A PROCESS FOR SOLIDIFYING SODIUM NITRATE WASTE IN POLYETHYLENE*

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ABSTRACT: A laboratory-scale process has been developed for the solidification of nitrate salt wastes in polyethylene. The process uses a commercially available single-screw extruder which continuously discharges prescribed polyethylene-waste mixtures from the hoppers to the output die, where it is extruded into a container while still in the molten form. The molten mixture ($-110-120^{\circ}\text{C}$) conforms to the shape of the container and solidifies upon cooling. Proportional feeders maintain waste to binder ratio and homogeneity of the waste form. Present studies use dry wastes, although wet solid wastes can be processed using vented extruders of the type used for the bitumen solidification process.

Tests were performed to determine leachability and mechanical stability. Emphasis is placed upon leaching of nitrates from the waste forms. Leach tests were performed according to ANS 16.1 as well as the EPA Extraction Procedure. For polyethylene waste forms containing 30-70 wt% sodium nitrate, ANS 16.1 leach indices range from 11 to 7.8, respectively. Compressive yield strengths range from 18 to 5 MPa (after 90 day water immersion). The results of the EPA Extraction Procedure indicate that the nitrate release levels for waste forms containing as much as 70 wt% sodium nitrate are not defined as characteristically hazardous waste.

Differential Scanning Calorimetry (DSC) was used to confirm the compatibility of polyethylene and simulated salt wastes at elevated temperatures. Components of the polyethylene/ NaNO_3 system, alone and in combination, were tested by DSC at temperatures to 400°C . At these temperatures, no chemical interaction were observed between polyethylene and nitrate waste compositions.

KEYWORDS: polyethylene, radioactivity, low-level waste, salt waste, hazardous waste, waste forms, extrusion process, leaching.

INTRODUCTION

Large quantities of nitrate salt waste are produced at various DOE facilities [1], as a result of nuclear fuel processing and reprocessing. Recent regulations regarding the amount of nitrates allowed into the ground has imposed severe restrictions on the types of solidification agents that can be used. In this study, polyethylene has been identified as an improved solidification agent for immobilization of nitrate wastes.

The selection of polyethylene was based on such considerations as materials properties, compatibility with the waste, solidification efficiency, ease of processibility, availability of materials and economic feasibility. Earlier studies at BNL have demonstrated the applicability of polyethylene for the solidification of PWR and BWR evaporator concentrates using the extruder process [2,3,4].

The use of polyethylene as an encapsulation material for LLW was originally suggested by researchers at Oak Ridge National Laboratory (ORNL) [5]. Polyethylene has also been used for solidification of low- and intermediate-level wastes in The Netherlands (unpublished) and Argentina [6,7]. Currently, researchers in Japan [8] have been investigating various methods for the encapsulation of low-level wastes in polyethylene.

TABLE 1--Nitrate waste composition [9]

SRP Nitrate Waste		RFP Nitrate Waste	
Component	Weight Percent	Component	Weight Percent
NaNO_3	48.9	NaNO_3	53.9
NaNO_2	12.2	KNO_3	33.9
NaOH	13.3	NaCl	3.2
Na_2CO_3	5.3	KCl	2.2
$\text{NaAl}(\text{OH})_4$	11.3	Na_2SO_4	2.8
Na_2SO_4	6.0	K_2SO_4	1.8
NaF	0.2	Na_3PO_4	0.9
NaCl	0.4	K_3PO_4	0.6
Na_2SiO_3	0.1	NaF	0.4
Na_2CrO_4	0.2	KF	0.3
$\text{Na}_2\text{C}_2\text{O}_4$	1.0		
Na_3PO_4	0.4		
$\text{NaB}(\text{C}_6\text{H}_5)_4$	0.2		
Other Salts	0.6		

Materials Compatibility

Differential scanning calorimetry (DSC) was used to determine the thermal behavior of nitrate wastes and waste components in the presence of polyethylene. Waste stream components comprising greater than 5 percent of the simulated waste compositions shown in Table 1 were characterized by DSC. Additionally, actual SRP nitrate waste was used. The waste solution obtained from SRP was vacuum dried and combined with polyethylene for thermal studies. Testing was performed at temperatures to 400°C, which is above the decomposition temperature of the major nitrate waste components, such as NaNO_3 and NaNO_2 . Several of the thermograms obtained using the DSC are shown in Figures 1 and 2. In all cases, the only observable peaks were characteristic endotherms corresponding to melting points or crystal transitions of the materials. The absence of exothermic peaks, at temperatures up to 400°C is an indication of the thermal stability of the polyethylene/nitrate waste mixtures.

