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SOLIDIFICATION OF DOE PROBLEM WASTES

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## SOLIDIFICATION OF DOE PROBLEM WASTES

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### ABSTRACT

Sodium nitrate waste has been successfully solidified in two types of polymeric materials: polyethylene, a thermoplastic material, and polyester styrene (PES), a thermosetting material. Waste form property evaluation tests such as ANS 16.1 leaching test and compressive strength measurements were performed on the waste forms containing various amounts of sodium nitrate. A single-screw extruder was employed for incorporating dry waste into polyethylene at its melt temperature of 120°C to produce a homogenous mixture. Results of the leaching test for polyethylene waste forms containing 30, 50, 60 and 70 wt% sodium nitrate are presented as cumulative fraction leached and leaching indices ranging from 11 to 7.8. Two PES systems are discussed. The first is for solidification of dry salt wastes and the second is a water extendible system that is compatible with wet waste streams. Leaching data for PES and water extendible PES waste forms containing 30 wt% sodium nitrate are presented as cumulative fraction leached and leaching indices of approximately 9. Results from compressive strength measurements are also included.

### INTRODUCTION

Many low-level radioactive wastes (LLW) generated at DOE facilities are routinely treated and/or immobilized prior to disposal by means of conventional techniques. A significant fraction of DOE defense wastes, however, either are incompatible with conventional solidification agents in their as-generated form, are solidified with poor efficiencies or form solidified products with poor performance properties in the disposal environment. Based on information obtained at various DOE waste producing sites and from the DOE Ad Hoc Contractors Committee<sup>1,2</sup>, sodium nitrate waste falls into this category. Because of the high volume of nitrate waste being produced and stored at DOE facilities and the more stringent restrictions being placed on the amount of nitrates allowed into the ground by several states, alternative options for the solidification

of nitrate wastes are being investigated. Two of these options, the use of polyethylene and polyester-styrene (PES) as solidification agents, will be discussed in this paper.

The selection of polyethylene and PES was based on such considerations as compatibility with waste, material properties (resistance to water permeability), solidification efficiency, ease of processibility, availability of materials and economic feasibility.

## SOLIDIFICATION OF SODIUM NITRATE WASTE IN POLYETHYLENE

### Polyethylene

Polyethylene is an inert thermoplastic organic polymer of crystalline-amorphous structure that solidifies upon cooling from the melt without dependence on complex chemical reactions. A variety of polyethylenes are commercially available, ranging from soft waxes to very tough plastics. The American Society for Testing and Materials (ASTM) grades polyethylene into three types: low, medium and high with respective density ranges of 0.910 to 0.925, 0.926 to 0.940, and 0.941 to 0.965 g/cm<sup>3</sup>.

In addition to density, other factors which affect polyethylene properties include molecular weight, molecular weight distribution and melt index. The melt index is probably the most important consideration since it determines the ease with which the molten polyethylene flows under prescribed conditions of temperature and pressure. The melt index, as specified by ASTM D-1238, is a measure of the viscosity of the melt at 190°C and is expressed in units of grams/10 minutes. Low-density polyethylene is preferred for the solidification of low-level radioactive waste since the processing temperatures and pressures are appreciably lower than those required for high-density polyethylene.<sup>3,4</sup> A low processing temperature is more desirable not only for economic reasons, but also for ease of processibility and prevention of volatilization and/or decomposition of the waste components.

### Formulation and Process Development Studies

Process development studies were conducted with a variety of low-density polyethylenes having densities between 0.917 and 0.924 g/cm<sup>3</sup>, melt indices between 2.0 and 55.0 g/10 min, and molecular weights between 19,000 and 70,000.<sup>3,4</sup> Based on a balance between achievable waste loadings, processing requirements and the results of waste form performance tests, the polyethylene found to be best suited for the solidification of sodium nitrate waste has a density of 0.924 g/cm<sup>3</sup> and a melt index ranging from 35 to 55 g/10 min.

For the incorporation of the waste into the polyethylene an extrusion method was selected based on such considerations as ease of processibility, quality control and the use of a proven available technology. The extrusion process employs a simultaneous mixing and heating of the waste and binder material to produce a homogeneous mixture.

For the production of laboratory-scale polyethylene waste forms, a commercially available 1-1/4 inch single-screw extruder, manufactured by Killion Extruders, Inc., Verona, NJ was used. The extruder was modified to accommodate a dynamic feed system consisting of two proportional hoppers to eliminate static premixing and gravity feeding of waste and binder materials into the extruder. These feeders improved the homogeneity of the product by closely regulating the rate at which both, waste and binder, are introduced into the extruder. A photo of the extruder is shown in Figure 1. Since the laboratory scale extruder was not equipped with vents to allow water vapor to escape, all waste materials were dried to facilitate mixing with polyethylene, which is not miscible with water. The process is described in more detail in References 3, 4, and 5.

