

**IT CORPORATION
TECHNOLOGY DEVELOPMENT LABORATORY
PROCESS DEVELOPMENT GROUP**

REPORT

For:

**Brookhaven National Laboratory
Decontamination of Dredged Estuarine Sediments
Bench-Scale Tests
BNL Contract No. 725047**

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ACRONYM LIST

ASTM	American Society for Testing and Materials
BNL	Brookhaven National Laboratories
BFS	Blast furnace slag
Cr	Chromium
DES	Dredged estuarine sediment
EC	
EPA	Environmental Protection Agency
FA	Fly ash
kg	Kilograms
HSP	Health and Safety Plan
LC	Lethal Concentrations
mg	Milligrams
mls	Milliliters
MTCLP	Modified Toxicity Characteristic Leaching Procedure
ND	Non detected
ngr/kg	Nanogram/kilogram
PC	Portland Cement
PCB	Polychlorinated biphenyls
PP	Pocket penetrometer
PR	Penetration resistance
psi	Pounds per square inch
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RTA	Rotary Thermal Apparatus

CONTENTS
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SAP	Sampling and Analysis Plan
SCFM	Standard cubic feet per minute
SF	Silica fume
S/S	Solidification/Stabilization
SVOC	Semi volatile organic compounds
SW-MTCLP	Sea Water Modified Toxicity Characteristic Leaching Procedure
TC	Toxicity Characteristic
TDL	Technology Development Laboratory
TOC	Total organic carbon
TOS	Concrete mortar penetrometer
tsf	Tons per square foot
UCS	Unconfined compressive strength
μg	Micrograms
VOC	Volatile organic compounds
WP	Work Plan
w/w	Weight/weight

1.0 INTRODUCTION

Sediments from the New York/New Jersey Harbor must be regularly dredged to maintain shipping channels and berthing areas for commerce and safe navigation. Ocean disposal has been the primary option for dredged sediments. The sediments that accumulate in the Harbor can contain contaminants such as organic compounds and heavy metals at concentrations high enough to prohibit ocean disposal.

Dredged sediments must pass testing criteria prior to ocean disposal. Recently revised regional guidance from the U.S. Army Corps of Engineers-New York District (NYDCOE) and the U.S. Environmental Protection Agency, Region 2 (EPA-Region 2), *Draft Regional Guidance for Performing Tests on Dredged Material Proposed for Ocean Disposal*¹ (Draft, December 1992) has established more stringent biological and chemical test criteria. As a result, the volume of contaminated dredged material prohibited from ocean disposal has increased.

The EPA-Region 2 and the NYDCOE are actively investigating technologies for dredged material management and disposal. Section 405 of the Water Resources and Development Act of 1992 authorized an investigation, including testing and demonstration, of decontamination technologies and their potential application to contaminated sediments to maintain harbor navigation in an environmentally-acceptable, cost-effective manner. Treatment may require several different procedures before disposal is possible due to the complex nature of the contaminants and their widespread spatial distribution within the Harbor. It has been estimated that approximately 500,000 cubic yards of dredged sediment will require treatment each year.

Dredged sediments from various areas of the harbor may contain elevated levels of a wide variety of contaminants, including heavy metals, polynuclear aromatic hydrocarbons (PAHs), and organochlorines such as dioxins, furans, polychlorinated biphenyls (PCBs), pesticides, and herbicides. Treatment systems must be capable of sufficiently reducing the contaminant levels by separation, destruction, immobilization, or other methods to render dredged sediments suitable for unrestricted ocean disposal, land disposal, or, preferably, beneficial use.

IT Corporation (IT) investigated a three stage treatment process. The three stages included dewatering the sediment, removing organic contaminants by thermal desorption, followed by cement based solidification/stabilization (S/S) of thermally treated sediment.

Two waste forms designed to meet different disposal options were investigated. The first waste form was a monolithic, high-strength block of treated material suitable for ocean disposal. These blocks would provide hard surfaces for reef development. Artificial reefs have proven to provide habitat for numerous fish and invertebrate species, and increase opportunities for recreational anglers. These stabilized blocks could be provided to state sponsored artificial reef programs. The second waste form was a thermally treated, dry soil-like material that was treated to reduce leachability of metals. This product is suitable for fill or road base construction.

The treatment process investigation was performed in two phases. In the initial phase of testing, covered by this report, bench-scale treatments were performed to evaluate methods for dewatering the sediment, to identify operating parameters for the thermal desorption of organics, and determine the reagents needed to solidify/stabilize the thermally treated sediment. Phase two (not funded at this time) involves pilot-scale testing of the treatment processes.

Prior to beginning the demonstration, IT prepared a Project Plan (October 1995). The IT Project Plan was inclusive of a Work Plan (WP), Health and Safety Plan (HSP), Quality Assurance Project Plan (QAPP), Sampling and Analysis Plan (SAP), and a Transportation and Waste Management Plan.

The program objectives, as established in the Brookhaven National Laboratory (BNL) Statement of Work and enumerated in the Project Plan, were as follows; to test methods of dewatering, thermally treating, and S/S dredged estuarine sediment (DES) to produce a final product that may be acceptable for unrestricted marine disposal and that provides beneficial use. To meet the first goal, the final product must meet disposal criteria as specified in *Draft Regional Guidance for Performing Tests on Dredged Material Proposed for Ocean Disposal*¹. To accomplish the second goal, the final product will be formed into blocks suitable for encouraging growth of marine organisms. To encourage the growth of marine organisms, the goals of the final product were: 1) an unconfined compressive strength (UCS) of 290 pounds per square inch (psi) or

greater and 2) metal leaching results below the Toxicity Characteristic (TC) regulatory threshold, minimize total metal, and minimize Lethal Concentrations or LC_{50} results.

An additional testing agenda was added to the program to investigate a land based disposal option. The objective of this option was to produce a nonhazardous material to be used as road or landfill. The goals of the land based material were: 1) no free liquid, 2) UCS of 20 psi, and 3) metal leaching results below TC regulatory threshold.

Data generated by this bench-scale study will be used by BNL to determine:

- treatment effectiveness as determined by a critical evaluation of the data from chemical and physical analyses and bioassay testing as well as their relative contribution to the assessment of the technology,
- composition of end product(s), effluent, and by-products,
- unit treatment cost estimates and time-scales for scale-up operations, and
- potential environmental and occupational hazards posed by the treatment technology or system.

This draft report describes the results of the bench-scale work performed. Only the bench-scale demonstration is covered by this draft report.

2.0 CONCLUSIONS

The results of the bench-scale testing, described in this report, indicate that the proposed treatment train, thermal treatment followed by stabilization, can lower the biotoxicity of the DES by removing hazardous organic contaminants and lowering the leachability of heavy metals. The process can, depending on selection of stabilization additives, produce either a high strength monolithic waste form that is suitable for ocean disposal or a soil-like material for use as fill. Based on a 100,000 cubic yard per year capacity, treatment of the DES to produce 62,725 tons of the fill material is estimated to cost \$72.64 per cubic yard of 'as received' DES. Producing the waste form for ocean disposal would cost \$88.64. Other conclusions from the testing are discussed in the following paragraphs.

The bench-scale tests indicate that the DES contain approximately 76% moisture and do not drain to any significant extent. They are also difficult to dewater using conventional pressure filtration. This is probably due to the high organic and high clay content of the DES. The high water content of the DES and lack of success with mechanical dewatering substantially increases the cost of treating this material. The increase in treatment cost is due to the capital and energy costs of thermal drying.

Treatment by thermal desorption at a temperature of 550°C for 5 minutes at temperature removes most of the PCBs, pesticides and PAHs from the DES. Dioxins are reduced but not eliminated. Thermal treatment also lowers the biotoxicity of the DES. Thermal treatment lowers Pcb in the DES from 5.3 mg (milligrams)/kilograms (kg) (dry basis) to 0.002 mg/kg. Removal of PCB greatly increases the options for beneficial reuse of the DES.

Treatment of the offgas from thermal desorption produces a condensate with both aqueous and organic components. Both these condensates contain organic contaminants. The condensate oil is very high in Pcb and dioxins. Treatment of 100,000 cubic yards of DES would produce 468.7 tons (~127,731 gallons or 2322 drums) of PCB contaminated oil. An additional 13,000 gallons per day of aqueous condensate would require biological treatment followed by carbon adsorption, which would produce spent carbon and biosludge contaminated with Pcb and

dioxins. The cost of treating or disposing of these offgas treatment residuals is high and favors the selection of a offgas treatment system that destroys the organic contaminants that are desorbed from the DES. This is described in the engineering evaluation.

3.0 ENGINEERING EVALUATION

This section of the report presents IT Corporation's conceptual design for the demonstration-scale (100,00 cubic yards per year) treatment system for the DES and an estimate of the treatment cost using the proposed process. The conceptual design and cost estimate are based on producing a dry soil-like final waste form that can be used as fill material. If the monolithic waste form, suitable for ocean disposal, is desired, minor process modifications to the stabilization system will be required and cost of stabilization reagents will increase. This is discussed further in section 3.1.2. The treatment train proposed by IT is shown on Figure 3.1. The treatment system described in the following paragraphs and is comprised of four primary unit operations:

- thermal drying of the dredged sediment,
- thermal desorption to remove the organic contaminants from the dewatered sediment solids,
- treatment of the contaminants in the off-gas from the thermal desorber in flameless thermal oxidizer, and
- stabilization of the thermally desorbed sediments to render the metals nonleachable and to produce a dry, soil-like waste form suitable for use as road or fill base construction.

Scale-up to higher production rates can be accomplished either by use of multiple treatment trains or by increasing the size of the process equipment.

3.1 PROPOSED DEMONSTRATION-SCALE TREATMENT TRAIN

The results of the bench-scale testing have been taken into consideration in developing the flow diagram for the proposed demonstration-scale treatment train. Primarily the lack of success in physically dewatering the dredged sediments necessitates the use of thermal drying to reduce the water content of the feed to the thermal desorber. The bench-scale testing also indicated that the desorption process would produce significant organic residuals that would require off-site treatment. This was not unexpected and confirmed that treatment of desorber off-gas in a flameless oxidizer was required in order to minimize process residuals. As noted above, the proposed treatment train includes thermal treatment of the dredged sediments to reduce the organic contaminants, especially PCBs and PAHs, and stabilization to fix toxic metals, primarily

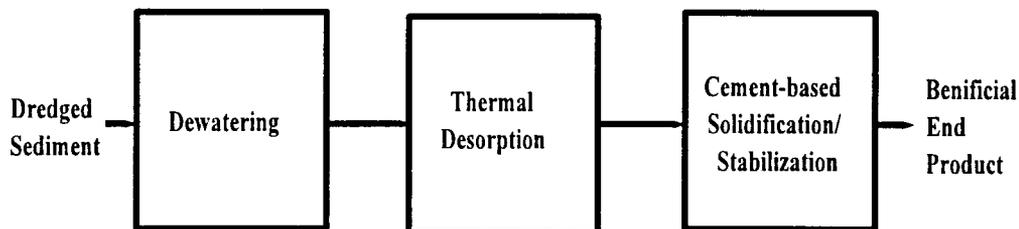


Figure 3.1. Three Stage Treatment Process

cadmium, copper and zinc, and produce a soil-like material suitable for use as fill. Figure 3.1 is a flow diagram for the proposed process with a mass balance for a demonstration-scale system designed to treat 100,000 cubic yards per year. This treatment rate is based on operating the system 12 months per year, 24 hours per day and 7 days per week. A two week maintenance shutdown and an operating factor of 90 percent have been assumed. This is based on IT Corporation's experience with our large-scale thermal treatment systems.

3.1.1 Thermal Treatment System Process Description

The proposed thermal treatment process is a multi-step operation that involves the drying of the sediments from 34 to 70 percent solids in a direct contact rotary drier, followed by thermal treatment at 1032°F in an indirectly fired calciner. This process includes treatment of all process residuals and destruction of desorbed organic contaminants in a Thermatrix® flameless oxidizer.

Dredged sediments will be stored in a concrete basin that will be sized to hold at least 5000 cubic yards of material. This will allow two weeks of continued operation of the treatment system when dredging operations are temporarily interrupted. Dredging operations and transfer of material from the storage basin must be conducted during adverse winter conditions. This will be accomplished by transferring the sediments from this basin to a feed hopper using a bucket excavator. The feed hopper will hold sediments sufficient for several hours of operation and will also be equipped with a bar screen to remove oversize debris.

The sediments will then be pumped into the rotary drier where the water will be removed by contact with hot combustion gases from a burner fired by natural gas. The solids will be dried

from 66 to 30 percent moisture (by weight) and heated to 212°F. The hot gases will leave the drier at 280°F, go through a baghouse to remove any entrained solids and then be cooled to condense the water from the off-gas. Both the non-condensable gases and the condensate will be treated by carbon adsorption before discharge. An induced draft fan will pull the off-gas through the drier, baghouse and the condenser. The condensate will be stored in a tank for use in the rest of the thermal treatment and stabilization process. Some of this condensate will be discharged to the ocean or to surface water. It will have been carbon treated and will contain negligible contaminants.

The dried sediments will be lifted by a conveyor and then drop, through a set of double tipping valves, into the rotary calciner (an indirectly fired thermal desorber). The double tipping valves will be needed to maintain the inert atmosphere in the calciner. The calciner is an alloy tube that rotates inside of a firebox. The flame does not contact the contaminated material, but heats the tube which transfers heat to solids. The calciner will heat the sediments to 1032°F, which will be sufficient to volatilize the organic contaminants from the sediments and to convert some of the sediment humic material (natural plant or microbial organic material) into light hydrocarbons. The sediments will drop from the calciner tube into a mixer cooler which is a screw mixer device. Water will be sprayed onto the hot sediments for dust control and cooling. The moistened or conditioned thermally treated sediments will then be transferred into bins using a radial stacker. They will then be fed to the stabilization facility.

Sweep gas (nitrogen or inert gas from a stoichiometric burner) will be used to purge the organics from the tube into the calciner off-gas treatment system, which will include a hot, ceramic fiber baghouse, to remove entrained solids, and a Thermatrix® flameless oxidizer. This device uses a bed of hot ceramic media to promote flameless non-incineration destruction of organics. Air will be added to the Thermatrix® unit to support oxidation of the organics. The oxidation of the light hydrocarbons formed by the decomposition of soil organics will raise the gas temperature to 1800°F which will destroy all contaminants. The hot gases from the Thermatrix® unit will then be cooled by dilution with ambient air and a partial water quench to 280°F. This will bring the temperature low enough for an induced draft fan to pull the off-gas through the Thermatrix® unit for discharge into the air through a stack.

