SOLIDIFICATION OF PROBLEM WASTES ANNUAL PROGRESS REPORT

October 1985 — September 1986

BNL--52078

DE88 001584

E.M. Franz, John H. Heiser, III and P. Colombo

February 1987

NUCLEAR WASTE RESEARCH GROUP
DEPARTMENT OF NUCLEAR ENERGY
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, LONG ISLAND, NEW YORK 11973

Prepared for the
NATIONAL LOW-LEVEL WASTE MANAGEMENT PROGRAM
UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency, contractor or subcontractor thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency, contractor or subcontractor thereof.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes:
Printed Copy: A03; Microfiche Copy: A01

TABLE OF CONTENTS

	Page
ABSTRACT.....	vii
1. INTRODUCTION.....	1
2. TYPES AND GENERATION SITES OF PROBLEM WASTE.....	3
2.1 Sites of Waste Generation.....	3
2.2 Problem Waste Types.....	3
2.2.1 Sodium Nitrate Waste.....	6
2.2.2 Compactible Waste.....	7
2.2.3 Sludge Waste.....	7
2.2.4 Incinerator Ash.....	8
3. SOLIDIFICATION OF SODIUM NITRATE WASTE.....	9
3.1 Polyethylene.....	9
3.1.1 Process Development Studies.....	9
3.1.2 Evaluation of the Properties of the Waste Form.....	12
3.1.2.1 Leachability Test.....	12
3.1.2.2 Compressive Yield Strengths.....	15
3.1.2.3 Water Immersion Test.....	16
3.2 Polyester-Styrene Resins.....	17
3.2.1 Ordinary Polyester-Styrene.....	18
3.2.2 Water Extendible Polyester-Styrene.....	19
3.2.3 Evaluation of the Properties of the Waste Form.....	21
3.3 Modified Portland Cement.....	23
3.3.1 Latex Modified Cement.....	24
3.3.2 Formulations.....	24
3.3.3 Evaluation of the Properties of the Waste Form.....	25
3.4 Thermal Stability of Waste Form Components.....	25
3.4.1 Analytical Procedure.....	28
3.4.2 Test Results.....	28
4. STABILIZATION OF COMPACTED WASTE.....	31
4.1 Formulations.....	31
4.1.1 Polymer Systems.....	31
4.1.2 Waste Compaction.....	31
4.2 Process Development Studies.....	32

TABLE OF CONTENTS cont.

	Page
4.3 Evaluation of the Properties of the Waste Form.....	32
4.3.1 Water Immersion Test.....	33
4.3.2 Compressive Strength.....	33
4.3.3 Biodegradation.....	33
5. CONCLUSIONS.....	35
REFERENCES.....	36

LIST OF TABLES

Table No.	Page
1. Summary of DOE Problem Wastes and Their Generation Sites.....	4
2. Average NaNO_3 Leaching Indices for Polyethylene Waste Forms.....	15
3. Compressive Yield Strengths of Polyethylene Waste Forms Containing Sodium Nitrate Waste.....	16
4. Formulations for Solidification of NaNO_3 Waste in Water- Extendible Polyester-Styrene.....	20
5. Average NaNO_3 Leaching Indices for Polyester-Styrene Waste Forms...	23
6. Compressive Yield Strengths of Polyester-Styrene Waste Forms Containing Sodium Nitrate Waste.....	24
7. Chemical Composition of Simulated Sodium Nitrate Wastes.....	26

LIST OF FIGURES

Figure No.	Page
1. Photograph of laboratory-scale, single-screw extruder with dual feed-hoppers.....	11
2. Cumulative fraction leached of sodium nitrate as a function of time from polyethylene waste forms.....	14
3. Cumulative fraction leached of sodium nitrate as a function of time from polyester-styrene waste forms.....	22
4. Cumulative fraction leached of sodium nitrate as a function of time from portland cement and latex modified portland cement waste forms.....	27
5. Differential scanning calorimeter (DSC) thermograms of: NaNO_3 ; polyethylene; mixture of NaNO_3 and polyethylene.....	29
6. Differential scanning calorimeter (DSC) thermograms of: NaNO_2 ; polyethylene; mixture of NaNO_2 and polyethylene.....	29
7. Differential scanning calorimeter (DSC) thermograms of: NaNO_3 ; polyester-styrene; mixture of NaNO_3 and polyester-styrene...	30
8. Differential scanning calorimeter (DSC) thermograms of: NaNO_2 ; polyester-styrene; mixture of NaNO_2 and polyester-styrene...	30
9. Sample A: Stabilized compacted waste after immersion in water for 195 days. Sample B: Unstabilized compacted waste not subjected to immersion in water. Sample C: Unstabilized compacted waste after immersion for 3 hours.....	34

SOLIDIFICATION OF PROBLEM WASTES

Abstract

This report describes initial work on the development of solidification systems for sodium nitrate waste and compacted waste. Sodium nitrate waste has been solidified in three types of materials: polyethylene, polyester-styrene (PES), and latex cement. Evaluations of the properties of the waste form, such as the ANS 16.1 leaching test, water immersion 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 melting temperature of 120°C to produce a homogeneous mixture. Results of the leaching test for polyethylene waste forms containing 30, 50, 60 and 70 wt% sodium nitrate are presented as the cumulative fraction leached and average leaching indices. The cumulative fraction leached in 90 days was 9.0×10^{-3} , 6.3×10^{-2} , 1.5×10^{-1} and 7.3×10^{-1} , respectively. From the lowest- to the highest-loaded samples, the leaching indices ranged from 11 to 7.8; the compressive yield strengths ranged from 2550 to 720 psi after 90-day immersion in water.