Dry sodium nitrate ( $\text{NaNO}_3$ ) was used to simulate the waste for most of the process development work and waste form testing. Two other types of simulated waste, one with the chemical composition of Savannah River Laboratory (SRL) nitrate waste and the other with the chemical composition of Rocky Flats Plant (RFP) nitrate waste, were used to determine whether the various chemical components present in actual waste, in particular sodium nitrate, potassium nitrate, and sodium nitrite, could result in chemical instability when combined with organic solidification agents such as polyethylene and PES at elevated processing temperatures. Since the hazard potential of chemical compounds can be assessed by their thermal behavior, a differential scanning calorimeter (DSC) was used to characterize the thermal behavior of the waste components, individually and in combination with the solidification agents.

Some of the results of the experiments using the DSC up to  $400^\circ\text{C}$  are shown in Figures 2 and 3. In the thermal profiles thus obtained, the only peaks which were observed were at the melting points of the various compounds, depicting endothermic reactions. The absence of peaks representing exothermic reactions indicates the stability of the polymer/waste mixtures over a range of temperatures to  $400^\circ\text{C}$ .

Laboratory size samples containing 30, 50, 60 and 70 wt% sodium nitrate were prepared for product testing and evaluation. The homogeneous extruded mixtures were solidified in cylindrical molds, yielding samples which measured approximately 4.8 cm in diameter and 9.0 cm in height.

### Waste Form Stability Evaluation

#### Testing

The stability of a waste form is an important factor in controlling the release of  $\text{NaNO}_3$  waste into the environment. A series of waste form

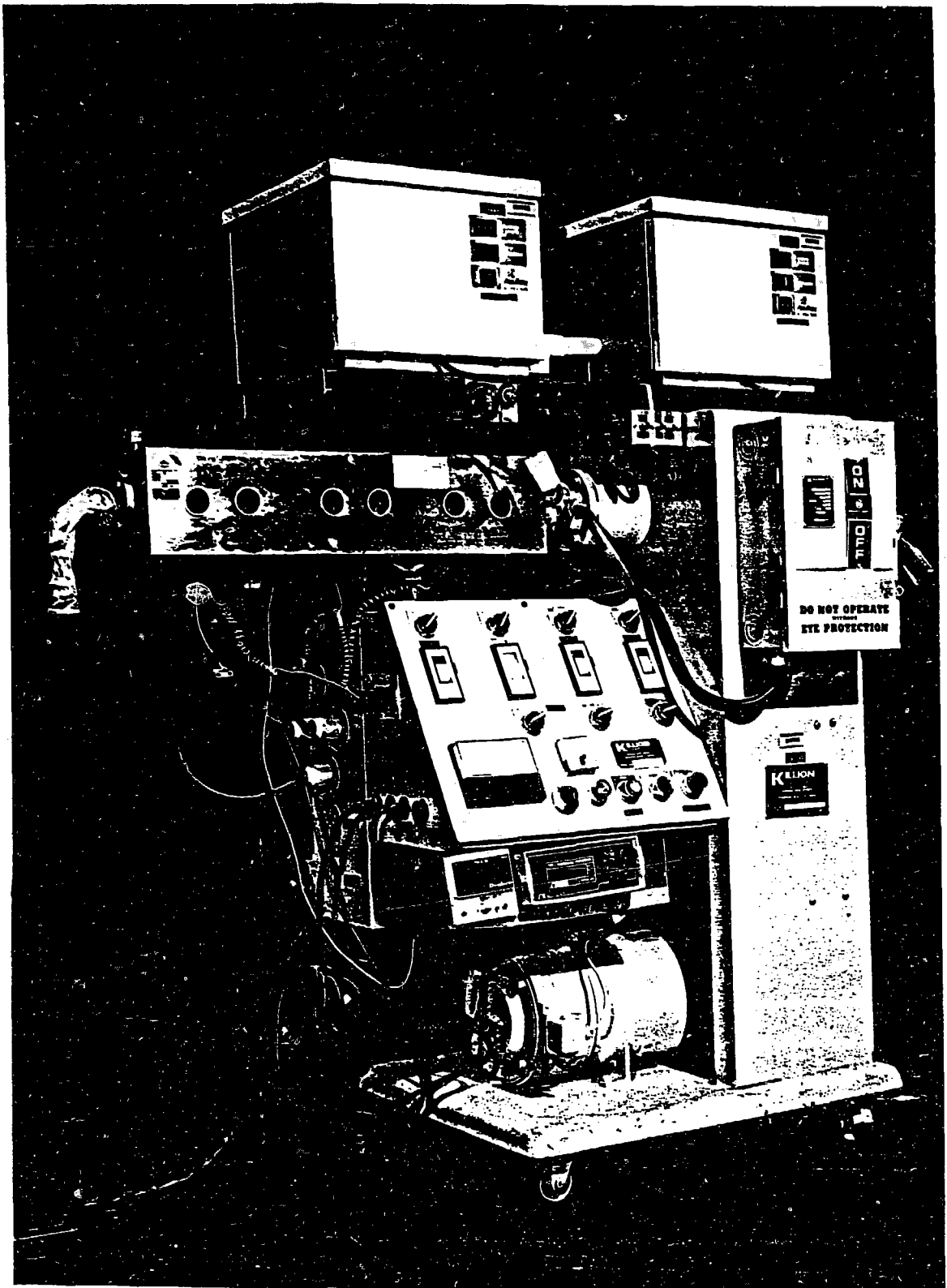


Figure 1. Photograph of laboratory-scale single-screw extruder with dual hopper/feeders.

