TREATABILITY STUDIES FOR POLYETHYLENE ENCAPSULATION OF INEL LOW-LEVEL MIXED WASTES

FINAL REPORT

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October 1995

**Prepared by:
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Department of Advanced Technology
Brookhaven National Laboratory
Upton, NY 11973**

**Prepared for:
Waste Reduction Operations Complex
Lockheed Idaho Technologies Company
Idaho Falls, ID 83415**

**United States Department of Energy
Contract No. DE-AC02-76CH00016**

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ABSTRACT

Treatability studies for polyethylene encapsulation of INEL low-level mixed wastes were conducted at Brookhaven National Laboratory. The treatability work, which included thermal screening and/or processibility testing, was performed on priority candidate wastes identified by INEL to determine the applicability of polyethylene encapsulation for the solidification and stabilization of these mixed wastes. The candidate wastes selected for this preliminary study were Eutectic Salts (ID#SMC-507), Ion Exchange Resins (ID#788), Activated Carbons (ID#562), Freon Contaminated Rags (ID#915), TAN TURCO Decon 4502 (ID#426), ICPP Sodium Bearing Liquid Waste (no ID#), and HTRE-3 Acid Spill Clean-up (ID#1055). Thermal screening was conducted for some of these wastes to determine the thermal stability of the wastes under expected pretreatment and processing conditions. Processibility testing to determine whether the wastes were amenable to extrusion processing included monitoring feed consistency, extruder output consistency, waste product homogeneity, and waste form performance. Processing parameters were not optimized within the scope of this study. However, based on the treatability results, polyethylene encapsulation does appear applicable as a primary or secondary treatment for most of these wastes.

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1. INTRODUCTION

Treatability studies were conducted at the Brookhaven National Laboratory (BNL) Environmental & Waste Technology Center for polyethylene encapsulation of low-level mixed wastes currently stored at Idaho National Engineering Laboratory (INEL). This work was sponsored by the Lockheed Idaho Technologies Company (LITCO), Waste Reductions Operation Complex (WROC), which is investigating the use of polyethylene for waste encapsulation in an effort to develop mixed waste treatment alternatives. BNL has developed the extrusion-based polyethylene encapsulation process as a waste solidification and stabilization technology, applicable to hazardous, low-level radioactive and low-level mixed wastes.

The treatability work was performed on candidate wastes identified and prioritized by INEL. For selected waste streams thermal stability screening was conducted to determine if the waste was amenable to polyethylene pretreatment and processing conditions. Other waste streams included processibility and waste form performance testing. Wastes generated during ongoing processing and maintenance operations or one-time cleanup operations, have been physically and chemically characterized at INEL enabling the preparation of surrogates. Treatability work was conducted using surrogates and actual mixed wastes. Each of the candidate wastes investigated is classified as a mixed waste due to the presence of radionuclides and heavy metals and/or organics. The wastes were identified by INEL as: Eutectic Salts (ID#SMC-507), Ion Exchange Resins (ID#788), Activated Carbons (ID#562), Freon Contaminated Rags (ID#915), TAN TURCO Decon 4502 (ID#426), ICPP Sodium Bearing Liquid Waste (no ID#), and HTRE-3 Acid Spill Clean-up (ID#1055).

All wastes were pretreated by size reduction or drying, as necessary, in order to make them amenable to feeding and processing with polyethylene. Successful microencapsulation generally requires a uniform particle size less than two millimeters and a moisture content below two weight percent. Wastes used in thermal screening were also pretreated, as necessary, in order to accurately represent the waste during encapsulation processing. Thermal testing by Thermal Gravimetric Analysis and Differential Scanning Calorimetry was used to screen wastes containing compounds volatile at extrusion processing temperatures (120-150°C). Extrusion processing of these wastes was not optimized but rather conducted at nominal waste loadings selected with respect to the materials' physical properties and processing experience with similar waste streams. For each waste, processibility work included monitoring material feed, processing consistency, waste form homogeneity, and waste form performance. In addition, Toxicity Characteristic Leaching Procedure (TCLP) analysis was conducted as part of waste form testing.

2. BACKGROUND

2.1 Thermal Gravimetric Analysis Description

Thermal analyses of INEL wastes were performed with a Shimadzu TGA-50 Thermogravimetric Analyzer to determine volatilization of hazardous constituents under process conditions expected for waste encapsulation or waste pretreatment. The TGA instrument operates as a highly sensitive mass balance yielding a weight or percent weight loss versus time for samples subjected to various thermal and atmospheric conditions. As a result, analysis of the subsequent impact on sample constituents is limited to quantitative interpretations of trends seen in the TGA weight loss curves. The TGA is applicable to measurement of adsorbed water, water of crystallization, studies of the thermal stability of substances and decomposition and oxidation reactions from solid (liquid) to gas and gas to solid (liquid)¹.

For this treatability study, small (10-40 mg) samples were placed in an aluminum sample cell then placed on a sample pan. The sample pan is suspended on a suspension wire hanging down in reaction tube where the atmosphere, typically nitrogen or compressed air, and temperature can be controlled. Deflections in the suspension wire, due to gaseous release from the sample, are detected by photoelectric elements, amplified and used to continually measure changes in the sample mass. Data acquisition is performed using a TA-50I and results shown as percent weight loss versus time. Volatilization of hazardous constituents is determined indirectly through quantitative interpretation of trends seen in the resulting TGA weight loss curves. Waste surrogates were prepared containing only a single volatile constituent allowing simple comparison of results from samples spiked with the hazardous constituent to samples without (baseline) to determine gaseous evolution of the hazardous component. Typically, the baseline weight loss curve represents loss of residual moisture due to thermal treatment. If total weight loss in the surrogate exceeds that seen in the baseline, it can be assumed that the difference is due to gaseous evolution of elements other than the residual moisture within the waste and most probably due to the volatile hazardous constituent. Additional quantitative conclusions may be drawn about the rate of release from differences in the slope between baseline and surrogate weight loss curves.

2.2 Differential Scanning Calorimetry Description

A Shimadzu DSC-50 Differential Scanning Calorimeter was used to test for potential liberation of waters of hydration and to evaluate possible oxidizer (waste) polyethylene interaction during processing. The DSC is an instrument for determining specific heat and enthalpy changes that may result from primary or secondary phase transitions and reactions². The instrument operates by adjusting heater block power based on temperature deviations detected between reference and sample sections. Samples weighing approximately 20 mg are placed in small aluminum sample cells with the reference consisting of an empty aluminum cell. Heat required to balance the sample temperatures to the programmed temperature is delivered through a known heat resistance and continually measured. Data acquisition is performed with a TA-50I with results presented on an energy versus time plot revealing exotherms and endotherms that occur

as the sample is subjected to the programmed heating profile. A quantitative interpretation of exotherms and endotherms can indirectly reveal potential liberation of waters of hydration or oxidizer/polyethylene reaction during waste encapsulation. For surrogates consisting of multiple components containing waters of hydration, separate analysis of each component is necessary to discern which, if any, contributes to the evolution of bound water in the waste.

2.3 Polyethylene Encapsulation Process Description

The polyethylene encapsulation process uses thermoplastic polyethylene to stabilize waste materials within a polymer matrix. This is accomplished by heating polyethylene above its melting point (120-150°C), then mixing the molten polyethylene with the waste. Solidification of the encapsulated matrix is assured upon cooling and is independent of the chemical nature of the waste materials. The BNL polyethylene encapsulation process utilizes a versatile, industry-tested single-screw plastics extruder. Dry waste and polyethylene are continuously fed to the extruder by individual dynamic feeders and accurately metered to maintain a constant waste loading. The feeders are either volumetric, designed to meter a constant volume of material at a given speed setting, or volumetric feeders retrofitted to a computer-controlled loss-in-weight system. Unlike loss-in-weight, volumetric feeding requires recalibration for each material. Within the extruder, a variable speed screw mixes the molten polyethylene with the waste material, builds pressure, and pumps the homogeneous mixture through a die directly into a waste container. The processing temperature is controlled through five independent extruder zones and a separate die zone, and can be tailored to achieve a particular temperature profile for different polymer and waste combinations.

Processibility testing with non-radioactive waste surrogates was conducted using a vented, Davis-Standard 38 mm (1.5 in.) single-screw extruder. A vacuum pump connected to the vent port removed volatiles (e.g., moisture) that may have evolved during processing. A Merrick loss-in-weight feed system consisting of a master feed controller and two slave controllers (one for waste and one for polyethylene) was used in conjunction with this extruder. Feeding was accomplished by simply entering the desired total feed rate as well as a recipe for the waste loading (percentage of waste compared to percentage of polyethylene). All surrogates were processed at a moderate screw speed (eg., 25 rpm). Grab samples of the extrudate were periodically taken to ensure waste product homogeneity by density analysis. Rate samples were taken to demonstrate processing consistency. Right cylindrical specimens measuring a nominal 5.1 cm (2 in.) by 10.2 cm (4 in.) were formulated for compressive strength testing.

Processing of low-level radioactive mixed wastes was conducted using a Killion 32 mm (1.25 in.) single-screw extruder. Material feed was accomplished using AccuRate volumetric feeders that required calibration with each waste material. A calibration curve was generated by recording the feeder output (in weight) at different feeder screw speed settings (percent of full speed). Five replicates were taken at a minimum of three separate feeder speed settings. A linear regression line was calculated and calibration data were plotted. Each mixed waste was processed for processibility confirmation and to fabricate waste form specimens for TCLP testing. TCLP specimens were cast as pellets (6 mm diameter x 6 mm height) from Teflon molds.

2.4 Compressive Strength Testing Description

Compressive strength testing of waste forms was conducted in accordance with ASTM D695, "Compressive Properties of Rigid Plastics" using a Soiltest Versatester³. Right cylindrical specimens fabricated during processibility testing were turned on a lathe to ensure flat surfaces on the top and bottom. These samples were compressed at a constant loading rate of 1.0 ± 0.5 mm/min. until the waste form failed or until the load within the samples no longer increased with continued loading. Typically, waste form failure by a crack or shear surface was not observed. For each waste stream, ten replicate samples were tested to determine the mean maximum compressive strength.

2.5 Toxicity Characteristic Leaching Procedure (TCLP) Description

Leachability of toxic metals from waste forms was conducted in accordance with 40 CFR 261--Identification and Listing of Hazardous Wastes, Appendix II--Toxicity Characteristic Leaching Procedure⁴. Waste form test samples were fabricated during processibility testing as 6 mm diameter by 6 mm height pellets, as per the 9.5 mm maximum size requirement. For each waste, TCLP testing was conducted on the encapsulated product and compared with the untreated waste to serve as a baseline. The TCLP test is an 18 hour extraction of 100 g of sample in 2000 g of a buffered leachant (either pH 2.88 or 4.93). A pre-test was conducted prior to initiation of each leach test to determine the appropriate extraction fluid to be used. Pre-tests consisted of measuring the pH of a 5.0 gram representative sample in 96.5 ml deionized water. Where pH of this solution was greater than 5.0, 3.5 ml 1.0N HCl was added, the slurry heated to 50°C for 10 min., and the pH remeasured. If pH of either solution was less than 5.0, the higher pH extraction fluid (5.7 ml glacial HOAc + 64.3 ml 1.0N NaOH diluted to 1000 ml) was used in the leach test. If pH of both pre-test solutions was greater than 5.0, the more acidic extraction fluid (5.7 ml glacial HOAc diluted to 1000 ml) was used.

Test samples were agitated in an end-over-end fashion at 30 ± 2 rpm for the test duration. On completion, the solutions were filtered using 0.6-0.8 micron glass fiber filter. An aliquot of the leachate (~100 ml) was placed in a polyethylene container and, if not immediately analyzed, refrigerated at 10°C until analysis was conducted.

Chemical analyses of non-radioactive samples containing Pb, Cd, Cr and Ni were done by inductively coupled plasma (ICP) spectroscopy using a Varian Liberty 100 emission analyzer. Non-radioactive samples containing Hg were analyzed using a Perkin Elmer 4000 Atomic Absorption Spectrophotometer fitted with a Perkin Elmer MHS-10 cold-vapor generator (EPA Method 7470). Radioactive samples were analyzed for Pb using a Hach DR/2000 Spectrophotometer.

3. TREATABILITY STUDIES

3.1 Eutectic Salts (INEL ID#SMC-507)

3.1.1 Waste Description

This waste is known as Cartecsal, formerly called Carbonate Eutectic Salt. It is a lead (Pb) contaminated salt mixture roughly comprised of 60 weight percent potassium carbonate, 30 weight percent lithium carbonate, and 10 weight percent sodium carbonate. Characterization conducted at INEL by TCLP analysis indicates a lead concentration between 4.8-5.8 mg/l. The salt mixture was described as a fine powder by the sampling personnel.

3.1.2 Scope

Thermal screening and processing feasibility testing were conducted on a surrogate of this waste stream. An actual INEL mixed waste sample was used for confirmation processing and TCLP testing. Thermal stability testing was conducted by Differential Scanning Calorimetry (DSC) on a Shimadzu DSC-50 to indicate whether decomposition of the carbonate salts occurs at extrusion processing temperatures, that is, whether any moisture (free water or bound water) is evolved. The eutectic salt surrogate used for extrusion processing feasibility testing was prepared according to the waste composition data except lead was not added. An additional surrogate was prepared that was spiked with lead (as PbCl_2) at a concentration of 120 ppm. This surrogate was processed to fabricate waste form pellets for TCLP testing. The eutectic salt mixed waste sample was also processed for TCLP testing.

3.1.3 Surrogate Preparation and Experimental Procedure

Potassium and sodium carbonate are available as hydrated compounds with bound moisture. Potassium carbonate can be anhydrous or sesquihydrated ($\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$). Sodium carbonate can be anhydrous or monohydrated ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). Lithium carbonate (Li_2CO_3) does not complex with water. The surrogate for thermal screening was prepared without lead using reagent grade hydrated salts from Brand-Nu Laboratories, Meriden, CT. Technical grade anhydrous carbonate salts were used, also from Brand-Nu Laboratories, during surrogate preparation for processibility confirmation testing.