3.1.2 Chemical Stabilization

The thermally treated DES contains leachable cadmium, copper and zinc at levels that are below the TC criteria but too high for beneficial use. The stabilization process will reduce the metals leachability to acceptable levels by mixing this material with lime, fly ash (FA) and condensate from the rotary drier system. Based on the bench-scale work, 5 percent lime and 10 percent FA will be required. This process has no by-product residuals other than the stabilized soil-like waste form that will be analyzed and demonstrated to be suitable for use as fill.

The stabilization system will be similar to a typical batch plant for mixing cement and consists of storage silos for the lime and FA and a mixer. The additives for the full-scale stabilization process will be bulk conveyed from large hopper trucks to standard commercial silos that will be equipped with baghouses for dust control. The thermally treated DES will then be transferred from a storage pile to the feed hopper by a loader. The DES, lime and FA will be transferred into the mixer by conveyors. Batch weights can be controlled by the load cells on the mixer. After the addition of solids is complete, the condensate will be added and the batch mixed. When mixing is complete the grout will be dumped into one of four bins in a cure pit. Upon curing the grout will become a dry, low strength, friable monolith that can readily be broken up by a front-end loader. The loader will transfer the stabilized material to a radial stacker that will mound the treated DES into a large storage pile. The treated material from the pile will be made available for use as fill.

3.1.3 Environmental Impacts

The environmental impacts of the proposed treatment process are expected to be minimal.

The thermal drying step of the process will have no negative environmental impacts. During the drying the solids temperature will not be high enough to volatilize significant levels of organics. The solids that are entrained from the drier will be collected in a baghouse and returned to the system, while water and trace organics that are evaporated will be condensed and collected by the gas phase carbon bed. The condensate will also be treated by carbon to remove any condensed organics. The condensate will be used in the S/S process, used for dust control or returned to surface waters.

The thermal desorption system includes a substantial gas cleaning system for the calciner offgas. The Thermatrix® flameless oxidizer will destroy the organics that are desorbed from the DES. The entire thermal treatment process operates under negative pressure to ensure that any leakage from seals, etc., enters the process rather than producing fugitive process emissions.

Fugitive dust emissions from the stabilization process will be controlled by the baghouses on the silos and the DES feed hopper and by water sprays that will maintain the thermally treated DES and cured grout in a non-dusty water content.

3.1.4 Site Requirements

Utility requirements will include a 750 kilowatt electrical supply (with average use of 300 to 400 kilowatt) and supply of 40,000 to 50,000 standard cubic foot per hour of natural gas. Process water will be supplied from the rotary drier condensate, but 10 gpm of potable water will be required for personnel and equipment washdown.

In terms of space requirements, the treatment system would require approximately 1.5 acres. Staging of dredging equipment, untreated sediments and treated DES and other material preparation activities can best be accomplished with an additional 3 to 5 acres of space.

3.2 TREATMENT COST ESTIMATE

The estimated DES treatment cost for the proposed treatment system, shown on Figure 3.1, is \$72.64 per cubic yard of untreated DES. This cost is higher than expected because of the high water content of the DES and our inability to mechanically dewater the solids. This cost could be decreased substantially if the need for thermal drying could be eliminated or reduced. This cost estimate is based on producing a dry soil-like treated DES for use as fill. The components of the treatment cost are shown in Table 3.1 and discussed in the following paragraphs.

3.2.1 Capital Cost

Capital cost for the treatment system is based on IT Corporation's experience in design, fabrication, installation and operation of large-scale thermal treatment systems. The total capital cost for the treatment system is estimated to be \$23,650,000. Most of this cost is for the thermal treatment system. This cost includes all equipment, installation, site improvements, storage

basins and piles, as well as all engineering, permitting and construction management costs. Based on a 10 year operating life, the capital cost for treating the DES is \$45,481 per week or \$23.65 per cubic yard.

3.2.2 Utilities

Utility costs are estimated to be \$41,311 per week and are primarily due to the cost of 40,814 SCFH of natural gas. Natural gas costs at \$5.25 per 1000 cubic feet, electric power at 300 KW, and water and sewer charges account for the remainder. Utility costs contribute \$21.48 per yard to the treatment cost.

Table 3.1 Components of the Treatment Cost

Capital Cost	\$23.65/yard
Utilities	\$21.48
Labor	\$19.99
Analytical	\$ 0.83
Lime/Fly ash	\$ 4.05
Maintenance Supplies	\$ 2.65
Total	\$72.64 per cubic yard of DES

3.2.3 Labor

The treatment facility will have a substantial staff that will include a plant manager, administrative assistant, a day shift utility operator, maintenance supervisor and two day shift maintenance mechanics. Shift positions will include a shift supervisor, a control room operator, two plant operators, two heavy equipment operators and a shift maintenance person. Labor cost is \$38,450 per week or \$19.99 per yard of untreated DES.

3.2.4 Analytical Cost

The treated DES will be analyzed for full TCLP, total PCBs and dioxins on a weekly basis. This cost is estimated to be \$1,600 per week or \$0.83 per yard.

3.2.5 Stabilization Reagent Cost

Lime and FA for stabilization will cost an estimated \$7,797 per week or \$4.05 per yard. This is based on a cost of \$38 per ton for FA and \$152 per ton for lime.

3.2.6 Maintenance Materials

The cost of spare parts, replacement parts and other maintenance supplies is assumed to be 5 percent of the original equipment cost per year. This includes contracts for maintenance of control system computers and the continuous emissions monitoring system. This cost is estimated at \$5,096 per week or \$2.65 per yard of DES.

3.3 MONOLITHIC WASTE FORM FOR OCEAN DISPOSAL ALTERNATIVE

If a high strength monolithic waste form, suitable for ocean disposal, is desired, treatment cost will increase. Producing a waste form meeting the criteria for this disposal option would increase treatment cost by \$16 per cubic yard of DES. This cost increase is for additional stabilization reagents and for equipment needed to mold and cure the monoliths. This cost does not include the cost of barging the monoliths to the offshore disposal site.

4.0 PROCEDURES AND EXPERIMENTAL OBSERVATIONS

The tests for this bench-scale study were conducted in three stages. Stage 1 was to dewater the received material. Stage 2 was to thermally desorb the remaining moisture and organics from the DES. Stage 3 was to solidify/stabilize (S/S) the thermally desorbed DES to prevent the leaching of the inorganic contaminants.

4.1 TEST PROGRAM OVERVIEW

4.1.1 Dewatering

The water content of the DES was in excess of 60 percent (by weight) which is too high for optimal operation of the thermal desorption system. High water content lowers the treatment capacity of a given desorber system and increases the energy requirements for treatment. High water content can also result in materials handling problems in typical desorber feed equipment. This all results in higher costs for treatment, therefore high moisture sediments are frequently dewatered before thermal treatment. The use of drainage beds and filter aids were options investigated for the dewatering process.

Drainage beds are simply concrete-lined pads or pits where piles of DES are allowed to release free-draining water. They are more likely to be effective on sandy materials than on the DES which have a high fines content. Plate and frame and belt filter presses have been used effectively on dredged sediments. Lime or filter aid were used as additives in an attempt to improve dewatering performance.

4.1.2 Thermal Treatment

The purpose of the thermal desorption testing was to identify treatment conditions (time/temperature) needed to remove pesticides and PCBs from the DES and to generate 13.7 kg of thermally treated soil for stabilization testing. The thermal desorption testing was conducted in IT's Rotary Thermal Apparatus (RTA), which is a bench-scale device that is used to treat up to

a kilogram of soil in an indirectly heated rotary tube. This device simulates the heat and mass transfer in a full scale rotary kiln or calciner.

The RTA is a batch device. Soil is charged to an alloy tube which is then bolted into the RTA. The tube drive for rotation is started and the tube is purged with air at a flow rate of 3 to 5 liters per minute. An electric furnace is raised into position and the furnace encloses the tube. As the DES heats to the treatment temperature, steam (from desorption of the soil moisture) and desorbed organics are evolved from the waste. These off-gases (purge gas and desorbed constituents) from the tube exit through a 3-foot-long quartz tube into the off-gas treatment system.

The normal off-gas treatment system for the RTA is a spray scrubber. This system uses recirculating water to chill and scrub the RTA off-gas. Acid gases, semivolatle organic compounds (SVOCs) and some oxygenated organics are removed in this scrubber. The spray scrubber is followed by a carbon absorber for removal of volatile organic compounds (VOCs). The gases are pulled through the off-gas treatment system by a vacuum pump that discharges into a laboratory fume hood. The flow rate of noncondensable gas through the system is measured by a rotameter in front of the vacuum pump and is controlled by a bypass valve at the pump. The flow rate is adjusted to maintain the required negative pressure at the inlet and outlet purge boxes of the rotary tube system. Figure 4.1 is a sketch of the RTA.

4.1.3 Solidification/Stabilization

One of the primary objectives of the bench-scale testing program was to determine the additive ratios and requirements for conversion of the thermally treated DES into a nonleachable durable matrix for evaluation of beneficial reuse or disposal. The preferred alternative for beneficial use and ultimate disposal is for unrestricted deposition into the ocean to form a fish aggregation area. The other alternative investigation for beneficial use was for disposal of the treated material as nonhazardous road or landfill.

S/S formulations were investigated to determine which formulations meet the required performance characteristics. Waste additive mixtures were generated to determine if the

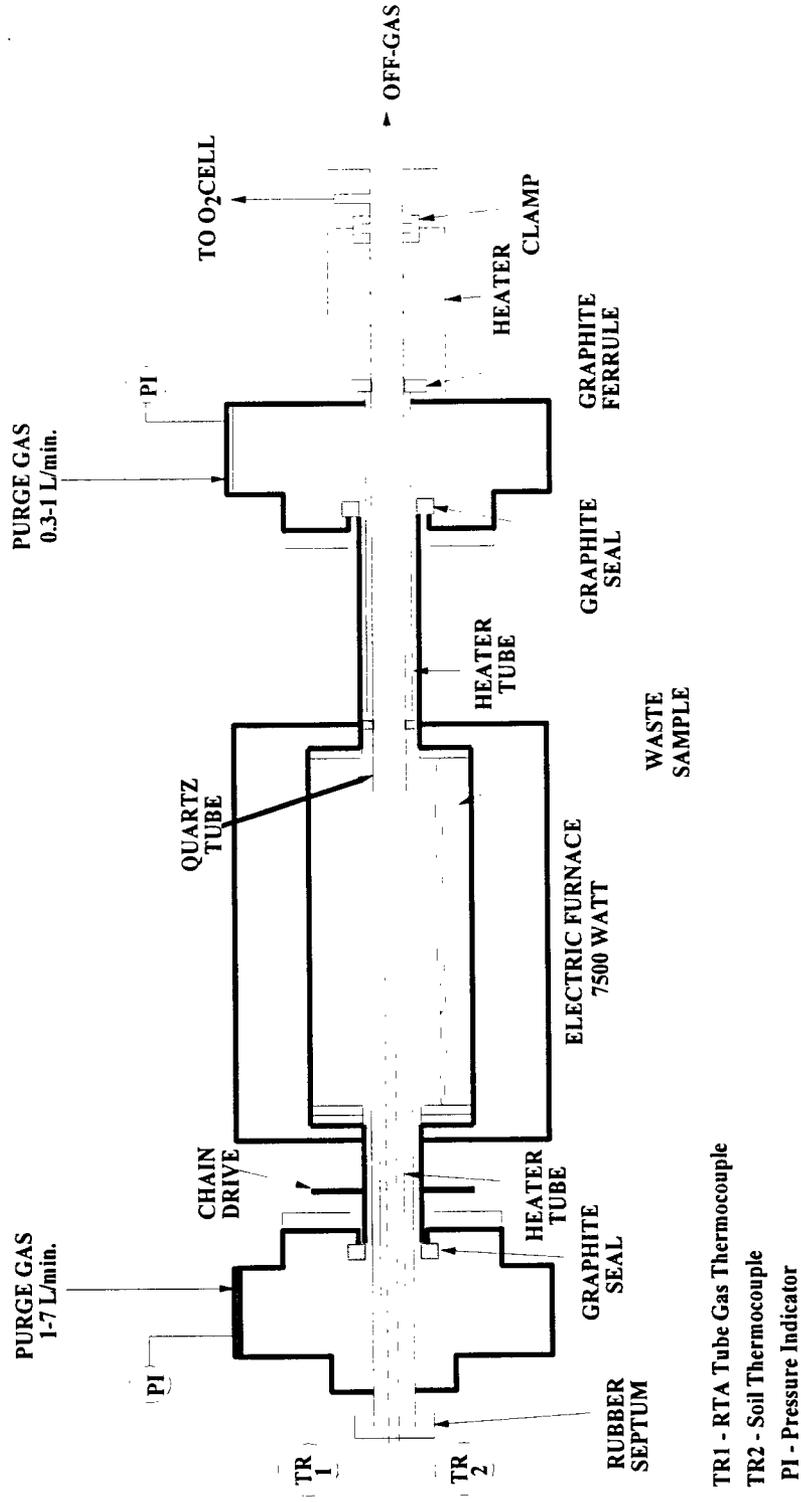


Figure 4.1. Rotary Thermal Apparatus (RTA) Schematic

waste form had acceptable UCS, metal leachability, and acceptably low LC_{50} values. The initial screening goals for the treated materials were that treated materials have a UCS greater than 290 psi and the metal leaching results were below the TC regulatory threshold. On the basis of the UCS and leaching results, three formulations were selected for LC_{50} analyses. The LC_{50} s of the stabilized materials were compared to each other and to the LC_{50} s of the untreated and thermally treated sediments. On the basis of the LC_{50} , UCS, and modified TCLP results, the best formulation was selected and scaled up to provide a five-kg sample for transfer to BNL.

4.2 DEWATERING TEST PROGRAM

4.2.1 Sample Preparation

IT received four 5-gallon buckets of material (70.143 kg) from BNL for treatability demonstrations at IT's Technology Development Laboratory (TDL), located in Knoxville, Tennessee. These samples were opened on October 18, 1995 and assigned TDL tracking numbers GG7002, GG7003, GG7004, and GG7005. Each sample had a dark black color with a strong sulfur smell and had approximately a ½-inch of standing water on top of the sludge. Each sample was thoroughly mixed to a "pudding like" consistency and the standing water was re-absorbed.

Many of the tests in this bench-scale program typically use small quantities of waste and can be adversely affected by stones, larger plant material or other debris. Accordingly, before any testing was started, the DES samples were hand-sorted to pick out large debris and then screened to remove material larger than ½". This material was then sieved through a ½-inch sieve and the samples were composited/homogenized. The oversize material removed during sieving had a weight of 60.70 grams. The segregated material consisted mainly of organic material (sticks and grass) and plastic garbage. Percent moistures in triplicate and ash contents for each bucket received were measured following compositing/homogenization. See Table 4.1 for results of the moisture analyses.