Two basic types of PES were used. One consists of PES resins which can be used to solidify dry wastes and the other is a water-extendible polyester (WEP) which is capable of immobilizing either dry or wet wastes. A promoter-catalyst system was chosen which facilitated curing at room temperature. The leaching of PES- and WEP-waste forms containing 25-33 wt% sodium nitrate resulted in a cumulative fraction leached which ranged between 8×10^{-2} and 1.8×10^{-1} . The leaching indices ranged between 9.3 and 8.9 and the compressive yield strength between 7710 and 2070 psi after 90-day immersion in water.

Waste forms of latex modified cement containing 13 and 23 wt% sodium nitrate were prepared and leach tested. The cumulative fraction leached was 5.1×10^{-1} and 6.8×10^{-1} and the leaching indices were 7.5 and 7.2, respectively.

Compacted waste was stabilized at room temperature with styrene monomer containing 10-40% trimethylolpropane trimethacrylate (TMPTMA) as a co-polymer in the presence of a promoter and catalyst. Laboratory-scale samples of stabilized compacted waste were immersed in water for 90 days: this caused dimensional changes of +3% in diameter and +8% in length. After immersion for 195 days their compressive strength averaged 2930 psi.

1. INTRODUCTION

In November, 1984, the DOE Ad Hoc Contractors Committee issued an informal Needs Assessment Document which identified "problem" wastes at the various DOE sites.

Problem wastes are defined as those low-level radioactive wastes (LLW) for which past or present solidification processes are deemed either technically or economically inadequate. Since a major objective of the Low-Level Waste Management Program (LLWMP) is to minimize the hazards associated with radioactive wastes consistent with economic and social requirements, a program sponsored by the U.S. DOE-LLWMP was initiated at Brookhaven National Laboratory (BNL) in FY 1986 to document and develop technology for improved treatment and solidification of such wastes.

A primary objective of this program was to supplement information given in the Needs Assessment Document by direct contact with site personnel. This was accomplished through site visits and telephone communications, specifically to obtain data on the characterization of wastes which is important in the selection/development of suitable solidification agents.

A compilation of the data resulting from this survey was submitted as a letter report to the LLWMP in July 1986. The report is entitled, "Identification, Characterization and Selection of DOE Low-Level Radioactive Problem Wastes," by E.M. Franz and P. Colombo, BNL-38496, April 1986.

Based on the results of the survey, the problem waste streams of most concern are sodium nitrate waste, compacted waste, sludges (primarily in ponds and basins) and incinerator ash. Criteria for the selection of these wastes were based on considerations such as the volumes produced, the commonality of the problem, as identified by the various DOE sites, and the severity of the problem, in terms of radioactivity content and storage problems.

Subsequent to the site survey, a decision was made to emphasize the development of solidification systems for sodium nitrate waste and to initiate studies on the stabilization of compacted waste. This report provides details of the progress made in FY 1986. The results of some waste form property evaluation tests are also given.

2. TYPES AND GENERATION SITES OF PROBLEM WASTE

Information on the identification and characterization of problem wastes was compiled from various sources, which included the informal Needs Assessment Document issued by the DOE Ad Hoc Operating Contractors Committee, November 1984, and data obtained by contacts with appropriate waste-management personnel at the major DOE facilities where waste is generated. A literature search indicated that information regarding the chemical composition, activity levels and generation rates for low-level waste streams generated at DOE sites was either sparse, non-existent or outdated.

2.1 Sites of Waste Generation

The major DOE sites visited by BNL are: Savannah River Laboratory (SRL), Oak Ridge National Laboratory (ORNL), Rocky Flats Plant (RFP), and the Idaho National Engineering Laboratory (INEL) which includes the Radioactive Waste Management Complex (RWMC) and the Westinghouse Idaho Nuclear Company (WINCO).

Information was also obtained through telephone conversations between BNL and the Feed Materials Production Center (FMPC), Goodyear Atomic Corporation (GAC), the Richland Hanford Operations (RHO), Los Alamos Scientific Laboratory (LASL) and the Monsanto Mound Facility. Although all of the sites generate numerous waste streams, the ones addressed here are those which were identified by the sites as being major problem waste streams.

2.2 Types of Problem Waste

In general, detailed information on the characterization of some of the problem wastes is unavailable. However, many of the sites have begun to analyze their waste streams in more detail to determine whether they contain materials which would place them in the mixed waste category. Mixed waste and transuranic (TRU) waste streams are not included in this study.

A summary of the DOE problem wastes, as identified at the various generation sites, is given in Table 1. The waste streams listed were categorized into groups which may be amenable to similar treatment/solidification options.

Table 1

Summary of DOE Problem Wastes and Their Generation Sites

Problem Waste Categories			DOE Waste Generation Sites																	
			ROCKY FLATS	MOUND	SANDIA	LASL	FERMI	SRL	OAK RIDGE X-10	OAK RIDGE Y-12	OAK RIDGE K-25	HANDFORD	FMPC	LAWRENCE LIVERMORE	INEL RMC	INEL WINCO	PADUCAH GAS DIF.	SANDIA LIVERMORE	GAC	
DRY	COMBUSTIBLE	COMPACTIBLE						.	.	.	.		.							
		COMBUSTIBLE (+ ASH)	.					.	.	.	.		.		.					
	NON-COMBUSTIBLE	COMPACTIBLE						.					.							
		NON-COMPACTIBLE				.		.					.							
WET	AQUEOUS	CONCENTRATE SALTS	.					.	.		.	.			.					
		SLUDGES	IN TANKS	.					.	.	.	.	.							
			IN PONDS, BASINS OR PITS						.	.	.	.	.							
		ACIDS & CORROSIVE LIQUIDS										.								
		DECON WASTES				.			.											
		ION EXCHANGE RESINS																.		
		MISC. LIQUIDS			.	.														
	ORGANIC	VOLATILES	.			.		.		.	.	.								
		NON-VOLATILES						.				.								
		METAL & METAL OXIDES	DRY	.								.	.	.			.			
WET			.									.								