The surrogates used for thermal screening were prepared by individually weighing, adding and mixing the hydrated carbonate salts in a small plastic cup. The salts were powdered with the exception of the potassium salt which appeared crystalline. After adding each salt, the mixture was well shaken to achieve a homogeneous surrogate. Two surrogates were prepared for processibility testing; one spiked with lead and one without. In either case, the ingredients were added to a one gallon can specially fabricated with interior baffles for mixing purposes. The can was then tumbled for 48 hours. The concentration of lead added to the surrogate (120 ppm) was based on the INEL characterization data which indicated a maximum lead concentration of 5.8 mg/l from TCLP results. Accounting for the 20:1 dilution, a TCLP concentration of 5.8 mg/l is

equivalent to 116 ppm in the waste. This number was rounded up to 120 ppm for surrogate preparation.

For DSC analysis, samples weighing approximately 20 mg were heated in the presence of nitrogen from ambient to 150°C at 3°C/min and held for 40 minutes. A slow heating rate (1-5°C/min) is suggested by the manufacturer for observing phase changes due to free or bound water evolution. Each individual carbonate salt and the homogeneous mixture were tested under these conditions.

For thermal testing, three (3) replicate samples of the eutectic salt surrogate were dried using a Sartorius Moisture Analyzer to determine the moisture content of the salts. Each test was conducted for 30 minutes at 150°C. A mass/mole balance was performed in order to determine if the weight loss corresponded with the quantity of bound water in the surrogate recalling that hydrated salts were used during thermal screening.

Processibility testing of the eutectic salt waste was conducted using a 38 mm (1.5 in.) single-screw Davis-Standard extruder for the surrogate. The INEL mixed waste eutectic salt was processed using a 32 mm (1.25 in.) single-screw Killion extruder contained in an enclosed HEPA filtered process facility. Material feed was accomplished through dry material volumetric feeders for the Killion extruder, and through volumetric feeders retrofitted to a loss-in-weight computer controlled system for the Davis-Standard extruder. The standard volumetric feeders were each calibrated with either the eutectic salt mixed waste or with low-density polyethylene pellets. To generate the calibration curves, five replicates were taken at three different feeder screw speed settings (indicated as manual %) for the eutectic salt mixed waste with five replicates at four feeder settings for the polyethylene pellets. The calibration curves with their tabulated data are shown in Figures 3.1.1 and 3.1.2, and Tables 3.1.1 and 3.1.2 for the eutectic salts and polyethylene, respectively.

Extrusion processing for the surrogates and for the mixed waste sample was conducted at a waste loading of 50 weight percent and at a screw speed of 25 rpm. These are not optimum nor maximum processing parameters but rather a conservative starting point that, based on previous experience with waste with similar physical properties, can be readily achieved. Processibility testing with the surrogate included fabricating nominal 5.1 cm (2 in.) by 10.2 cm (4 in.) right cylindrical specimens for compressive strength testing, taking periodic grab samples for density analysis (monitor waste product homogeneity), and timed one minute samples for processing consistency. Compressive strength testing was conducted in accordance with ASTM D695, "Compressive Properties of Rigid Plastics." The densities of the grab samples were determined by weighing each grab sample and using a multipycnometer to determine their volumes. Processibility testing with the actual eutectic salt mixed waste was limited to confirmation processing while fabricating waste form pellets for TCLP testing. All of the mixed waste sample received from INEL was used for this task. Following TCLP testing, the concentration of lead in the extraction fluids was determined by Inductively Coupled Plasma Spectroscopy (ICP) for the nonradioactive surrogate (spiked with 120 ppm lead) and by Hach

UV-Spectroscopy for the mixed waste sample. For both TCLP tests, encapsulated waste forms were compared with the untreated samples which served as baselines.

3.1.4 Results and Discussion

DSC experiments were conducted on the individual component salts of the eutectic salt waste and on the surrogate mixture. The DSC results, shown as plots of energy (mW) versus time (min), are shown in Figures 3.1.3 through 3.1.6. Endothermic peaks representing the evolution of bound water can be observed for potassium carbonate sesquihydrate, Figure 3.1.3, and sodium carbonate monohydrate, Figure 3.1.5. The DSC plot for lithium carbonate, Figure 3.1.4, does not reveal any phase change for the same heating profile, as seen with potassium carbonate and sodium carbonate. This is due to the fact that lithium carbonate is not hydrated. The DSC plot for the eutectic salt surrogate, Figure 3.1.6, shows an endothermic peak as expected since it is comprised of the hydrated potassium and sodium carbonate salts.

Although DSC results can be used to observe a phase change in a material and to calculate the enthalpy change associated with this phase change, quantitative results, such as calculating the quantity of water evolving from a hydrated material, can not be determined. Therefore, in order to quantitatively determine if the endothermic peaks observed in DSC plots correspond to the quantity of bound moisture in the surrogate, a mass/mole balance was performed based on weight loss experiments using a Sartorius Moisture Analyzer. Three replicate samples of the eutectic salt surrogate were dried in the moisture balance at 150°C resulting in a mean weight loss of 11.6 ± 0.27 percent. Using a basis of one mole, hydrated water represents 16.4 weight percent of the compound potassium carbonate sesquihydrate ($K_2CO_3 \cdot 1\frac{1}{2}H_2O$) and 14.5 weight percent of the compound sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$). The weight percent of water in the eutectic salt surrogate is calculated by multiplying these percent numbers by their respective component percents in the surrogate (i.e., $0.6 \times 16.4 + 0.10 \times 14.5$) and is equal to 11.3 percent. This number is in close agreement with the weight loss observed on the moisture analyzer. It is therefore assumed that if the salts comprising the actual eutectic salt mixed waste are hydrated that all waters of hydration will evolve at the temperature required for extrusion processing.

Pretreatment of waste streams is generally required in order to make the wastes amenable to processing with polyethylene. This often includes drying to achieve a moisture content less than two percent and size reduction to attain a particle size distribution between approximately 50 to 2000 microns. This range is somewhat flexible and is dependent upon the type of material feeders, the size of the extruder and the physical properties of the waste. Processibility testing of this waste was conducted using a surrogate prepared with anhydrous salts. As previously shown, potassium and sodium carbonate are available in hydrated form and that the bound moisture will evolve. However, anhydrous salts were used in preparation of this surrogate to eliminate the need for pretreatment drying.

Processing of the eutectic salt surrogate was successful. This waste was observed to process most effectively when the feed materials (polyethylene pellets and salt powder) were allowed to back up (i.e., create a small head) above the feed screw. Starve feeding the extruder

resulted in a more erratic output/processing rate. During waste processing, compressive strength specimens were formulated, grab samples were taken for density analysis and periodic rate samples were taken for processing consistency. The consistency of the extruder output rate is summarized in Table 3.1.3. The mean output rate at a screw speed of 25 rpm was 77.30 ± 2.79 g/min. The small percent error of 2.58% is an excellent reflection on how well the material processed. Generally, materials that vary in output rate as much as 15-20% can still be successfully processed. The densities of waste forms containing 50 wt% eutectic salt surrogate are shown in Table 3.1.4. The mean waste form density was 1.35 ± 0.02 g/cm³. The maximum compressive strength of the waste forms was $1.56 \times 10^4 \pm 345$ kPa (2259 ± 50 psi), as shown in Table 3.1.5. This is similar to compressive strength data for other polyethylene final waste forms and is well above the NRC waste form compressive strength requirement of 414 kPa (60 psi).

TCLP results are summarized in Table 3.1.6. All tested samples were within the RCRA limit of 5 mg/l for lead concentration. The concentration of lead in the encapsulated surrogate (spiked with 120 ppm lead) was undetectable based on two replicate ICP Spectroscopy analyses, compared with concentrations of 4.1 and 4.2 mg/l for the untreated surrogate. The detection limit of the ICP Spectrometer for lead is 0.14 mg/l. A marked improvement in leachability was also seen in samples of the encapsulated eutectic salt mixed waste. Based on HACH UV-Spectroscopy, the baseline or untreated mixed waste sample leached to a lead concentration of 4.1 mg/l compared to 1.8 mg/l for the encapsulated mixed waste samples.

3.1.5 Conclusions

Processing of the eutectic salts was successful. This waste is amenable to stabilization by polyethylene encapsulation. Due to the limited scope of this study, processing parameters were not optimized. At a waste loading of 50 weight percent the leachability of encapsulated waste forms was effectively reduced below RCRA limits. Higher waste loadings should be achievable from a processing standpoint and based on the successful waste form testing results achieved to date. Thermal screening showed that potassium and sodium carbonate may contain waters of hydration and, if so, would require pretreatment drying to prevent evolution of these waters during extrusion processing. It is recommended that additional processibility work be conducted on this waste stream in order to optimize processing variables and maximize waste loading potential.

Table 3.1.1 Killion feeder calibration data for eutectic salts.
(Feedrate given as g/min)

Sample	Percent of Full Speed		
	10%	25%	40%
1	10.70	29.82	51.02
2	10.65	30.05	50.43
3	10.34	28.59	50.82
4	10.47	30.32	50.22
5	10.48	30.60	50.71
Mean	10.53	29.88	50.64
Std. Dev.	0.13	0.69	0.28
2 σ	0.16	0.86	0.35
% Error	1.54	2.88	0.70

Figure 3.1.1 Killion feeder calibration curve for eutectic salts.

**Table 3.1.2 Killion feeder calibration data for polyethylene.
(Feedrate given as g/min)**

Sample	Percent of Full Speed			
	10%	25%	50%	75%
1	10.53	35.58	73.47	111.45
2	10.07	34.69	72.74	112.80
3	9.48	34.83	73.55	112.16
4	9.67	34.85	74.81	113.76
5	9.52	36.09	74.71	110.51
Mean	9.85	35.21	73.86	112.14
Std. Dev.	0.40	0.54	0.79	1.11
2 σ	0.49	0.67	0.98	1.38
% Error	5.00	1.90	1.33	1.23

Figure 3.1.2 Killion feeder calibration curve for polyethylene.

Potassium carbonate sesquihydrate

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
3.0	150.0	40.0

Detector Type: Shimadzu DSC-50

Sample Name: Potassium carbonate (1.5 H₂O)

Cell: Aluminum

Atmosphere: Nitrogen

Rate Flow: 20.00[ml/min]

Figure 3.1.3. DSC plot showing phase change representing water evolution from potassium carbonate sesquihydrate

Lithium carbonate

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
3.0	150.0	40.0

Detector Type: Shimadzu DSC-50

Sample Name: Lithium Carbonate

Cell: Aluminum

Atmosphere: Nitrogen

Rate Flow: 20.00[ml/min]

Figure 3.1.4. DSC plot showing no phase change for lithium carbonate

Sodium carbonate monohydrate

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
3.0	150.0	40.0

Detector Type: Shimadzu DSC-50

Sample Name: Sodium carbonate (1 H₂O)

Cell: Aluminum

Atmosphere: Nitrogen

Rate Flow: 20.00[ml/min]

Figure 3.1.5. DSC plot showing phase change representing water evolution from sodium carbonate monohydrate

Eutectic salt surrogate

Temp Program
Rate Hold Temp Hold Time
[C/min] [C] [min]
3.0 150.0 40.0

Detector Type: Shimadzu DSC-50
Sample Name: Eutectic Salt Surrogate
Cell: Aluminum
Atmosphere: Nitrogen
Rate Flow: 20.00[ml/min]

Figure 3.1.6. DSC plot showing phase change representing water evolution from eutectic salt surrogate

Table 3.1.3 Process rates of eutectic salt surrogate at waste loading of 50wt% and screw speed of 25 rpm.

Sample	Rate (g/min)
1	74.86
2	74.55
3	79.50
4	80.55
5	78.82
6	81.43
7	72.49
8	77.04
9	78.63
10	75.17
Mean	77.30
Std. Dev.	2.79
2 σ	2.00
% Error	2.58

Table 3.1.4 Densities of grab samples representing encapsulated eutectic salt waste forms at a waste loading of 50wt%.

Sample	Density (g/cc)
1	1.36
2	1.31
3	1.35
4	1.35
5	1.36
6	1.39
7	1.37
8	1.36
9	1.34
10	1.35
Mean	1.35
Std. Dev.	0.02
2 σ	0.01
% Error	1.10

Table 3.1.5 Maximum compressive strength of 50 wt% eutectic salt waste forms.

Sample	Max. Comp. Strength (psi)
1	2342
2	2223
3	2214
4	2229
5	2232
6	2252
7	2243
8	2248
9	2239
10	2371
Mean	2259
Std. Dev.	50.00
2 σ	35.87
% Error	1.59

Table 3.1.6 TCLP results comparing encapsulated eutectic salts with untreated samples. (RCRA limit for Pb: 5 mg/l)

Sample	Extraction Fluid	Pb Concentration (mg/l)
Encapsulated surrogate spiked with 120 ppm lead	1	<0.14 ¹²
Untreated surrogate spiked with 120 ppm lead	2	4.2/4.1 ¹
Encapsulated mixed waste sample	1	1.8
Untreated mixed waste sample	2	4.1

¹ two replicate samples analyzed

² detection limit of ICP spectrometer

3.2 PWTU Spent Ion Exchange Resins (INEL ID#788)

3.2.1 Waste Description

This mixed waste is comprised of spent styrene-divinyl benzene resin beads containing approximately 10 weight percent water. This waste contains the radionuclides Co-60 and Ag-108, as well as the toxic metals lead (Pb) at 102,000 ppm (total) and mercury (Hg) at 2,850 ppm (total). The low-level radioactive mixed waste sample received at BNL contains white, brown and black beads and appears to be from a mixed bed ion exchange column.

3.2.2 Scope

Thermal screening, processing feasibility testing and TCLP testing were conducted on this waste. However, since BNL has previously conducted extensive process development studies on similar ion exchange resin waste streams, extrusion process evaluation and compressive strength testing were not repeated for this project. Thermal screening was conducted on a surrogate spiked with lead and mercury and on the actual mixed waste resins in order to determine the effect of thermal pretreatment on the resins and evaluate metal retention. Pretreated resins were processed and waste form pellets were fabricated at a 40 weight percent loading for TCLP testing.

