# POLYETHYLENE ENCAPSULATION OF SINGLE SHELL TANK LOW-LEVEL WASTES

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## ABSTRACT

Polyethylene encapsulation is being explored for potential use in treating nitrate salts and sludges at U.S. Department of Energy (US DOE) underground storage tank facilities. Some of these wastes contain high concentrations of fission products and are expected to maintain equilibrium temperatures of 50 - 70°C for many years. The potential effects of elevated temperature and high radiation conditions on key waste form properties (e.g., mechanical integrity, leachability) are examined. After 6 months of thermal conditioning, waste form test specimens show no degradation in mechanical integrity. Leaching at elevated temperature resulted in a small increase in leach rate (a factor of less than two), while diffusion remained the dominant mechanism of release. Full-scale polyethylene waste forms containing 50 - 70 wt% nitrate salt can be expected to leach a total of 5 - 17% of the original contaminant source term after 300 years of leaching under worst-case conditions (fully saturated at 70°C).

## INTRODUCTION

Polyethylene encapsulation, developed at Brookhaven National Lab (BNL), is an improved process for solidification of radioactive and mixed wastes that are not satisfactorily treated by conventional solidification technologies.(1,2,3) Polyethylene is an inert thermoplastic material that can be processed at relatively low temperatures (130 - 150°C) and combined with waste to form a homogenous molten mixture. On cooling, the mixture forms a monolithic solid waste form with excellent properties. The BNL process utilizes a modified single-screw extruder, a technology that has been well proven in the plastics industry. Bench-scale research and development has demonstrated process applicability to a wide range of waste types including nitrate salts, evaporator concentrates, sludges, incinerator ash, and ion exchange resins. Waste loadings as high as 70 wt% nitrate salt have been achieved while still maintaining waste form performance well above minimum regulatory criteria for commercial low-level waste. Compared with maximum loadings of only about 20 wt% nitrate salt for conventional hydraulic cement processes (i.e., grout), this process can provide significant improvements in volume reduction, resulting in large overall cost savings.

Polyethylene encapsulation has been identified as one of seven potential solidification technologies for remediation of leaking underground storage tanks at the Hanford site in Richland, WA.(4,5) Although the predominant chemical constituent in these tanks (sodium nitrate) is similar to other nitrate salts treated by this process, the SST wastes contain sufficient levels of fission products such as Sr-90 and Cs-137, that the waste is self-heating. Preliminary estimates place maximum equilibrium temperatures of the tank wastes between 50°C - 70°C for several hundred years, assuming no further separation of these isotopes. Under the sponsorship of the Department of Energy's Office of Technology Development Underground Storage Tank Integrated Demonstration, the focus of this work is to investigate the potential effects of elevated thermal conditions and high radiation doses on key waste form performance parameters including mechanical strength and leaching.(6) Leaching studies at elevated temperature and the effects on mechanical integrity of waste forms after 6 months of thermal conditioning have been completed. The investigation of radiation effects is on-going.

On completion of this effort to investigate thermal and radiation effects, waste form development activities will examine processing and waste form performance issues using surrogate salt waste that closely resembles actual Hanford SST waste in chemical and physical composition. Scale-up feasibility will be demonstrated at the BNL Polyethylene Encapsulation Demonstration and Test Facility.

## SAMPLE PREPARATION

Samples were prepared using a bench-scale plastics extruder with a 32 mm (1.25 in.) screw diameter and a maximum output rate of about 35 kg/hr (16 lb/hr). The BNL extruder, shown in Fig. 1, is equipped with two volumetric feeders calibrated to deliver precise quantities of simulated waste and polyethylene binder. The materials are mixed and heated at about 150°C within the extruder, forming a homogeneous molten mixture. The mixture is then extruded into a suitable mold and forms a monolithic solid waste form on cooling.

Separate feeders for the polyethylene and simulated salt waste were calibrated using the materials that were employed for test specimens. Each feeder was calibrated at five different speeds covering the complete operating range (10, 25, 50 75 and 90% of full speed). Output rate at each speed was measured for at least 10 trials. Mean output rates, associated $2\sigma$ error, and linear regression lines were calculated.

Waste form test specimens were prepared using sodium nitrate (to simulate the major constituent in SST waste) and low-density polyethylene, with nominal salt loadings of 50, 60 and 70 wt%. Mechanical integrity test specimens were extruded and machined to a nominal size of 50 mm diameter x 100 mm height. Densities were calculated from dimension and weight data. Average densities were 1.280 ± .005 (50 wt% salt), 1.371 ± .005 (60 wt% salt), and 1.544 ± .011 (70 wt% salt). Leach test specimens were extruded and machined to a nominal size of 2.5 cm in diameter x 2.5 cm in height. Cut surfaces at the tops and bottoms of test specimens exposed unencapsulated salt to leachate and thus were re-sealed by heating to more closely replicate the normally sealed surfaces of cast waste forms.