4.2.2 Drainage Tests

Drainage tests were performed on the composited/homogenized sample to simulate an approximate 6-foot bed height of waste on a 25 standard cubic feet per minute (SCFM) filter

Table 4.1 As Received Moisture and Ash Percents

Sample Number	Percent Moisture	Percent Moisture	Percent Moisture	Average Percent Moisture	Percent Ash	Percent Ash	Percent Ash	Average Percent Ash
GG 7003	66.5	67.0	66.8	66.8	70.6	73.3	70.8	71.6
GG 7002	65.3	65.5	65.8	65.5	69.0	69.0	70.0	69.3
GG 7004	66.8	66.8	66.8	66.8	71.1	71.0	71.3	71.1
GG 7005	65.8	66.6	66.2	66.2	70.1	70.4	70.5	70.3

mesh. This was accomplished by placing the waste into a 4-inch diameter by 6-inch high proctor permeameter mold. A 25 SCFM filter cloth was used and a head pressure of 3 psi was applied. This pressure simulated the pressure of a 6-foot bed height. When the pressure was applied, only 11 milliliters (mls) of liquid was collected in 61 seconds. At that point no further liquid was collected. From these results, it was determined that this material was not drainable.

4.2.3 Filtration Tests

High pressure filtration was tested using a 6-inch diameter pressure leaf filter. Approximately 500 grams of the composited/homogenized sample was placed into the filter apparatus and a pressure of 120 psi was slowly applied. At 120 psi, only 30 mls of liquid had been collected in 15 minutes. Hyflo diatomaceous earth was added as a filter aid at a five percent concentration for the second test. Approximately 44 mls were collected at 120 psi after 15 minutes. The filter blinded off completely at this point.

The final test used lime as a filter aid at a two percent concentration. This provided the worst results yielding only 22 mls at 120 psi after 15 minutes. It was determined that the material was not filterable, therefore it would be air-dried prior to any thermal treatment.

4.3 THERMAL TREATMENT TESTING

4.3.1 Sample Pretreatment

Since the dewatering experiments described earlier were not successful in producing a suitable feed material for thermal testing, the sludge was air dried to a consistency suitable for feeding to the test equipment. The air drying was performed by emptying the contents of the four pails into two large plastic trays with a total surface of about 1200 square inches (in²). The sludge in the trays was about 2.5 to 3 inches deep. The trays were placed on the floor of a walk-in hood and the hood fan was placed on high. The material developed a scale on the surface resulting in very poor drying below the surface without constant mixing. Therefore, the material was dried in stages by smaller volumes. The depth of the sludge dried in each stage was 1/4 to 3/4 inch. The material was replaced in the hood and allowed to dry with the hood fan again on high. The layer was turned over, scraped into a pile, mixed, and respread two or three times over a two day period for each stage. At this time the material was again combined and the moisture content was checked and found to be about 45 percent. The sludge was still slightly gummy with some crumbly material. The sludge was returned to the pails after mixing the spread layer and the results reported. After evaluation, the consistency was considered to be too sticky and further drying was ordered. The contents of the pails were spread onto the trays again and allowed to dry for another 24 hours. The moisture was now around 40 percent and the material was mostly crumbly and fairly free flowing. The lumps were crumbled by hand, mixed once more and the final material was returned to two of the pails. This air dried material was used as the feed for the RTA testing.

4.3.2 Thermal Testing

The thermal testing consisted of four RTA screening tests to determine the best treatment conditions. The predetermined conditions were used in 26 RTA runs that were conducted to produce thermally treated soil for the stabilization testing.

Treatment Matrix RTA Tests - The RTA test matrix consisted of four tests spanning a range of conditions typical for low level semivolatile and PCB contaminated soils. Table 4.2 shows the four range finding runs tested.

Table 4.2 Thermal Testing Parameters

Test Number	Temperature (°C)	Time Maintained at Temperature (minutes)
1	350	5
2	450	0
3	450	5
4	550	5

The feed was weighed into a plastic tray and transferred to the RTA tube. The transferred weight was recorded and the tube system assembled. The preheated furnace was raised and clamped around the tube and data collection started. When the sample temperature was about 100°C from the desired end point, the controller temperature was lowered to the run temperature set point. When the sample temperature reached the final set point, the furnace was opened and closed as necessary to keep the sample temperature from overshooting the set point. When the time at temperature was satisfied, the furnace was lowered away from the tube and cooling was begun by a fan and by spraying the tube with a fine spray of cold tap water. The use of the spray cooling allowed the entire run to be completed in 45 to 50 minutes. The off gas treatment system consisted of the spray column scrubber followed by a bed of vapor phase carbon. The scrubbing system was not cleaned between runs. When all of the runs were complete aliquots of the treated material were submitted for pesticide, PAH and PCB analysis and for leaching tests to determine toxicity of the leachate to marine life.

RTA Sample Production Runs - After the results of the LC₅₀ toxicity testing and the contaminant analyses were complete, the run condition giving the lowest residual contaminant content, and the least toxic leachate was chosen as the condition to generate sufficient treated sludge for stabilization testing. This condition was 550°C for 5 minutes at temperature. In order to generate enough material for the stabilization testing, 26 runs treating 25 kg of DES produced 13.7 kg of thermally treated sediments.

To generate residuals for mass balance determination, the scrubber system was replaced by a series of water impingers followed by a small carbon trap. The impingers were kept in an ice bath with the first impinger containing only enough water to act as a condenser. The first impinger was emptied after each run and the other impinger levels were adjusted as necessary between runs. The weights of liquid removed from the system were recorded. The transfer lines from the RTA to the first impinger were cleaned as necessary between runs and the weights of the scrapings were recorded. The scrapings from these connections were into the pail containing the collected liquids. When all of the runs were complete, the oil phase which had accumulated in the pail with the liquid phase, was separated and the volume of each phase was estimated. The carbon from several trap content changes was composited into one jar. The aqueous phase, the carbon, and the separated oil phase were submitted to BNL for analysis. The weights of the collected phases from the complete set of runs were provided for mass balance.

4.4 SOLIDIFICATION/STABILIZATION

The primary objectives of the S/S bench-scale testing program were to determine the additive ratios and requirements for conversion of the thermally treated DES into a nonleachable durable matrix for evaluation of beneficial reuse or disposal. The preferred alternative for beneficial use and ultimate disposal is for unrestricted deposition into the ocean to form a fish aggregation area. The other alternative investigation for beneficial use was for disposal of the treated material as non-hazardous road or landfill.

S/S formulations were investigated to determine which formulations meet the required performance characteristics for both alternatives. Waste additive mixtures were generated to determine if the waste form had acceptable UCS, metal leachability, and acceptably low LC_{50} values. The initial screening goals for the treated materials for ocean disposal were:

- treated materials having a seven-day UCS greater than or equal to 290 psi,
- the metal leaching results were below the TC regulatory threshold, and
- minimization of metal concentration in the dynamic leaching tests.

On the basis of the UCS and leaching results, three formulations were selected for LC₅₀ analyses. The LC₅₀ analysis of the stabilized materials were compared to each other and to the LC₅₀ data of analyses from the untreated and thermally treated sediments. Using these LC₅₀, UCS, and modified TCLP results, the best formulation was selected and scaled up to provide a 5-kg sample for transfer to BNL.

The goals for the road or landfill alternative materials were:

- no free liquid,
- seven-day UCS values greater than 20 psi, and
- metal leaching results below the TC regulatory threshold.

Values for LC₅₀ analysis were determined for comparison to the ocean disposal alternative samples. For fill materials, there is no regulatory LC₅₀ threshold for comparison or evaluation.

On the basis of the expected waste contaminants, IT's technical experience indicates that multiple additives are needed to produce a saltwater durable waste form, fixate the metal contaminants and solidify the waste form. Work performed by the French government on potential waste disposal in the oceans indicated that the treated materials needed to be dense and have low permeability to maximize its durability in sea water (personal communication). These two parameters are improved by moderate to high loadings of activated blast furnace slag (BFS) and lower water additions in the formulations. This information was used in the selection of the eight experiments to investigate. The additives evaluated are: Portland cement (PC), Class C FA, BFS, and silica fume (SF). The additives and their minimum and maximum percentage loadings used in the program are listed in Table 4.3. The amount of water was added was selected to provide enough water for hydration of the DES and reagents and to make the grout into a workable paste. A statistical experimental design was used to isolate the most important additives and to reduce the number of additives necessary to treat the thermally treated DES. The experimental design matrix is a basic 2⁴⁻¹ fractional factorial design. The design matrix uses eight formulations instead of 16 for the full factorial design. There are no centroid data points in the design. The amount of water to be added to the samples was determined by the consistency

of the thermally treated DES-grout mixture. The experimental design matrix is shown in Table 4.4. The program analyzed the treated samples for the parameters listed in Table 4.5

Two formulations for the fill alternative were formulated using the leaching and UCS data from the statistically designed experiments, and IT experience. These formulations used significantly less reagents since they do not require the durability for being submerged in sea water. The reagents used were PC, BFS, and lime (reagent CaO). The program analyzed the treated samples for the parameters listed in Table 4.5.

4.5 SOLIDIFICATION/STABILIZATION TEST PROGRAM

The S/S test program was performed to determine the additive ratios or formulations to convert the thermally treated DES into a nonleachable durable matrix. Two beneficial reuse or disposal options were investigated, artificial reefs to form fish aggregation areas in the ocean, and nonhazardous road or landfill.

4.5.1 Solidification/Stabilization DES Preparation

Approximately 13 kg of thermally treated material was agitated by hand in a five-gallon bucket. This material had the physical appearance of chard dry clay balls the size of road gravel. It was ground with a hand cranked meat grinder to reduce the size to powder and small granules (less than 4.75 mm). Size reduction was performed to improve mixing efficiently and the rate of

Table 4.3 Ranges of Major Additives

Additive	Minimum Loading (%)	Maximum Loading (%)
Portland Cement	20	50
Fly Ash	4	30
Blast Furnace Slag	4	50
Silica Fume	0	3

Table 4.4 Formulation Matrix

Run Number	Portland Cement (g)	Blast Furnace Slag (g)	Silica Fume (g)	Fly Ash (g)	Sediment (g)
1	20	4	0	4	100
2	20	4	3	30	100
3	20	50	3	4	100
4	20	50	0	30	100
5	50	50	0	4	100
6	50	50	3	30	100
7	50	4	3	4	100
8	50	4	0	30	100

Table 4.5 BNL Solidification/Stabilization Analysis - Initial Screening Tests

Analysis	Method	Number of Analyses	Matrix	Sample Container	Sample Quantity	Sample Preservation Requirement	Reporting units	Detection Limit Required
Penetration Resistance	Pocket Penetrometer	32	Solid	4-oz cup	50 G	None	Tons/Ft ² (tsf)	0.25 tsf
Field Rate of Set	Concrete Mortar Penetrometer	32	Solid	4-oz cup	200 g	None	lbs/in ² psi	100 psi
Unconfined Compressive Strength	ASTM D2216	8	Solid	2"x4" plastic mold	400 g (approx.)	None	psi	Not applicable
Modified TCLP	SW 846 Method 1311, Modified	8	Solid	Plastic wide-mouth	25 g	None	mg/L	Analyte specific
Modified TCLP using Sea Water as Extractant	SW 846 Method 1311, modified	8	Solid	Plastic wide-mouth	20 g	None	mg/L	Analyt specific

chemical reactions in the initial DES-grout mixture. In addition, the American Society for Testing and Materials (ASTM) D-2166 UCS procedure requires that the largest solid particle be less than 1/10th the ID of the mold, i.e., 5.08 mm for an 50.8 mm ID mold. Homogeneity of the thermally treated sediment was determined through visual inspection. The approximate amount of water adsorbed by the sediment was determined by ascertaining the Atterberg limits for the material.

4.5.2 Solidification/Stabilization Waste Form Preparation

The S/S testing program is divided into three phases: initial screening tests, intermediate tests, and production of a 5-kg sample for BNL analysis.

4.5.2.1 Phase 1: Solidification/Stabilization Initial Screen Tests

This phase consisted of preparing ten formulations. The first eight formulations were from a half factorial statistical design matrix for the ocean disposal option. Two additional formulations were prepared for the nonhazardous fill disposal options.

The reagents tested for the ocean disposal options were PC, FA, BFS, and SF. The reagents were tested in various combinations and loadings to test the effects of the mixture composition on the S/S of the thermally treated material. Table 4.6 contains the formulation matrix. After completion of the statistical design matrix, the samples for the nonhazardous fill disposal option were prepared using PC, BFS, and lime (reagent CaO). Grouts were made in 1 to 1.5 kilogram batches. Typically, 300 to 500 grams of thermally treated DES were used in each batch. Thermally treated material was dry blended with the reagent additives, except SF, with a whisk in a four-quart planetary mixer. When necessary, the dry blend was dampened with water and the SF was then folded into the mixture to eliminate potential SF dust emissions. Water was added with mixing until the mixture became a stiff but plastic paste. As a first approximation, the amount of water added equals 0.5 times the sum of the weights of DES plus all reagents. The water and dry materials were cut into each other with a hand held spatula prior to operations of the mechanical mixer. The mixer was initially operated at low speed to blend the dry material with the water to form a paste. The grout was mixed until it was visually homogeneous, approximately 5 minutes of mixing. Each formulation was made to about the same mixing consistency. The temperature rise of the DES-grout was measured by placing a thermometer into the mixture in the mixing bowl until the temperature reached a maximum level. The temperature rise is the difference between the room temperature and the maximum temperature achieved in the mixer. Historically, temperature rises less than 8°C are not a problem in the field. Laboratory temperature rises $\geq 15^\circ\text{C}$ indicate the potential for relatively large temperature rises in the field that may lead to problems such as rapid set. Measured temperature rises between 8 and 15°C, indicate that further analysis of the size of pours and types of equipment may need further evaluation. All ocean disposal alternative samples had temperature rises less than 8°C.

Table 4.6 Formulations for Ocean Disposal Experiments

Formulation Number	Grams of Reagent Per 100 Grams of Thermally Treated DES				
	Portland Cement	Fly Ash	Blast Furnace Slag	Silica Fume	Water
1	20	4	4	0	66
2	20	30	4	3	85
3	20	4	50	3	105
4	20	30	50	0	100
5	50	4	50	0	102
6	50	30	50	3	129
7	50	4	4	3	101
8	50	30	4	0	92
9	5	0	5	0	53
Modified 3	20	14	40	0	87
10	Lime 5	10	0	0	58

After the temperature rise measurements the mixture was aliquoted into sample containers for further analyses. The DES-grout was placed into two-8 ounce plastic specimen cups, two Ziploc® bags and one-2 inch by 4 inch plastic cylindrical mold as described in the following paragraphs.