SOLIDIFICATION PROCESS

An extrusion process was developed which simultaneously heats and blends the polyethylene and waste materials to produce a solid homogeneous waste form. Laboratory scale specimens were produced using a commercially available 3.2 cm single-screw extruder. A photograph of the extruder and hoppers is shown in Figure 3. A simplified schematic of the polyethylene extrusion process is given in Figure 4.

The extrusion process for solidification of radioactive waste in polyethylene involves the heating, mixing and extrusion 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 either a single hopper or individual hoppers in which they are stored 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 controlled at a temperature below the polyethylene melting point of 120°C. This serves to gradually pre-heat the materials but at the same time assures proper transport of the mixture.
3. As the waste-binder mixture moves forward past the initial pre-heating zone, it is masticated under pressure due to the compressive effects of a gradual reduction in the channel area between the screw and cylinder. Screw rotation also assists in the mixing of the materials to a homogeneous state.
4. The gradual transfer of thermal energy by the combined effects of the barrel heaters and frictional heat serves to melt the polyethylene. The frictional heat input is difficult to control and must be compensated for by the regulation of the resistance band heaters. In some cases it is necessary to remove excessive heat by the use of external blowers.
5. The melted thermoplastic-waste mixture is forced through an output die into a mold and is allowed to cool and solidify.

Based on experience, a processing temperature of -120°C was established. At this temperature, good processibility is obtained and problems associated with the decomposition-volatilization of wastes and waste form components are minimized.

The extruder employed in this study was not vented, requiring pre-drying of the aqueous nitrate waste prior to mixing with polyethylene. Commercially available vented extruders of the type used in bitumen processes would allow incorporation of wet nitrate waste as feed material.

PRODUCT EVALUATION

Stability of a waste form is an important factor in controlling the release of NaNO_3 waste into the environment. A series of waste form evaluation tests were suggested in NRC's Branch Technical Position Paper on Waste Form [10] in support of 10 CFR 61. Two of these tests, the 90-day immersion in water and the ANS 16.1 Leach Test [11], were used in this study to evaluate the polyethylene/ NaNO_3 waste forms. The method outlined in ASTM D-695 was used to measure the compressive yield strength after immersion testing. Since some of the States have adopted the EPA drinking water standards as a guideline for the amount of nitrates allowed to be released into the environment, the EPA Extraction Procedure [12] was performed to determine compliance.

ANS 16.1 Leach Test

Leach testing was performed for 90 days in accordance with the procedures in ANS 16.1 Standard, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes" [11]. The 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 waste form leaching under actual burial conditions, it allows a comparison of the relative leachability of various waste/binder combinations. This test addresses specifically the leaching of radionuclides, but it is also applicable to non-radioactive chemical species and is used in these studies to determine the release rate of NaNO_3 from the waste form.

Cylindrical specimens, measuring 4.5-4.9 cm in diameter and ~9 cm in length and containing 30, 50, 60 and 70 weight percent sodium nitrate, were leached in a volume of deionized distilled water such that the leachant volume to specimen surface area was 10 ± 0.2 (cm). The leachant was changed at prescribed time intervals and the leachate was analyzed for sodium using Atomic Absorption Spectrophotometry (AA). Since the only source of Na in the samples is NaNO_3 , the amount of Na released from the specimens corresponds directly to the amount of NaNO_3 released. At the end of 90 days the leach data was calculated as cumulative fraction leached (CFL), leach rate, and leach index. The CFL data is presented as a function of time in Figure 5 and clearly shows the dependence of leaching on increased waste loadings. Arithmetic averages of CFL, leach rate, and leach index are given in Table 2. The indices were calculated according to ANS 16.1 and ranged from 11.1 to 7.8 for 30 to 70 weight percent NaNO_3 loaded specimens, respectively. The leach index is a dimensionless figure-of-merit, which quantifies the relative leachability for a given waste type/solidification agent combination. Since the index is inversely proportional to the effective diffusivity, higher index values represent better retention and reduced leachability of a waste species.

TABLE 2--ANS 16.1 Leach Test data for sodium nitrate in polyethylene
waste forms

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

EPA Extraction Procedure

The EPA Extraction Procedure (EP) for hazardous wastes was designed to characterize leaching performance of hazardous waste packages under landfill conditions [12]. In order to take into account the attenuation and dilution expected during migration of the leachate to the groundwater, the amount of contaminant released during the test is to be combined with a generic attenuation/dilution factor of 100 [13].