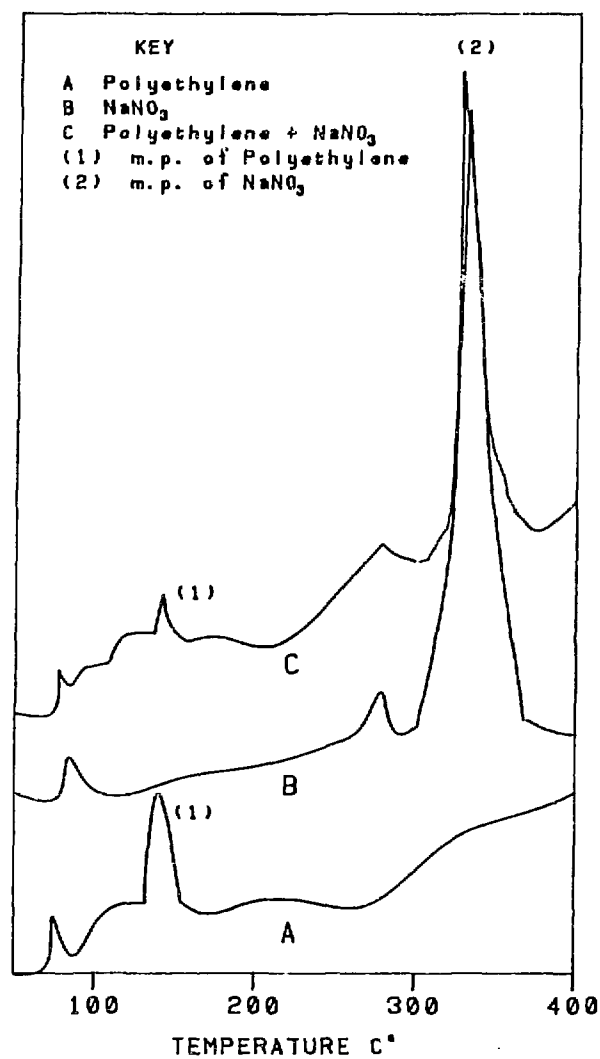


Figure 2. Differential Scanning Calorimeter (DSC) Thermograms of: NaNO<sub>3</sub>; polyethylene; mixture of NaNO<sub>3</sub> and polyethylene.

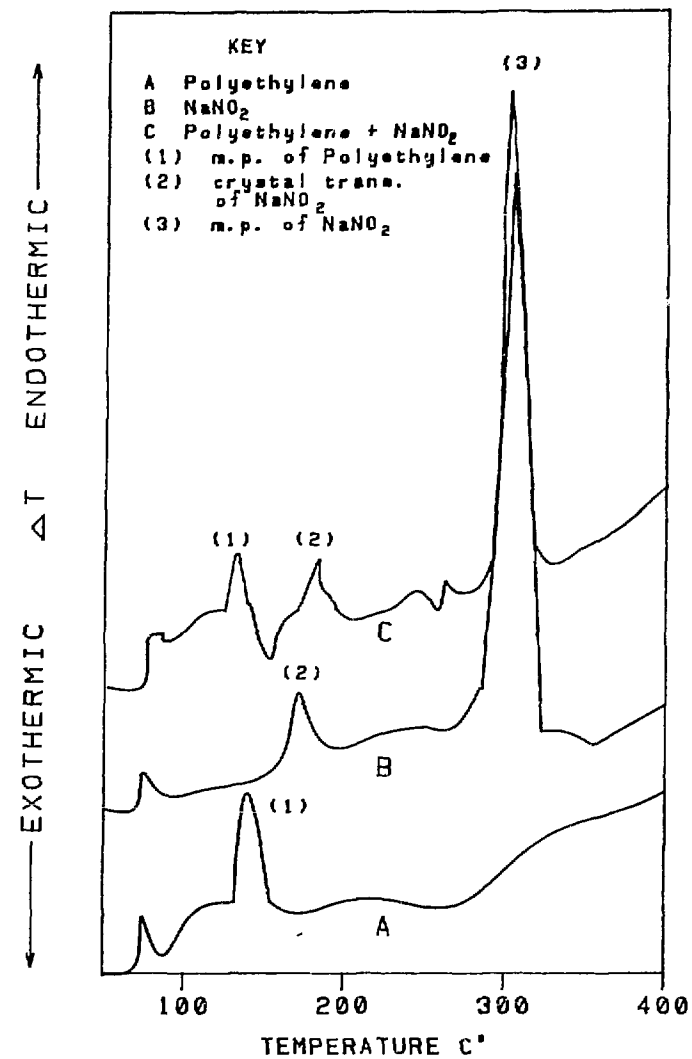


Figure 3. Differential Scanning of Calorimeter (DSC) Thermograms of: NaNO<sub>2</sub>; polyethylene; mixture of NaNO<sub>2</sub> and polyethylene.