One hundred grams of material was placed into an eight-ounce specimen cup. The cup was tapped on the bench top to flatten the surface and remove the air bubbles from the mixture. This cup sample was used to measure the penetration resistance (PR) using a pocket penetrometer (PP). Three hundred grams of material were placed into the other cup in the same manner to measure PR with a concrete mortar penetrometer (TOS). Both cups were capped. Penetrometer measurements on both aliquots were taken at 4 hours, 1, 2, and 7 days. Visual observations were made to determine if there was any free standing liquid on the curing materials after 24 hours. In all cases, there was no free liquid after a 24 hour cure.

PP measures the resistance of a 1/4 inch rod driven 1/4 inch in the material. The instrument is a spring loaded penetrometer with a range of 0.25 to 4.5 tons per square foot (tsf). This test is used to predict the UCS. The concrete mortar penetrometer is measured similarly but the penetration distance is 4 times longer, 1-inch, and the scale ranges from 20 psi to 700 psi. This measurement is generally used to measure the amount of set throughout the specimen or to find the amount of time a specimen takes to reach initial set. Generally cement is considered set or unworkable at a TOS reading of 500 psi. If the PP and TOS values at 24-48 hours are less than 4.5 tsf and 160 psi, respectively, the grouted samples may not meet the greater than or equal to 290 psi requirement at 7 days for ocean disposal. The data may also be used to define the amount of time the DES-grout is workable prior to initial set.

Thirty grams of grout was placed into two separate baggies and each was flattened into a pancake for metal leaching tests. After curing seven days, each aliquot was crushed to less than 3/8 inch for extraction in the modified Toxicity Characteristic Leaching Procedure (MTCLP) and Sea Water modified Toxicity Characteristic Leaching Procedure (SW-MTCLP). The MTCLP and SW-MTCLP are dynamic leaching procedures utilizing acetic acid/sodium acetate and synthetic sea water as extraction fluids, respectively. The extraction vessels are agitated for 18 ± 2 hours.

The MTCLP extraction followed the TCLP procedure (EPA SW-846 method 1311) except that the sample size was reduced from 100 grams in 2 liters of extraction fluid to 20 grams in 400 ml of extraction fluid. In addition, the extraction was agitated on a platform shaker instead of a rotary tumbler. SW-MTCLP followed the same method as the MTCLP except that a three percent solution of Instant Ocean® was used instead of the TCLP acetic acid solutions. The Instant Ocean® solution was stirred a minimum of 12 hours prior to use in the extraction procedure. Both sets of extracts were filtered through a 0.6 to 0.8 micron filter and preserved with nitric acid to pH less than two. The extracts were digested for metals analysis following SW-846 method 3015, microwave digestion for water samples. Analysis of the digestates followed SW-846 method 6010A, inductively coupled plasma analysis. The metals analyzed were arsenic, barium, cadmium, chromium, copper, lead, nickel, selenium, silver, and zinc.

A 2 inch by 4 inch Jatco, Inc. brand cylinder mold was filled by transferring enough material to fill the mold 1/3 full. The material was then compacted by tapping the mold on the bench top followed by tamping the material with a tamper. This process was repeated until the mold was full. The top of the grout was then smoothed with a spatula and the mold was covered with a lid and sealed with tape. UCS using method ASTM D2166 was performed on the demolded specimen at seven days of cure.

4.5.2.2 Phase 2: Solidification/Stabilization Intermediate Tests

Sample selection for the LC_{50} analysis was based on a UCS greater than 290 psi, and leachate metal concentrations less than TC regulatory limits in both the MTCLP and the SW-MTCLP. The criteria for the two land disposal samples, formulations 9 and 10, were passage of the TC regulatory limits only, since they were not intended for ocean disposal. Comparison of the trends

from data analysis with the cost of the reagents assisted IT in determining if reagents should be eliminated or the formulation modified. This allowed formulations to be chosen that would be most effective and financially sound. Five formulations were chosen to create material for LC₅₀ tests. Table 4.7 contains these five formulations with their corresponding formulation number from Section 4.4.2.1. One thousand gram batches of grout were mixed as in the initial tests of the first ten formulation mixes. Each sample for LC₅₀ was prepared by filling by three 2 inch by 4 inch cylinders filling in thirds until they were filled to a height of about 3.8 inches. As before, the material was compacted by tapping the mold on the bench top followed by tamping the material with a tamper. The molds were covered and sealed with tape to minimize moisture loss. An additional mold was completely filled for modified formulation 3 to perform UCS by ASTM D2166. The cylinders were allowed to cure for seven days prior to extraction for the LC₅₀ testing. At seven days the cylinders were demolded and measured for height and width using a caliper to determine the volume of each cylinder. Each cylinder was then placed into a one liter plastic wide mouth bottle. Enough three percent Instant Ocean® was added to each bottle to equal four times the volume of the treated specimen. The Instant Ocean® solution was stirred a minimum of 12 hours prior to use. The cylinders were extracted by tumbling on the rotary tumbler for one hour. The extracts were then centrifuged at 2000 rpm for 30 minutes to separate the supernatant from the solids. The extracts were then shipped to IT Sommerset, New Jersey, under chain of custody, for LC₅₀ testing using *mysidopsis bahia* (mysid shrimp), *menidia berylina* (silverside minnows) and *mytilus edulis* (mussel larvae).

4.5.2.3 Phase 3: Solidification/Stabilization BNL Sample for Analysis

The final formulation selection for confirmation analysis was based on the LC₅₀ results. Ten kilograms of grout was mixed in a five-gallon Hobart mixer using a spade shaped blade. The temperature of the wet grout was measured. The sample was aliquoted into three-2 inch cube molds, three-3 inch by 6 inch cylinder molds, two drinking straws and one-one gallon Ziploc® bags. The samples were sent to BNL at seven days of cure for confirmation analysis.

Table 4.7 Solidification/Stabilization Intermediate Test Formulations

Formulation Number	Grams of Reagent Per 100 Grams of Thermally Treated Material			
	Portland Cement	Fly Ash	Blast Furnace Slag	Water
Modified 3	20	14	40	87
4	20	30	50	100
5	50	4	50	102
9	5	0	5	60
10	Lime 5	10	0	61

5.0 RESULTS AND DISCUSSION

5.1 DEWATERING

A limited dewatering study was conducted on materials having the physical properties described in Table 5.1. This data was provided by BNL. The table also contains data on the final IT product after thermal treatment and stabilization. The analysis of the final product was done in duplicate. These are IT-1 and IT-2 in Table 5.1. These tests results showed that the DES were not amenable to normal physical dewatering methods. The results of the filtration tests are summarized on Table 5.2. This is probably due to the high proportion of the fine fractions in the sediments, which are 80 percent clays and silts. The sediments also contain high levels of organic matter, see Table 5.1. The carbon content of the untreated material was 8.3 percent (dry basis) as measured by the ultimate analysis conducted by Galbraith Laboratories in Knoxville, Tennessee for IT. Organic matter derived from plant or microbial cellular material can be very difficult to dewater.

5.2 THERMAL TREATMENT

5.2.1 Treatment Matrix RTA Tests

The untreated and thermally treated sediments, from the first four RTA runs, were analyzed for organochlorine pesticides, PCBs, PAHs and biotoxicity. They were also submitted for ultimate analysis which includes moisture, ash and an elemental analysis (C,H,Cl,S,N). The results of the chemical analyses are shown on Table 5.3 and the ultimate analysis is shown in Table 5.4. The results of the biotoxicity testing are shown on Figure 5.1.

The analyses for organochlorine pesticides, PAHs and PCBs showed that the untreated DES contained low levels of these contaminants. The untreated DES contained aldrin, dieldrin, DDD and DDE at levels below 200 µg/kg. Treatment at all conditions lowered pesticides to below detection limits. Initial individual PAHs ranged from 1.0 to 10.0 mg/kg, while total PAHs were 58.1 mg/kg. The individual PAHs in the treated DES from all four RTA runs were typically below the detection limit of 0.660 mg/kg, which shows reductions in PAHs of 50 to 80 percent. The elevated detection limits for the individual PAHs preclude a more precise determination of percent removal. The PCB analysis of the initial DES, using the EPA Method 8080, showed 1.4 mg/kg of Aroclor 1242 and 1.5 mg/kg of Aroclor 1254. Aroclors in all treated DES were below detection limits of 66 µg/kg. All of the final concentrations of contaminants in the treated DES are consistent with past experience. The initial concentrations are so low that even the mildest treatment conditions (350°C for 5 minutes at temperature) were effective in reducing pesticides, PCBs and PAHs to below detection limits.

From the chemical analyses, discussed in the previous paragraph, it was not possible to select conditions for producing the thermally treated DES for stabilization testing. The results of the

Table 5.1 Physical Parameters on Untreated and Thermal-S/S Treated DES

Analyte	Initial Concentration	IT-1	IT-2	Mean	Percent Reduction (%)
Particle size (% wt [dry])					
Medium Gravel > 4.75 mm	0.04	0.54	3.73	2.135	
Fine gravel 2.0 - 4.75 mm	0.38	20.2	25.70	22.95	
V. coarse sand 0.85 - 2.0 mm	0.83	26.7	22.10	24.4	
Coarse sand 0.425 - 0.85 mm	2.15	13.3	12.50	12.9	
Medium sand 0.24 - 0.425 mm	5.05	6.94	6.52	6.73	
Fine sand 0.106 - 0.24 mm	9.57	7.64	6.84	7.24	
V. fine sand 0.075 - 0.106 mm	2.8	1.92	1.75	1.835	
Clay < 2.0 μm	35.57	5.14	5.19	5.165	
Silt 2.0 - 75 μm	44.95	15.8	15.30	15.55	
pH (std. units)	7.9	11.67	11.62	11.645	
Total Solids (% wt [dry])	33.05	70.8	71.00	70.9	
Total Sulfides (mg/kg [dry])	7,833.38	210	370.00	290	96.30
Total Organic Carbon (mg/kg [dry])	7.32	3.43	3.44	3.435	53.07

Table 5.2 Filtration Test Results

Test Number	Sample Weight (grams)	Filter Aid Added	Pressure (psi)	Time of Test (minutes)	Volume of Liquid Collected (ml)	Percent Moisture Removed (%)
1	500	None	120	15	30	9.0
2	500	Hyflo diatomaceous earth @ 5%	120	15	44	13.3
3	500	Lime @ 2%	120	15	22	6.6

**Table 5.3 Total Pesticides ($\mu\text{g}/\text{kg}$ dry)
 Thermally Treated Dredged Estuary Sediment**

Analyte	Untreated	Treatment Temperature ($^{\circ}\text{C}$) /Residence Time (min)			
		350/5	450/0	450/5	550/5
Aldrin	75	<3.4	<3.4	<3.4	<3.4
4,4'-DDD	162.1	<3.4	<3.4	<3.4	<3.4
4,4'-DDE	150.6	<3.4	<3.4	<3.4	<3.4
Dieldrin	74.5	<3.4	<3.4	<3.4	<3.4

**Table 5.3 (continued) Total Arochlors (PCBS) ($\mu\text{g}/\text{kg}$ dry)
 Thermally Treated Dredged Estuary Sediment**

Analyte	Untreated	Treatment Temperature ($^{\circ}\text{C}$) /Residence Time (min)			
		350/5	450/0	450/5	550/5
Arochlor 1016	< 930	< 66	< 66	< 66	< 66
Arochlor 1221	< 930	< 66	< 66	< 66	< 66
Arochlor 1232	< 930	< 66	< 66	< 66	< 66
Arochlor 1242	1400	< 66	< 66	< 66	< 66
Arochlor 1248	< 930	< 66	< 66	< 66	< 66
Arochlor 1254	1500	< 66	< 66	< 66	< 66
Arochlor 1260	< 930	< 66	< 66	< 66	< 66

**Table 5.3 (continued) Total Petroleum Aromatic Hydrocarbons ($\mu\text{g}/\text{kg}$ dry)
 Thermally Treated Dredged Estuary Sediment**

Analyte	Untreated	Treatment Temperature ($^{\circ}\text{C}$) /Residence Time (min)			
		350/5	450/0	450/5	550/5
Naphthalene	2729	< 660	86	< 660	67
Acenaphthylene	1288	< 660	< 650	< 660	< 650
Acenaphthene	1042	< 660	< 650	< 660	< 650
Fluorene	1389	< 660	< 650	< 660	< 650
Phenanthrene	6588	< 660	< 650	< 660	< 650
Anthracene	3702	< 660	< 650	< 660	< 650
Fluoranthene	10324	< 660	< 650	< 660	< 650
Pyrene	7102	< 660	< 650	< 660	< 650
Benzo(a)anthracene	4484	< 660	< 650	< 660	71
Chrysene	4585	< 660	< 650	< 660	< 650
Benzo(b)fluoranthene	2922	< 660	< 650	< 660	220
Benzo(k)fluoranthene	1107	< 660	< 650	< 660	< 650
Benzo(a)pyrene	2550	< 660	< 650	< 660	86
Indeno(123-cd)pyrene	1076	< 660	< 650	< 660	< 650
Dibenz(a,h)anthracene	397	< 660	< 650	< 660	< 650
Benzo(ghi)perylene	1255	< 660	< 650	< 660	< 650

Table 5.4 Ultimate Analysis Of Thermally Treated Dredged Estuary Sediments¹

Ultimate Analysis	Untreated Sediment		Thermally Treated (450°C/5 min)		Thermally Treated (450°C/0 min)		Thermally Treated (550°C/5 min)		Thermally Treated (350°C/5 min)	
	as received	dry basis	as received	dry basis	as received	dry basis	as received	dry basis	as received	dry basis
Moisture (%)	65.88	-	0.33	-	0.18	-	1.26	-	0.35	-
Carbon (%)	2.82	8.26	6.54	6.56	9.28	9.30	5.20	5.27	11.50	11.54
Hydrogen, (%)	5.44	15.94	<0.5	<0.5	0.64	0.64	<0.5	<0.5	0.64	0.64
Nitrogen (%)	<0.5	<1.47	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Chlorine (%)	0.91	2.67	2.65	2.66	2.70	2.70	2.68	2.71	2.62	2.63
Sulfur (%)	0.83	2.43	2.16	2.17	2.49	2.49	2.26	2.29	2.15	2.16
Ash (%)	28.52	83.59	90.45	90.75	89.99	90.15	91.53	92.70	88.51	88.82
BTU/lb ¹	162	475	1005	1008	1034	1036	887	898	1137	1141

¹ Samples analyzed by Galbraith Laboratories in Knoxville, TN for IT.