Prior to leaching, specimens (3.3 cm diameter x 7.1 cm length) containing 30, 50, 60 and 70 weight percent NaNO_3 were subjected to the EPA Structural Integrity Procedure (SIP) as specified in the EP. The SIP involves dropping a 0.33 Kg weight fifteen times onto the face of the specimen to be leached. This procedure is designed to ascertain the specimen's mechanical ability to remain a monolith. Details of the procedure and a schematic of the SIP apparatus are found in 10 CFR 40 Part 261, Appendix II. None of the samples subjected to the SIP showed any signs of damage.

The specimens were leached in demineralized water, equal to sixteen times the specimen weight. The leachate was made acidic ($\text{pH} = 5.0 \pm 0.2$) using 0.5N acetic acid and monitored as prescribed to maintain a constant pH of 5. After the initial pH correction further acid additions were not required. The leachate was agitated by tumbling at 30 rpm (± 2 rpm). At the end of the 24 hour leaching period the leachate was analyzed for sodium using AA. The calculated nitrate release levels given in Table 3, are below the drinking water standard of 44 ppm of nitrate [14], when the attenuation/dilution factor of 100 is applied. This indicates the specimen would not be classified as a characteristically hazardous waste under RCRA.

TABLE 3--Sodium nitrate releases from polyethylene waste forms using EPA
Extraction Procedure

Waste Loading (wt%)	Nitrate in Leachate (ppm)	Passes Drinking Water Standard With Attenuation/Dilution Factor of 100
30	11	yes
50	40	yes
60	64	yes
70	492	yes

Mechanical Integrity

Water immersion tests were performed on cylindrical specimens (-4.6 cm diameter and 9 cm length) using deionized distilled water. After 90 days of immersion the specimens were destructively tested to determine compressive yield strength. All measurements were made according to ASTM D-695, "Standard Test Method for Compressive Properties of Rigid Plastics." The results, which are given in Table 4, are compared to compressive yield strengths of similar specimens which had not been exposed to water. In the case of LLW disposal, the NRC recommends a minimum compressive strength of 0.35 MPa (50 psi) to ensure that a waste form remains stable under the compressive loads inherent in a disposal environment. As can be seen from the data in Table 4, the compressive yield strength does not change when waste loadings are increased from 30 to 60 wt% or when the samples are immersed in water for 90 days. Only the 70 weight percent loaded samples exhibited reduced compressive yield strength at -5 MPa.

Dimensional changes due to swelling were also investigated after 90 days immersion. The average dimensional change in length was +0.2%, the average change in diameter was -0.1%. These are negligible differences and show no swelling problems for the polyethylene/sodium nitrate samples investigated. Figure 6 shows a 70 weight percent specimen before and after 90 day immersion in water.

TABLE 4--Compressive yield strength of polyethylene/sodium nitrate waste forms

Waste Loading (weight percent)	Compressive Strength (MPa)	
	no treatment	after 90 days immersion
30	16.3	17.6
50	13.2	13.2
60	15.4	15.9
70	7.03	4.96

CONCLUSIONS

Polyethylene is an effective solidification agent for nitrate salt wastes. High loading efficiencies are achievable using simple processing techniques. Leaching indices calculated, for polyethylene/sodium nitrate waste forms ranged from 11.1 to 7.8, for 30 to 70 weight percent waste loadings respectively. All specimens subjected to the EPA Extraction Procedure were classified as a "characteristically hazardous waste" according to RCRA.

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FIG. 1--Differential scanning calorimeter (DSC) thermograms for polyethylene containing 50% NaNO_3 or NaNO_2 .

FIG. 2--Differential scanning calorimeter (DSC) thermograms for polyethylene containing 50% actual or simulated waste.

FIG. 3--Photograph of laboratory-scale single-screw extruder with dual hopper/feeders.

FIG. 4--Schematic of extrusion process for incorporating nitrate waste into polyethylene.

FIG. 5--Cumulative fraction leached of sodium nitrate from polyethylene waste forms as a function of time.

FIG. 6--Polyethylene waste forms containing 70 wt% sodium nitrate, untreated (left) and after 90 day immersion in water (right).

DO NOT OPERATE
EYE PROTECTION

Leaching of Sodium Nitrate from Polyethylene Waste Forms