The only types of problematic waste streams reported by the Sandia Livermore Laboratories and the Fermi Laboratories were categorized as mixed wastes, therefore, this information was not included in Table 1. However, several of the those included in Table 1 have been since categorized as mixed wastes.

Based on the data presented in Table 1, problem waste streams identified by most sites are:

- dry bulk waste - compactible and/or combustible (yielding incinerator ash)
- concentrate salts - mainly nitrates
- sludges - most importantly those in ponds, basins and pits
- volatile organic liquids
- dry metals and metal oxides

By volume, the dry bulk wastes, concentrate salts and sludges in ponds exceed the other two categories. The dry bulk wastes and concentrate salts are produced continuously, therefore, their solidification will involve long-term efforts. The use of sludge ponds will be totally discontinued within a few years and consequently their stabilization will be a relatively short-term but extensive undertaking because of the large amounts of material involved. The effluent wastes which were stored and treated in these ponds are still being produced. Instead of putting them into ponds, the wastes will be treated at effluent treatment plants or stored until such plants are built. In general, the treatment of effluent wastes involves such steps as filtration, precipitation, ion exchange and evaporation. The resultant sludge will be stored or solidified prior to disposal. However, the technology for the suitable solidification of some of these sludges is not presently available.

The level of radioactivity of incinerator ash and dry metals may exceed that of the other categories. Because of the reduction in volume achieved during incineration, the specific activity of the incinerated waste is greatly increased. Although dry metals often include parts of equipment which contain

high levels of induced activity, the problem with the large pieces of activated metal is more often in the handling and shielding rather than in the immobilization of the waste.

There is a question regarding the classification of some of the volatile organic liquids listed as problem LLW in Table 1. Recent communications with the sites suggest that some may be considered mixed wastes.

Of the wastes identified as needing improved treatment/solidification prior to disposal, the following were assigned the highest priority: concentrate salts (primarily sodium nitrate wastes), compacted waste, incinerator ash and sludges (in ponds and basins). This selection was based on the volumes of waste produced, the severity of the problems encountered and the commonality of the problem to the greatest number of sites.

2.2.1 Sodium Nitrate Waste

Nitrate waste is the product of a variety of operations that utilize nitric acid, such as reprocessing of spent fuel, the purification and enrichment of uranium, regeneration of ion exchange resins, and the decontamination and volume reduction of HLW. Over 250 million kilograms of nitrate wastes¹ are stored, primarily in DOE facilities, with more being produced each day.

Various methods for treatment or disposal of this waste are under consideration. These include thermal destruction of nitrate salts, chemical reduction of nitrate compounds, biodenitrification and physical disposal. At the present time, however, aqueous NaNO_3 slurries are incorporated into modified portland cements for disposal.

The inherent porosity of cement, in combination with a highly soluble salt such as NaNO_3 , results in high NaNO_3 leaching rates. Where site or state regulations restrict the release of NaNO_3 into the environment, cement admixtures are used, along with significant reductions in the amount of NaNO_3 which can be incorporated into the cement matrix. In selecting improved solidification processes, the specific site requirements placed on the properties

of the solidified waste have to be considered, as well as the compositional variations of the waste from site to site. For example, the salts at some sites (SRL) contain nitrites while others do not (RFP). Also, other constituents such as phosphates, sulfates, ammonia, fluorides and organics are present in some salt wastes while not in others.

2.2.2 Compactible Waste

Large volumes of compactible dry bulk waste, although usually with low levels of radioactivity, are produced at most of the DOE sites. This waste consists of contaminated paper, plastics, glassware, protective clothing, wood and rubber.

Much of this waste is subject to biodegradation under shallow land burial conditions and has been identified as a major cause of the subsidence of burial trenches and the deterioration of trench caps, particularly at humid or semi-humid sites. Such deterioration also is caused by the presence of voids in compactible waste packages and by the inability of some of these waste packages to sustain overburden loads. The need for stabilization of compactible wastes has been recognized by several sites (ORNL, SRL, INEL-RWMC) as an important consideration for trench stability. Similar problems have been reported at the Nevada Test Site (NTS).

2.2.3 Sludge Waste

Ponds and basins have been in use for over twenty years at many DOE sites for treatment of effluent wastes. Since the use of these ponds is being discontinued, the sludges contained in them will have to be stabilized to minimize dispersion of contamination. Although not as high in radioactivity as some of the other types of problem waste, the sludges represent a high volume waste. Recently, several of these pond wastes were classified as mixed wastes. Although the waste in many of the ponds has not yet been completely characterized, it is recognized that the ponds vary from each other in their gross radiological and chemical composition, depending on which part of the plant they served. The pH values range from 2 to 10, with most of the ponds being in

the upper part of this range. However, the pH varies from time to time, depending on chemical treatment such as the addition of oxalic acid or sodium hydroxide.

2.2.4 Incinerator Ash

Many of the sites are considering incineration of dry bulk waste in the near future as a viable option to reduce the volume of waste. The RWMC at INEL already incinerates most of its combustible waste. Because of the higher specific activity of the residue ash and its dispersive characteristics, solidification of the ash is considered important for minimizing trench subsidence and for preventing dispersion of radioactivity into the environment.

3. SOLIDIFICATION OF SODIUM NITRATE WASTE

This section describes preliminary work on the use of various types of matrix materials for the encapsulation of simulated NaNO_3 wastes, as a dried powder and as a slurry. These materials include polyethylene, polyester-styrene, water-extendible polyester-styrene and a modified latex cement. Tests of leachability, compressive strength and immersion in water, were performed to evaluate the integrity of the waste forms.

3.1 Polyethylene

The present studies on the development of polyethylene as a solidification agent for sodium nitrate waste are an extension of previous work performed at BNL on the immobilization of simulated PWR and BWR evaporator concentrates, using an extruder process^{2,3}.