evaluation tests were suggested in NRC's Branch Technical Position Paper on Waste Form<sup>6</sup> in support of 10 CFR 61. Two of these tests, 90-day immersion in water and ANS 16.1 Leach Test<sup>7</sup>, were used in this study to evaluate the polyethylene/ $\text{NaNO}_3$  waste forms. In addition, to evaluate the compressive yield strength of the waste forms, the method outlined in ASTM D-695, "Standard Test Method for Compressive Properties of Rigid Plastics," was used.

## Results

The leaching data for  $\text{NaNO}_3$  from replicate sets of polyethylene waste forms was calculated in terms of the cumulative fraction leached (CFL), the leach rates at 90 days of leaching and the leaching indices.

The CFL is presented graphically as a function of leaching time (in days) and is shown in Figure 4. The data in Figure 4 clearly demonstrate the dependence of leachability upon increased waste loadings of 30, 50, 60 and 70 wt%  $\text{NaNO}_3$ . The average CFL at the end of 90 days is 0.9%, 6.3%, N.A. % and 73.4%, respectively.

The leach rate at 90 days of leaching is shown in Table 1 as rate per second and rate per day. The values are averages of data from replicate samples and range from  $7.2 \times 10^{-5} \text{ day}^{-1}$  to  $8.5 \times 10^{-4} \text{ day}^{-1}$  for 30 wt% to 70 wt% waste loading, respectively.

The leaching indices were calculated as recommended in the ANS 16.1 method. This index is a dimensionless figure of merit which quantifies the relative leachability for a given waste type-solidification agent. It can thus be used as a basis for comparison of the various waste component retention capabilities of different solidification matrix-waste type combinations.

Average leaching indices were calculated for each of the replicate sets of polyethylene waste forms which had been leached. An average of the leaching indices of replicate samples is listed in Table 2. Since the leaching index is inversely proportional to effective diffusivity, higher index values represent reduced leachability.

TABLE 1.  $\text{NaNO}_3$  LEACHING RATES FROM POLYETHYLENE WASTE FORMS

$\text{NaNO}_3$ Loading (wt%)	Leach Rate at 90 Days	
	$\text{sec}^{-1}$	$\text{day}^{-1}$
30	$8.4 \times 10^{-10}$	$7.3 \times 10^{-5}$
50	$6.0 \times 10^{-9}$	$5.2 \times 10^{-4}$
60	N.A.	N.A.
70	$9.8 \times 10^{-9}$	$8.5 \times 10^{-4}$

N.A. = data not available at this time.