3.2.3 Thermal Screening Procedure and Results

Dried, untreated resins typically swell when hydrated. Inevitable permeation of water through a waste form under saturated conditions results in significant internal tensile stresses, caused by swelling beads, potentially leading to waste form failure. In previous work, BNL has shown thermal pretreatment of ion exchange resins at a temperature of 300°C effectively prevents resin swelling by breaking down the resin's molecular structure, thereby optimizing polyethylene waste form performance⁵. Considering performance under water immersion testing, maximum waste loadings for waste forms containing pretreated ion exchange resins can be as high as approximately 70 weight percent compared to 30 weight percent for untreated resins⁶.

Ion exchange resins were characterized for lead and mercury retention following thermal pretreatment. Rohm and Haas Amberlite IRN-77 (strong acid) cation exchange resins were used as baseline samples in addition to actual mixed bed ion exchange resin waste received from INEL. Initially, mercury retention during thermal pretreatment was investigated through batchwise resin loading and eluting. A 500 g batch of IRN-77 was first conditioned by hydrating in 1.0N HCl overnight. Following rinsing and dewatering, nine 20 g samples were weighed into separate containers. To each, 100 ml of a stock solution containing 200 ppm Hg and 200 ppm Pb was pipetted. After immersion in the stock solution for at least 18 hours, each sample was individually dewatered while retaining the post-loading solution for analysis. The concentrations of Hg in these post-loading solutions are shown in Table 3.2.1. Mercury concentrations were determined by cold-vapor atomic absorption (EPA Method 7470) which has a detection limit of 0.2 µg/l (0.2 ppb). It can be seen that nearly all the mercury (greater than 99%) was loaded onto

the IRN-77 resin, inferred by the low mercury concentration in the loading solution following completion of resin loading. The nine dewatered resin samples were handled as follows: three were left untreated, three were treated at 110°C for 18 hours, and three were treated at 300°C for one hour. Treatment at 110°C was conducted to dry the resins without altering their chemical or physical composition. Samples dried at 110°C turned from light brown to dark brown. Samples treated at 300°C turned uniformly black. Six 20 g samples of INEL resin were similarly weighed into separate containers. Three samples were left untreated as controls, and three were treated at 300°C for one hour. Treated INEL samples showed some smoke evolution on removal from the furnace in contrast to IRN resin which did not show any off-gassing. The INEL mixed waste resin which originally contained white, brown and black resin particles darkened to brown and black.

Following treatment, all IRN-77 and INEL treated samples and controls were eluted using 25ml of 0.1N H₂SO₄ to drive off Pb or Hg remaining on the resin. IRN resin dried at 110°C crackled and self-heated on rehydration, whereas samples treated at 300°C did not. The mercury concentrations in the eluting solutions are also shown in Table 3.2.1. The concentration values in the eluting solution for the untreated IRN-77 resin is a good reference for gauging the effectiveness of the elution. The elution was not successful in desorbing the ion exchange resins as seen in the low mercury concentrations (on the order of 9 mg/l). This concentration should be on the order of 200 mg/l since this sample was simply loaded, then desorbed without any treatment. The elution probably was unsuccessful due to the low acid concentration and the use of sulfuric acid. Mercury sulfate, resulting from reaction with sulfuric acid, is not very soluble and most likely precipitated so the mercury was not detectable by AA Spectroscopy.

Due to inconclusive results from batchwise thermal screening, and in order to further elucidate metals retention during thermal pretreatment, an alternative experimental procedure was employed. A column technique was used for loading and eluting metals on/from the ion exchange resins (loading conducted on surrogate only) and a stronger acid was used during the elution step. During this procedure, nine columns of IRN-77 ion exchange resins were prepared. Columns consisted of 5.00 g dewatered resins sluiced into 10 ml glass columns. Resin beads were supported with glass wool plugs. IRN columns were loaded with 25 ml of an approximately 200 ppm Hg/Pb stock solution. Solutions were dripped at 1.0 ml/min, the flow controlled by a thumbscrew clamp on a short piece of tygon tubing at the outlet. Loading solutions were collected in separate containers after passing the resin columns. Columns were then dewatered by briefly blowing a low pressure stream of air through the column.

Upon dewatering, the columns were given one of three different thermal pretreatments: three samples were heated at 110° for 24 h to simulate a low temperature drying process; three samples were heated at 300°C for 1 h to dehydrate and destroy the swelling capacity of the resins; and three samples were left at ambient conditions as controls (control samples were not dewatered following loading). Following pretreatment, the columns were re-wetted by backwashing once again with deionized water, after which Pb and Hg were eluted using 50 ml of 1.0N HCl to quantify the retained mass of these metals.

Nine 5.00 g samples of actual INEL mixed waste ion exchange resin were weighed into plastic cups. As with the IRN resins, three samples were heated at 110° for 24 h, three samples were heated at 300°C for 1 h, and three samples were left untreated. Following treatment, resin samples were weighed, then sluiced into 10 ml glass columns as described above. Samples were eluted using 1.0N HCl for analysis of Pb and Hg. Mercury concentrations were determined by atomic absorption, as done previously, with lead concentrations determined by inductively coupled plasma spectroscopy.

The percent weight losses from dewatered surrogate IRN resins and INEL resins during thermal pretreatment are shown in Table 3.2.2. Similar results were obtained for the surrogate IRN resins and the INEL resins. The mean weight losses at the low temperature pretreatment (110°C@24h) are $59.55 \pm 0.04\%$ and $60.16 \pm 0.14\%$ for the IRN resin and the INEL resin, respectively. Additional weight loss was observed from the resins during the higher temperature pretreatment (300°C@1h): $74.17 \pm 0.04\%$ for the IRN resin and $73.41 \pm 0.59\%$ for the INEL resin. The additional volatilization observed from the resins during the higher temperature pretreatment is likely due to additional moisture evolution and evolution of resin decomposition products. Possible evolution of metals can not be concluded since, based on the low metal concentrations, the weight loss due their evolution would be inconsequential compared to the total weight loss.

The effect of thermal pretreatment on the resin size and swelling capability is shown in Table 3.2.3 which summarizes the mean bed volume occupied by each resin following pretreatment. The mean bed volumes were determined after re-wetting the resins and are based on three replicates. The bed volume for untreated (control) IRN surrogate resin was $6.43 \pm 0.05 \text{ cm}^3$ and $6.67 \pm 0.05 \text{ cm}^3$ following low temperature pretreatment at 110°C. The desired impact of thermal pretreatment at 300°C to reduce resin swelling ability is shown by the reduction of bed volume to $2.33 \pm 0.19 \text{ cm}^3$. Comparable results were obtained following pretreatment of the INEL mixed waste resins. The untreated INEL resin had a bed volume of $6.30 \pm 0.08 \text{ cm}^3$. The bed volume was $6.27 \pm 0.13 \text{ cm}^3$ following pretreatment at 110°C and $3.5 \pm 0.22 \text{ cm}^3$ following pretreatment at 300°C.

The lead retention of the surrogate and INEL resins are indicated in Table 3.2.4. This table summarizes for the surrogate IRN resins, the concentration of lead loaded onto the resins, the concentration of lead eluted from the resins following thermal treatment and, based on this data, the percent lead eluted. The percent eluted is the percentage of the original lead concentration loaded onto the resins that was successfully eluted after pretreatment. Each reported value is the statistical mean based on three replicates. For the control samples (untreated), 95.8% of the original lead loaded onto the resins was successfully eluted using 1.0N HCl. Following low temperature pretreatment, 102.1% lead was eluted. As expected, it can be concluded that no lead evolved during the low temperature pretreatment. The fact that this percentage is greater than 100% is likely due to experimental error. Following thermal pretreatment at 300°C, only 0.4% of the original lead concentration on the resin was successfully eluted. The reason for this may be that the lead either evolved during pretreatment, is still bound to the resin and was not successfully removed using a strong acid elution, or the lead is in a chemical form non-detectable by ICP. It is believed that the lead did not evolve, since 300°C

is below the expected volatility point for lead, and was eluted but was not detected during spectroscopic analysis. The IRN resin is a strong acid cation resin containing sulfite functional groups. During thermal pretreatment at 300°C, it is possible that the functional groups are removed which, in turn, react with the lead forming lead sulfate; a compound with low solubility. If this were the case, the lead (as lead sulfate) would not be detectable by ICP. This potential mechanism could be conclusively established by acid digesting the eluting solution prior to chemical analysis for lead concentration, but this is beyond the scope of the project.

Thermal screening results for lead retention of the INEL mixed waste ion exchange resins are also summarized in Table 3.2.4. The lead concentration eluted from these resins is shown for control samples and for samples following pretreatment. The exact concentration of lead on the INEL resins was not known prior to pretreatment so in order to calculate the percent lead eluted from each sample, the control samples were used as a basis. The percent lead eluted from the control samples was assumed to be 100%. This does not mean that the elution step was 100% effective, rather the control samples are taken as a benchmark for the other samples. The concentration of lead eluted from the control samples were taken as the maximum and were used to determine the percents eluted from the resin samples following pretreatment at both 110°C and 300°C. If the pretreated samples were calculated to have a percent of lead eluted less than 100%, this would indicate that the lead had evolved or was still bound to the resin and could not be successfully removed by elution. However, following pretreatment at 110°C, 114.6% lead was eluted, and after pretreatment at 300°C, 122.9% lead was eluted. This indicates that the lead did not evolve during pretreatment and the elutions were more effective on the pretreated samples.

The mercury retention of the surrogate and INEL resins are indicated in Table 3.2.5. This table summarizes for the surrogate IRN resins, the concentration of mercury loaded onto the resins, the concentration of mercury eluted from the resins following thermal treatment and the percent mercury eluted. As with Table 3.2.4, the percent eluted is the percentage of the original lead concentration loaded onto the resins that was successfully eluted after pretreatment. Each reported value is the statistical mean based on three replicates. The percent of mercury eluted from the untreated (control) samples was limited to 26.3%, despite using 1.0N HCl as suggested by a Rohm and Haas.^{7,8} Since the elution step for mercury is not effective, it is difficult to draw conclusions as to the evolution of mercury during pretreatment based on eluting any/all mercury remaining on the resins. The percent of mercury eluted is less for the pretreated samples than for the untreated samples. Two possibilities exist to explain this trend. If it is assumed that each sample can be eluted to the same effectiveness, then the observed differences between the percentages of mercury eluted from the untreated samples compared to the pretreated samples is due to evolution of mercury. On the other hand, the observed differences may be due to a chemical or physical effect caused by thermal pretreatment that prevents elution of the mercury. The same procedure was employed to determine the percent mercury eluted from the INEL resins as for calculating the percent lead eluted. The percent mercury eluted from the untreated INEL resins was again assumed to be 100%. Following the low temperature pretreatment, an improvement in the percent of mercury eluted was observed. Following pretreatment at 300°C, only 0.2% of the mercury was successfully eluted compared to the untreated sample. This may indicate that mercury has evolved during the higher temperature pretreatment or, as with the lead,

has reacted with resin decomposition products to form an insoluble compound. This conclusion can not be verified since the type of functional groups on the INEL resin is not known. Again, the results are inconclusive, but an acid digestion of the eluting solution is recommended. This step may elucidate whether insoluble compounds are present.

3.2.4 Spent Ion Exchange Resin Pretreatment and Extrusion Processing

Pretreatment of the as-received INEL resins was conducted by heating two glass trays containing the resin beads in a muffle furnace at 300°C for one hour. Upon opening the oven door, following thermal pretreatment, significant quantities of billowing white smoke were observed. Additional resin pretreatment was not conducted since the cause of the off-gassing is not known and since precautions were not in place to trap and analyze the composition of the smoke. Off-gassing of ion exchange resins has not been observed with any previous resin types. Muffle furnaces are not vented so the quantity of off-gas generated during the thermal pretreatment exited when the door was opened. Oil was observed dripping down the back of the oven, probably a result of condensed off-gas. BNL Health Physics personnel checked the oven for contamination and analyzed the oil for PCB contamination. Both results were negative.

The INEL resin that was pretreated (approximately 130 g by dry weight), was processed on a Killion 32 mm (1.25 in.) single-screw extruder at a waste loading of 40 weight percent. This waste loading was selected to ensure sufficient material to fabricate waste form pellet specimens for TCLP testing. Feed metering to the extruder was accomplished with volumetric feeders that were calibrated with either the mixed waste ion exchange resin or with low-density polyethylene pellets. To generate the calibration curves, five replicate one minute rate samples were taken at four different feeder screw speed (manual percent) settings. The tabulated data and the calibration curve for the ion exchange resins are shown in Table 3.2.6 and Figure 3.2.1, respectively. The calibration results for polyethylene were previously shown in Table 3.1.2 and Figure 3.1.2. Processibility testing with this waste was limited to confirmation processing while fabricating waste form pellets for TCLP testing. Successful processing of this waste confirmed that ion exchange resins are amenable to extrusion processing with polyethylene.

TCLP testing was conducted on the encapsulated waste forms and compared with untreated samples to serve as baselines. Due to the pH of the waste forms and the untreated ion exchange resins determined during TCLP pre-test, extraction fluid #1 was used for both samples. Leachates were analyzed for lead concentration using a Hach UV-Spectrometer. Mercury concentrations were not analyzed since thermal screening was inconclusive for possible mercury evolution during pretreatment. TCLP results are summarized in Table 3.2.7. The encapsulated waste forms dramatically decreased lead leachability compared to the untreated ion exchange resins and passed the TCLP test with a lead concentration of 1.6 mg/l. The lead concentration in the untreated leachate was 1,200 mg/l, well above the RCRA limit of 5 mg/l.

3.2.5 Conclusions

Thermal screening testing did not conclusively determine the fate of mercury on pretreated ion exchange resins. It is assumed that lead does not evolve. The observed percents of lead eluted following pretreatment from both the surrogate resins and the INEL resins contributed to this assumption. However, the discrepancy for the low percent of lead eluted from the surrogate samples pretreated at 300°C can be resolved by acid digesting these elution solutions. Acid digestions of mercury elution solutions may also help draw conclusions on the fate of mercury. Additional testing should also be performed to improve the mercury elution effectiveness, e.g. identify a better eluting solution.

