboratory and pilot-scale waste materials containing simulated sodium nitrate salt or actual nitrate salt waste from Rocky Flats. Other studies performing similar tests on sodium sulfate, boric acid, incinerator ash and ion exchange resins were cited by Kalb *et al.*, i.e., Kalb and Colombo, 1984; Franz and Colombo, 1984; Franz *et al.*, 1987; and Heiser *et al.*, 1989.

Waste-binder Compatibility

Waste streams of more than 5% nitrate salt compositions were tested with polyethylene at temperatures up to 400°C (three times higher than the standard processing temperature of 120°C). Several thermograms obtained by differential scanning calorimetry were obtained. The only peaks observable in these thermograms 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.

Compressive Strength

Compressive strength was tested to show the ability of the encapsulated waste to withstand loading pressures common with stacking of waste forms and burial under soil or barrier materials. ASTM D-695, the Standard Method of Test for Compressive Properties of Rigid Plastics, was used to test the waste form strength. The compressive yield strength was shown to vary with waste loading, from 7.03 MPa for 70 wt% sodium nitrate to 16.3 MPa for 30 wt% sodium nitrate. These results were well above the minimum 0.41 MPa Nuclear Regulatory Commission (NRC) strength criteria. Figure 4 shows the compressive strength of various wt% sodium nitrate untreated and after 90 days of water immersion.

Water Immersion Testing

The polyethylene encapsulated waste forms were immersed in water for 90 days and then tested for compressive strength as stated above. Figure 4 depicts the results of this test and clearly shows that in general no loss of compressive yield strength was observed. Only the 70 wt% sodium nitrate salt waste form exhibited an approximate 30% reduction in compressive strength. However, all samples still exceeded the minimum compressive strength criteria by at least one order of magnitude (Kalb *et al.*, 1991b).

Thermal Cycling

The thermal cycling tests were conducted according to ASTM B-553, Standard Method of Test for Thermal Cycling of Electroplated Plastics. "Cored specimens from the pilot-scale waste form

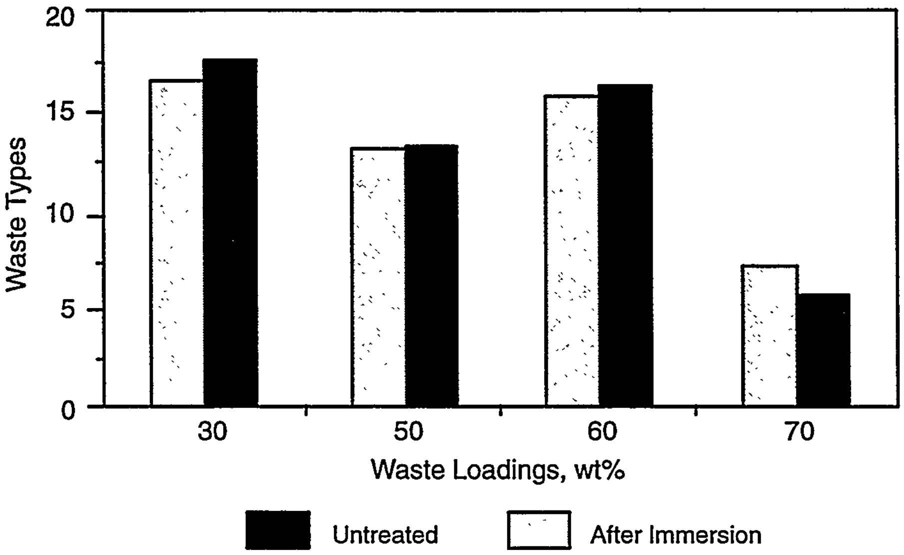

Figure 4. Compressive yield strength of polyethylene waste forms containing sodium nitrate salt, untreated and after 90 days in water immersion (from Kalb *et al.*, 1991b).

were cycled between temperature extremes of -40° C and +60° C for a total of 30, five-hour periods" (Kalb *et al.*, 1991b). Table 3 lists the results of this test and indicates that no statistically significant changes in compressive yield strength were produced by the thermal cycling.

TABLE 3. COMPRESSIVE YIELD STRENGTH OF CORED PILOT-SCALE POLYETHYLENE WASTE FORMS CONTAINING 60 WT% SODIUM NITRATE (from Kalb *et al.*, 1991b).