### LEACHING OF SODIUM NITRATE FROM POLYETHYLENE

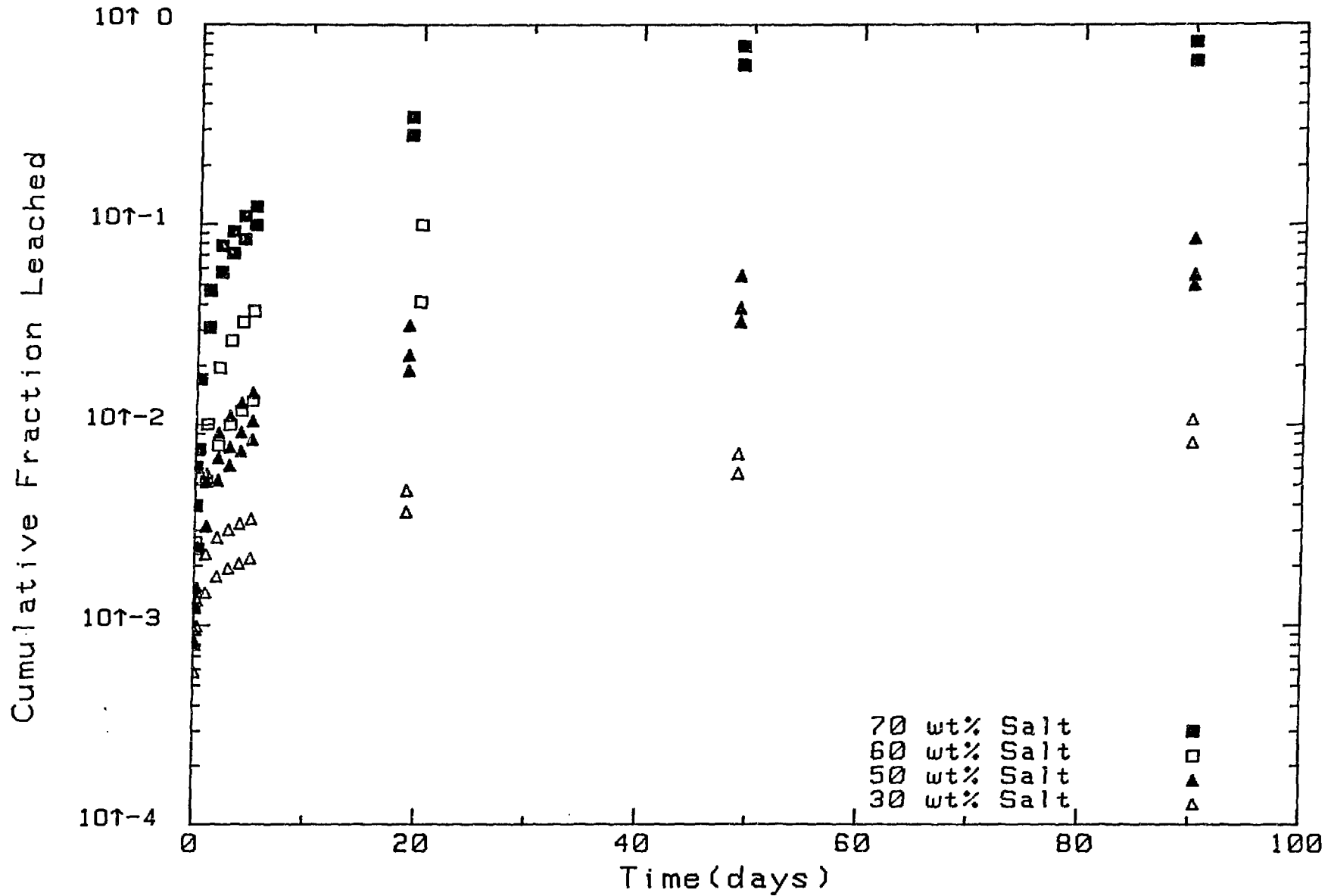


Figure 4. Cumulative fraction leached of sodium nitrate as a function of time from polyethylene waste forms.



TABLE 2. AVERAGE NaNO<sub>3</sub> LEACHING INDICES FOR POLYETHYLENE WASTE FORMS

Waste Loading NaNO <sub>3</sub> (wt%)	Average Leaching Index
30	11.1
50	9.7
60	9.1*
70	7.8

The compressive yield strength of polyethylene waste forms containing various amounts of NaNO<sub>3</sub> waste were measured before and after 90-day immersion in deionized water. These results are presented in Table 3. Even the waste forms with highest waste loadings (70 wt% NaNO<sub>3</sub>) retained a high compressive yield strength of 720 psi.

TABLE 3. COMPRESSIVE YIELD STRENGTHS OF POLYETHYLENE WASTE FORMS CONTAINING SODIUM NITRATE WASTE

Waste Loading wt% NaNO <sub>3</sub>	Compressive Yield Strength (psi)	
	Before	After 90 Days Immersion
30	2370 + 280	2290
50	1920 + 160	1720 + 40
60	2200 + 70	N.A.
70	N.A.	720

#### SOLIDIFICATION OF SODIUM NITRATE WASTE IN POLYESTER-STYRENE

##### Polyester-Styrene

The essential ingredients in commercial unsaturated polyester resins are a linear polyester resin, a cross-linking monomer, such as styrene, and inhibitors to retard cross-linking until the resin is ready for use. The process of converting polyester resins from the liquid to the solid involves a catalyst promoted chemical reaction between the polyester resin and the monomer in which the polyester is dissolved, to form a cross-linked, thermoset polymer. Once a thermoset material is formed the plastic

\*Based on 20 days of leaching.

N.A. = data not available at this time.

cannot be reformed or remelted as in the case of thermoplastic materials. In these studies a promoter was used for curing the resin mixture at room temperature.

### Formulation and Process Development Studies

Several types of commercially available polyester-based thermosetting resins were investigated. Two basic types which were used in these studies are polyester-styrene (PES) resins which can be used to solidify dry wastes and those which can be used to immobilize aqueous waste by forming an emulsion with the water in the waste. The latter type is called a water extendible polyester (WEP) and is usually capable of immobilizing either dry or wet (slurries, solutions) wastes. The physical and chemical form of the waste, other site specific factors and economics determine which of these two types of polyester resins are to be used in a specific solidification process.

For process development work, dry sodium nitrate was used to simulate nitrate salt waste. Slurries and solutions of the salt were prepared to simulate wet wastes. As discussed earlier in the polyethylene section, two other types of simulated waste (with the chemical composition of SRL and RFP waste) were used in experiments to determine the hazard potential of some of the compounds when combined with organic solidification agents at elevated processing temperatures. Examples of the thermal profiles obtained using the DSC at temperatures up to 400°C are shown in Figures 5 and 6. No exothermic reactions were observed.

The polyester-styrene resin used to solidify dry salt waste was promoted with dimethyl aniline. The catalyst was benzoyl peroxide. Laboratory scale samples (4.6 cm diameter x 9.0 cm length) were prepared containing 33 wt% sodium nitrate, 4.7 wt% thixotropic agent, 0.38% promoter, and 1% catalyst. In the process which involved the solidification of dry salt or salt slurries, a thixotropic agent was added to increase the viscosity of the mixture to keep the waste salt dispersed during curing.