² Duplicate analysis was performed on BTU analysis of treated sediments.

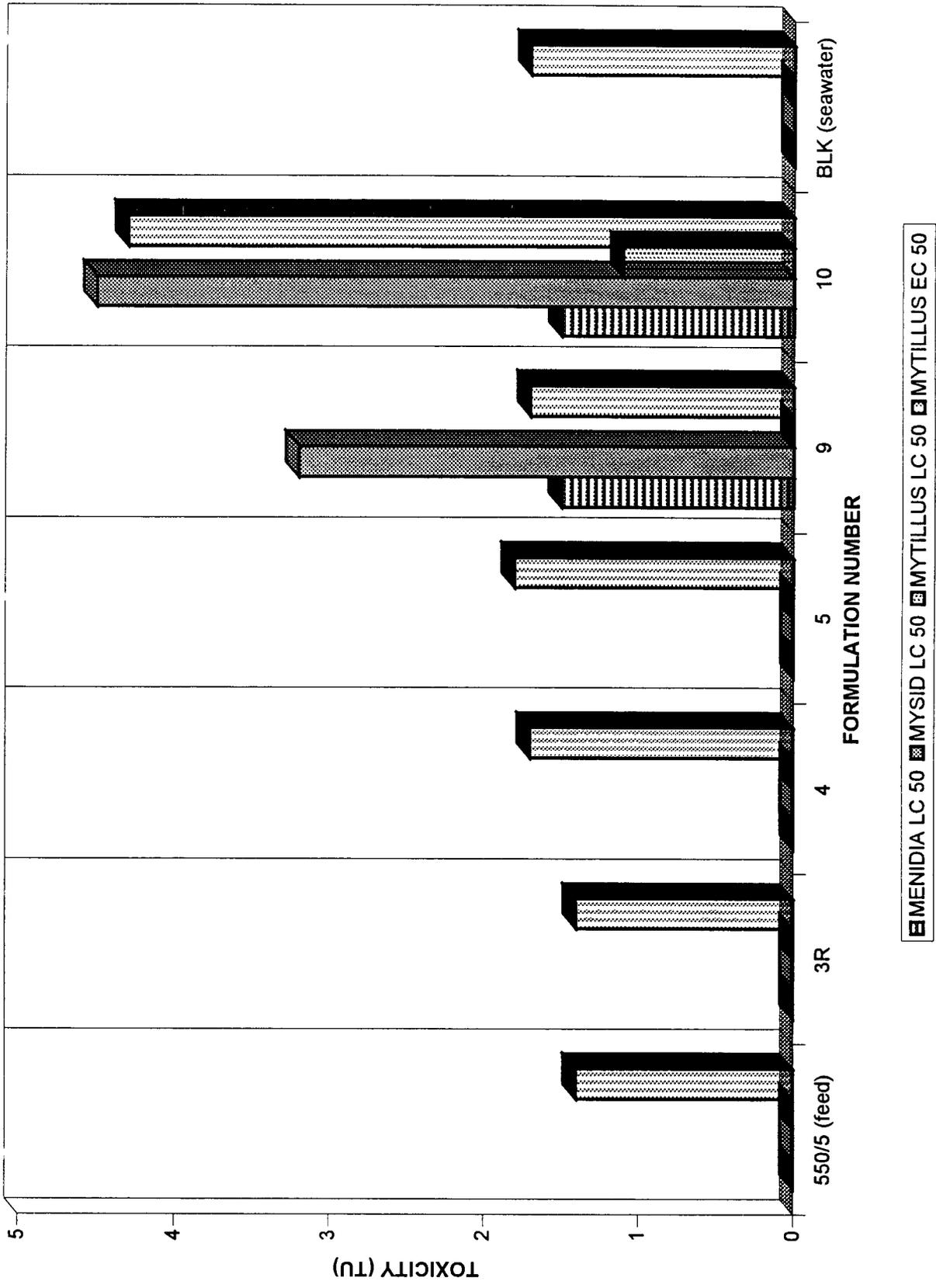
Table 5.4 Ultimate Analysis of Thermally Treated Dredged Estuary Sediments¹

Ultimate Analysis	Untreated Sediment		Thermally Treated (450° C/5 min)		Thermally Treated (450° C/0 min)		Thermally Treated (550° C/5 min)		Thermally Treated (350° C/5 min)	
	as received	dry basis	as received	dry basis	as received	dry basis	as received	dry basis	as received	dry basis
Moisture (%)	65.88	-	0.33	-	0.18	-	1.26	-	0.35	-
Carbon (%)	2.82	8.26	6.54	6.56	9.28	9.30	5.20	5.27	11.50	11.54
Hydrogen, (%)	5.44	15.94	<0.5	<0.5	0.64	0.64	<0.5	<0.5	0.64	0.64
Nitrogen (%)	<0.5	<1.47	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Chlorine (%)	0.91	2.67	2.65	2.66	2.70	2.70	2.68	2.71	2.62	2.63
Sulfur (%)	0.83	2.43	2.16	2.17	2.49	2.49	2.26	2.29	2.15	2.16
Ash (%)	28.52	83.59	90.45	90.75	89.99	90.15	91.53	92.70	88.51	88.82
BTU/lb ¹	162	475	1005	1008	1034	1036	887	898	1137	1141

¹ Samples analyzed by Galbraith Laboratories in Knoxville, TN for IT.

² Duplicate analysis was performed on BTU analysis of treated sediments.

Figure 5.1. Toxicity of Seawater Leachates of Stabilized Thermally Treated Dredged Estuary Sediments



biotoxicity testing, shown on Figure 5.1, provided data that revealed a significant effect from treatment at the four different conditions. The data show the results of acute and short term chronic bioassay testing of salt water leachates of the untreated DES and the treated DES from the four RTA tests. These bioassays used three common salt water arthropods and Figure 5.1 shows the relative toxicity of the leachates compared to the Instant Ocean® salt mix used to generate the leachates. All of the leachates from the treated DES showed lowered toxicity compared to the untreated material. Toxicity decreased as the severity of the thermal treatment increased and the lowest toxicity was exhibited by the leachate produced from the DES treated at 550°C for 5 minutes. These conditions were selected for treatment of the DES for stabilization testing.

The results of the ultimate analysis of the DES are shown on Table 5.4. These analyses show that the organic content (as measured by percent carbon and hydrogen) of the DES is reduced by thermal treatment at the selected conditions of 550°C/5 minutes. Chlorine is not reduced, which means that hydrochloric acid gas emissions from the thermal desorber should not be a significant problem. Sulfur in the DES treated at 550°C/5 minutes is slightly lower than in the dry untreated DES, 2.29 percent compared to 2.43 percent. This is within the variability of the analytical method but pilot-scale studies should include testing to determine sulfur gas emissions from the desorber.

5.2.2 RTA Sample Production Runs

The 26 sample production RTA runs produced 13.7 kg of thermally treated DES for the stabilization tests. These runs also produced residual condensate, both aqueous and oil phases. Mass balance data for these runs are shown on Table 5.5. This table also includes PCB and dioxin data, supplied by BNL, on the condensate residuals. The overall mass balance and component balances for ash, carbon, PCBs and dioxins show reasonable closure of the mass balance. The data for the 2,3,7,8 substituted dioxins is reported as 2,3,7,8-tetrachloro-dioxin Total Toxicity Equivalents (TTE). Since no sample of thermally treated DES was submitted to BNL for dioxin analysis, the dioxin content of this fraction was estimated by assuming that all of the dioxins in the final stabilized material came from the DES.

The data showed near complete removal of the PCBs from the DES and showed that dioxins, as measured by 2,3,7,8-tetrachloro-dioxin TTE, were lowered from 525 ng/kg to 154 ng/kg (dry solids basis). This represents a 70 percent reduction in dioxin toxicity.

Treatment of 25.0 kilograms of the DES, by thermal desorption, produced 170 grams of a black condensate oil that contained high levels of PCBs and dioxins (452 mg/kg PCBs and 28 micrograms (µg)/kg of dioxin TTE). The aqueous condensate and carbon trap also contained dioxins, but were not analyzed for PCBs. This data is shown on the mass balance on Table 5.5. These contaminant levels in the condensate oil, e.g., 0.04 percent PCB, mean that the offgas treatment system residuals, from a large-scale system, would require treatment at a substantial cost. Treatment of the offgas in a flameless oxidizer as the offgas is produced would significantly reduce cost, see Section 3.

5.3 SOLIDIFICATION/STABILIZATION INITIAL GROUT AND UCS

Several analyses/observations were performed on the grout mixture containing the thermally treated additives. The observations included inspection of grout consistency and presence of liquid bleed. The analyses included PP, TOS, and temperature rise. UCS was performed after the grout cured seven days. Table 5.6 presents the formulations, PP, TOS, grout descriptions and UCS data in tabular form. The PP and TOS measure the force of driving a 1/4 inch rod, 1/4 and 1 inch into the material, respectively. The maximum values for the instruments are 4.5 tsf and 700 psi, respectively. The PRs are used to predict the strength development and workability. Generally, if the PP and TOS values at 24 to 48 hours are less than 4.5 tsf and 160 psi, respectively, the grouted samples will not meet the greater than or equal to 290 psi requirement at seven days for ocean disposal. Also for a fluid cementitious waste form (i.e., non-compactable

Table 5.5 Mass Balance Data For Thermal Treatment Of Dredged Estuarine Sediments

Stream Description	Mass (g)		Carbon ^{Note 5}		Ash ^{Note 5}		PCBS ^{Note 5}		Dioxin, TTE ^{Note 3,5}					
	(wt%)	(g)	(wt%)	(g)	(%)	(g)	(µg/kg)	(mg)	(ng/kg)	(µg)				
Feed DES		24,989		1,177.0		11,919.8		2,996.7		74.9		299		7.47
Scrubber Water		2,082												
Total In		27,071		1,177.0	47.7	11,919.8		2,996.7		74.9		299		7.47
Treated DES		13,744	5.5	714.7	91.5	12,579.9		1.8		0.0		154		2.12
Condensate Aqueous		12,536	0.5	62.7				na ^{Note 4}				63		0.79
Condensate Oil		170	85.0	144.5				452,370.0		76.9		28,147		4.78
Offgas Solids		147	5.2	7.6	85.0	125.0								0.00
Offgas				211.9										
Carbon Traps		498						na ^{Note 4}				1,845		0.92
Glassware Rinse		640						8,692.6		5.6		888		0.57
Total Out		26,597 ^{Note 1}		1,141.4 ^{Note 2}		12,704.8				82.5				9.18
Recovery %		98.2		97.0		106.6				110.2				122.9

Note 1: Overall mass balance was completed around the desorber and impingers and does not include the carbon traps and solvent rinse of the glassware.

Note 2: Carbon (organic) content of aqueous condensate and offgas are estimated from earlier work on other soils.

Note 3: dioxin is reported as nanogram/kg of 2,3,7,8-tetrachloro-dioxin Total Toxicity Equivalents.

Note 4: Not Analyzed.

Note 5: Wt% carbon, ash, PCB, Dioxins have been corrected for 57% moisture content of partially dried DES used in the RTA tests.

Table 5.6 S/S Formulations and Results for the Ocean Disposal Alternative

Formulation Number	Grams of Reagent Per 100 Grams of Thermally Treated Material						4 HOUR			24 HOUR			UCS (psi)
	Portland Cement	Fly Ash Class C	Blast Furnace Slag	Silica Fume	Water		PP ¹ (tsf)	TOS ² (psi)		PP ¹ (tsf)	TOS ² (psi)		
1	20	4	4	0	66		3.0	320		> 4.5	> 700		310
2	20	30	4	3	85		4.25	480		> 4.5	> 700		240
3	20	4	50	3	105		1.75	200		> 4.5	> 700		360
4	20	30	50	0	100		< 0.25	< 20		> 4.5	660		420
5	50	4	50	0	102		0.65	20		> 4.5	> 700		550
6	50	30	50	3	129		0.75	60		> 4.5	> 700		460
7	50	4	4	3	101		2.0	240		> 4.5	> 700		330
8	50	30	4	0	92		0.25	< 20		> 4.5	> 700		380
Modified 3	20	14	40	0	87		-	-		-	-		300

Table 5.6 (continued) S/S Formulations and Results for the Land Disposal Alternative

Formulation Number	Grams of Reagent Per 100 Grams of Thermally Treated Material						4 HOUR		24 HOUR		UCS (psi)
	Portland Cement	Fly Ash Class C	Blast Furnace Slag	Silica Fume	Water		PP ¹ (tsf)	TOS ² (psi)	PP ¹ (tsf)	TOS ² (psi)	
9	5	0	5	0	53		> 4.5	580	> 4.5	> 700	40
10	Lime 5	10	0	0	58		370	370	> 4.5	> 700	34

Table 5.6 (continued) S/S Formulations and Results for the Ocean Disposal Alternative

Formulation Number	Grout Description	Liquid Bleed	Temperature Rise (°C)
1	Not fluid, Compactable	None	2
2	Not fluid, Compactable; Less fluid than #1	None	3
3	Sticky; Wetter than #1 or #2	None	1.5
4	Fluid, Consistency of cement truck grout	None	1.5
5	Fluid, Consistency of cement truck grout	None	2.5
6	Thick coarse grout, Not fluid	None	1.5
7	Thick coarse grout, Stiff	None	1.5
8	Fluid, Consistency of cement truck grout	None	3
Modified 3	Semifluid, can pour in clumps, not sticky	None	2.5

Table 5.6 (continued) S/S Formulations and Results for the Land Disposal Alternative

Formulation Number	Grout Description	Liquid Bleed	Temperature Rise (°C)
9	Formed balls, Compactable	None	0
10	Formed balls, Compactable	None	0

soil-like materials) the material generally needs to be placed prior to achieving a TOS value greater than approximately 300 psi for maximum strength development. The four-hour TOS values indicate that formulations 3 through 8 are still reasonable workable at four-hours of cure. In addition, the four-hour PP values are less than 2.0 tsf for the same formulations. This also indicates that mixtures are reasonably workable after a four-hour cure. Formulations 1, 2, 9, and 10 were non-fluid and were compacted into the cups and molds. The four-hour TOS value may not adequately provide information on the workability of the mixtures. The workability and fluidity of these latter mixtures may be increased by addition of more water and/or plasticizers. Further testing of the formulations to optimize the workability of the mixtures was beyond the scope of this project.