Test Description	Compressive Yield Strength, Mpa
Initial	14.2 ± 0.3
Post Thermal Cycling	13.3 ± 0.5
Post Irradiation	16.7 ± 0.7
Post Biodegradation	10.1 ± 1.8

Biodegradation

A literature review conducted by Kalb *et al.* (1991b) indicated that polyethylene is not susceptible to biodegradation, particularly LDPE. Testing of polyethylene waste forms containing sodium sulfate, boric acid, incinerator ash, and ion exchange resin resulted in no growth of microorganisms (Franz and Colombo, 1984). The tests were performed according to ASTM G-21, Standard Practice for Determining Resistance of Plastics to Bacteria. In addition to pilot-scale core samples, blank control samples of polyethylene were tested. After 21 days of incubation, no fungal or bacterial growth was observed on any of the samples. However, compressive yield strength tests resulted (see Table 3) in a 29% reduction of strength for the incubated samples (note: the compressive yield strength was still above the minimum required). Because no microorganism growth was observed, the decline in compressive yield strength could not have been due to biodegradation. The authors re-examined the samples and found that some solubilization of the nitrate salts had occurred in both the nutrient agar and sterilization solvent. Because the coring process resulted in fresh-cut surfaces, solubilization was accelerated. This would not occur under normal processing conditions.

Radiation Stability

Pilot-scale core samples of sodium nitrate waste form were exposed to a ^{60}Co gamma source at a dose rate of 3.6 x 10^6 rad/hr, for a total dose of 10^8 rad. Irradiation resulted in an 18% increase in compressive yield strength as indicated in Table 3. These results confirm the prediction of other studies that irradiation would increase polyethylene strength. Therefore, encapsulation of low-level waste/mixed waste with polyethylene should result in a compliant waste form.

Leachability of Radioactive Constituents

Kalb *et al.* (1991b) performed the EPA Toxicity Characteristic Leaching Procedure (TCLP) on encapsulated sodium nitrate salt wastes from the Rocky Flats Plant in Colorado. The tests were designed to simulate probable sanitary landfill conditions. In particular, the TCLP requires vigorous agitation. The results of this test are compared with the untreated waste and reported in Table 4. Polyethylene encapsulated wastes were below the EPA leachate allowable limits for the metals reported.

TABLE 4. RESULTS FROM THE EPA TCLP FOR ROCKY FLAT. PLANT (RFP) NITRATE SALT ENCAPSULATED IN POLYETHYLENE (from Kalb *et al.*, 1991b).

	Concentration 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
EPA Allowable Limit	5.0	1.0	5.0	100

Kalb and Colombo (1984) prepared simulated radioactive waste containing 10, 30 and 50 wt% sodium sulfate, 25 and 35 wt% incinerator ash, and ^{137}Cs, ^{60}Co and ^{85}Sr tracers. Leaching tests were performed according to the American Nuclear Society (ANS) 16.1 Standard "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes." The samples were leached for 91 days in demineralized water at a temperature of 20 ± 2°C. While Kalb and Colombo (1984) do not specify whether the ANS procedure requires agitation, it is highly probable that the ANS procedure is not as conservative as the more recent TCLP. In general, Kalb and Colombo found that all three tracers leached at similar rates with larger amounts of tracers leaching from the higher waste load samples and with increased exposure to the leaching solution. It was also found that higher amounts of tracer leached from the sodium sulfate in comparison to the incinerator ash. The authors hypothesized that the highly soluble nature of the sodium sulfate salt resulted in dissolution of the salt and hence an increased porosity within the waste. The solubility of the salt and the increased porosity provided more pathways for tracer migration. Unfortunately, Kalb and Colombo do not provide any information about allowable radioactive leachate amounts and therefore it is not possible to ascertain whether the amounts of tracer measured were environmentally significant or not.

While the Kalb and Colombo (1984) data limit interpretation, a study by Kalb, Fuhrmann and Colombo (1993) provides information that permits long-term assessment of leaching. Kalb, Fuhrmann and Colombo (1993) performed an accelerated leach test (ALT) to model cumulative fractional releases of waste after 300 years of leaching under fully saturated conditions. Table 5 lists the projected releases of wastes treated by polyethylene encapsulation after 300 years of leaching. The only limitation of this model is the assumption that the treated wastes remained structurally stable during that time interval. Their results indicate that approximately 5 - 17% of the contaminant source will be leached after 300 years of exposure to saturated conditions. They state that in contrast, portland cement waste forms would release about 17% of the contaminant source after only 11 years. Therefore, polyethylene binder provides 27 times the leaching longevity as portland cement.

TABLE 5. PROJECTED CUMULATIVE FRACTION LEACHED (CFL) AND DIFFUSIONS RATES (D_e) AFTER 300 YEARS OF LEACHING FOR FULL-SCALE POLYETHYLENE WASTE FORMS[a] CONTAINING NITRATE SALT WASTES (from Kalb, Fuhrmann and Colombo, 1993).