Confirmation processing of INEL PWTU spent ion exchange resins was successful. This waste is amenable to polyethylene encapsulation following thermal pretreatment. At a waste loading of 40 weight percent the leachability of lead from encapsulated waste forms was effectively reduced below RCRA limits. Additional work is suggested to maximize waste loading potential and to optimize processing conditions for the thermally pretreated resins. Alternatively, additional work could be conducted for processing dry ion exchange resins that have not been treated at 300°C. Dried resins are also amenable to encapsulation processing if waste loading potential is reduced to 20-30 wt%.

Table 3.2.1 Analytical results of mercury concentrations from IX resin elutions.

Solution	Sample 1 (mg/l)	Sample 2 (mg/l)	Sample 3 (mg/l)	Mean Conc. (mg/l)
Pb/Hg Stock Solution	212 219	na ¹	na	216
Loading Solution ² (IRN-77, Untreated)	na	2.35	na	2.35
Loading Solution ² (IRN-77, 110°C)	0.14	na	na	0.14
Loading Solution ² (IRN-77, 300°C)	na	na	na	na
Eluting Solution (IRN-77, Untreated)	9.73, 9.43 9.15	7.81	10.9	9.40
Eluting Solution (IRN-77, 110°C)	2.28	2.27	2.28	2.28
Eluting Solution (IRN-77, 300°C)	nd ³	nd	nd	nd
Eluting Solution (INEL, Untreated)	0.17	0.17	0.23	0.19
Eluting Solution (INEL, 300°C)	nd	nd	nd	nd

¹ na = not analyzed

² analyzed following at least 18 hours in contact with resins

³ nd = not detected

Table 3.2.2 Percent weight loss from dewatered ion exchange resins following thermal pretreatment.

Ion Exchange Resin Sample¹	Mean % Weight Loss²
IRN-77 (low-temp, 110° C@24 h)	59.55±0.04
IRN-77 (high-temp, 300° C@1 h)	74.17±0.04
INEL#788 (low-temp, 110° C@24 h)	60.16±0.14
INEL#788 (high-temp, 300° C@1 h)	73.41±0.59

¹ 25.00 g samples

² based on 3 replicates

Table 3.2.3 Ion exchange resin bed volumes following thermal pretreatment.

Ion Exchange Resin Sample¹	Column Bed Volume (cc)²
IRN-77 (untreated)	6.43 ± 0.05
IRN-77 (low-temp, 110°C@24 h)	6.67 ± 0.05
IRN-77 (high-temp, 300°C@1 h)	2.33 ± 0.19
INEL#788 (untreated)	6.30 ± 0.08
INEL#788 (low-temp, 110°C@24 h)	6.27 ± 0.13
INEL#788 (high-temp, 300°C@1 h)	3.50 ± 0.22

¹ 5.00 g samples

² based on 3 replicates

Table 3.2.4 Thermal testing results for lead (Pb) volatilization during pretreatment.

Pretreatment	Concentration loaded onto resin¹ μg Pb/ grams resin	Concentration eluted after pretreatment² μg Pb/ grams resin	% Pb eluted³
Control (IRN-77, Untreated)	965.9	925.5	95.8 %
Low Temperature (IRN-77, 24h @110°C)	965.9	986.1	102.1 %
High Temperature (IRN-77, 1h @ 300°C)	965.9	3.7	0.4 %
Control (INEL, Untreated)	-	2139.2	100.0 %
Low Temperature (INEL, 24h @110°C)	-	2450.7	114.6 %
High Temperature (INEL, 1h @ 300°C)	-	2628.5	122.9 %

¹ Average based on 3 replicate trials. Loading calculated from concentration analysis of 25 ml Pb solution before and after being passed through a column containing 5 grams of resin.

² Average based on 3 replicate trials for each pretreatment. Eluted using 50ml of 1.0 N HCL solution.

³ Percent eluted for IRN-77 resin based on the calculated Pb loading (965.9 μg Pb/ grams resin) and for INEL resin based on total Pb eluted from control.

Table 3.2.5 Thermal testing results for mercury (Hg) volatilization during pretreatment.

Pretreatment	Concentration loaded onto resin ¹ $\mu\text{g Hg/ grams resin}$	Concentration eluted after pretreatment ² $\mu\text{g Hg/ grams resin}$	% Hg eluted ³
Control (IRN-77, Untreated)	899.1	236.7	26.3 %
Low Temperature (IRN-77, 24h @110°C)	899.1	32.9	3.7 %
High Temperature (IRN-77, 1h @ 300°C)	899.1	0.0	0.0 %
Control (INEL, Untreated)	-	45.4	100 %
Low Temperature (INEL, 24h @110°C)	-	70.2	154.7 %
High Temperature (INEL, 1h @ 300°C)	-	0.1	0.2 %

¹ Average based on 3 replicate trials. Loading calculated from concentration analysis of 25 ml Hg solution before and after being passed through a column containing 5 grams of resin.

² Average based on 3 replicate trials for each pretreatment. Eluted using 50ml of 1.0 N HCL solution.

³ Percent eluted for IRN-77 resin based on the calculated Hg loading (899.1 $\mu\text{g Hg/ grams resin}$) and for INEL resin based on total Hg eluted from control.

**Table 3.2.6 Killion feeder calibration data for INEL ion exchange resins.
(feedrate given as g/min)**

Sample	Percent of Full Speed			
	10%	15%	20%	25%
1	4.96	8.29	11.62	14.90
2	5.01	8.36	11.45	14.80
3	5.08	8.16	11.71	15.14
4	5.11	8.23	11.67	14.78
5	5.10	8.28	11.50	14.83
Mean	5.05	8.26	11.59	14.89
Std. Dev.	0.06	0.07	0.10	0.13
2 σ	0.07	0.08	0.12	0.16
% Error	1.42	1.00	1.06	1.10

Figure 3.2.1 Killion feeder calibration curve for INEL ion exchange resins.

Table 3.2.7 TCLP results comparing encapsulated spent ion exchange resins with untreated samples. (RCRA limit for Pb: 5 mg/l)

Sample	Extraction Fluid	Pb Concentration (mg/l)
Encapsulated IX Resin (40 wt%)	1	1.6
Untreated IX Resin	1	1200

3.3 Activated Carbon (INEL ID#562)

3.3.1 Waste Description

Consisting primarily of granular activated carbon in the 4-12 mesh range this waste was characterized with leachable levels of the volatile organics trichloroethylene and tetrachloroethylene as well as the radionuclides Cs-137, Co-60 and Sr. The most recent characterization data for this waste indicates three TCLP contaminants of concern at concentration levels of 0.3 ppm tetrachloroethylene, 33 ppm of trichloroethylene and 314 ppm barium in the waste stream.

3.3.2 Scope

A series of thermal screening tests were conducted on prepared surrogates to examine the volatility of both tetrachloroethylene and trichloroethylene from the carbon matrix. Thermal testing conditions were chosen to simulate expected waste encapsulation processing conditions. Several surrogates were prepared with either exaggerated amounts of 50,000-300,000 ppm (5-30 wt%) tetrachloroethylene or 50,000-100,000 ppm (5-10wt%) trichloroethylene (compared to the 0.3 ppm tetrachloroethylene and 33 ppm trichloroethylene found in the actual waste). A more representative surrogate was not produced due to the combined difficulties in accurately measuring the minute amounts of organics that would be required as well as the complexity of having to evenly sorb a small organic quantity onto a significantly larger carbon matrix without creating large variations in concentrations. In addition, any weight loss attributed to a 0.3 or 33 ppm quantity would not be detectable within the sensitivity of the instrumentation to be used for thermal screening. Barium was not added to the surrogate since the relatively low processing temperatures of 150°C preclude the gaseous evolution of the metal from the waste. The purpose of analyzing the two organics individually is to ascertain which, if any, will leave the carbon matrix and the relative propensity of each to do so.

3.3.3 Surrogate Preparation and Experimental Procedure

A total of five surrogates were produced containing either trichloroethylene or tetrachloroethylene at varying organic contents. They included surrogates containing 5, 10 and 30wt% tetrachloroethylene and 5 and 10wt% trichloroethylene. The surrogates were prepared by individually weighing each ingredient on an analytical balance and adding them to a 120 ml capped plastic cup. In order to better achieve a homogenous product within the 10-40 mg sample size range (required for thermal testing using a TGA analyzer) the activated carbon was ground to a fine powder using a mortar and pestle. After weighing and adding the ground activated carbon, the appropriate amount of organic material was carefully added using a plastic dropper. The added organics were immediately sorbed by a small fraction of activated carbon on the surface as seen in the formation of clumps. Vigorous shaking appeared to disperse the clumps. Using this process a 10 gram batch of each surrogate was prepared. During surrogate preparation the adsorption of the tetrachloroethylene and trichloroethylene onto the carbon matrix resulted in a release of heat causing the cup to warm. This may be evidence of chemical adsorption

(chemisorption) for which relatively large releases of heat of adsorption are usually encountered. The alternative, physical adsorption, generally has considerably lower heat releases due to lower heats of adsorption⁹. As a comparison during thermal screening, a baseline surrogate was prepared simply containing ground activated carbon.

Each surrogate was tested using the TGA analyzer by heating the samples in an air atmosphere (supplied through a compressed air cylinder) at 20°C/min to 150°C and holding for 90 minutes or longer for some runs. This is the maximum temperature that would be incurred and far exceeds the average residence time of 10 minutes that would occur during extrusion processing. TGA runs continually measure the weight of the sample over time as it is heated, thus revealing volatilization of various constituents in a weight or weight loss vs. time plot. Comparison of TGA results between samples containing the organics and those without (baseline) reveal whether the organics leave the carbon matrix under the simulated thermal conditions for waste encapsulation. For each surrogate three runs were conducted to confirm repeatability of TGA results as well as to ensure homogeneity of the prepared surrogate.

3.3.4 Results and Discussion

Three baseline TGA runs were conducted for samples containing 100% activated carbon, shown in Figure 3.3.1. The weight loss curves indicate a rapid initial drop which quickly levels off within the first ten minutes of the TGA run. Total weight loss ranged between 3.56 - 3.95 wt%, all of which can be attributed to the water content of the hygroscopic activated carbon.

Surrogates containing 5 and 10 wt% trichloroethylene were analyzed using the TGA analyzer with the results shown in conjunction with the three baseline runs in Figure 3.3.2 and Figure 3.3.3. Gaseous evolution of trichloroethylene from the carbon matrix is evident since percent weight loss exceeds that associated with moisture content alone (baseline). In fact, trichloroethylene continues to evolve after 90 minutes at a constant temperature of 150°C. TGA runs conducted beyond the 90 minute time frame (Figure 3.3.4) show a gradual leveling of the weight loss curve, with the rate of trichloroethylene evolution decreasing as concentration of the organic decreases. Similar trends can be seen for the surrogate containing 5, 10 and 30 wt% tetrachloroethylene (Figures 3.3.5 - 3.3.8) with the rate of loss of tetrachloroethylene being less than that for trichloroethylene. This rate difference is expected since trichloroethylene has a higher vapor pressure and lower boiling point compared to tetrachloroethylene. Variations in total weight loss between replicate runs for each surrogate may be attributed to variations in surrogate homogeneity.

Thermal screening results more importantly indicate gaseous evolution of both trichloroethylene and tetrachloroethylene within the initial ten minutes of thermal testing, the time frame required for waste encapsulation. This is indicated by the change in slope of the weight loss curve. The initial sharp decrease is associated with water loss as seen in the baseline and the more gradual decrease caused by the evolution of organics. A decreasing pattern in this initial sharp weight loss (associated with water volatilization) is seen in both the trichloroethylene and tetrachloroethylene for surrogates with increasing organic loading. This trend may be explained

by the progressively larger heat generated (larger heats of adsorption) when preparing surrogates with higher tetrachloroethylene or trichloroethylene concentration. Not only is there a lower moisture content with higher organic loadings, since the organic component represents a greater weight fraction of the total sample weight, but the increase in generated heat may serve to liberate a larger percentage of moisture prior to the TGA analysis.

The vapor pressures for trichloroethylene and for water at ambient conditions are 58 mm Hg and 18 mm Hg, respectively, with the boiling point for trichloroethylene being 87°C, lower than that for water (100°C). The relatively higher vapor pressure and lower boiling point suggests that the trichloroethylene should evolve at a faster rate than water, contrary to what was observed. Two explanations exist for the slow evolution of trichloroethylene; (1) the observed heat generated when preparing the surrogate is due to chemisorption for which activation energies for desorption are generally greater resulting in a decrease in the rate of desorption, and/or (2) the heat generated is a result of an exothermic reaction in which case the weight loss may be due to the gaseous evolution of the products of reaction and not the trichloroethylene. Similar reasoning may apply to the trends seen in the tetrachloroethylene surrogate despite the lower vapor pressure (13 mm Hg at 20°C) and higher boiling point (121°C).

3.3.5 Conclusions

Despite having clearly demonstrated gaseous evolution of tetrachloroethylene and trichloroethylene for surrogates containing exaggerated amounts of the organics, a conclusive answer regarding desorption of 0.3 ppm and 33 ppm concentrations levels in the actual waste cannot be drawn. However, the TGA thermal screening tests do reveal many favorable factors that may act to retard or prevent gaseous evolution within the ten minute time frame required for waste encapsulation:

- 1) Extended runs of both the trichloroethylene and tetrachloroethylene demonstrated that gaseous evolution of the organics is diffusion limited, in that the rate of gaseous evolution decreases with concentration of organics. This is supported by the gradual flattening of the weight loss curve as the organics leave the carbon matrix. Since actual waste contains 0.3 and 33 ppm levels of tetrachloroethylene and trichloroethylene, the rate of organic evolution is expected to be very low.
- 2) Chemisorption of the organics to the carbon matrix will further impede volatilization by increasing the required activation energy for desorption. Therefore, the relatively high vapor pressures for both the trichloroethylene and tetrachloroethylene are no longer indicative of the volatility of these organics.
- 3) Higher than atmospheric pressures are encountered during the encapsulation process. Higher pressures will further inhibit trichloroethylene and tetrachloroethylene desorption. In addition, the simultaneous heating and mixing of polymer and waste will also deter the escape of gaseous molecules.