Polyethylene is a thermoplastic polymer of crystalline-amorphous structure consisting of linear molecular chains that normally are not cross-linked. At elevated temperatures polyethylene goes from a hard material to a rubbery or flowable liquid. On cooling, the polymer reverts to its original state. Since the solidification process is not dependent upon complex chemical reactions, as in the case of hydraulic cements and thermosetting polymeric systems, processing is simplified and solidification is assured upon cooling.

3.1.1 Process Development Studies

For incorporating the waste into the polyethylene an extrusion method was selected based on such considerations as ease of processibility, packing efficiency, quality control and available technology.

This process employs a commercially available 1 1/4 inch single-screw extruder, manufactured by Killion Extruders, Inc., Verona, NJ. The extruder was modified to accommodate a dynamic feed system with two 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 the waste and the binder are introduced into the extruder. A photograph of the extruder is shown in Figure 1.

The process is especially well suited for incorporation of dry wastes resulting from advanced volume-reduction systems. Although these studies were performed with simulated dry salt waste, the processing equipment can be modified to accommodate wet wastes. This would result in a system similar to the type presently used in the United States and abroad for processing and encapsulating wet solid wastes in bitumen.

Based on previous work involving the solidification of simulated sodium sulfate waste in polyethylene^{2,3} a low-density (0.924g/cc) polyethylene with a melt index of 55gm/10 minutes was chosen. A low-density polyethylene is preferred for the solidification of radioactive waste, since the processing temperatures and pressures are appreciably lower than those required for high-density polyethylene^{2,3,4}. Low processing temperatures are more desirable not only for economic reasons, but also for ease of processibility and prevention of volatilization/decomposition of the waste components.

The extrusion process for solidification of radioactive waste in polyethylene involves the heating, mixing and extruding of materials in one basic operation. The process is broken down into the following steps:

1. The polyethylene binder and dry waste materials are transferred from storage in either a single hopper or individual hoppers to the extruder feed throat. Metering of waste-to-binder ratios is accomplished at this step.
2. The mixture is conveyed through a heated cylinder by the motion of the rotating screw. The initial portion of the cylinder is kept at a temperature below 120°C, the melting point of polyethylene. This serves to gradually pre-heat the materials but, at the same time, assures proper transport of the mixture.

Figure 1.

Photograph of laboratory-scale single-screw extruder with dual feed-hoppers.

3. As the waste-binder mixture moves forward past the initial pre-heating zone, it is masticated under pressure by compression as the channel area between the screw and cylinder is gradually reduced. The rotation of the screw also assists in mixing the materials into a homogeneous state.
4. The gradual transfer of thermal energy by the combined effects of the barrel heaters and frictional heat melts the polyethylene. The frictional heat is difficult to control and must be compensated for by regulating the resistance band heaters. In some cases, excessive heat must be removed by the use of external blowers.
5. The melted thermoplastic-waste mixture is forced through an output die into a container where it cools and solidifies.

3.1.2 Evaluation of the Properties of the Waste Form

The stability of a waste form is an important factor in controlling the release of NaNO_3 waste into the environment. A series of evaluation tests were suggested in NRC's Branch Technical Position Paper on Waste Form⁵, in support of 10 CFR 61. Two of these tests, the 90-day immersion in water and the ANS 16.1 Leach Test, were used in this study to evaluate polyethylene- NaNO_3 waste forms. The method outlined in ASTM D-695 was used to evaluate the compressive yield strengths.

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

3.1.2.1 Leachability Test. Leaching tests were performed for a minimum duration of 90 days in accordance with the procedures in ANS 16.1 Standard, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes"⁶. This test was designed to provide a standardized laboratory method

for characterizing the leaching behavior of low-level waste forms. Although the test procedures do not necessarily simulate the leaching of the waste form under actual burial conditions, they allow a comparison of the relative leachability of various waste and binder combinations. This test specifically addresses the leaching of radionuclides, however, it also is applicable to non-radioactive chemical species and is used in these studies to determine the release rate of NaNO_3 from the waste forms.

Replicate samples of polyethylene waste forms containing 30, 50, 60 and 70 wt% NaNO_3 were leached in demineralized water. The volume of leachant employed ranged between 1500 and 1700 ml, as specified by the ratio of 10 ± 0.2 cm of leachant volume to external geometric surface area of the waste form. The temperature was maintained at $20 \pm 2^\circ\text{C}$. After rinsing the specimens for an initial 30 seconds, the leachant was replenished at the following time intervals: 2 hour, 5 hour, 17 hour, 24 hour intervals for the next four days, 13 day, 28 day and 45 day, for a total of ten leachate samplings. Aliquots of the leachates were analyzed for sodium (Na) using atomic absorption spectrophotometry. Since the only source of Na in the samples is NaNO_3 , the amount of Na released from the samples corresponds directly to the amount of NaNO_3 released. The leaching data for NaNO_3 from polyethylene waste forms are presented in Figure 2 as the cumulative fraction leached vs. leaching time (days).

These data clearly demonstrate the dependence of leachability upon increased waste loadings of 30, 50, 60 and 70 wt% NaNO_3 . The average cumulative fraction leached at the end of ninety days is 9×10^{-3} , 6.3×10^{-2} , 1.5×10^{-1} and 7.3×10^{-1} , respectively.

The leaching indices were calculated as prescribed in the ANS 16.1 method⁶. 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 between different solidification materials.

Figure 2. Cumulative fraction leached of sodium nitrate as a function of time from polyethylene waste forms.

Average leaching indices were calculated for each of the replicate sets of polyethylene waste forms. These values are listed in Table 2. Since the leaching index is inversely proportional to effective diffusivity, higher index values represent reduced leachability.