Temp°C	50 wt% Salt		60 wt% Salt		70 wt% Salt	
	D_e (cm^2/s)	CFL (%)	D_e (cm^2/s)	CFL (%)	D_e (cm^2/s)	CFL (%)
20	3.05×10^{-9}	3.7	8.6×10^{-9}	5.0	5.58×10^{-8}	9.5
35	2.65×10^{-9}	3.6	1.90×10^{-8}	6.3	7.63×10^{-8}	10.7
50	5.32×10^{-9}	4.3	3.10×10^{-8}	7.6	1.34×10^{-7}	13.4
70	9.69×10^{-9}	5.1	2.40×10^{-8}	6.9	2.33×10^{-7}	16.8

[a] Projected releases for 6.3 cubic meter full-scale waste form (2 m diameter x 2 m in height)

Flammability

Kalb *et al.* (1993) state that flammability is not a concern for treated wastes after they have been deposited in shallow landfills, because there is not sufficient oxygen available for combustion. However, during the treatment and transportation phases, combustion may occur. Samples of LDPE were tested according to ASTM D-1929 "Standard Method of Test for Ignition Properties of Plastics." The flash ignition temperature for polyethylene was 409°C and the self-ignition temperature was 430°C. Because polyethylene is heated to only 120°C for extrusion purposes, it is highly unlikely that a fire will occur during the treatment process. If the polyethylene waste form should be ignited, polyethylene burns slowly in a controlled manner, i.e., 1.0 in/min (Kalb *et al.*, 1993).

Environmental Stress Cracking and Photodegradation

Environmental stress cracking of polyethylene may occur under conditions of stress when exposed to soaps, detergents, wetting agents, or oils (Kalb *et al.*, 1993). It is not probable that polyethylene encapsulated waste forms would be exposed to high stress and the above mentioned chemical agents according to Kalb *et al.* (1993). Deterioration of polyethylene's mechanical properties will occur when exposed to sunlight and oxygen for long periods of time. However, the photodegradation effect would only impact the surface of the waste form, if the wastes were stored in an exposed manner. Because wastes are typically buried in a shallow landfill, photodegradation is not likely to occur (Kalb *et al.*, 1993).

Microencapsulation Treatment Facilities

Table 6 provides a list of microencapsulation treatment system facilities. To date, no polyethylene extrusion processes are permitted for mixed wastes (Faucette, 1996). It is anticipated that this will change as DOE works with private industry to commercialize encapsulation waste treatment.

TABLE 6. POLYMER MICROENCAPSULATION TREATMENT SYSTEMS (from Roach, 1996).

System Name	Site and State
Pantex Mobile Stabilization Skid	Pantex, TX
Oak Ridge Commercial Option	Oak Ridge, TN
CTMP System 3-LLW Miscellaneous Waste Form Immobilization	RFETS, CO

Macroencapsulation

Macroencapsulation coats bulk wastes such as radioactive lead and debris with an encapsulant. According to 40 CFR 268.42, macroencapsulation is defined as encapsulation "...with surface coating materials such as polymeric organic (e.g., resins and plastics) or with a jacket of inert inorganic materials to substantially reduce surface exposure to potential leaching media." 40 CFR 268.40 states that macroencapsulation is a treatment standard for radioactively contaminated lead solids. Because macroencapsulation is simply the application of a surface coating to a solid rather than mixing with fine particles, macroencapsulation is not governed by as many regulations as microencapsulation. For sleeve-type (i.e., the fusing of a polymer lid onto a polymer sleeve which contains the debris) macroencapsulation, the final waste form must pass the DOT drop tests specified in 49 CFR 173.461 through 465 (Roach, 1996). In addition, containerized waste must not exceed a 10% void volume according to 40 CFR 264.315, and any state requirements.

Because the most difficult and abundant DOE waste streams are composed of fine particles which contain mixed wastes, most of the research conducted by the DOE laboratories has focussed on microencapsulation technology. In fact, INEL, BNL and RFETS did not provide any reports or articles that discussed test results for macroencapsulation. However, based on the information provided in the previous microencapsulation section, it is possible to extrapolate test results to macroencapsulated waste forms.