## THERMAL EFFECTS ON MECHANICAL INTEGRITY

Simulated waste form specimens were weighed and measured prior to thermal conditioning. Samples were then placed in two environmental chambers and were held at 50

Fig. 1. BNL bench-scale extruder used to produce nitrate salt waste forms for testing.

and 70°C. Thermocouples were installed inside the chambers and in the center of several waste forms to monitor temperatures over the course of the experiment.

After periods of thermal conditioning at 50°C and 70°C for 3 and 6 months, 5 replicates of each waste loading (a total of 30 specimens at each time interval) were removed from the chambers and allowed to equilibrate to ambient temperature. Following thermal conditioning, specimens were weighed and measured again to check for changes in mass or dimensions resulting from storage at elevated temperatures. Changes in weight were very slight - the maximum weight gain or loss was $<0.08\%$. Small changes in physical dimensions were recorded resulting in volume changes and density variations of up to about 4%. However, the average change in density for all samples was less than 1%. These variations are within the limits of normal measurement error and do not represent any real change in the physical size of the waste forms.

Thermally conditioned specimens were then tested for changes in mechanical strength according to ASTM Method D-695, "Standard Method of Test for Compressive Properties of Rigid Plastics." Since polyethylene specimens do not always fail catastrophically, stress was plotted as a function of time. Compressive yield strength was determined at the point where the slope decreased to zero. A typical plot of compressive stress vs. time is shown in Fig. 2. Compressive yield strength for UST-ID polyethylene/sodium nitrate waste forms stored at elevated temperatures for 3 and 6 months is compared with yield strength data for control specimens stored at ambient temperature in Table I. These data represent the average of 5 replicates with the associated error reported at the 95% confidence limit. Compressive yield strength data are represented graphically in Fig. 3 in terms of the percent of original strength. Although percent of original strength ranged from 91% to 111%, no statistically significant changes in compressive yield strength were observed as a result of thermal conditioning at these anticipated temperatures for periods of 3 and 6 months. The effects of elevated temperatures for longer times will be examined with the remaining test specimens, still undergoing thermal conditioning.

## ACCELERATED LEACH TESTING

Leaching was conducted according to the Accelerated Leach Test (ALT) procedure developed at BNL.(7,8) Replicate test specimens containing 50, 60, and 70 wt% simulated sodium nitrate waste encapsulated in polyethylene were leached at 20°C, 35°C, 50°C, and 70°C. Leaching was conducted in distilled water with a leachant volume to specimen surface area ratio of 100 cm. Sampling and leachant replacement were performed at pre-set intervals over a period of 11 days. Leachate samples were analyzed for sodium concentration by atomic absorption. Cumulative fraction released, and effective diffusivity were calculated using the ALT computer program. This program also calculates the predicted release

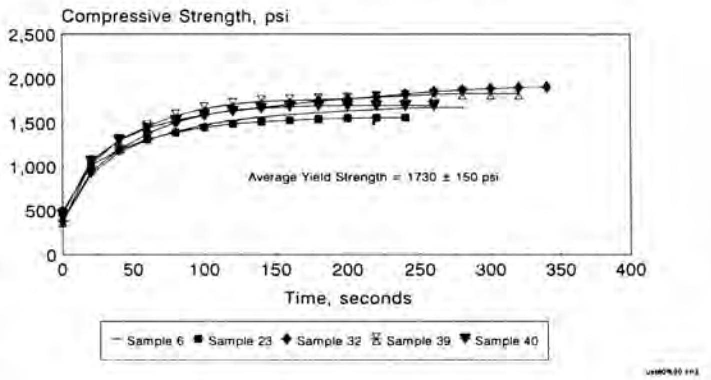


Fig. 2. Typical compressive yield stress data plotted as a function of time for 5 replicate polyethylene waste form specimens containing sodium nitrate (60 wt% $NaNO_3$, stored at 50°C for 3 months).

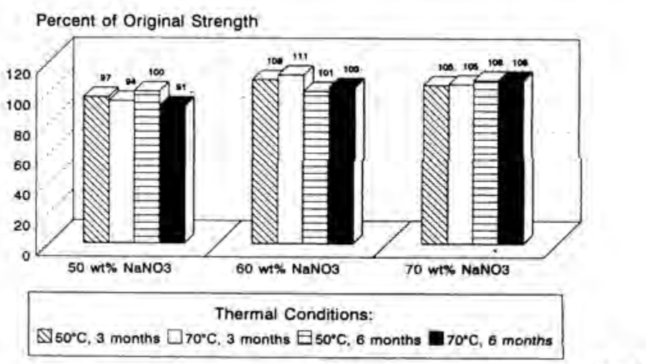


Fig. 3. Percent of original compressive yield strength for thermally conditioned polyethylene waste forms containing sodium nitrate.