Table 2

Average NaNO_3 Leaching Indices for Polyethylene Waste Forms^a

<u>Waste Loading NaNO_3 (wt%)</u>	<u>Average Leaching Index</u>
30	11.1
50	9.7
60	9.0
70	7.8

a. Calculated in accordance with ANS 16.1 Leach Test.

3.1.2.2. Compressive Yield Strengths. To ensure that a waste form remains stable under the compressive loads inherent in a disposal environment, NRC has recommended that solidified waste forms should have compressive strengths of at least 50 psi when tested in accordance with ASTM C-39 or ASTM D-1074. Since polyethylene does not have a discrete brittle fracture yield point under compressive load, the standard compressive strength tests recommended by the NRC are not applicable. Instead, the ASTM D-695 "Standard Test Method for Compressive Properties of Rigid Plastics," was used as an alternative. Prior to testing, the samples were machined so that the ends were parallel, as prescribed in Section 6.1 of ASTM D-695. The compressive yield measurements were performed using a Soiltest AP1000 Universal Testing Machine. The compressive yield strength in pounds per square inch was determined by dividing the vertical load obtained at the plateau of the

stress-strain curve (yield point) by the original cross-sectional area of the test specimen. The compressive yield strength of polyethylene samples containing 30, 50, 60 and 70 wt% NaNO_3 are given in Table 3.

Table 3

Compressive Yield Strengths Of Polyethylene Waste Forms Containing
Sodium Nitrate Waste

Waste Loading wt.% NaNO_3	Compressive Yield Strength (psi)	
	Before Immersion	After 90 Day Immersion
30	2370	2550
50	1920	1920
60	2200	2310
70	1020	720

3.1.2.3 Water Immersion Test. Waste forms disposed by shallow land burial may encounter periods of exposure to aqueous conditions in the form of percolate/groundwater. Depending upon the composition of the waste and solidification material, water may cause swelling, cracking, dissolution or exfoliation of the waste form and subsequent deterioration of the disposal trench.

Immersion tests were performed on simulated waste forms for ninety days. Specimens were immersed in deionized water in sealed polypropylene containers. At the end of ninety days the compressive yield strength of the specimens was measured and compared to the control specimens. These data also are included in Table 3.

3.2 Polyester-Styrene Resins

The essential ingredients in commercial unsaturated polyester resins are a linear polyester resin, a cross-linking monomer and inhibitors to retard cross-linking until the resin is ready for use. The usual cross-linking monomers are styrene, methyl methacrylate, vinyl toluene, alpha-methyl styrene, and diallyl phthalate. However, the cross-linking monomer most extensively used is styrene. Polyester-styrene mixtures are available from the manufacturer in varying proportions depending on its use. Resin manufacturers make other modifications of the basic resins before shipment, such as the addition of promoters for initiating cures at room temperature and incorporation of thixotropic agents, such as pyrogenic silica, for increasing the viscosity of the resin mixture. Other additives may be added for fire retardance, improved chemical resistance, better weathering characteristics and for minimizing shrinkage during curing.

The process of converting polyester resins from liquids to solids involves a chemical reaction between the polyester resin and the monomer in which the polyester is dissolved, to form a cross-linked, thermoset polymer. This chemical reaction is activated by a free radical mechanism which opens the unsaturated (double) bonds in the polyester chain or styrene monomer. Once a thermoset material is formed, the plastic cannot be reformed or remelted as can thermoplastic materials, such as polyethylene.

Ordinary polyester-styrene (PES) is not compatible with water. Therefore, dried wastes must be used to form suitable waste forms. However, modified polyester-styrene resins capable of immobilizing aqueous wastes also are commercially available. These are called water-extendible polyester-styrenes (WEP) and can be used, provided that the pH of the aqueous waste is adjusted between 7-9 and that high speed, high-shear agitation is used to form a water-in-oil emulsion between the aqueous waste and the organic polymer. The emulsion is solidified by addition of suitable combinations of a peroxide catalyst and promoter.

3.2.1 Ordinary Polyester-Styrene

Formulations

A typical formulation used to prepare polyester-styrene- NaNO_3 samples is:

Ingredients	Wt. %
polyester-styrene (Ashland 1289-2)	63
sodium nitrate (NaNO_3)	31
thixotropic agent	5.0
dimethylaniline (promoter)	0.4
benzoyl peroxide (catalyst)	1.0

The above formulation is based on preliminary work. It is anticipated that the use of more viscous polyester-styrene mixtures will effectively result in increased waste loadings.

Process Development Studies

The following laboratory procedure was developed for the encapsulation of simulated, dried NaNO_3 waste in ordinary polyester-styrene:

- A preferred promoter is added in the proper proportion to the base polyester-styrene resin.
- A measured amount of thixotropic (thickening) agent is added to adjust the viscosity of the base resin. Depending on the density of the dried waste, this may be necessary for minimizing segregation of the waste and binder mixture during curing.
- Dried NaNO_3 salt waste is stirred into the resin, to form a homogeneous mixture.

- A compatible catalyst is subsequently mixed in to evenly distribute the catalyst throughout the mixture.
- The mixture is cured in place, or is cast into appropriate containers and then cured.

3.2.2. Water-Extendible Polyester-Styrene

Water-extendible polyester-styrene (WEP) has an advantage over PES in that it is compatible with wet wastes, such as slurries or solutions of nitrate salts.

Formulations

Trial formulations which have proven satisfactory using NaNO_3 slurries and solutions are given in Table 4. Further studies are planned to determine maximum waste loadings.

Process Development Studies

The procedure for the fabrication of WEP- NaNO_3 waste forms is as follows:

- The specified promoter, in this case cobalt naphthenate, is added to the base WEP.
- Where required, a predetermined amount of thixotropic agent is added to adjust viscosity.
- Salt slurry or solution is slowly added to the WEP mixture, using high-shear mixing to form an emulsion.
- Catalyst (i.e., methyl ethyl ketone peroxide) is slowly added using high-shear mixing.
- The mixture is cured in place, or cast into appropriate containers and allowed to cure.