Water extendible polyester resins obtained from two different manufacturers (A and B) were used to solidify  $\text{NaNO}_3$  slurries and solutions. Both resins were promoted with cobalt naphthenate and methyl ethyl ketone peroxide (MEKP) was used as the catalyst (1%). Laboratory-scale samples (4.6 cm diameter x 9.0 cm length) containing salt slurry waste had 27 wt% and 25 wt% sodium nitrate in WEP resin A and WEP resin B, respectively. Samples containing salt solutions had 28 wt% sodium nitrate in both types of resins. Resins used for salt slurries also contained 7-8 wt% (~ 4 wt% of the total waste form) thixotropic additives. The resin and waste were mixed together with a laboratory-scale high-shear mixer. The catalyst MEKP was added to the mixture during mixing.

Table 4 summarizes the various resin/waste/additive combinations and the relative amounts of each used in this study for the solidification of

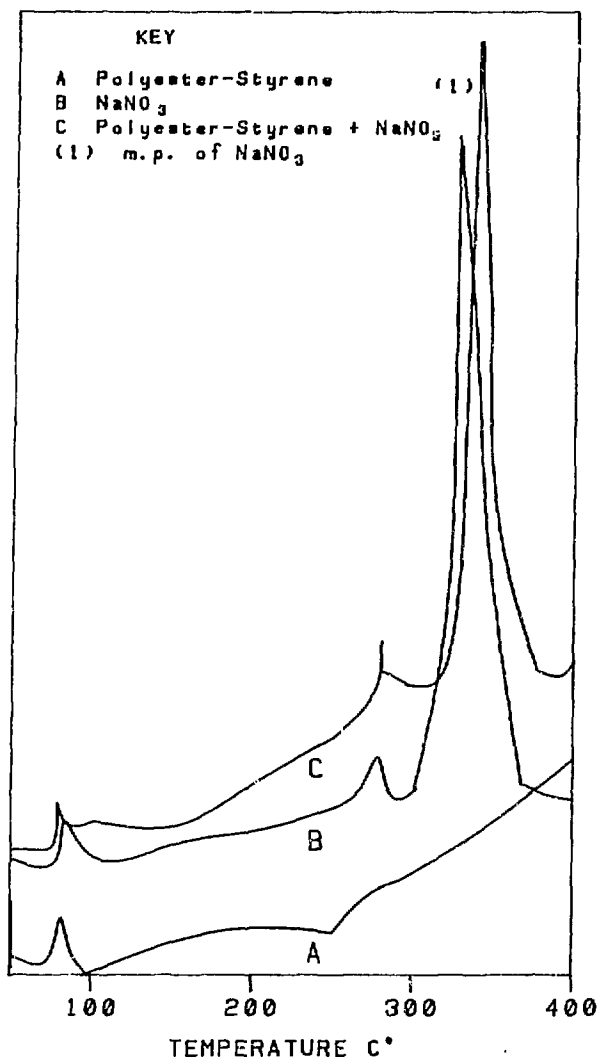


Figure 5. Differential Scanning Calorimeter (DSC) Thermograms of:  $\text{NaNO}_3$ ; polyester-styrene; mixture of  $\text{NaNO}_3$  and polyester-styrene.