For conclusive results, further testing with the actual waste containing 0.3 ppm tetrachloroethylene and 33 ppm trichloroethylene is recommended. Testing would entail an alternative method of collecting the off-gas leaving the carbon matrix and analyzing for the trace quantities of organics. However, considering the presence of such small concentrations of these organics, additional testing may not be warranted. Trichloroethylene and tetrachloroethylene leaving the waste may be safely discharged through a vent port and passed through a filter or cold trap to prevent release during waste encapsulation. Furthermore, this waste stream contains the heavy metal barium and radionuclides for which polyethylene is recommended for waste stabilization. The 4-12 mesh granular activated carbon appears to be amenable to the extrusion process.

Activated Carbon (baseline)

Plotted: 3 baseline and temperature profiles
Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H
Cell: Aluminum
Atmosphere: Air
Rate Flow: 10.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
20.0	150.0	65.0

Figure 3.3.1. TGA plot showing weight loss from baseline surrogate.

Activated Carbon with 5wt% Trichloroethylene

Plotted: 3 baseline and 3 surrogate runs
Surrogate contains: 5wt% trichloroethylene,
95wt% activated carbon
Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H
Cell: Aluminum
Atmosphere: Air
Rate Flow: 10.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
20.0	150.0	90.0

Figure 3.3.2. TGA plot showing weight loss from surrogate containing 5wt% trichloroethylene compared to baseline.

Activated Carbon with 10wt% Trichloroethylene

Plotted: 3 baseline and 3 surrogate runs

Surrogate contains: 10wt% trichloroethylene
90wt% activated carbon

Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H

Cell: Aluminum

Atmosphere: Air

Rate Flow: 10.00[ml/min]

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
20.0	150.0	90.0

Figure 3.3.3. TGA plot showing weight loss from surrogate containing 10wt% trichloroethylene compared to baseline.

Activated Carbon with Trichloroethylene - Extended Runs

Plotted: 2 extended surrogate runs

Surrogate-1 contains: 10wt% trichloroethylene
90wt% activated carbon

Surrogate-2 contains: 5wt% trichloroethylene
95wt% activated carbon

Detector Type: Shimadzu TGA-50H

Cell: Aluminum

Atmosphere: Air

Rate Flow: 10.00[ml/min]

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
20.0	150.0	200.0, 330.0

Figure 3.3.4. TGA plot showing weight loss for runs beyond 90 minutes for 5 and 10wt% trichloroethylene.

Activated Carbon with 5wt% Tetrachloroethylene

Plotted: 3 baseline and 3 surrogate runs

Surrogate contains: 5wt% tetrachloroethylene
95wt% activated carbon;

Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H

Cell: Aluminum

Atmosphere: Air

Rate Flow: 10.00[ml/min]

Temp Program

Rate [C/min]	Hold Temp [C]	Hold Time [min]
20.0	150.0	90.0

Figure 3.3.5. TGA plot showing weight loss from surrogate containing 5wt% tetrachloroethylene compared to baseline.

Activated Carbon with 10wt% Tetrachloroethylene

Plotted: 3 baseline and 2 surrogate runs
 Surrogate contains: 10wt% tetrachloroethylene
 90wt% activated carbon
 Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H
 Cell: Aluminum
 Atmosphere: Air
 Rate Flow: 10.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
20.0	150.0	90.0

Figure 3.3.6. TGA plot showing weight loss from surrogate containing 10wt% tetrachloroethylene compared to baseline.

Activated Carbon with 30wt% Tetrachloroethylene

Plotted: 3 baseline and 3 surrogate runs
Surrogate contains: 30wt% tetrachloroethylene
70wt% activated carbon
Baseline contains: 100% activated carbon

Detector Type: Shimadzu TGA-50H
Cell: Aluminum
Atmosphere: Air
Rate Flow: 10.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
20.0	150.0	90.0

Figure 3.3.7. TGA plot showing weight loss from surrogate containing 30wt% tetrachloroethylene compared to baseline.

Activated Carbon with Tetrachloroethylene - Extended Runs

Plotted: 2 extended surrogate runs

Surrogate-1 contains: 10wt% tetrachloroethylene
90wt% activated carbon

Surrogate-2 contains: 5wt% tetrachloroethylene
95wt% activated carbon

Detector Type: Shimadzu TGA-50H

Cell: Aluminum

Atmosphere: Air

Rate Flow: 10.00[ml/min]

Temp Program

Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
20.0	150.0	330.0, 420.0

Figure 3.3.8. TGA plot showing weight loss for runs beyond 90 minutes for 5 and 10wt% tetrachloroethylene.

3.4 Freon Contaminated Rags (INEL ID #915)

3.4.1 Regulatory Issues for Conducting Treatability Studies on Listed Wastes

Hazardous wastes are categorized as either characteristic or listed. A characteristic waste is considered a hazardous waste when one or multiple components of the waste meet specific criteria for corrosivity, toxicity, etc. However, if the hazardous nature of the component is removed, for example, stabilizing the waste, then the waste is no longer considered a hazardous waste. On the other hand, listed wastes are always considered hazardous regardless of any treatment. Materials that contact listed wastes, in turn, also become classified as listed wastes. Listed wastes are defined based on their original use including spent solvents (F list), specific source (K list) or commercial product (U and P list). All listed wastes have an associated EPA code, depending on how the waste was originally used, which determines the Land Disposal Restrictions (LDR) found in 40CFR268. The LDR is a treatability standard that is required in order to dispose of the listed waste. Freon 113 (trichlorotrifluoroethane) is only classified as a listed waste if its original use was as a solvent, since it appears on the spent solvent list (F002). The corresponding treatment standard for a F002 waste is concentration based and requires a waste concentration below 30 mg/Kg for land disposal. For quantities less than 1,000 kg treatability studies may be carried out under the RCRA Part B treatability exemption. A memorandum issued by BNL's Safety and Environmental Protection Division on "Requirements for Conducting Treatability Studies on Hazardous and Mixed Wastes at BNL" is attached as Appendix A.

3.4.2 Waste Description

This waste was characterized by INEL as a heterogeneous mix of different materials including debris such as different paper and plastic products, kitty litter and carbon. It is considered a listed waste due to elevated concentrations of freon 113 (trichlorotrifluoroethane). The waste contains the radionuclides cobalt-60, antimony-125, cesium-134 and cesium-13, and the metals cadmium (139 ppm), chromium (345 ppm) and lead (2020 ppm). During characterization analysis, the debris waste was separated from the powdered solid waste (i.e. kitty litter/carbon). VOC monitoring indicated that the freon resided primarily in the kitty litter/carbon mix with a concentration ranging from 180-180,000 ppm.

3.4.3 Scope

Thermal screening tests were conducted on this mixed waste stream to determine the organic constituent volatility (Freon 113) under solidification processing conditions. A surrogate of this waste was prepared at BNL containing 18 weight percent freon (181,000 ppm) obtained from the BNL A/C Shop, 77 weight percent kitty litter (Clean Paws cat box filler) and 5 weight percent activated carbon (Calgon Carbon Corp.). This composition was agreed upon by INEL and BNL to represent the powdered solid waste deemed to contain the freon. Metals were not added to the surrogate for thermal screening testing since evolution of gaseous metal products is not expected to occur during the relatively low processing temperatures required for polyethylene

extrusion ($\leq 150^{\circ}\text{C}$). Furthermore, the focus of these thermal screening tests was to observe freon volatility.

3.4.4 Surrogate Preparation and Experimental Procedure

Thermal screening testing by Thermal Gravimetric Analysis (TGA) requires small sample sizes of approximately 10-40 mg. The surrogate was prepared by individually weighing each ingredient on an analytical balance then adding them to a 120 ml capped plastic cup. The kitty litter and carbon were each ground to a fine particle size prior to mixing using a mortar and pestle in order to achieve a homogeneous surrogate. After weighing and adding the freon, which was conducted quickly in order to minimize any volatilization, the sample was vigorously shaken. It was observed when adding the freon that most of the freon was sorbed by a small portion of the kitty litter/carbon resulting in the formation of a small clump. Shaking appeared to thoroughly disperse this clump. Surrogate prepared for baseline experiments with the TGA did not contain freon but maintained the kitty litter to carbon ratio.

Thermal screening experiments were conducted by heating the surrogate in an air atmosphere (supplied by a compressed air cylinder) at $20^{\circ}\text{C}/\text{min}$ to 150°C and holding for 90 minutes. This is the maximum temperature that would be incurred and far exceeds the approximate residence time of 10 minutes that would occur during extrusion processing.

3.4.5 Results and Discussion

A series of TGA baselines were conducted to provide a reference for successive runs that were spiked with freon. Three replicate baseline runs show a weight loss between 7.2 - 7.6 wt% equivalent to the moisture content of the hygroscopic kitty litter. The moisture content of the kitty litter determined using a Sartorius Moisture Balance at 150°C averaged 7.47 ± 0.16 percent. TGA results from three surrogate replicates containing 18 wt% freon are shown in Figure 3.4.1 in conjunction with the three baseline runs. Total weight loss for the surrogate containing freon ranged from 8.8 - 9.8 percent. Accounting for the weight loss due to moisture seen in the baselines, only a small fraction of the freon (1.2 - 2.6%) was observed to volatilize. This is far less than the initial concentration of 18 wt%. Three possibilities exist for the small observed weight loss: (1) the remainder of the freon is still bound in the surrogate and did not evolve, (2) the remaining freon is volatilizing very quickly such that it is lost during the transfer of the surrogate from the closed container to the TGA sample pan (a process that takes approximately 3-5 minutes), or (3) when adding the freon to the kitty litter/carbon after weighing, it is absorbed by only a small portion of the material on top (the clump formation). Vigorous shaking may not have produced a homogeneous surrogate and the samples removed for TGA analysis did not contain the prescribed 18 wt% freon.

Freon 113 is a volatile organic with a vapor pressure of 277 mm Hg at ambient conditions. This is a high vapor pressure so freon would be expected to volatilize readily, especially under elevated temperatures. TGA results did not conclusively establish the evolution of the freon from the surrogate at processing conditions. Therefore, in order to further gauge freon volatility from

the surrogate, three replicate experiments were conducted to observe weight loss from the surrogate at standard temperature and pressure. For this experiment, small quantities (6.25 g) of surrogate were prepared by weighing and adding each ingredient to a 20 ml plastic vial. Upon addition of the freon, which was added last, the vial was closed and shaken to evenly disperse the freon. The surrogate was then placed on an aluminum tray resting on an analytical balance. The weight loss, caused by volatilizing freon, was recorded versus time. Plots of these results are shown in Figures 3.4.2 and 3.4.3. The tabulated data for these curves is shown in Table 3.4.1. Figure 3.4.2 shows the decrease in weight of the surrogate as the freon volatilizes with time while Figure 3.4.3 shown the percent weight loss of the surrogate with time. It was noted that as each replicate experiment was initiated, the weight of the surrogate had already decreased in comparison with the quantity of material initially added. This can be seen in the plot at the zero point on the abscissa or time axis since there was a weight loss before the first timed weight measurement. The weight loss is very rapid during the initial few minutes then decreases to an asymptotic value equaling the initial freon weight fraction. Within the first five minutes approximately 16 wt% of the initial 18 wt% freon volatilized and after 30 minutes, the surrogate lost a total of 17.24 ± 0.51 weight percent. The total weight loss is expected to approach 18 wt% at longer times. At elevated temperatures the rate of freon volatilization would be even greater.

3.4.6 Conclusions

Although the TGA was not capable of accurately recording all the freon volatilization from the surrogate, the TGA results are in agreement with the ambient temperature weight loss experimental results when considering the weight loss versus time. As seen in the ambient temperature weight loss curves, Figures 3.4.2 and 3.4.3, freon volatilizes from the surrogate almost entirely within the first few minutes. Since sample preparation for TGA analysis normally requires a few minutes, each TGA experiment was not able to record the total freon volatilization from the surrogate because the majority of the freon had volatilized prior to starting each TGA experiment. The freon weight loss and the weight loss curve recorded by the TGA is equivalent to the weight loss results observed in Figure 3.4.3 following the approximate four minute mark.

Freon was observed to readily volatilize at standard temperature and pressure when exposed to the atmosphere. In an enclosed environment such as a covered container, freon will evolve until achieving equilibrium at its corresponding vapor pressure for any given temperature. Freon's high vapor pressure (277 mm Hg@20°C) resulted in its near complete volatilization after 30 minutes at room temperature. It is expected that all the freon will volatilize at the thermal processing conditions for polyethylene encapsulation. However, since this waste stream is a mixed waste containing heavy metals and radionuclides, polyethylene encapsulation is recommended for stabilization. The physical characteristics of this waste appear to make it amenable to extrusion processing. Successful polyethylene encapsulation would require special precautions to be introduced to capture any freon 113 evolved during waste processing. An alternative treatment option may be to use encapsulation as a second treatment step to stabilize the debris and sorbent components of this waste stream following desorption of the freon. It is important to note that all components of this waste stream, whether treated or untreated, must be disposed of as a listed waste due to the freon's listed waste designation.

Freon Contaminated Rags

Plotted: 3 baseline and 3 surrogate runs

Surrogate contains: 38.5g kitty litter

2.5g activated carbon

9.0g freon 113

Baseline contains: 19.3g kitty litter

1.3g activated carbon

Detector Type: Shimadzu TGA-50H

Cell: Aluminum

Atmosphere: Air

Rate Flow: 10.00[ml/min]

Temp Program

Rate	Hold Temp	Hold Time
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[C/min]	[C]	[min]
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20.0	150.0	90.0
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Figure 3.4.1. TGA plot showing weight loss from surrogate containing 180,000 ppm freon compared to baseline.

Table 3.4.1 Evolution of freon from surrogate at ambient conditions. Surrogate contains: 5wt%carbon, 77wt% kitty litter, 18wt%freon 113.