Table 4

Formulations for Solidification of NaNO_3 Waste in Water-Extendible Polyester-Styrene

RESIN ¹ TYPE	WT%	NaNO ₃ WASTE		THIXO- TRIPOC MATERIAL WT%	CATAYLST (Initiator) Methyl Ethyl Ketone Peroxide (MEKP) WT%	PROMOTER (Accelerator) Cobalt Naphthenate (CoN) WT%
		NaNO ₃ WT %	WATER WT%			
TYPE A ²	36	28	35	-	0.5	0.4
TYPE B ³	35	29	36	-	0.4	-
TYPE A	62	27	6.0	4.4	0.6	0.6
TYPE B	56	25	15	4.0	0.5	-

¹Pre-promoted

²Ashland WEP-662

³Alpha Altek 78-50ERM

3.2.3 Evaluation of the Properties of the Waste Form

The evaluation of the properties of the waste form was based on the ANS 16.1 Leach Test, the ASTM D-695 compressive strength test and the 90-day water immersion test.

Leach Tests

Samples containing 33 wt.% NaNO_3 as dry salt were prepared using PES. Samples containing 25 to 27 wt.% NaNO_3 as a slurry were prepared using WEP as the solidification agent. WEP also was used for samples containing 28 wt.% NaNO_3 as solution waste. All of the samples were leached in demineralized water according to the ANS 16.1 Leach Test. The volume of the leachate was 10 ± 0.2 times the surface area of the samples and ranged between 1500 and 1700 ml. Temperature was maintained at $20 \pm 2^\circ\text{C}$. Aliquots of the leachate were analyzed for sodium using atomic absorption spectrophotometry.

The resultant data are calculated as cumulative fraction leached (CFL). The CFL plotted as a function of leaching time is shown in Figure 3. These curves show that all waste forms have similar leaching characteristics, whether the waste was incorporated as a dry salt, salt slurry or salt solution. The CFL at the end of 90 days of leaching ranged between 8×10^{-2} and 1.8×10^{-1} . The calculated average leaching indices, presented in Table 5, fall into a narrow range between 8.9 and 9.3.

Compressive Yield Strengths

Triplicate samples taken from the same lots used in the leach test were tested for compressive yield strength according to ASTM D-695. The results, given in Table 5, show that PES- NaNO_3 and WEP- NaNO_3 waste forms have compressive yield strengths that exceed 2000 psi.

Leaching of Sodium Nitrate from Polyester-Styrene Waste Forms

Figure 3. Cumulative fraction leached of sodium nitrate as a function of time from polyester-styrene waste forms.

Table 5

Average NaNO_3 Leaching Indices for Polyester-Styrene Waste Forms

Resin Type	Waste Loading NaNO_3 (wt%)	Average Leaching Index
PES	33 (dry)	9.2
WEP-A	25 (as slurry)	9.3
WEP-B	27 (as slurry)	9.1
WEP-A	28 (as solution)	8.9
WEP-B	28 (as solution)	9.3

Water Immersion (90 day) Test

Water immersion tests were performed on PES and WEP samples to determine their mechanical stability following exposure for 90 days. Samples, taken from the same lots as the leaching samples, were placed in deionized water, and after 90 days, compressive yield strengths were measured according to ASTM D-695. Measurements were made immediately upon removal of the samples from the water. The data is presented in Table 6. All of the samples tested exceed 2000 psi in compressive yield strength.

3.3 Modified Portland Cement

Portland cement, with and without additives, is used extensively in the solidification of radioactive wastes. Most cement additives are selected primarily for their ability to retard the leaching of radionuclides. These materials include adsorbers such as clays, fly ash, and do little towards restricting the movement of soluble salts without compromising either the properties of the waste forms or the waste loadings.

Table 6

Compressive Yield Strengths of Polyester-Styrene Waste Forms Containing Sodium Nitrate Waste

Resin Type	NaNO ₃ Wt%	Water Wt%	Compressive Yield Strength (psi)	
			Before Immersion	After (90 Days) Immersion
PES	33 ^a	--	7730	7710
WEP-A	25 ^b	5.5	3180	3050
WEP-B	27 ^b	14.9	5420	3440
WEP-A	28 ^c	35.4	2440	2120
WEP-B	28 ^c	35.6	2400	2070

a. Dry salt waste.

b. Salt slurry.

c. Salt solution.

3.3.1 Latex Modified Cement

Latex modified cement has been in use for some time to retard the corrosion of steel reinforcements in concrete^{7,8}. The "modifier" is a styrene butadiene latex admixture that acts as a water reducer. Water-reducers or plasticizers reduce by about 25-35% the amount of water needed to make a workable, mixable cement, thereby decreasing its porosity and hence permeability to water. Since latex has been shown to retard chloride ion movement in cement^{8,9}, the latex may also retard nitrate releases.

3.3.2 Formulations

The latex modifier used was an aqueous emulsion containing ~48% solids. Normal practices were followed to make the cement with a water/cement ratio of 0.30 to 0.40. This ratio includes the water present in the latex emulsion. The latex emulsion was added to yield a latex/cement ratio of 0.15.

Laboratory-scale samples were prepared using portland type II cement. Two lots were prepared, the first contained 13 wt% and the second 23 wt% sodium nitrate. Both lots had a water/cement ratio of 0.30 and a latex/cement ratio of 0.15. The ingredients were mixed together in a 3-quart laboratory cement mixer. The cement was transferred to plastic containers and allowed to set for one day in the containers and an additional 7 days in air. Samples measured 4.8 cm diameter and 9.0 cm in length.