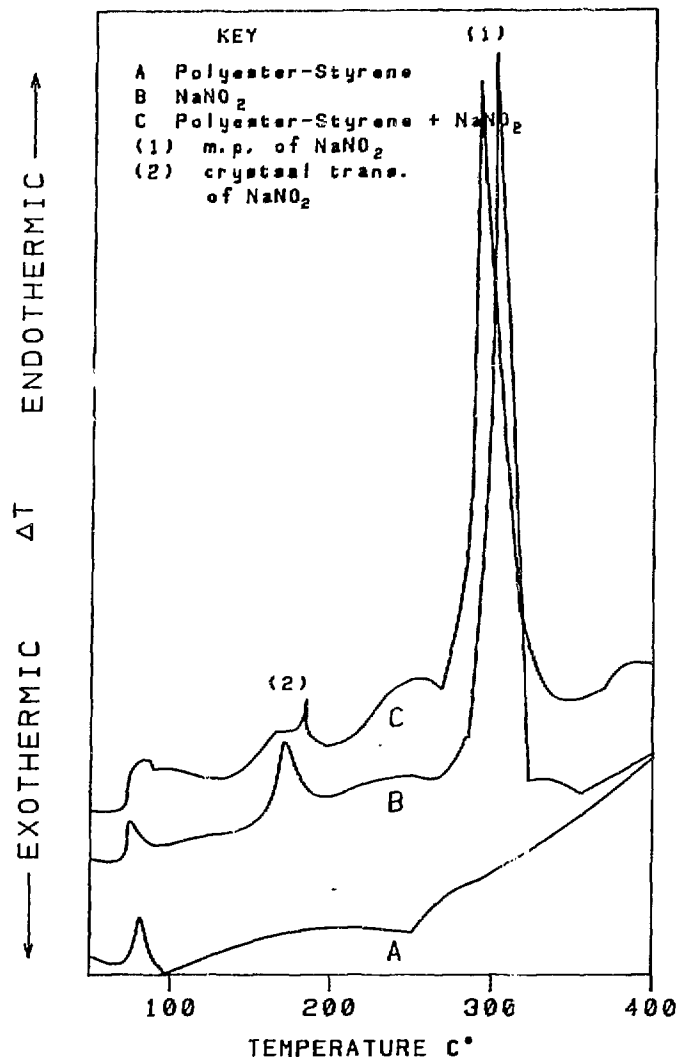


Figure 6. Differential Scanning Calorimeter (DSC) Thermograms of:  $\text{NaNO}_2$ ; polyester-styrene; mixture of  $\text{NaNO}_2$  and polyester-styrene.

TABLE 4. FORMULATIONS FOR SOLIDIFICATION OF  $\text{NaNO}_3$  WASTE IN POLYESTER-STYRENE

RESIN TYPE	WT %	$\text{NaNO}_3$ WASTE		THIXO- TROPIC MATERIAL WT%	CATAYLST (Initiator)		PROMOTER* (Accelerator)	
		$\text{NaNO}_3$ WT %	WATER WT %		TYPE	WT %	TYPE	WT %
POLYESTER STYRENE	62.7	31.3	-	4.7	BENZOYL PEROXIDE (BFF-50)	0.94	DIMETHYLANILINE (DMA)	0.38
WATER EXTENDIBLE POLYESTER STYRENE TYPE A	35.4	28.3	35.4	-	MEKP**	0.5	COBALT NAPHTENATE (CoN)	0.35
WATER EXTENDIBLE POLYESTER STYRENE TYPE B	35.6	28.5	35.6	-	MEKP	0.36	CoN	-
WATER EXTENDIBLE POLYESTER STYRENE TYPE A	61.5	27.4	5.5	4.4	MEKP	0.6	CoN	0.6
WATER EXTENDIBLE POLYESTER STYRENE TYPE B	55.7	24.9	14.9	4.0	MEKP	0.5	CoN	-

\*Additions to as-received resins.

\*\*Methyl Ethyl Ketone Peroxide.

nitrate waste. Since many of the resins already contain promoters when received from the manufacturer, the amount of promoter listed in Table 4 refers to the additional amount that was added during formulation studies.

### Waste Form Stability Evaluation

#### Testing

The same tests that were performed on polyethylene/ $\text{NaNO}_3$  samples were also used to evaluate the stability of PES/ $\text{NaNO}_3$  and WEP/ $\text{NaNO}_3$  samples. These three tests are: a 90-day immersion in water, the ANS 16.1 Leach Test and a compressive yield strength measurement according to ASTM D-695.

#### Results

The leaching data for PES and WEP waste forms is presented as CFL, the leach rate at 90 days of leaching and the average leaching indices.

In Figure 7 the CFL is plotted as a function of leaching time (in days). As can be seen from these leaching curves, all of the waste forms have similar leaching characteristics, whether the waste they contain was incorporated as a dry salt, salt slurry or salt solution. The CFL at the end of 90 days of leaching for these waste forms range between  $9 \times 10^{-2}$  and  $1.8 \times 10^{-1}$ .

The leach rate at 90 days of leaching and the average leaching indices, calculated according to the ANS 16.1 method, are also very similar for all of the waste forms tested. The data is presented in Table 5. The leach rates range between  $7.3 \times 10^{-4}$  and  $1.6 \times 10^{-3} \text{ day}^{-1}$  and the average leaching indices between 8.9 and 9.3.

TABLE 5. AVERAGE  $\text{NaNO}_3$  LEACHING INDICES AND LEACHING RATE

Resin type	Waste Loading $\text{NaNO}_3$ (wt%)	Leaching Rate at 90 days		Average Leaching Index
		$\text{sec}^{-1}$	$\text{day}^{-1}$	
PES	33 (dry)	$1.8 \times 10^{-8}$	$1.6 \times 10^{-3}$	9.2
WEP-A	25 (as slurry)	$8.6 \times 10^{-9}$ *	$7.4 \times 10^{-4}$ *	9.3*
WEP-B	27 (as slurry)	$1.4 \times 10^{-8}$	$1.2 \times 10^{-3}$	9.1
WEP-A	28 (as solution)	$1.3 \times 10^{-8}$ *	$1.1 \times 10^{-3}$	8.9*
WEP-B	28 (as solution)	$8.4 \times 10^{-9}$	$7.3 \times 10^{-4}$	9.3

\*Data represents only 47 days of leaching.