Time (min)	Run 1		Run 2		Run 3	
	Weight (g)	%Wt. Loss	Weight (g)	%Wt. Loss	Weight (g)	%Wt. Loss
0	6.25	0.00	6.25	0.00	6.26	0.00
0	5.71	8.64	5.93	5.12	5.83	6.87
0.17	5.60	10.40	5.82	6.88	5.75	8.15
0.33	5.53	11.52	5.70	8.80	5.64	9.90
0.50	5.46	12.64	5.60	10.40	5.58	10.86
0.67	5.40	13.60	5.53	11.52	5.52	11.82
0.83	5.35	14.40	5.44	12.96	5.47	12.62
1.00	5.34	14.56	5.40	13.60	5.42	13.42
1.33	5.29	15.36	5.34	14.56	5.35	14.54
1.67	5.27	15.68	5.29	15.36	5.32	15.02
2.00	5.26	15.84	5.27	15.68	5.31	15.18
2.50	5.24	16.16	5.24	16.16	5.28	15.65
3.00	5.24	16.16	5.23	16.32	5.27	15.81
3.50	5.24	16.16	5.21	16.64	5.25	16.13
4.00	5.24	16.16	5.22	16.48	5.25	16.13
4.50	5.23	16.32	5.20	16.80	5.25	16.13
5.00	5.23	16.32	5.20	16.80	5.25	16.13
5.50	5.23	16.32	5.20	16.80	5.24	16.29
6.00	5.23	16.32	5.19	16.96	5.24	16.29
6.50	5.23	16.32	5.20	16.80	5.23	16.45
7.00	5.22	16.48	5.20	16.80	5.23	16.45
7.50	5.21	16.64	5.19	16.96	5.22	16.61
8.00	5.22	16.48	5.20	16.80	5.22	16.61
8.50	5.22	16.48	5.20	16.80	5.23	16.45
9.00	5.22	16.48	5.19	16.96	5.23	16.45
9.50	5.22	16.48	5.19	16.96	5.22	16.61
10.00	5.22	16.48	5.19	16.96	5.21	16.77
11.00	5.21	16.64	5.18	17.12	5.22	16.61
12.00	5.21	16.64	5.18	17.12	5.20	16.93
13.00	5.21	16.64	5.18	17.12	5.20	16.93
14.00	5.20	16.80	5.18	17.12	5.20	16.93
15.00	5.20	16.80	5.18	17.12	5.20	16.93
20.00	5.20	16.80	5.17	17.28	5.20	16.93
30.00	5.20	16.80	5.15	17.60	5.18	17.25
60.00	5.18	17.12	5.15	17.60

Figure 3.4.2 Weight loss from freon contaminated rags surrogate at ambient conditions.

Figure 3.4.3 Percent weight loss from freon contaminated rags surrogate at ambient conditions.

3.5 TAN TURCO Decon 4502 (INEL ID#426)

3.5.1 Waste Description

This is a mixed waste stream comprised of 77% potassium hydroxide (KOH), 20% potassium permanganate (KMnO₄) and 3% potassium chromate (K₂CrO₄), the radionuclides K-40 and Cs-137, and chromium (Cr) at greater than 5 mg/l. The sample of mixed waste received at BNL appeared as black agglomerated pieces in a wide range of particle sizes, some as large as 7.6 cm (3 in.) in diameter.

3.5.2 Scope

The anticipated treatability plan for this waste was to conduct compatibility testing to evaluate whether the oxidizers in the waste (KMnO₄ and K₂CrO₄) impact the thermal stability of polyethylene and to perform processability testing with this waste. Due to difficulties handling the mixed waste sample, this could not be successfully accomplished. However, some interesting information regarding the nature of this waste was obtained.

3.5.3 Waste Sample Testing

Compatibility testing was to be conducted using Differential Scanning Calorimetry (DSC) to investigate the thermal behavior of the mixed waste in the presence of polyethylene. Thermograms would be obtained by running polyethylene, samples of the mixed waste, and various mixtures of polyethylene with the waste to simulate various waste loadings. The polyethylene and the mixed waste sample would each have characteristic endotherms corresponding to their respective phase changes (i.e., melting points or crystal transitions). If additional or greatly enhanced endotherms were observed when running mixtures of the polyethylene and waste, this would be indicative that an interaction occurred and that the thermal stability of polyethylene may be adversely affected. Previous compatibility testing at BNL with polyethylene and nitrate salt wastes showed no impact on thermal stability due to the presence of oxidizers¹⁰.

A portion of the as-received mixed waste sample was manually crushed within plastic bags in preparation for DSC testing. A 10 mg sample was placed in an aluminum DSC crucible. Almost immediately, a rapid reaction was observed in which the waste became a sludge and bubbled continuously. The mechanism for this reaction is most likely due to the absorption of moisture from the air and the reaction of the aluminum pan with potassium hydroxide and with the oxidizers potassium chromate and potassium permanganate. To demonstrate this, a series of experiments were conducted by placing samples of the waste on various surfaces including glass, plastic and aluminum in either a dry, pure oxygen atmosphere or at standard room conditions. Results indicated that the waste liquifies due to absorption of moisture from air and that the waste only adversely reacted with aluminum.

3.5.4 Conclusions

It was not possible to further characterize the nature of this waste stream within the time frame of this project. Future work to pursue thermal stability testing of this waste would require special precautions to prevent the waste from absorbing moisture and from reacting with the experimental testing materials. In the case of DSC testing, which requires crucible sample holders to be conductive for heat transfer, a noble metal crucible such as platinum could be used. From a polyethylene encapsulation processing standpoint, pretreatment of the waste by size reduction and drying would be required. Special care would be required between transferring the dried waste materials to the extruder. Processing of the dry waste can be accomplished by maintaining a dry inert atmosphere within the waste feeder/feeder hopper and in the feed throat to the extruder. These precautions were used during extrusion processing of the hygroscopic ICPP sodium bearing liquid waste, as discussed in the ICPP sodium bearing liquid waste treatability write up. An alternative treatment for this waste could be to chemically alter the waste by acid neutralization. Although this would produce significant heat as well as water, it might make the waste more amenable to the aforementioned testing and treatment methods.

3.6 ICPP Sodium Bearing Liquid Waste

3.6.1 Waste Description

This waste stream is a low-level liquid mixed waste resulting from the processing of sodium-bearing waste that is currently stored in the Tank Farm at the Idaho Chemical Processing Plant (ICPP). Characterized by INEL, the waste consists of several toxicity characteristic heavy metals such as Cd, Cr, Pb and Hg along with an unknown number of radionuclides. In addition, the waste is strongly acidic with a pH less than one. Two additional waste streams exist resulting from the thermal de-nitration of the ICPP liquid waste, one at temperatures greater than a 600°C and the second at temperatures of approximately 850°C with clay and silica additives used to form insoluble minerals.

3.6.2 Scope

An initial investigation was conducted to examine the corrosive impact of ICPP sodium bearing liquid waste ($\text{pH} < 1$) on BNL pretreatment and encapsulation process equipment and to determine if neutralization is needed prior to drying/encapsulation. Based on this study minimal to no damage was anticipated to existing BNL laboratory process equipment. Consequently, pretreatment and processability tests were performed on waste surrogates provided by INEL. Liquid wastes are not directly amenable to the polyethylene encapsulation process. A pretreatment dryer test was conducted on an INEL prepared ICPP liquid waste surrogate using a laboratory-scale vacuum dryer, as an alternative to the batch oven drying technique used by INEL. Processing feasibility testing was performed on an ICPP dried surrogate, a product of ICPP liquid waste de-nitration performed in aluminum crucibles at 600°C. TCLP testing was conducted on encapsulated waste forms and compared with the untreated surrogate to serve as a baseline.

3.6.3 Corrosive Impact on Dryer and Extruder

Due to the low pH of this waste, the corrosive impact on processing equipment is an important concern. Waste pretreatment by drying at BNL is primarily accomplished using vacuum dryers. These vessels are type 304 stainless steel and contain welds that have not been post-weld annealed. Exposure to low pH liquids like the ICPP sodium bearing liquid waste may induce intergranular stress corrosion cracking at the weld joints. Post-weld annealing performed on the existing drying vessel could reduce, but not eliminate, the potential for this type of attack. INEL's drying method currently uses a 304L material in their drying and storage vessels for handling of the ICPP liquid waste. This material exhibits improved resistance to stress corrosion cracking, but is still susceptible.

Corrosion is also a potential concern for the construction materials of the extruder. Two main parts of an extruder, the barrel liner and the screw, may contact the waste, and be susceptible to corrosive failure. The barrel liner in the Davis-Standard 38mm (1.5 in.) extruder used for bench-scale processability testing at BNL is made from X-101 containing approximately 75% iron. This material has excellent wear resistance but can be adversely affected by pH extremes, according to the manufacturer.¹¹ The representative at Xaloy Inc. was unable to predict long-term effects, but felt that short term use of dried materials should not present a problem. For conditions under which the X-101 alloy is not suitable, Xaloy Inc. does produce liners with alternate materials which have higher corrosion resistance. In order of increasing corrosion resistance, the materials are X-102 (boron-iron alloy), X-800 (Ni-Carbide), X-306 (Ni with 10-15% Fe), and X-309 (<1% Fe). The materials are proprietary, so that exact compositions are not available. The extruder screw is chrome-plated 4140 steel. The chrome plating provides good corrosion resistance, but if the plating integrity is compromised, such as by chipping, the corrosion resistance will be reduced.

It is suggested that during the design of a production-scale polyethylene encapsulation process that the use of corrosion resistant materials be a priority. Long-term continuous processing may require more frequent replacement of the vessel and liner and will demand strict monitoring of vessel, liner and screw integrity. However, for the limited runs required for process testing, the existing BNL extruder and dryer equipment will suffice since minimal to no equipment damage is expected.

3.6.4 Experimental Procedure

Waste pretreatment of the liquid ICPP sodium bearing waste was performed using a laboratory-scale, indirectly heated, vacuum dryer with dual planetary orbital mixing (Ross, Hauppauge, NY). The dryer/mixer is a jacketed cylindrical vessel with a swing mount lid. Two motor driven intermeshing paddles, attached to the dryer top, rotate to agitate the materials being mixed or dried. Heating is provided by a circulating hot oil bath while a vacuum roughing pump maintains a maximum vacuum pressure of 30 inches Hg. Vapor is continuously removed, condensed through a series of water cooled condensers, and collected. Waste surrogate

temperature is monitored by a flush mounted thermocouple in the process vessel. A glass view-port allows for visual observation of the drying cycle. For the test, two liters of the ICPP liquid waste were placed inside the dryer/mixer vessel, the hot oil heater was set to 130°C and a maximum 30 inches Hg vacuum pressure drawn. These operating parameters were chosen based on successfully drying a test solution of sodium carbonate and potassium carbonate. Hot oil temperature, surrogate temperature and vacuum pressure gauge were periodically monitored throughout the dryer test. Upon completion of the dryer test the condensate and the as-received ICPP liquid waste surrogate were tested for metals concentrations using Inductively Coupled Plasma Spectroscopy (ICP) to determine if any metals evolved during the drying process.

Dried ICPP waste surrogate prepared by INEL was used during processibility testing. Pretreatment of this waste was required in order to make it amenable to processing with polyethylene. Since as-received surrogate contained 3.5 wt% moisture, this included drying to a moisture content of less than two percent. The waste contains potassium hydroxide, a hygroscopic material. The composition of the waste surrogate is shown in Table 3.6.1. As a result, a moisture sorption rate test was conducted by placing a small crushed sample of the waste in an aluminum pan on an analytical balance. The weight gain due to the absorption of moisture was recorded over an 85 minute time frame. A Sartorius Moisture Analyzer was used to determine the moisture content of the as-received ICPP dried waste. Results indicated an initial as-received moisture content of 3.5 wt% and a rapid rate of moisture gain, shown in Table 3.6.2 and Figure 3.6.1, more than doubling its initial moisture content by gaining 3.7 wt% over the 85 minutes of exposure to ambient air. The ICPP dried surrogate, as-received from INEL, consisted of agglomerated particles varying in size from fine powder to large aggregates up to 8 cm (3.2 inches) in diameter. It was therefore determined that pretreatment in the form of oven drying and size reduction to achieve a particle size distribution between 50-2000 microns would be necessary.

The hygroscopic ICPP dried waste surrogate was oven dried in several Pyrex glass dishes at a temperature of 110°C for at least 24 hours to remove the 3.5 wt% residual moisture. Drying was performed prior to size reduction in order to facilitate breaking up the large particles as well as to prevent size reduced particles from re-agglomerating. Precautions were taken during pretreatment to prevent exposure to the surrogate due to potential health hazards. Small quantities of the material were crushed by placing in 0.004 inch thick polyethylene plastic bags, then double bagging and placing under an aluminum plate. Operating in a vent hood, a hammer was used to repeatedly strike the plate which served to distribute the load of the impact and crush the surrogate. To ensure a particle size amenable to polyethylene encapsulation the crushed ICPP dried surrogate was sieved using a 2000 micron sieve and placed back in the oven to prevent the waste from re-absorbing moisture, as well as to remove any moisture that may have been absorbed during size reduction. A final moisture analysis of the pretreated ICPP dried waste was found to be 0.95 weight percent.

Processibility testing of the pretreated ICPP dried waste was conducted using a 38 mm (1.5 in.) single-screw Davis-Standard extruder. Material feed was accomplished through volumetric feeders retro-fitted to a loss-in-weight PID controlled system. To reduce moisture absorbance by the hygroscopic waste surrogate additional precautions were taken. For example, a dry atmosphere

(2.4% relative humidity) was created inside the feed hopper by delivering purge gas at a rate of three cubic feet per hour from a compressed air cylinder through a desiccant tube. The dry atmosphere served to eliminate moisture absorbance by the ICPP surrogate and ensured processibility.