**TABLE I**

**Compressive Yield Strength for UST-ID Polyethylene Waste Forms Containing Sodium Nitrate Stored at Elevated and Ambient Temperatures[a]**

| | Yield Strength, psi | Yield Strength, psi Stored at 50°C | | Yield Strength, psi Stored at 70°C | |
|---|---|---|---|---|---|
| Waste Loading, wt% | Control (ambient temperature) | 3 months | 6 months | 3 months | 6 months |
| 50 | 2080 ± 260 | 2010 ± 280 | 2090 ± 310 | 1960 ± 130 | 1890 ± 150 |
| 60 | 1600 ± 140 | 1730 ± 150 | 1610 ± 140 | 1780 ± 200 | 1650 ± 110 |
| 70 | 1500 ± 200 | 1570 ± 200 | 1620 ± 130 | 1580 ± 200 | 1620 ± 90 |

[a]Average of 5 replicates. Error calculated at 95% confidence limit.

based on diffusion and compares actual leach data with those expected by the model. In this way, the effects of elevated temperature on the leaching mechanism and rate can be assessed.

Cumulative fraction leached varied as a function of waste loading and increasing temperature, as predicted. Cumulative releases at a given temperature increased by a factor of approximately 2 for each waste loading increase of 10 wt%. Samples containing 50 wt% nitrate salt leached at 20 and 35°C exhibited the lowest leach rates with average final cumulative fractional releases of about 0.15. Specimens containing 70 wt% nitrate salt leached at 70°C had the highest leach rates with average final cumulative fractional releases of 0.85. Most of the tested specimens closely follow the diffusion model indicating that diffusion is the dominant leaching mechanism and that elevated temperature does not appear to alter the leaching mechanism. Cumulative fractional release data for each waste loading and temperature were plotted on an Arrhenius plot as a function of the inverse of absolute leaching temperature. Regression lines through these data show a relatively flat slope, indicative of low activation energies corresponding to diffusion/dissolution processes. These data also corroborate that the dominant leaching mechanism does not change with increases in temperature up to 70°C. Since diffusion was the predominant mechanism of release, the ALT computer model was used to project releases for full-scale (6.3 cubic meter) waste forms over time. Predicted cumulative fraction releases after 300 years of leaching under fully saturated conditions are given in Table II. These predictions are based on the assumption that the waste forms remain structurally stable over this time.

## CONCLUSIONS

Results to date have indicated that polyethylene waste forms are not adversely affected at temperatures up to 70°C. For example, mechanical integrity and strength of polyethylene waste forms containing sodium nitrate would not be affected by anticipated thermal loads associated with SST wastes. Extrapolation of accelerated leaching data at 70°C indicate that full-scale polyethylene waste forms containing 50 to 70 wt% nitrate salt will release between 5 and 17% of the contaminant source term after 300 years leaching under saturated conditions. In contrast, portland cement (i.e., grout) waste forms are projected to release about 17% of the total source term after only 11 years. Following successful completion of thermal and radiation stability testing, bench-scale treatability studies using surrogate single shell tank wastes will be conducted. Finally, a full-scale demonstration of the polyethylene encapsulation system for single shell tank wastes will be performed to ensure process viability under production conditions.

## REFERENCES

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**TABLE II**

**Projected Cumulative Fractional Releases After 300 Years of Leaching for Full-Scale Polyethylene Waste Forms Containing Nitrate Salt Wastes**

| Projected Releases After 300 Years[a] | | | | | | |
|---|---|---|---|---|---|---|
| | 50 wt% Salt | | 60 wt% Salt | | 70 wt% Salt | |
| Temperature °C | $D_e$ (cm$^2$/s) | CFL (%) | $D_e$ (cm$^2$/s) | CFL (%) | $D_e$ (cm$^2$/s) | CFL (%) |
| 20 | $3.05 \times 10^{-9}$ | 3.7 | $8.6 \times 10^{-9}$ | 5.0 | $5.58 \times 10^{-8}$ | 9.5 |
| 35 | $2.65 \times 10^{-9}$ | 3.6 | $1.90 \times 10^{-8}$ | 6.3 | $7.63 \times 10^{-8}$ | 10.7 |
| 50 | $5.32 \times 10^{-9}$ | 4.3 | $3.10 \times 10^{-8}$ | 7.6 | $1.34 \times 10^{-7}$ | 13.4 |
| 70 | $9.69 \times 10^{-9}$ | 5.1 | $2.40 \times 10^{-8}$ | 6.9 | $2.33 \times 10^{-7}$ | 16.8 |

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

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