3.3.3 Evaluation of the Properties of the Waste Form

Samples of latex-modified cement were tested to determine the rate of nitrate release. Samples containing 13 and 23 wt% sodium nitrate were leached in deionized water according to the ⁰ANS 16.1 Leach Test. The data, which is plotted as the cumulative fraction leached (CFL) vs. leaching time, is shown in Figure 4 and is compared to the leaching data of plain portland cement sample containing 9 wt% NaNO_3 . For modified cement samples containing 13 and 23 wt% NaNO_3 , the CFL is 5.1×10^{-1} and 6.8×10^{-1} respectively, and the average leaching index (LI) is 7.5 and 7.2 respectively, at the end of 90 days of leaching. For the unmodified cement sample, the CFL is 2.9×10^{-1} and $\text{LI}=8.0$. When normalized for differences in waste loading, the leach rates for latex-modified cement and unmodified cement are similar. This may be the result of instability of the latex during sample preparation. Further work is needed on latex and other cement admixtures which inhibit or retard water permeability.

3.4 Thermal Stability of Waste Form Components

The radionuclide content and the chemical composition of sodium nitrate waste can vary, depending on the process used to generate the waste and its subsequent treatment for storage or disposal. Typical chemical composition of NaNO_3 waste streams, generated at the Savannah River Plant (SRL) and the Rocky Flats Plant (RFP) are shown in Table 7. Both waste streams contain a substantial amount of NaNO_3 , however, notable differences exist in the types and concentration of chemical constituents in the waste. Of particular interest to this study is the presence of sodium nitrite (NaNO_2) in SRL waste and potassium nitrate (KNO_3) in RFP waste. Both compounds, along with sodium nitrate (NaNO_3), are categorized as strong oxidizers and are considered to be unstable at elevated temperatures and/or in combination with organic materials.

Figure 4. Cumulative fraction leached of sodium nitrate as a function of time from portland cement (PC) and latex modified portland cement (LMC) waste forms.

Table 7

Chemical Composition of Simulated Sodium Nitrate Wastes¹
 ROCKY FLATS PLANT
 (Spray-Dried Nitrate Waste)

<u>COMPOUND</u>	<u>(WT %)</u>
NaNO ₃	53.9
KNO ₃	33.9
NaCl	3.2
KCl	2.2
Na ₂ SO ₄	2.8
K ₂ SO ₄	1.8
Na ₃ PO ₄	0.9
K ₃ PO ₄	0.6
NaF	0.4
KF	0.3

 SAVANNAH RIVER PLANT
 (Decontaminated, Aged Salt Solution)

<u>COMPOUND</u>	<u>SOLUTION (WT%)</u>
H ₂ O	68
NaNO ₃	15.6
NaNO ₂	3.9
NaOH	4.2
NaCO ₃	1.7
NaAlO ₂	3.6
Na ₂ SO ₄	1.9
NaF	0.06
NaCl	0.12
Na ₂ SiO ₃	0.04
Na ₂ CrO ₄	0.05
Na ₂ C ₂ O ₄	0.31
Na ₃ PO ₄	0.13
NaB(C ₆ H ₅) ₄	0.06
Other Salts	0.20

Since the solidification agents considered for this study are organic materials (polyethylene, polyester-styrene), a series of experiments were conducted to determine the thermal stability of the waste components of interest and the polymer materials, alone and in combination.

3.4.1 Analytical Procedure

A Perkin-Elmer Differential Scanning Calorimeter (DSC) was used to determine the thermal behavior of selected waste components, individually, and in combination with the solidification agents. Samples were analyzed at a scanning rate of 40°C/min, over a range from 50°C to 400°C.

3.4.2 Test Results

The thermograms, shown in Figures 5-8, describe the thermal behavior of the various components at temperatures to 400°C. Thermograms for polyethylene, NaNO_3 and NaNO_2 , are compared in Figures 5 and 6. Similar techniques were used for comparing sets of data in Figures 7-8.

In each case, the thermal profiles depict endothermic reactions characteristic of the melting points and transition temperatures of the respective compound. The absence of exothermic reactions, at temperatures in excess of the melting point of the materials, attests to their stability when exposed to high temperatures in the presence of polyethylene and polyester-styrene. For comparison, processing temperatures for polyethylene- NaNO_3 waste forms is approximately 120°C, while exotherm temperatures resulting from monomer-polymer conversion of polyester-styrene- NaNO_3 waste forms is below 150°C.

Further thermal stability studies are underway which include the use of actual waste, as generated at SRL.

Thermograms

Figure 5

Figure 6

Differential Scanning Calorimeter (DSC)
Thermograms

Figure 7

Figure 8

4. STABILIZATION OF COMPACTED WASTE

The stabilization of compacted waste is unique in that mixing/stirring techniques cannot be utilized. Instead, in-situ impregnation or prewetting techniques must be used to produce a satisfactory waste form.

This section describes preliminary investigations on stabilization methods and testing of waste forms. A more concentrated effort is planned for FY 1987.

4.1 Formulations

4.1.1 Polymer Systems

Styrene monomer was selected as a base system because of its low, near-water viscosity, low cost and availability. The use of a low-viscosity monomer is important to facilitate penetration of the compacted waste.

Styrene is not amenable to polymerization by catalyst-promoter combinations, therefore, external heating is required to initiate the polymerization reaction for an effective cure in a reasonable time. However, in combination with other types of monomers, styrene can be cured at room temperature through the use of catalyst-promoter systems. Two materials which have been effective are trimethylolpropane-trimethacrylate (TMPTMA) and a polyester resin. Styrene-TMPTMA mixtures normally contain 20-40 wt% TMPTMA. Polyester-styrene mixtures contain 50-70 wt% polyester.

Styrene-TMPTMA was preferred for initial studies since it has a lower viscosity and better wetting properties than the polyester-styrene mixture. The monomer mixture was used in conjunction with a promoter-catalyst system which induced polymerization at room temperature in 15-20 minutes.