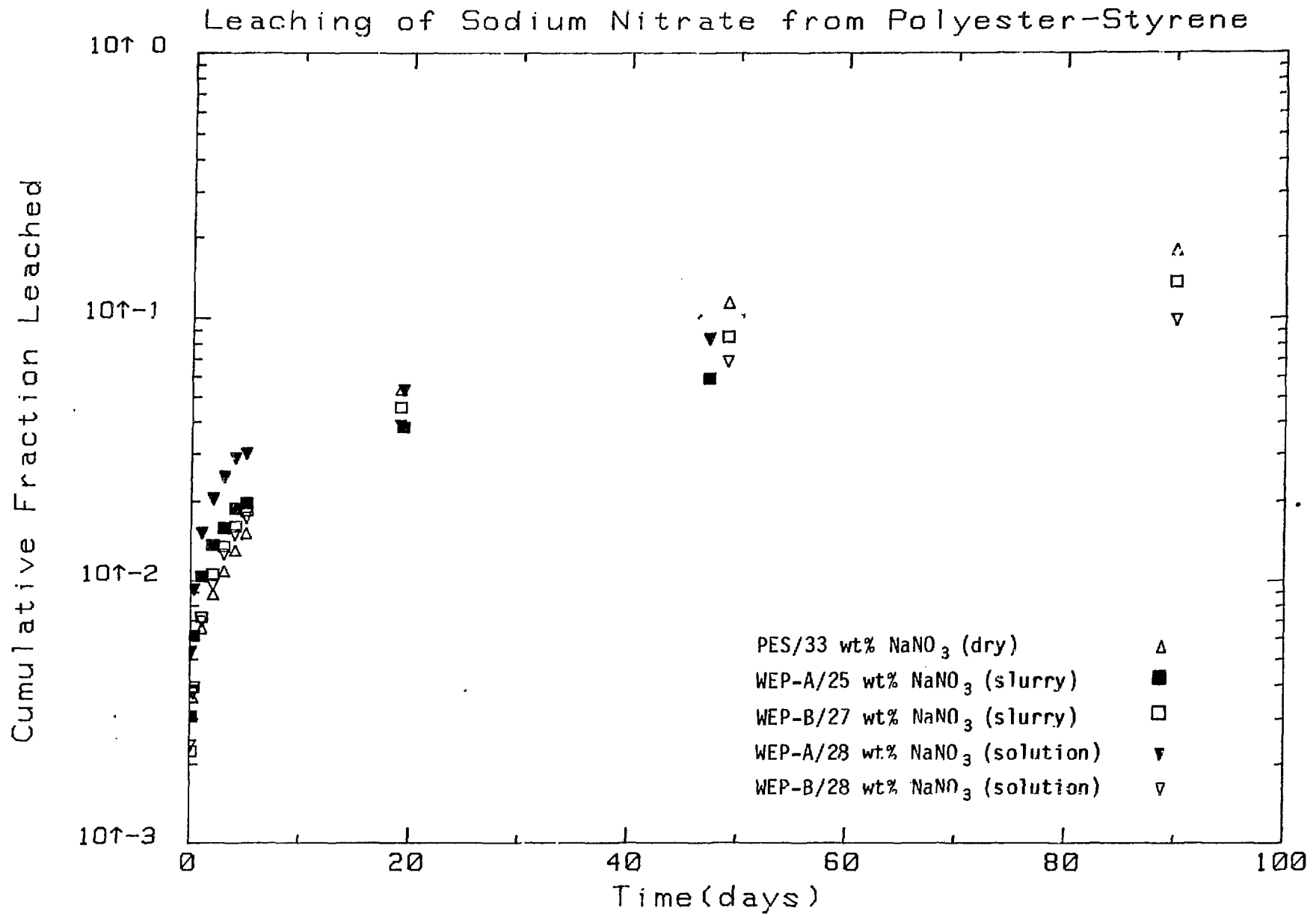


Figure 7. Cumulative fraction leached of sodium nitrate as a function of time from polyester-styrene waste forms.

The compressive yield strength of PES and WEP waste forms containing approximately 30 wt% NaNO<sub>3</sub> waste was measured before and after 90-day immersion in deionized water. The results are presented in Table 6. Even the lowest value measured after immersion was relatively high at 1300 psi.

TABLE 6. COMPRESSIVE YIELD STRENGTHS OF POLYESTER-STYRENE WASTE FORMS

Resin Type	Wt% NaNO <sub>3</sub>	Compressive Yield Strength (psi)	
		Before	After 90 Days Immersion
PES	33 (dry)	7730 ± 490	7540
WEP-A	25 (as slurry)	3180 ± 130	2744
WEP-B	27 (as slurry)	5420 ± 40	1300
WEP-A	28 (as solution)	2440 ± 130	2125
WEP-B	28 (as solution)	2400 ± 40	1930

#### CONCLUSIONS

The work described in this paper demonstrates the feasibility of polyethylene and polyester-styrene as potential solidification agents for sodium nitrate waste.

Both materials demonstrated good leaching characteristics and high compressive yield strength. High loading efficiencies (up to 70 wt%) are shown for polyethylene. To date, waste loading studies have not been completed in the case of polyester-styrene above 33 wt% loading.

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