A target waste loading of 40 weight percent and screw speed of 25 rpm were selected as a conservative starting point considering the hygroscopic nature of the ICPP waste surrogate. These are not optimal nor maximum processing parameters but can be readily achieved based on past experience with wastes with similar physical properties. Optimizing these parameters would require additional processing tests, beyond the scope of this project. Processibility testing included fabricating 5.1cm (2 in.) by 10.2cm (4 in.) right cylindrical specimens for compressive strength testing, grab samples to monitor product homogeneity through density analysis and taking one minute rate samples for processing consistency. Compressive strength testing was conducted in accordance with ASTM D695, "Compressive Properties of Rigid Plastics." Grab sample densities were determined by weighing each grab sample and using a multipycnometer to analyze their volumes. TCLP tests were performed on both encapsulated waste form pellets, fabricated using Teflon dies, and the untreated ICPP dried waste surrogate (serving as baseline) to evaluate waste form performance. The TCLP extraction fluid was analyzed for concentrations of Cd, Cr, Ni and Pb using ICP Spectroscopy and Hg using a Atomic Absorption Spectrometer fitted with a Perkin-Elmer MHS-10 cold-vapor generator (EPA Method 7470).

3.6.5 Results and Discussion

The ICPP liquid waste surrogate dryer trial was initiated using the vacuum dryer/mixer with a circulating oil bath temperature of 130°C and 30 inches of Hg vacuum. Drying was performed for a total of eight hours with a maximum surrogate temperature of 82°C. The existing dryer setup was found to be inadequate in its ability to handle the highly corrosive waste surrogate and consequently drying was stopped prior to reaching complete dryness to avoid further risk of damage to equipment from prolonged contact. Corrosive effects were strongly evident in rust seen on the bottom of the lid and a hole that was formed through a brass fitting during testing. Drying was halted with the ICPP surrogate reduced to an orange sludge at which point a red vapor was also observed evolving inside the dryer vessel. Condensate from the condenser tubes was found to be green in color, similar to the untreated ICPP liquid waste surrogate, suggesting the presence of Ni. ICP Spectroscopy was performed for metals concentration in both the as-received ICPP liquid surrogate and in the collected condensate with the results shown in Table 3.6.3. Concentrations of metals were clearly detected in the condensate with the levels of Ni, Mn, Fe, Mg, Mo, Cr and Cd considerably less than that found in the ICPP liquid surrogate and the levels of Pb being only slightly less. Elevated concentrations of Cu and Zn are also evident in the condensate, likely due to the corrosion of the brass (a Cu and Zn alloy) fitting. With melting points of all these metals being considerably higher than maximum process temperatures achieved, 82°C, the most probable explanation of their presence in the condensate is through carry over by vapor droplets pulled through the vacuum tube. To eliminate this mode of mobilization, a demister may be used to break apart the vapor droplets in the vacuum line.

Successful extrusion processing of the pretreated ICPP dried waste surrogate was accomplished at 40 weight percent loading. The extrudate was observed to be continuous, uniform and free of vapor bubbles, proving waste pretreatment to be effective. Process rate results (summarized in Table 3.6.4) support these observations, indicating a mean output rate of 65.61 ± 1.64 g/min and a relatively small 1.79 percent error. Density results, summarized in Table 3.6.5, show the mean waste product density to be 1.25 ± 0.03 g/cm³ with a 1.79 percent error. Density variations between replicates taken as grab samples during processing are indicative of product homogeneity. The low percent error is evidence of good mixing and wetting of individual waste particles, thus indicating a homogenous final waste form. Mean compressive strength results for the encapsulated waste forms are shown in Table 3.6.6. The mean maximum compressive strength of $1.85 \times 10^4 \pm 593$ kPa (2684 ± 86 psi) is well above the NRC waste form compressive strength requirement of 414 kPa (60 psi) and similar to that of other polyethylene waste forms.

TCLP leach testing results for the encapsulated ICPP dried surrogate compared with that of the untreated surrogate (baseline) are shown in Table 3.6.7. Leachates from both the treated and untreated surrogates were found to contain concentrations of Cd, Hg and Pb below current RCRA limits (1, 0.2, and 5 mg/l, respectively). The concentrations for Cr, on the other hand, were detected at 108 mg/l in the untreated surrogate, well above the current RCRA limit of 5 mg/l. This was successfully reduced below the current RCRA limit to a concentration of 2.4 mg/l in the encapsulated ICPP dried waste surrogate. Mercury was detected at a concentration of 0.02 mg/l for the untreated surrogate and was undetectable in the treated surrogate. The detection limit of the Perkin-Elmer cold-vapor technique used for Hg analysis is 0.2 µg/l (ppb). Concentrations of both Pb and Ni were also below detection limits for both the treated and untreated surrogates for which ICP Spectroscopy detection limits are set at 0.14 mg/l for Pb and 0.06 mg/l for Ni. Results for Cd were surprising in that concentrations were below ICP detection limits (0.015 mg/l Cd) in the untreated surrogate yet detectable at 0.34 ppm in the leachate of the treated surrogate. This appears to indicate that more Cd leached from the encapsulated surrogate compared to the untreated surrogate. A pH test on untreated ICPP dried surrogate revealed an approximate pH of 11.4, highly basic compared to the original ICPP liquid surrogate characterized with a pH of less than one. This is possibly a result of the greater than 600°C thermal de-nitration process. High pH wastes are known to reduce metals solubility in TCLP tests. Due to the stronger buffering capacity of the untreated waste compared to the encapsulated waste, the pH of the leachate for the untreated surrogate (pH 11.5) was considerably greater than that of the encapsulated waste (pH 5.1). This occurred despite having tested the untreated baseline surrogate in a lower pH extraction fluid (fluid #2 - pH 2.88) compared to the treated surrogate, which was leached using extraction fluid #1 (pH 4.93). The encapsulated ICPP surrogate has reduced buffering capacity since the waste is surrounded by polyethylene and has limited contact with the extraction fluid. Metals leaching into a higher pH solution, as occurred with the untreated waste, probably precipitated and were consequently removed during the 0.7µm filtration step. As a result, concentrations of all the metals (Cd, Cr, Hg, Ni and Pb) that leached into the untreated baseline extraction fluid may be greater than the results indicated in Table 3.6.7. Despite this bias, both Cr and Hg have shown considerably less metals concentrations, indicating a marked improvement in leachability for the encapsulated ICPP surrogate.

3.6.6 Conclusions

Pretreatment drying of the ICPP liquid surrogate was not fully demonstrated using vacuum drying due to the material limitations in the existing equipment. However, past experience suggests that complete drying is possible using this methodology. In addition, the corrosive impact of the waste, evident during testing, suggests that waste neutralization should also be investigated. This could be accomplished by combining the ICPP liquid waste with the highly basic INEL ID# 1055 acid spill clean-up waste (pH 12.3) to buffer its corrosive effect prior to pretreatment.

Processing of the ICPP dried surrogate, with appropriate waste pretreatment and precautions, was successful at a waste loading of 40%. This waste stream is an excellent candidate for stabilization by polyethylene encapsulation. Higher waste loadings should be readily achievable based on favorable processing results. Due to the limited scope of this study, the processing parameters were not optimized. Further testing is recommended to optimize all processing parameters and maximize waste loading potential. Feasibility studies should also be conducted with an actual mixed waste sample.

Table 3.6.1 INEL analysis of ICPP sodium bearing liquid waste sent to BNL.

Constituent	Quantity	Unit
Aluminum	18200	mg/l
Boron	173	mg/l
Cadmium	246	mg/l
Chromium	351	mg/l
Iron	1480	mg/l
Manganese	764	mg/l
Molybdenum	129	mg/l
Nickel	120	mg/l
Zirconium	146	mg/l
Calcium	1440	mg/l
Acid	1.8	Normal
Sodium	32000	mg/l
Potassium	6600	mg/l
Lead	218	mg/l
Mercury	242	mg/l
Fluoride	0.0922	Molar
Chloride	1312	mg/l
Sulfate	1.48	Molar
Nitrate	3.76	Molar
Cesium	11	mg/l
Cerium	53.5	mg/l
Total Strontium	16	mg/l

Table 3.6.2 Rate of moisture absorbance by ICPP dried waste surrogate at ambient conditions.

Time (min)	Weight (g)	Wt% Gained
0	9.07	0.00
5	9.09	0.22
10	9.13	0.66
15	9.15	0.87
20	9.18	1.20
25	9.20	1.41
35	9.25	1.95
45	9.29	2.37
55	9.32	2.68
85	9.42	3.72

$$\text{Wt\% Gained} = (\text{current weight} - \text{initial weight}) / \text{current weight} * 100$$

Figure 3.6.1 Weight percent gained from moisture absorbed from ambient air.

Table 3.6.3 Metal concentrations in ICPP liquid surrogate and condensate from pretreatment dryer trial determined by ICP Spectroscopy.

Metals	Condensate (ppm)	Waste (ppm)
Ti	1.814	0.9989
Ni	18.32	106.2
Pb	166.5	200.7
Mn	2.658	717.1
Fe	394.4	1348
Mg	7.405	83.25
Mo	0.7588	120.9
Cr	9.06	314.6
Be	0.7629	0.1203
Zn	2194	9.158
Cu	7902	13.2
Cd	13.57	212.8

Table 3.6.4 Process rates of ICPP dried surrogate at waste loading of 40wt% and screw speed of 25 rpm.

Sample	Rate (g/min)
1	67.29
2	65.69
3	67.15
4	65.20
5	63.28
6	64.06
7	67.08
8	67.97
9	63.22
10	65.18
Mean	65.61
Std. Dev.	1.64
2 σ	1.17
% Error	1.79

Table 3.6.5 Densities of grab samples representing encapsulated ICPP sodium bearing liquid waste forms at a waste loading of 40wt%.

Sample	Density (g/cc)
1	1.30
2	1.27
3	1.27
4	1.23
5	1.20
6	1.27
7	1.26
8	1.20
9	1.23
10	1.25
Mean	1.25
Std. Dev.	0.03
2 σ	0.02
% Error	1.79

Table 3.6.6 Maximum compressive strength of 40wt% ICPP sodium bearing liquid waste forms.

Sample	Max. Comp. Strength (psi)
1	2795
2	2611
3	2602
4	2770
5	2534
6	2733
7	2653
8	2804
9	2691
10	2646
Mean	2684
Std. Dev.	86.00
2 σ	61.33
% Error	2.29

Table 3.6.7 TCLP Results comparing encapsulated ICPP dried surrogate with untreated samples.

Sample	Extraction Fluid	Metals Concentration (mg/l)				
		Cd	Cr	Hg	Pb	Ni
Untreated ICPP dried surrogate	2	<0.015	108	0.02	<0.14	<0.06
Encapsulated ICPP dried surrogate	1	0.336	2.4	<0.0002	<0.14	<0.06

3.7 HTRE-3 Acid Spill Cleanup (INEL ID#1055)

3.7.1 Waste Description

HTRE-3 Acid Spill Cleanup is a mixed waste primarily composed of the absorbent Spill-X and nitric acid (HNO_3). Additionally, nine radionuclides are present (Co-60, Cs-137, Pb-212, Th-228, Th-230, Th-232, U-234, U-235 and U-238), as well as lead (Pb) at 397 ppm (total) and mercury (Hg) at 737 ppm (total). The physical appearance of this waste is a white powder with a pH of 12.3.

3.7.2 Effects of Moisture Content and pH on Encapsulation Process

Physical characterization of this waste by INEL indicates that this waste contains approximately 25 weight percent water. In order to make this waste amenable to controlled feed metering and extrusion processing, the moisture content must be reduced to less than approximately two weight percent. Pretreatment does not present a problem, however, due to the high pH (12.3) of this waste, corrosion resistive materials would need to be incorporated into the design of the pretreatment system. Drying could be accomplished through the use of direct dryers (e.g., spray dryers) or indirect dryers (e.g., vacuum dryers). In either case, the materials of construction would be a priority. Vacuum dryers at BNL are constructed of type 304 stainless steel, which has good corrosion resistance to high pH materials but is susceptible to stress corrosion cracking. This could be partially remedied by performing post-weld annealing.

Corrosion is also a potential concern for the construction materials of the extruder. This is less significant since all excess water is removed during pretreatment and the waste is essentially "wetted" with polyethylene while being processed through the extruder barrel. However, two main parts of an extruder, the barrel liner and the screw, may contact the waste. For processing corrosive materials, the materials of construction of the liner and the screw should be carefully selected. The barrel liner in the Davis-Standard 38mm (1.5 in.) extruder used for bench-scale processibility testing at BNL is made from an alloy X-101, containing approximately 75% iron. This material has excellent wear resistance but can be adversely affected by exposure to high pH materials¹¹. Other possible liner materials with increasing corrosion resistance, listed with their primary composition, are X-102 (boron-iron alloy), X-800 (nickel-carbide), X-306 (nickel with 10-15% iron), and X-309 (less than 1% iron). The extruder screw is chrome-plated 4140 steel with good corrosion resistance. However, chipping of the chrome may occur with wear, thereby, compromising the plating integrity and reducing corrosion resistance.

3.7.3 Scope

Processing feasibility testing was conducted on a surrogate of this waste stream that was prepared according to the characterization data provided by INEL. A waste composition containing three parts Spill-X to one part nitric acid was agreed upon by INEL and BNL to accurately represent the actual mixed waste. Experiments were also conducted to determine the concentration of nitric acid required at the correct waste composition ratio to achieve a waste with

the desired pH of 12.3. An additional surrogate, spiked with lead and mercury, was processed to fabricate waste form pellets for TCLP testing.

3.7.4 Surrogate Preparation and Experimental Procedure

It was determined by experimentation that mixing one part 0.1M (molar) nitric acid with three parts Spill-X (Ansul Incorporated, Marinette, WI) resulted in a waste surrogate with a pH of 12.3. Spill-X is primarily composed of magnesium aluminum silicate and magnesium oxide. The actual composition percentages are proprietary. A surrogate weighing a total of approximately 7.5 kg was prepared for processibility testing. Following the addition of nitric acid, the surrogate was dried in a convection oven at 110°C. Some clumping did occur during drying necessitating size reduction. This was accomplished by placing the dried surrogate in plastic bags and manually hammering the clumps which easily crumbled and broke apart. Size reduction and drying are often required of wastes prior to extrusion processing to achieve a moisture content less than two percent and a particle size distribution between approximately 50 to 2000 microns, as mentioned previously. Two kilograms of this pre-treated surrogate were set aside in order to prepare a second surrogate to be used for confirmation processing and TCLP waste form pellet fabrication. This surrogate was spiked with 397 ppm lead (as $PbCl_2$) and 737 ppm mercury (as $HgCl_2$).