4.1.2 Waste Compaction

It is common practice at waste generation sites to compress certain waste materials in containers, as a volume reduction (VR) process. Several factors that affect VR include the applied force, the bulk density of the waste, the voids in the container, and the springback of the material.

All of these factors are important in considering the amount of monomer required to effectively stabilize the waste form, since the economic feasibility of such a process largely depends on the volume and cost of the monomer. Volume reduction can be improved by preshredding, using anti-spring devices and increasing compaction pressures.

In this study, waste was compacted to ~40-50 psi using a laboratory-scale hydraulic press. This is comparable to commonly used low-pressure 55-gallon drum compactors used in the nuclear industry. Future work will also include supercompacted waste.

4.2 Process Development Studies

Several methods are being considered for stabilizing compacted waste with polymer materials. These include:

- 1) impregnation of contained (55-gallon drums) compacted waste using a vacuum technique;
- 2) tumbler-mixing of monomer and shredded or "as-is" waste prior to compaction;
- 3) placing a prescribed amount of monomer in the drum, sufficient to saturate waste during compaction; and
- 4) simultaneous shredding and "wetting" of waste directly into drum prior to compaction.

4.3 Evaluation of the Properties of the Waste Form

The performance of stabilized compacted waste was evaluated using test procedures which simulate disposal environments. These include water immersion, compressive strength, and biodegradation. Leach tests were not performed pending results of the above tests.

4.3.1 Water Immersion Test

Samples of stabilized compacted waste, containing 75g waste and 70g of a styrene-TMPTMA mixture, were prepared for water immersion testing. The cylindrical samples (7.0 cm in diameter x 4.2 cm in length) were placed in deionized water, at room temperature, for a period of 90 days. Only slight dimensional changes (+3% in diameter and +8% in length) were detected at the end of this time period. The samples were re-immersed for a total of 195 days, at the end of which no further dimensional changes were noted. Figure 9 compares relative volumes for: stabilized compacted waste after immersion in water for 195 days (A), compacted waste, "as is" (B), and compacted waste after 3 hour exposure to water (C). A twofold increase in volume can be seen between samples B and C.

The stabilized compacted waste samples (60-40 styrene-TMPTMA), with waste-to-binder ratios of 1.1-1.2, had compressive strengths of ~2900 psi after 195-day immersion in water.

4.3.2 Compressive Strength

The compressive strength of stabilized waste forms was measured in accordance with ASTM C-39, "Compressive Strength of Cylindrical Concrete Specimens." Initial compressive strengths for these samples averaged 3100 psi.

4.3.3 Biodegradation

Samples containing a waste to binder ratio of 1.2 were subjected to biodegradation testing according to test methods described in ASTM G-21, "Determining Resistance of Synthetic Polymeric materials to Fungi" and ASTM G-22, "Determining Resistance of Plastics to Bacteria."

No fungal or bacterial growth was observed on the specimens after testing. Furthermore, their compressive strengths remained essentially the same, at 3100 psi.

Figure 9. Sample A: Stabilized compacted waste after immersion in water for 195 days.
Sample B: Unstabilized compacted waste not subjected to immersion in water.
Sample C: Unstabilized compacted waste after immersion for 3 hours.

5. CONCLUSIONS

- Laboratory-scale process development studies demonstrate the feasibility of polyethylene, polyester-styrene and water-extendible polyester-styrene as potential solidification agents for sodium nitrate waste.
- Polyethylene waste forms exhibit good leaching characteristics, high-compressive yield strength (700-2600 psi) and high-loading efficiencies (70 wt% NaNO_3).
- Initial studies with polyester-styrene and water-extendible polyester-styrene resins demonstrate good leaching characteristics and high-compressive yield strength (2100-7700 psi) at ~30 wt% NaNO_3 loading.
- Modified latex cement, when compared to ordinary portland cement, did not exhibit improved leaching characteristics for sodium nitrate waste.
- Compacted waste was successfully stabilized with a mixture of styrene and TMPTMA. Immersion in water for 195 days produced only slight dimensional changes (+3% in diameter and +8% in length) while the compressive strength remained at ~3000 psi.

REFERENCES

1. Johnson, A.J. and P.M. Arnold, Waste Generation Reduction - Nitrates, Comprehensive Report of Denitrification Technologies, Rockwell International, RFP-3899, March 15, 1986.
2. Kalb, P.D. and P. Colombo, "Polyethylene Solidification of Low-Level Wastes, Topical Report," BNL-51867, Brookhaven National Laboratory, Upton, NY, October, 1984.
3. Franz, E.M. and P. Colombo, Waste Form Evaluation Program, Final Report, BNL-51954, Brookhaven National Laboratory, Upton, NY, September, 1985.
4. Moriyama, N., et al, "Incorporation of an Evaporator Concentrate in Polyethylene for a BWR," Nuclear and Chemical Waste Management 3, 1982.
5. U.S. NRC, "Technical Branch Position on Waste Forms." Final Waste Classification and Waste Form Technical Position Papers. U.S. Nuclear Regulatory Commission, Washington, DC, May 1983.
6. ANS Standards Committee, Working Group 16.1, Measurement of the Leachability of Solidified Low-Level Wastes, American Nuclear Society, June, 1984.
7. Sprinkel, M.M., "Overview of Latex Modified Concrete Overlays," Final Report, Virginia Highway and Transportation Research Council, January 1985.
8. A Handbook on Portland Cement Concrete and Mortar Containing Styrene/Butadiene Latex, The Dow Chemical Company.
9. Kuhlmann, L.A., "The Effect of Cure Time on Chloride Permeability of Latex Modified Cement," Presentation at 1984 Fall Convention, American Concrete Institute, New York, New York, October 28-November 2.