All of the 24-hour PP values are greater than 4.5 tsf. There was no liquid bleed in any of the samples. All samples achieved initial set, TOS values greater than 500 psi, in less than or equals to 24 hours cure. Therefore, based on the four- and 24-hour results, most of the ocean disposal alternative formulations are easily workable and may be poured into molds for curing. The nonhazardous road or landfill alternative samples appear to be near the plastic limit for the mixture and form balls during mixing. These balls may be poured out of a cement mixer/batch plant and compacted to achieve the desired no-free standing water material and cure to a low UCS waste form.

The UCS values are also presented in Table 5.6. All ocean disposal alternative formulations, except formulation 2, achieved the desired 290 psi. Formulation 2, which did not achieve the 290 psi goal, had 20 percent PC, 30 percent FA, 4 percent BFS, and 3 percent SF. All other 20 percent PC formulations and all formulations with 50 percent PC had UCS results greater than 300 psi. Analysis of the data indicates that increasing the loadings of PC, BFS, and SF increases the UCS values. The effect of FA on the 7-day UCS value is uncertain. This is not unexpected since FA is known to mostly effect the long term, not short term, strength. Comparison of grout descriptions with the DES-grout compositions shows that when the DES-grout was made to approximately the same water percentage, the fluidity of the grout was increased with increasing FA loadings. Since the UCS criterion was met by most formulations, the selection of formulations for LC₅₀ was based on the leaching results and the workability of the mixture.

The nonhazardous road or landfill alternative samples had nominal UCS values of 30 to 40 psi. The selection for LC₅₀ was based on the leaching results.

5.3.1 Solidification/Stabilization MTCLP & SW-MTCLP Leaching Results

The MTCLP and SW-MTCLP results are listed in Tables 5.7 and 5.8. Both tables have the results for the eight ocean disposal alternative formulations, air dried DES (before high temperature treatment), and the thermally treated DES material (heated at 550°C for five minutes). The MTCLP table, Table 5.7, also contains the leaching results for the nonhazardous road or landfill alternative samples. The SW-MTCLP and MTCLP values are similar. Generally, the SW-MTCLP values are slightly higher. All Resource Conservation and Recovery Act (RCRA) metal concentrations are below the TC regulatory threshold. The air dried DES and the thermally treated DES materials had

detectable metal concentrations for barium, cadmium, copper, lead, nickel, and zinc. The presence of these metals in the leachate is not unexpected since the total metal concentrations, except for cadmium, ranged from 134 to 1140 mg/kg in the feed. The cadmium concentration ranged from 24 to 37 mg/kg (IT internal screening and BNL official results, respectively). See Table 5.9 for BNL total metal concentrations in the DES and stabilized DES materials. All of these leachate values are less than would be expected from the 1:20 weight/weight (w/w) solid to leachate ratio and the pH of the leachate solutions after 18 plus or minus 2 hours of extraction. The low metal concentrations in the leachate are likely due to the high clay content in the feed of 35.6 percent, and the high sulfide content of 0.78 percent in the air dried material, see Table 5.1. In addition, the high total organic carbon (TOC) content of the waste would be expected to reduce most or all of the soluble Chromium (Cr) VI to the less soluble Cr(III) species. Clays are known to adsorb metal from aqueous systems and reduce their concentration in many leaching tests. Sulfide reacts with many of the RCRA metal ions to form sparingly soluble salts. As a consequence, the availability of the metals to leach would be decreased. On the basis of the data in Table 5.1, it is unlikely that the low metal concentration in the leachate is solely due to the sulfide content since most of the sulfide was removed from the DES during the thermal treatment. The sulfide content was lowered from 0.78 percent to 0.029 percent by the thermal then S/S processes. The extent of any given metal sulfide removal depended on the vapor pressure of the salt at the treatment temperature, interactions with other anions in the sample, and the redox potential of the mixture at the treatment temperature. Analysis of data on the thermally treated products, Table 5.4, before S/S indicate that the sulfur

Table 5.7. S/S MTCLP Leaching Results

Formulation Number	Arsenic (mg/L)	Barium (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Lead (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Zinc (mg/L)	pH ¹ (std. units)
1	<0.178	0.308	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.076	10.44
2	<0.178	0.371	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.100	8.97
3	<0.178	0.429	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.087	10.10
4	<0.178	0.451	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.076	9.4
5	<0.178	0.477	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.096	11.32
6	<0.178	0.491	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.104	11.36
7	<0.178	0.513	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.098	11.69
8	<0.178	0.604	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.120	11.75
9	<0.178	0.412	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.115	7.11
10	<0.178	0.361	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.100	7.22
Air Dried DES	<0.178	0.277	0.325	<0.028	0.286	0.242	2.43	<0.147	<0.017	18.2	5.19
Thermally Treated DES ²	<0.178	0.305	0.665	<0.028	1.58	0.159	1.75	<0.147	<0.017	26.1	5.39

¹ Result using pH electrode.
² 550°C for 5 minutes.

Table 5.8 SW-MTCLP Leaching Results

Formulation Number	Arsenic (mg/L)	Barium (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Lead (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Zinc (mg/L)	pH ¹ (std. units)
1	<0.178	0.869	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.127	6
2	<0.178	0.944	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.084	7
3	<0.178	0.980	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.130	7
4	<0.178	0.961	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.103	6
5	<0.178	1.13	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.176	6
6	<0.178	0.921	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.242	6
7	<0.178	0.992	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.213	6
8	<0.178	0.974	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.225	6
Air Dried DES	<0.178	0.452	0.438	<0.028	0.197	<0.201	2.21	<0.147	<0.017	14.5	5
Thermally Treated DES ²	<0.178	0.521	<0.026	<0.028	<0.011	<0.201	<0.03	<0.147	<0.017	0.145	7

¹ Results using pH paper.

² 550 °C for 5 minutes.

Table 5.9 Total Metals on Untreated and Thermal-S/S Treated DES

Analyte Metals: (mg/kg (dry))	Untreated DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Silver	18.42	6.57	5.88	6.23	66.21
Arsenic	33.48	14.10	13.00	13.55	59.53
Berillium	0.56	<0.195	<0.1875	<0.19	66.52
Cadmium	37.05	13.10	12.50	12.80	65.45
Chromium	376.67	126.00	111.00	118.50	68.54
Copper	1171.67	449.00	367.00	408.00	65.18
Nickel	297.17	142.00	97.70	119.85	59.67
Lead	617	241.00	193.00	203.50	67.02
Antimony	10.29	6.72	5.25	5.99	41.84
Selenium	3.24	1.57	1.07	1.32	59.26
Thallium	2.77	2.95	2.12	2.54	8.48
Zinc	1726	629.00	549.00	589.00	65.87
Mercury (Total)	1.29	<0.082	<0.09	<0.086	93.33

content of the untreated and thermally treated materials, dry weight basis, are about the same. The indicates that sulfur was not removed. The metals may therefore still be in the sulfide form. The low sulfide values in Table 5.1 maybe due to matrix interference. However, the total sulfur in Table 5.4 maybe as sulfate, or other anions besides sulfide. Determination of which salts were in the feed or products was beyond the scope of this project.

In the S/S treated material, the only two metals that had detectable leachate concentrations were barium and zinc. Barium ranged from 0.3 to 0.6 and 0.869 to 1.13 mg/l in the MTCLP and SW-MTCLP, respectively. Zinc ranged from 0.76 to 1.2 and 0.084 to 0.242 mg/l in the MTCLP and SW-MTCLP, respectively. Arsenic, cadmium, chromium, copper, lead, nickel, selenium, and silver were all non-detected. All formulations used TCLP Fluid 1. TCLP Fluid number 1 has an initial pH of 4.98 and is an acetic acid-sodium acetate buffer solution. There is no obvious correlation of leachate metal concentration with the pH of the leachate after extraction of the waste form. This supports the hypothesis that the presence of clays and sulfide are limiting the leaching of the treated waste form.

The variability of the metal concentration is too small to assign correlation between each of the additives and the leachate concentrations. For the ocean disposal alternative formulations, there may be a trend with the cement loading. The three highest MTCLP barium concentrations and the two highest SW-MTCLP barium concentrations are at 50 percent cement loadings. Four of the five highest MTCLP zinc and the four highest zinc SW-MTCLP concentrations are at 50 percent cement loadings. The higher cement loading may therefore cause slightly higher barium and zinc concentrations in the leachate.

5.3.2 Solidification/Stabilization Selection of Formulations for LC₅₀ Analyses

Sample selection for the LC₅₀ analysis was based on a UCS greater than 290 psi, and leachate metal concentrations less than TC regulatory limits, in both the MTCLP and the SW-MTCLP for the ocean disposal alternative samples. The criteria for the two land disposal samples, formulations 9 and 10, were passage of the TC regulatory limits and no free water.

Comparison of the trends from data analysis with the cost of the reagents assisted IT in determining if reagents should be eliminated or the formulation modified. This allowed formulations to be chosen that would be most effective and financially sound. Five formulations were chosen to perform LC₅₀ tests. Table 5.10 contains these five formulations with their corresponding formulation number from Table 5.6.

5.3.2.1 Ocean Disposal Alternative

As indicated previously the only formulation that did not meet the UCS criteria was formulation 2. Formulation 1 had a UCS value of 310 psi. It was decided that this was too close to the 290 psi criteria to select. All other formulations, i.e., 3 through 8, were potential candidates. The next two

criteria for selection were leaching performance and cost of additives. All formulations had metal leachate concentrations less than the TC regulatory threshold. Therefore the selection was based on minimization of leachate concentrations. The 20 percent PC samples generally had slightly lower barium and zinc concentrations and the reagent cost would be lower than the 50 percent cement samples. Therefore the selection of formulations was limited to formulations 3 and 4. However formulation 5 was also selected since it had the highest UCS value and would be used as a point of comparison to formulations 3 and 4.

As seen in Table 5.6, formulation 3 was sticky and wetter than formulations 1 and 2. The composition of formulation 3 was modified to make it more workable in the field. As previously indicated, increasing the FA loading increased the fluidity of the DES-grout mixture. Increasing the FA had uncertain effects on the 7-day UCS result. In order to maintain approximately the same total loading of reagents, the BFS loading was decreased from 50 to 40 percent and the FA loading was increased from four to 14 percent. Since SF is a relatively expensive reagent it was also removed from the formulation composition. On the basis of previous correlations, the UCS value of modified formulation 3 was expected to decrease since the BFS and SF loadings were decreased from their values in formulation 3.

The expected trends were observed for modified formulation 3 when compared to the original formulation 3. The modification of formulation 3 caused the DES-grout material to be a semi-fluid material but not sticky (See Table 5.6). In addition the UCS value was decreased from 360 to 300 psi.

Table 5.10 Selected Formulations for LC₅₀ Analysis

Formulation Number	Grams of Reagent Per 100 Grams of Thermally Treated DES ¹			
	Portland Cement	Fly Ash	Blast furnace Slag	Water
Modified 3	20	14	40	87
4	20	30	50	100
5	50	4	50	102
9	5	0	5	60
10	Lime 5	10	0	61

¹ 550°C for 5 minutes.

The three selected formulations for the ocean disposal alternative all had high concentrations of BFS, (i.e. ≥ 40 percent loading) which should make them dense with a high silica to lime ratio. These compositions will make the formulations more durable in sea water.

5.3.2.2 Road or Landfill Alternative

Due to project time constraints and for comparison of the UCS data to formulations 1 through 8, the measurement of UCS for the road or landfill samples were set at 7-days cure. Formulations therefore had to be selected that would be relatively inexpensive and would achieve moderate UCS, (i.e., greater than 20 psi) in seven days.

Formulation 9 was design to use PC to provide strength and BFS to react with the calcium hydroxide byproduct made by cement hydration reactions. BFS was chosen over FA since it was previously observed that BFS had a beneficial effect on the UCS while the effect of FA was uncertain at 7-day cure. By the BFS reacting with the calcium hydroxide, the treated sample would be more dense and potentially less toxic in the LC₅₀ analyses. Formulation 9 had 5 percent loadings of PC and BFS.

Formulation 10 was designed based on IT's experience with treating soils and oily materials. Often a dry blend of 50:50 (w/w) lime (calcium oxide) to FA is used when low strength, low cost treatment is desired. The 50:50 dry blend composition was modified to 33.3:66.6 (w/w) lime to FA to lower the alkalinity and treatment costs of the treated material. It was speculated that the lower alkalinity of the treated mixture would be less detrimental to the specimens in the LC₅₀ analyses. The final formulation had 5 percent lime and 10 percent FA loadings.

5.3.3 Solidification/Stabilization LC₅₀ Results

The LC₅₀ test was performed on the synthetic sea water leachate of air dried DES, thermally treated at 550°C for five minutes, and samples from formulations 4, 5, 9, 10 and modified 3. Three different organisms were used to test the toxicity of each leachate, i.e., *Menidia berylina* (Silverside Minnows), *Mysidopsis bahia* (Mysid Shrimp), and *Mytilus edulis* (Mussel Larvae). The EC₅₀ was also determined by these tests. The results of these tests are in Table 5.11 and 5.12 and Figure 5.2. In Table 5.11 "LC50 (% Sample)" is the percentage of leachate necessary to be lethal to 50 percent of the population. "Mortality in 100 percent Sample (%)" is the percentage of organism, out of 20 per batch, that die in a solution that is 100 percent leachate from the DES and treated DES materials.

In Table 5.11 and 5.12, the air dried DES is the feed to the RTA. The RTA is the operation unit that produced the thermally treated DES material for the S/S process. Formulations modified 3, 4, and 5 were specifically designed for ocean disposal and low toxicity. Formulations 9 and 10 were designed to produce material that are nonhazardous and can be used as fill, e.g., road beds and landfills. Comparison of the air dried DES with the thermally treated DES shows that toxicity, in TU, is reduced by thermal treatment for all three species. See Tables 5.11 and 5.12 and Figure 5.2.