As stated in the previous section, thermoplastic binders (e.g., polyethylene) meet or exceed all requirements for compression strength, biodegradation, leachability, flammability, irradiation, photodegradation, and chemical interaction. The most important test that would be required of any binding agent used in macroencapsulation would be its ability to resist stress fracturing with weight loading or during transportation. The same will probably hold true for most thermosetting polymers except as noted previously, the resins used for thermosetting polymers can often react with components in the waste debris. The likelihood of chemical interactions with large pieces of waste debris are likely to be reduced in occurrence and effect due the nature of most lead and debris wastes and the decreased surface area in contact with the polymer. It is self evident that polymer encapsulants would have a higher resistance to stress fracture than cements and would be less likely to degrade from saturated conditions or biodegradation. But because the weight loading of macroencapsulation would be the same for cements and polymers, the cost of polymer macroencapsulation would probably be higher. The treatment systems that are presently providing macroencapsulation processing are listed in Table 7.

TABLE 7. POLYMER MACROENCAPSULATION TREATMENT SYSTEMS (from Roach, 1996).

System Name	Type	Site and State
Envirocare of Utah, Inc.	Extrusion	Various
WROC Macroencapsulation	Extrusion	INEL, ID
Macroencapsulation in a Permitted Containment Building	Extrusion	SRS, SC
Commercial Macroencapsulation (was part of WRAP IIA)	Sleeve	Hanford, WA
CTMP System 3-LLW Misc Waste Form Immobilization	Extrusion	RFETS, CO
Mobile Macroencapsulation	Sleeve	Pantex, TX

CONCLUSIONS

Mixed waste encapsulation treatment using polymers has been adopted by DOE researchers from existing processes developed within the polymer industry. Researchers at BNL and RFETS have performed several tests on the applicability and durability of polymers (predominantly polyethylene) for encapsulation of DOE mixed waste streams. The encapsulation of fine particle waste streams such as incinerator fly ash, evaporator concentrates (e.g., nitrate salt wastes), and ion exchange resins has been one of the primary concerns of the researchers. This is due to the fact that these wastes contain chemical components, such as metals, that increase the difficulty of producing a cost-effective compliant waste form for storage.

Most of the research that has been reported addresses microencapsulation of powdered wastes; limited research has been performed on macroencapsulation. This is due to the fact that there are more risks associated with microencapsulation, e.g., leachability, degradation, and potential for chemical interaction between the polymer binder and the fine wastes. The primary concerns for macroencapsulation are the durability of the encapsulating polymer and the potential for stress fracture. Because macroencapsulation is the encapsulation of a bulk waste such as lead debris, leaching and chemical interaction with the solid waste are not of concern.

Although polymer encapsulation is not as widely used as cementation, polymers offer several advantages over the typical cement encapsulation processes. The most important advantages are the increased waste loadings, the increased durability of the waste form, and the relative insensitivity to variations in the waste stream chemistry. These advantages also make it possible for polymer encapsulation, particularly polyethylene, to provide an overall treatment cost savings. The increased waste form durability is a result of the fact that polyethylene is highly resistant to biodegradation, attack by aggressive chemicals, and radiation doses. In fact, radiation doses through 10^8 rad increase the crosslinking and improve strength and other physical properties of polyethylene (Kalb *et al.*, 1993). Other advantages include: it has passed all EPA and NRC tests for compressive strength and leachability; the fact that it is an off-the-shelf technology where all of the equipment and materials are already available from private vendors; the technology is relatively simple; it is a non-thermal treatment process and therefore no secondary waste streams are produced; the polymer industry has decades of experience in polymer processing; and it provides a market for recycled polymers.

The only disadvantage of this technology is, at this point in time, no pilot- or full-scale tests have been performed using polyethylene encapsulation to treat actual low-level mixed waste streams. All tests have been conducted with surrogates. Faucette (1996) notes that extended hot pilot-scale tests using actual waste streams were planned for 1996 and results should soon be forthcoming.

If the "hot" tests with actual waste streams at RFETS yield successful results and given the favorable results summarized in this report, polymer encapsulation of low-level mixed wastes should be strongly considered for treatment of wastes from the Nevada Test Site.

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APPENDIX A

THE APPLICATION OF POLYETHYLENE RESINS IN VARIOUS CHEMICAL ENVIRONMENTS[a] (from Kalb *et al.*, 1991b).

	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 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

Chemical	Polyethylene can be used at 25°C	 60°C
Carbon tetrachloride	No	No
Carbonic acid	Yes	Yes
Chlorine gas, wet or dry	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
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
Mercurous nitrate	Yes	Yes
Mercury	Yes	Yes
Methyl chloride	No	No
Methyl ethyl ketone	No	No
Mixed acids	Yes	No

Chemical	Polyethylene can be used at 25°C	60°C
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
Potassium chlorate	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

Chemical	Polyethylene can be used at 25°C	60°C
Sodium nitrite	Yes	Yes
Sodium sulfate	Yes	Yes
Sodium sulfide	Yes	Yes
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 Raff and Allison, 1956.

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