Processibility testing was conducted using a 38 mm (1.5 in.) single-screw Davis-Standard extruder. The waste surrogate was fed along with polyethylene pellets using individual volumetric feeders retrofitted to a loss-in-weight computer controlled system. Waste processing was conducted at a waste loading of 50 weight percent and at a screw speed of 25 rpm. As with the processibility testing of the eutectic salt waste and the ICPP sodium bearing liquid waste, these are not optimum nor maximum processing parameters but rather a conservative starting point. Additional processibility testing would be required beyond the scope of this project to optimize the processing parameters. Processibility testing included formulating nominal 5.1 cm (2 in.) by 10.2 cm (4 in.) waste form specimens for compressive strength testing, taking periodic grab samples for density analysis (monitor waste product homogeneity), and timed one minute samples for processing consistency. Compressive strength testing was conducted in accordance with ASTM D695, "Compressive Properties of Rigid Plastics." Grab sample densities were calculated by weighing each sample and determining their volumes using a multipycnometer. The metals spiked surrogate was processed for TCLP purposes in an effort to determine leachability of polyethylene/acid spill cleanup waste forms. TCLP testing was also conducted on an untreated surrogate sample to serve as a baseline. The lead concentration in the TCLP leachates was determined by ICP Spectroscopy. Atomic Absorption (AA) Spectroscopy was used to determine mercury concentrations.

3.7.5 Results and Discussion

Following surrogate preparation and pretreatment, the acid spill cleanup surrogate was successfully processed at a waste loading of 50 weight percent. Rate samples, taken periodically during processing, indicated a mean output rate of 76.47 ± 3.05 g/min with a 2.85 percent error, at an extruder screw speed of 25 rpm. Table 3.7.1 summarizes the rate sampling results. The

extrudate (product exiting extruder die) was continuous and consistent, as indicated by the low percent error between replicate process rate samples. These results are a direct indication that this waste is amenable to polyethylene encapsulation by extrusion processing. The densities of the encapsulated product, taken as grab samples during processing, are shown in Table 3.7.2. The mean waste product density was $1.38 \pm 0.03 \text{ g/cm}^3$. The maximum compressive strength of the waste forms are shown in Table 3.7.3. The mean maximum compressive strength was $1.60 \times 10^4 \pm 165 \text{ kPa}$ ($2315 \pm 24 \text{ psi}$), similar to other polyethylene final waste forms and well above the NRC waste form compressive strength requirement of 414 kPa (60 psi).

The leachability results of the encapsulated product compared to the untreated surrogate are shown in Table 3.7.4. All samples were within the RCRA limit of 5 mg/l for lead concentration. The lead concentration in the leachate of the untreated surrogate (spiked with 397 ppm Pb) was 4.2 mg/l compared to 0.18 mg/l for the encapsulated surrogate. Although the untreated surrogate passed the TCLP test for lead leachability, a marked decrease in lead leaching was achieved with the encapsulated product. The untreated surrogate (spiked with 737 ppm Hg) failed the TCLP test with a mercury concentration of 11.37 mg/l, above the RCRA limit of 0.2 mg/l. The polyethylene encapsulated surrogate dramatically reduced leaching and passed the TCLP test for mercury with a concentration of 0.02 mg/l. These results may actually be better than they appear when considering the pH conditions during the TCLP test. The TCLP test required the use of extraction fluid #2 (pH 2.88) for the untreated surrogate and extraction fluid #1 (pH 4.93) for the encapsulated surrogate. Following tumbling during the TCLP test, the extraction fluid containing the encapsulated surrogate recorded a pH of 5.0 while a pH of 11.0 was recorded for the extraction fluid containing the untreated surrogate. Even though the untreated surrogate required an extraction fluid with a low pH of 2.88, the surrogate, starting with a pH of 12.3, had a high buffering capacity thereby maintaining a high pH throughout the TCLP test. Considering metals are mostly insoluble at a high pH, most of the metals probably had precipitated and were removed during the filtration step ($0.7 \mu\text{m}$) in the TCLP test. It is likely that some of the metals were not present in the aliquots removed from the extraction fluid (removed during filtration) and therefore were not present during analysis for metal concentrations. On the other hand, the extraction fluid containing the encapsulated surrogate recorded a pH of 5.0 following tumbling. This pH was much lower because the surrogate was unable to buffer the solution since it was encapsulated in polyethylene. The solubility of metals at a pH of 5.0 is much greater than at a pH of 11.0.

3.7.6 Conclusions

Processibility of the INEL ID#1055 acid spill cleanup surrogate was successful. This waste stream is a prime candidate for polyethylene encapsulation. At a waste loading of 50 weight percent, the leachability of waste forms was shown to be effectively reduced and within RCRA TCLP limits for lead and mercury. Higher waste loadings should be readily achievable based on processing considerations and the successful waste form testing. Due to the limited scope of this project, processing parameters were not optimized but additional work is recommended to optimize all processing parameters and to conduct feasibility testing with an actual mixed waste sample.

Table 3.7.1 Process rates of acid spill cleanup surrogate at waste loading of 50wt% and screw speed of 25 rpm.

Sample	Rate (g/min)
1	78.34
2	80.87
3	78.30
4	79.36
5	76.71
6	73.67
7	78.73
8	70.79
9	73.72
10	74.16
Mean	76.47
Std. Dev.	3.05
2 σ	2.18
% Error	2.85

Table 3.7.2 Densities of grab samples representing encapsulated acid spill cleanup waste forms at a waste loading of 50wt%.

Sample	Density (g/cc)
1	1.35
2	1.43
3	1.42
4	1.41
5	1.42
6	1.40
7	1.36
8	1.34
9	1.35
10	1.35
Mean	1.38
Std. Dev.	0.03
2 σ	0.02
% Error	1.73

Table 3.7.3 Maximum compressive strength of 50wt% acid spill cleanup waste forms.

Sample	Max. Comp. Strength (psi)
1	2319
2	2313
3	2313
4	2300
5	2297
6	2293
7	2291
8	2376
9	2315
10	2333
Mean	2315
Std. Dev.	23.83
2 σ	17.04
% Error	0.74

Table 3.7.4 TCLP results comparing encapsulated acid spill cleanup surrogate with untreated surrogate. (RCRA limit for Pb: 5 mg/l; Hg: 0.2 mg/l)

Sample	Extraction Fluid	Pb Concentration (mg/l)	Hg Concentration (mg/l)
Encapsulated surrogate ¹	1	0.18	0.02
Untreated surrogate ¹	2	4.2	11.37

¹ Surrogate spiked with 397 ppm Pb and 737 ppm Hg

4. CONCLUSIONS AND RECOMMENDATIONS

Eutectic Salt (INEL ID#SMC-507)

Surrogate and actual mixed waste samples were successfully encapsulated at waste loading of 50 weight percent. Both surrogate, spiked with lead, and actual mixed waste forms passed current TCLP limits for lead leachability as shown in the TCLP summary Table 4.1. Pretreatment of this waste is required because waters of hydration in the carbonate salts evolve at extrusion processing temperatures. Additional processability work is recommended for this waste stream in order to optimize processing parameters, maximize waste loading, and to improve TCLP results (through optimization, additives, etc.) to meet proposed RCRA limits¹². Following optimization, full-scale confirmation testing is also recommended.

PWTU Spent Ion Exchange Resins (INEL ID#788)

Thermal screening testing did not conclusively determine the fate of mercury on pretreated ion exchange resins. However, testing did strongly suggest that lead does not evolve, as expected. To help draw conclusions for mercury volatilization, additional testing should be performed to identify improved eluting solutions and acid digestions should be conducted on the elution solutions for more accurate chemical analyses. Confirmation processing of actual INEL resins was successful. Dried ion exchange resins are amenable to polyethylene encapsulation. At a waste loading of 40 weight percent the leachability of lead from encapsulated waste forms was effectively reduced below current limits (Table 4.1). Additional work is suggested to maximize waste loading potential and to optimize processing conditions for the thermally pretreated resins. Optimization and additives can also be used to successfully reduce TCLP results below the proposed RCRA standards for lead. Alternatively, additional work could be conducted for processing dry ion exchange resins that have not been treated at 300°C. Resins dried at 110°C are amenable to encapsulation processing if waste loading potential is reduced to 20-30 wt%.

Activated Carbon (INEL ID#562)

Gaseous evolution of tetrachloroethylene and trichloroethylene was demonstrated. It is inconclusive whether the organics will evolve during encapsulation processing due to inhibiting factors such as their low concentration in the actual waste, possible chemisorption on the carbon substrate and extrusion conditions (i.e., high pressures, gaseous entrapment in melt). However, additional testing to quantify the evolution of organics may not be warranted due to their low concentrations. Since this waste stream does appear amenable to encapsulation, based on its physical characteristics, processability testing of this waste is recommended. A properly designed off-gas treatment train could trap and concentrate any volatilized organics. Barium and the radionuclides in this waste would be effectively encapsulated.

Freon Contaminated Rags (INEL ID#915)

Freon volatilization was demonstrated at ambient temperature and pressure. At encapsulation processing conditions, it is expected that freon will completely evolve. It is recommended that processability testing be conducted for encapsulation of the metals (Cd, Cr, Pb) and radionuclides in this waste since the physical characteristics of this waste appear to make it amenable to polyethylene encapsulation. The stabilization of this waste by polyethylene encapsulation can be a second treatment step following controlled desorption of the freon.

TAN TURCO Decon 4502 (INEL ID#426)

The impact of oxidizers in this waste on polyethylene and processability testing was not completed due to the highly reactive nature of the waste. The waste reacted with the aluminum pans during thermal stability testing and formed a sludge due to moisture sorbed from ambient air. Continued thermal stability testing for oxidizer impact by differential scanning calorimetry would require using inert crucibles. Pending successful stability testing results, encapsulation tests are recommended following pretreatment of this waste by size reduction and drying. Special precautions to prevent the waste from sorbing moisture would be implemented. If alternative treatability testing with this waste is desired, it is recommended that acid neutralization be investigated.

ICPP Sodium Bearing Liquid Waste

Dried waste surrogate was successfully encapsulated at a waste loading of 40 weight percent. Drying and size reduction made the waste amenable to stabilization by polyethylene encapsulation. Leachability of chromium and mercury from encapsulated waste forms compared to untreated surrogate was reduced below current TCLP limits. Two other metals (Pb and Cd) were within current TCLP limits for both untreated samples and encapsulated waste forms. Pretreatment drying of the liquid waste surrogate was not fully demonstrated using vacuum drying due to construction material limitations. ICPP liquid waste was noted to have a corrosive impact on pretreatment process equipment but a long-term deleterious impact of the dried surrogate on extruder materials is not anticipated. Further testing is recommended to optimize all processing parameters, maximize waste loading potential, improve TCLP results to meet proposed RCRA limits for cadmium and chromium and to conduct feasibility studies with an actual mixed waste sample. For pretreatment, testing is recommended with corrosion resistant dryer equipment and/or waste neutralization.

HTRE-3 Acid Spill Cleanup (INEL ID#1055)

This waste stream is a prime candidate for polyethylene encapsulation and was successfully processed at a 50 weight percent waste loading. Waste form leachability was effectively reduced and within both current and proposed RCRA TCLP limits for lead and mercury (Table 4.1). Additional processability work is recommended for this waste stream in order to optimize processing parameters and maximize waste loading, and for full-scale confirmation testing.

Table 4.1 Summary of TCLP results

INEL Waste	Metal	Untreated (mg/l)	Polyethylene Encapsulated (mg/l)	Current RCRA Limit (mg/l)	Proposed RCRA Limit (mg/l)
Eutectic Salts (surrogate)	Pb	4.2 / 4.1	<0.14 / <0.14	5	0.37
Eutectic Salts (mixed waste)	Pb	4.1	1.8	5	0.37
PWTU Ion Exchange Resins	Pb	1200	1.6	5	0.37
ICPP Sodium Bearing Waste	Pb	<0.14	<0.14	5	0.37
	Hg	0.02	<0.0002	0.2	0.2
	Cd	<0.015	0.336	1	0.19
	Cr	108	2.4	5	0.86
HTRE-3 Acid Spill Cleanup	Pb	4.2	0.18	5	0.37
	Hg	11.37	0.02	0.2	0.2

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APPENDIX

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: January 3, 1994
TO: P. Kalb
FROM: G. Goode *G. G.*
SUBJECT: Treatability Studies, Mixed Waste

Per your request for information on the regulatory requirements for conducting Treatability Studies at BNL on mixed waste from off-site, I put together the attached information package titled "Requirements for Conducting Treatability Studies on Hazardous and Mixed Waste at Brookhaven National Laboratory".

The regulations governing conduct of treatability studies are found in NYSDEC regulations, 6NYCRR Part 371.1(e)(4)(v) "Samples Undergoing Treatability Studies at Laboratories and Testing Facilities", see Attachment #1 of the package for the full text of the regulations. Samples undergoing treatability studies and the laboratory conducting the study are not subject to any of the requirements of the Part 370 Series regulations (the hazardous waste reg's) provided the conditions of Part 371.1(e)(4)(v)(a - k) are met. The package explains the details and in bold after some of the requirements, I've added some helpful hints, forms, and sample letters....

After you've had a chance to review the attached materials, give me a call and I'll work with you to make sure we've got all the bases covered. If you have any questions, please don't hesitate to contact me on ext. 4549.

GAG/med/RM312094

Attachment: "Requirements for Conducting Treatability Studies on Hazardous and Mixed Wastes at Brookhaven National Laboratory"

cc: W. R. Casey
L. C. Emma
B. Royce
K. Shurberg
G. Todzia