Table 5.11 LC₅₀ Results

Biological Species	Procedure	Formulation										Instant Ocean Blank
		Air Dried DES	Thermally Dried DES ¹	Modified 3	4	5	9	10				
Menidia beryllina (Silverside Minnows)	LC ₅₀ (% Sample) Mortality in 100% Sample (%)	58.79	> 100.0	> 100.0	> 100.0	> 100.0	65.7	66.39	> 100.0	> 100.0		
		95	0	15	25	10	100	82.5	17.5	17.5		
Mysidopsis bahia (Mysid Shrimp)	LC ₅₀ (% Sample) Mortality in 100% Sample (%)	82.78	> 100.0	> 100	> 100	> 100	31.57	22.36	> 100	> 100		
		65	2.5	27.5	42.5	17.5	70	100	0	0		
Mytilus edulis (Mussel Larvae)	LC ₅₀ (% Sample) Mortality in 100% Sample (%)	75.02	> 100.0	> 100	> 100	> 100	> 100	87.06	> 100	> 100		
		77.0	15.8	44.0	35.0	30.0	41.5	52.5	42.0	42.0		
	EC ₅₀ (% Sample) Effected in 100% Sample (%)	24.04	71.2	> 100	58.38	54.68	58.44	23.41	59.22	59.22		
		100	92.3	94.9	97.1	97.1	100.0	100.0	94.9	94.9		

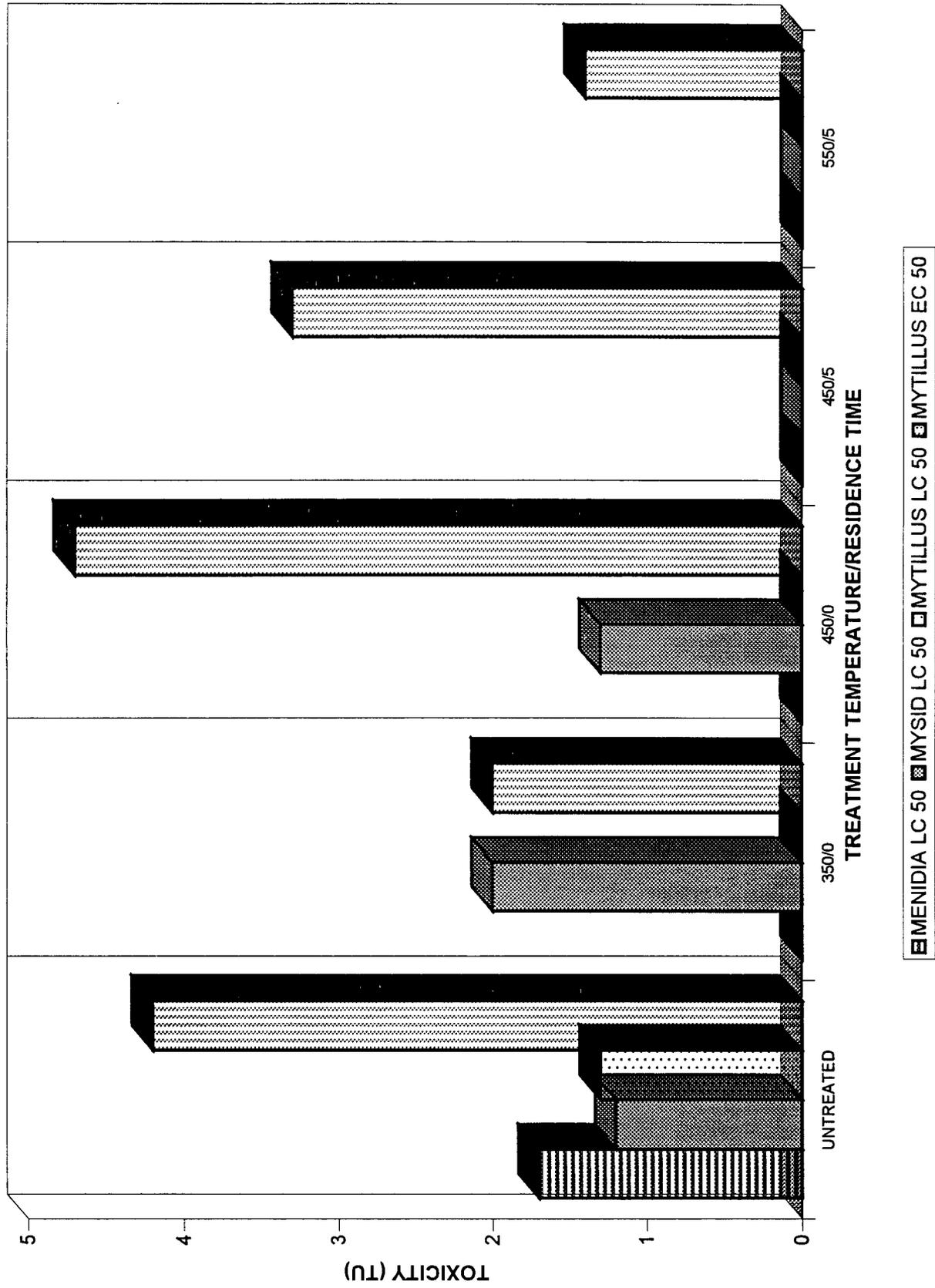
¹ 550°C for 5 minutes.

Table 5.12 Toxicity Measured In Toxicity Units (TU)

Biological Species	Formulation										Instant Ocean Blank
	Air Dried DES	Thermally Treated DES ¹	Modified 3	4	5	9	10				
<i>Menidia berylina</i>	1.7	<1	<1	<1	<1	1.5	1.5	<1			
<i>Mysidopsis bahia</i>	1.2	<1	<1	<1	<1	3.2	4.5	<1			
<i>Mytilus edulis</i> LC ₅₀	1.3	<1	<1	<1	<1	<1	1.1	<1			
<i>Mytilus edulis</i> EC ₅₀	4.2	1.4	1.4	1.7	1.8	1.7	4.3	1.7			

¹ 550 °C for 5 minutes.

Figure 5.2. Toxicity of Seawater Leachates of Thermally Treated Dredged Estuary Sediments



VALUES LESS THAN 1 TU ARE GRAPHED AS 0 TU

Formulation modified 3 has identical toxicity as the thermally treated DES. Formulations 4 and 5 have higher EC_{50} values than the thermally treated DES or formulation modified 3. The amount of leachate that effected 50 percent of the population was always greater than 100 percent leachate, for the EC_{50} (% Sample) and for all LC_{50} (% Sample). Therefore, this could not be used to differentiate between formulations. In addition, the metal concentration of the original formulation 3 in the MTCLP and SW-MTCLP, both of which uses ground particles instead of monoliths, were very low. Lastly, the UCS value for formulation modified 3 was greater than 290 psi. These three factors indicate that this formulation has significant potential for regulatory acceptance for unrestricted ocean disposal. Formulation modified 3 was therefore selected as the formulations to scale up for the >5 kg sample to send to BNL for official analysis.

Formulations 9 and 10, the fill alternative samples, have higher sea water specimen LC_{50} toxicity values than the ocean disposal alternative samples. The toxicity, measured in toxicity units, is similar to the air dried DES except for the *Mysidopsis bahia* (Mysid Shrimp) specie. For the latter specie, the toxicity is higher for the treated material than the feed. This may be due to the expected high alkalinity and salinity of leachates from the low UCS formulations 9 and 10.

5.3.4 BNL Thermally Treated Solidificaton/Stabilization Results

Analysis of the data supplied by BNL indicates that most all organic compounds were removed from the DES by the process and that the organic and metal compounds are either sparingly or insoluble in the TCLP. All TCLP analytes are below the TC regulatory threshold. See Tables 5.9 and 5.13 for total's analyses. See Table 5.14 for TCLP analyses. These tables contain data on the untreated DES and on the DES material after thermal-S/S treatment. The analysis of the treated product was conducted in duplicate. These are indicated as IT-1 and IT-2. The mean values for IT-1 and IT-2 are reported. When untreated and treated values are available a percent reduction due to the treatment process are calculated and presented in the tables. The symbol "NV" (i.e., no value) is used in the tables to indicate that the concentration is below the detection limit and that the detection limit value was not reported to IT.

5.3.5 Totals Analysis

All PCB, pesticides, and herbicides have not detected (ND) concentrations in the total analysis. When data on the untreated DES material was supplied, percentage reductions were calculated using the listed ND values. For PCB and pesticides, the percentage reduction was >99.6 and >90.9 percent, respectively. The SVOC were all ND except for naphthalene (47.9 in the product and 2729 $\mu\text{g}/\text{kg}$ in the feed), 2-methylnaphthalene (25.0 in the product and 2304 $\mu\text{g}/\text{kg}$ in the feed), Diethylphthalate (33.4 $\mu\text{g}/\text{kg}$ in the product), Di-n-butylphthalate (60.4 $\mu\text{g}/\text{kg}$ in the product), and bis-2-ethylhexylphthalate (243.3 in the product and 48631 $\mu\text{g}/\text{kg}$ in the feed). Diethylphthalate and Di-n-butyl phthalate are common laboratory contaminants often arising from the gloves, rubber O-rings, and plastic containers in contact with the sample or a leachate of the sample. All of these

Table 5.13 Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES ¹			percent reduction (%)
		IT-1	IT-2	Mean	
PCBs: (µg/kg [dry])					
2-Mono	57.33	<0.01	<0.01	<0.01	99.98
44'-Di	64.67	<0.002	<0.02	<0.011	99.98
244'-Tri	168.17	0.0200	0.0200	0.0200	99.99
22'55'-Tetra	269.33	0.0100	0.0200	0.0150	99.99
33'44'-Tetra	13.83	<0.006	<0.002	<0.004	99.97
2344'5-Penta	6	<0.003	<0.002	<0.0025	99.96
233'44'-Penta	66.87	0.0200	0.0100	0.0150	99.98
233'44'5-Hexa	0.42	0.007	0.01	0.0085	97.98
33'44'55'-Hexa	17.12	<0.008	<0.005	<0.0065	99.96
22'344'55'-Hepta	73.67	<0.003	<0.004	<0.0035	100.00
22'33'44'55'-Octa	17.17	0.0300	0.1000	0.0650	99.62
22'33'44'55'6-Nona	12	<0.008	<0.005	<0.0065	99.95
Deca	7.33	<0.01	0.0100	0.0100	99.86
PCB Totals: (µg/kg [dry])					
Mono	108.67	0.0400	0.0500	0.0450	99.96
Di	379.3	0.0900	0.1300	0.1100	99.97
Tri	727.83	0.1600	0.1200	0.1400	99.98
Tetra	1586.33	0.1300	0.0500	0.0900	99.99
Penta	1236.67	0.1300	0.0700	0.1000	99.99
Hexa	808.83	0.1600	0.0400	0.1000	99.99
Hepta	294.5	0.0800	0.0400	0.0600	99.98
Octa	95	<0.02	<0.02	<0.02	99.98
Nona	20.17	0.0100	0.0100	0.0100	99.95

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Dioxins and Furans: (ng/kg [dry])					
2378-TCDD	40.83	<0.45	<0.3	<0.375	99.08
12378-PeCDD	67.33	2.50	2.00	2.25	96.66
123478-HxCDD	55.92	3.20	3.20	3.20	94.28
123678-HxCDD	141.67	3.50	3.50	3.50	97.53
123789-HxCDD	139	Rejected		0.00	
1234678-HpCDD	2091.67	<29.6	36.20	32.90	98.43
OCDD	17463.3	110.00	297.00	203.50	98.83
2378-TCDF	340	71.60	67.40	69.50	79.56
12378-PeCDF	310.83	24.40	22.20	23.30	92.50
23478-PeCDF	152.17	47.40	43.60	45.50	70.10
123478-HxCDF	1303.33	Rejected			
123678-HxCDF	464	74.30	74.40	74.35	83.98
234678-HxCDF	184.33	119.00	82.10	100.55	45.45
123789-HxCDF	25.13	Rejected	0.00	0.00	
1234678-HpCDF	4969.33	715.00	729.00	722.00	85.47
1234789-HpCDF	110.52	36.40	30.50	33.45	69.73
OCDF	4418.33	395.00	473.00	434.00	90.18

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Totals: Dioxins (ng/kg [dry])					
TCDD	246.1	8.30	7.60	7.95	96.77
PeCDD	378.17	20.30	19.10	19.70	94.79
HxCDD	4370	35.20	38.00	36.60	99.16
HpCDD	4450	67.70	80.90	74.30	98.33
Totals: Furans (ng/kg [dry])					
TCDF	2371.67	365.00	389.00	377.00	84.10
PeCDF	2853.33	568.00	602.00	585.00	79.50
HxCDF	5175	985.00	948.00	966.50	81.32
HpCDF	6068.83	893.00	899.00	896.00	85.24

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
SVOCs: ($\mu\text{g}/\text{kg}$ [dry])					
Phenol	585	<24.03	<21.7	<22.865	96.09
bis(2-Chloroethyl)ether		<68.8	<67.6	<68.2	
2-Chlorophenol		<76.7	<75.4	<76.05	
1,3-Dichlorobenzene		<69.3	<68.1	<68.7	
1,4-Dichlorobenzene		<70.6	<69.4	<70	
1,2-Dichlorobenzene		<77.4	<76.1	<76.75	
Benzyl alcohol		<123.5	<121.4	<122.45	
2,2'-oxybis(1-Chloropropane)		<57.1	<56.2	<56.65	
2-Methylphenol		<79.5	<78.2	<78.85	
3/4-Methylphenol	1389.57	<70.8	<69.6	<70.2	94.95
N-Nitroso-di-n-propylamine		<94.5	<92.9	<93.7	
Hexachloroethane		<93.3	<91.8	<92.55	
Nitrobenzene		<53.9	<52.4	<53.15	
Isophorone		<32.4	<31.4	<31.9	
2-Nitrophenol		<133.3	<129.5	<131.4	
2,4-Dimethylphenol		<62.3	<60.6	<61.45	
bis(2-Chloroethoxy)methane		<53.7	<52.2	<52.95	
Benzoic acid		<118.1	<114.8	<116.45	
2,4-Dichlorophenol		<83.5	<81.1	<82.3	
1,2,4-Trichlorobenzene		<73.5	<71.4	<72.45	
Naphthalene	2728.57	50.96	44.84	47.90	98.24
4-Chloroaniline	1002.83	<64.3	<62.4	<63.35	93.68
Hexachlorobutadiene		<97.3	<94.6	<95.95	
4-Chloro-3-methylphenol		<64.9	<63	<63.95	
2-Methylnaphthalene	2304	27.01	23.06	25.04	98.91

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
SVOCs: ($\mu\text{g}/\text{kg}$ [dry])					
Hexachlorocyclopentadiene		< 96	< 90.9	< 93.45	
2,4,6-Trichlorophenol		< 114.2	< 108.1	< 111.15	
2,4,5-Trichlorophenol		< 122.8	< 116.2	< 119.5	
2-Chloroanphthalene		< 44.1	< 41.7	< 42.9	
2-Nitroaniline		< 117.5	< 111.1	< 114.3	
Dimethylphthalate		< 38.1	< 36	< 37.05	
2,6-Dinitrotoluene		< 175.5	< 166.1	< 170.8	
2,4-Dinitrotoluene		< 128.3	< 121.4	< 124.85	
Acenaphthylene	1288.5	< 27.8	< 26.3	< 27.05	97.90
3-Nitroaniline		< 187.7	< 177.6	< 182.65	
Acenaphthene	1042.33	< 44.4	< 42	< 43.2	95.86
2,4-Dinitrophenol		< 322.6	< 305.2	< 313.9	
4-Nitrophenol		< 122.8	< 116.2	< 119.5	
Dibenzofuran	1172	< 31.7	< 30	< 30.85	97.37
Diethylphthalate		32.84	33.98	33.41	
4-Chlorophenyl-phenylether		< 88.4	< 83.7	< 86.05	
Fluorene	1389.17	< 44.8	< 42.4	< 43.6	96.86
4-Nitroaniline		< 181.1	< 171.3	< 176.2	
4,6-Dinitro-2-methylphenol		< 210.2	< 224.9	< 217.55	
N-Nitrosodiphenylamine		< 67.4	< 72.1	< 69.75	
4-Bromophenyl-phenylether		< 145.4	< 155.6	< 150.5	
Hexachlorobenzene		< 109.9	< 116.54	< 113.22	
Pentachlorophenol		< 153.5	< 164.2	< 158.85	
Phenanthrene	6588	< 13.1	< 33.5	< 23.3	99.65
Anthracene	3702.17	< 33.3	< 35.6	< 34.45	99.07

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
SVOCs: ($\mu\text{g}/\text{kg}$ [dry])					
Di-n-butyl phthalate	1226.6	68.08	52.73	60.41	95.08
Fluoranthene	10323.7	<24.5	<26.2	<25.35	99.75
Pyrene	7101.67	<23	<23.6	<23.3	99.67
Butylbenzylphthalate	1473.17	<27.2	<27.9	<27.55	98.13
3,3'-Dichlorobenzidine		<76	<78	<77	
bis-2-ethylhexylphthalate	48630.9	243.33		243.33	99.50
Benzo(a)anthracene	4484.17	<25.3	<25.9	<25.6	99.43
Chrysene	4585.33	<27.8	<28.5	<28.15	99.39
Di-n-octylphthalate	3522.5	<18.1	<19.4	<18.75	99.47
Benzo(b)fluoranthene	2922.17	<34.7	<37.2	<35.95	98.77
Benzo(k)fluoranthene	1107.33	<38.9	<41.7	<40.3	96.36
Benzo(a)pyrene	2550.83	<38.7	<41.6	<40.15	98.43
Indeno(123-cd)pyrene	1075.67	<34	<36.4	<35.2	96.73
Dibenz(a,h)anthracene	397	<4.1	<49.4	<26.75	93.26
Benzo(ghi)perylene	1254.83	<35.6	<38.2	<36.9	97.06
Benzo(e)pyrene		<37.6	<40.4	<39	
Perylene	948.5	<41.9	<44.9	<43.4	95.42

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Pesticides: ($\mu\text{g}/\text{kg}$ [dry])					
a-BHC	<NV ¹	<3.43	<3.38	<3.405	
a-Chlordane	<NV ¹	<3.43	<3.38	<3.405	
Aldrin	75	<3.43	<3.38	<3.405	95.46
beta-BHC	<NV ¹	<3.43	<3.38	<3.405	
delta-BHC	<NV ¹	<3.43	<3.38	<3.405	
4,4'-DDD	162.1	<6.86	<6.76	<6.81	95.80
4,4'-DDE	150.57	<6.86	<6.76	<6.81	95.48
4,4'-DDT	<NV ¹	<6.86	<6.76	<6.81	
Dieldrin	74.45	<6.86	<6.76	<6.81	90.85
Endrin	<NV ¹	<6.86	<6.76	<6.81	
Endrin aldehyde	<NV ¹	<6.86	<6.76	<6.81	
Endosulfan I	<NV ¹	<3.43	<3.38	<3.405	
EndosulfanII	<NV ¹	<6.86	<6.76	<6.81	
Endosulfan sulfate	<NV ¹	<6.86	<6.76	<6.81	
g-BHC (Lindane)	<NV ¹	<3.43	<3.38	<3.405	
g-Chlordane	<NV ¹	<3.43	<3.38	<3.405	
Heptachlor	<NV ¹	<3.43	<3.38	<3.405	
Heptachlor epoxide	<NV ¹	<3.43	<3.38	<3.405	
Methoxychlor	<NV ¹	<34.3	<33.78	<34.04	
Toxaphene	<NV ¹	<343.03	<337.81	<340.42	
Herbicides: (mg/kg [dry])					
2,4-D		<0.2	<0.2	<0.2	
2,4,5-TP (Silvex)		<0.05	<0.05	<0.05	
2,4,5-T		<0.05	<0.05	<0.05	

¹ NV: Less than detection limit. No Value provided for detection limit.

Table 5.13 (continued) Analytical Results with Percent Reductions

Analyte	Air Dried DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Metals: (mg/kg [dry])					
Silver	18.42	6.57	5.88	6.23	66.21
Arsenic	33.48	14.10	13.00	13.55	59.53
Beryllium	0.56	<0.195	<0.18	<0.1875	66.52
Cadmium	37.05	13.10	12.50	12.80	65.45
Chromium	376.67	126.00	111.00	118.50	68.54
Copper	1171.67	449.00	367.00	408.00	65.18
Nickel	297.17	142.00	97.70	119.85	59.67
Lead	617	214.00	193.00	203.50	67.02
Antimony	10.29	6.72	5.25	5.99	41.84
Selenium	3.24	1.57	1.07	1.32	59.26
Thallium	2.77	2.95	2.12	2.54	8.48
Zinc	1726	629.00	549.00	589.00	65.87
Mercury (total)	1.29	<0.082	<0.09	<0.086	93.33

Table 5.14 TCLP Results

Analyte Metals (TCLP): (mg/L [extract])	Untreated DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Arsenic	<NV ¹	<0.1	<0.1	<0.1	
Barium	<NV ¹	<0.5	<0.5	<0.5	
Cadmium	<NV ¹	<0.01	<0.01	<0.01	
Chromium	0.03	<0.01	<0.01	<0.01	66.67
Lead	<NV ¹	<0.05	<0.05	<0.05	
Mercury	<NV ¹	<0.001	<0.001	<0.001	
Selenium	<NV ¹	<0.1	<0.1	<0.1	
Silver	<NV ¹	<0.01	<0.01	<0.01	

¹ NV: Less than detection limit. No Value provided for detection limit.

Table 5.14 (continued) TCLP Results

Analyte	Untreated DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
Pesticides (TCLP): (mg/L [extract])					
Chlordane	<NV ¹	<0.005	<0.005	<0.005	
Endrin	<NV ¹	0.0005	0.0005	0.0005	
Heptachlor	<NV ¹	0.0005	0.0005	0.0005	
Heptachlor epoxide	<NV ¹	0.0005	0.0005	0.0005	
Lindane (g-BHC)	<NV ¹	0.0005	0.0005	0.0005	
Methoxychlor	<NV ¹	0.001	0.001	0.001	
Toxaphene	<NV ¹	0.01	0.01	0.01	
Herbicides (TCLP): (mg/L [extract])					
2,4-D	<NV ¹	<0.1	<0.1	<0.1	
2,4,5-TP (Silvex)	<NV ¹	<0.01	<0.01	<0.01	

¹ NV: Less than detection limit. No Value provided for detection limit.

Table 5.14 (continued) TCLP Results

Analyte	Untreated DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
VOCs (TCLP): (mg/L [extract])					
Benzene	<NV ¹	<0.2	<0.2	<0.2	
Carbon tetrachloride	<NV ¹	<0.2	<0.2	<0.2	
Chlorobenzene	<NV ¹	<0.2	<0.2	<0.2	
Chloroform	<NV ¹	<0.2	<0.2	<0.2	
1,4-Dichlorobenzene	<NV ¹	<0.2	<0.2	<0.2	
1,2-Dichloroethane	<NV ¹	<0.2	<0.2	<0.2	
1,1-Dichloroethene	<NV ¹	<0.2	<0.2	<0.2	
Methyl ethyl ketone	<NV ¹	5	<5	<5	
Tetrachloroethene	<NV ¹	<0.2	<0.2	<0.2	
Trichloroethene	<NV ¹	<0.2	<0.2	<0.2	
Vinyl chloride	<NV ¹	<0.1	<0.1	<0.1	
SVOCs (TCLP): (mg/L [extract])					
Hexachloroethane	<NV ¹	<0.1	<0.1	<0.1	
Nitrobenzene	<NV ¹	<0.1	<0.1	<0.1	
Hexachlorobutadiene	<NV ¹	<0.1	<0.1	<0.1	
2,4-Dinitrotoluene	<NV ¹	<0.1	<0.1	<0.1	
Hexachlorobenzene	<NV ¹	<0.1	<0.1	<0.1	
2,4,6-Trichlorophenol	<NV ¹	<0.1	<0.1	<0.1	
2,4,5-Trichlorophenol	<NV ¹	<0.1	<0.1	<0.1	
Pentachlorophenol	<NV ¹	<0.25	<0.25	<0.25	
Pyridine	<NV ¹	<0.25	<0.25	<0.25	
o-Cresol	<NV ¹	<0.1	<0.1	<0.1	
m,p-Cresols	<NV ¹	<0.1	<0.1	<0.1	
Total Cresols	<NV ¹	<0.1	<0.1	<0.1	

¹ NV: Less than detection limit. No Value provided for detection limit.

Table 5.14 (continued) TCLP Results

Analyte	initial conc	IT-1IT-2mean			percent reduction
PAHs (TCLP): (mg/L [extract])					
Naphthalene	< NV ¹	<0.1	<0.1	<0.1	
2-Methylnaphthalene	< NV ¹	<0.1	<0.1	<0.1	
Acenaphthylene	< NV ¹	<0.1	<0.1	<0.1	
Acenaphthene	< NV ¹	<0.1	<0.1	<0.1	
Dibenzofuran	< NV ¹	<0.1	<0.1	<0.1	
Fluorene	< NV ¹	<0.1	<0.1	<0.1	
Phenanthrene	< NV ¹	<0.1	<0.1	<0.1	
Anthracene	< NV ¹	<0.1	<0.1	<0.1	
Fluoranthene	< NV ¹	<0.1	<0.1	<0.1	
Pyrene	< NV ¹	<0.1	<0.1	<0.1	
Benzo(a)anthracene	< NV ¹	<0.1	<0.1	<0.1	
Chrysene	< NV ¹	<0.1	<0.1	<0.1	
Benzo(b)fluoranthene	< NV ¹	<0.1	<0.1	<0.1	
Benzo(k)Fluoranthene	< NV ¹	<0.1	<0.1	<0.1	
Benzo(a)pyrene	< NV ¹	<0.1	<0.1	<0.1	
Indeno(123-cd)pyrene	< NV ¹	<0.1	<0.1	<0.1	
Dibenz(a,h)anthracene	< NV ¹	<0.1	<0.1	<0.1	

¹ NV: Less than detection limit. No Value provided for detection limit.

Table 5.14 (continued) TCLP Results

Analyte	Untreated DES	Treated DES			Percent Reduction (%)
		IT-1	IT-2	Mean	
PCBs (TCLP): (µg/L [extract])					
2-Mono	<NV ¹	<NV ¹	<NV ¹		
44'-Di	<NV ¹	<NV ¹	<NV ¹		
244'-Tri	<NV ¹	<0.00003	<0.00003	<0.00003	
22'55'-Tetra	<NV ¹	<0.00003	<0.00004	<0.000035	
33'44'-Tetra	<NV ¹	<0.00003	<0.00003	<0.00003	
2344'5'-Penta	<NV ¹	<0.00002	<0.00003	<0.000025	
233'44'-Penta	<NV ¹	<0.00002	<0.00003	<0.000025	
33'44'5'-Penta	<NV ¹	<0.00002	<0.00003	<0.000025	
233'44'5'-Hexa	<NV ¹	<0.00003	<0.00003	<0.00003	
33'44'55'-Hexa	<NV ¹	<0.00003	<0.00004	<0.000035	
22'344'55'-Hepta	<NV ¹	<0.00004	<0.00002	<0.00003	
22'33'44'55'-Octa	<NV ¹	<0.00004	<0.00005	<0.000045	
22'33'44'55'6'-Nona	<NV ¹	<0.00005	<0.00006	<0.000055	
Deca	<NV ¹	<0.00005	<0.00006	<0.000055	
PCB Totals:(µg/L [extract])					
Mono	<NV ¹	<0.00003	<0.00003	<0.00003	
Di	<NV ¹	<0.00003	<0.00003	<0.00003	
Tri	<NV ¹	<0.00003	<0.00003	<0.00003	
Tetra	<NV ¹	<0.00003	<0.00003	<0.00003	
Penta	<NV ¹	0.00003	0.00002	0.00003	
Hexa	<NV ¹	0.00007	0.00004	0.00006	
Hepta	<NV ¹	<0.00004	<0.00002	<0.00003	
Octa	<NV ¹	<0.00004	<0.00005	<0.000045	
Nona	<NV ¹	<0.00005	<0.00006	<0.000055	

¹ NV: Less than detection limit. No Value provided for detection limit.

total organic compound concentrations are small, ≤ 0.243 mg/kg. The percentage reductions were calculated for all SVOC with measured initial concentrations. The percentage reduction was >93.7 percent. This percentage reduction value is limited by all the ND values in the product.

There are multiple dioxins present in the total analysis. The total toxicity equivalent as 2,5,7,8-TCDD was 59.0 ng/kg (dry). This is well below the normal EPA guideline of 1.0 $\mu\text{g}/\text{kg}$ for unrestricted landfill. If the treated material is disposed of in the ocean, then the total toxicity equivalent as 2,5,7,8-TCDD value may indicate that a bioaccumulation test may be appropriate on a monolithic material.

The process does not remove or destroy metals. The total metal concentration may be closely accounted for by the dilution with reagents.

5.3.6 TCLP Analysis

All metals, pesticides, herbicides, VOC, SVOC, dioxins, and furans were all ND in the TCLP. This shows that even though there are metals and organic compounds in the treated material, very little is leaching out. This coincides with the very low LC_{50} and EC_{50} values for formulation modified 3. The official TCLP results also compare favorably with the MTCLP results for similar formulation.

The thermal process effectively removed most of the hazardous organic compounds from the DES. It appears that the metal compounds are partially held or fixated by clay and sulfide in the DES and that the addition of S/S reagents, PC with BFS, FA, and SF or Lime with FA, combine to effectively immobilize metals making them practically non-leachable.