

Demonstration of New Technologies Required for the Treatment of Mixed Waste Contaminated with ≥ 260 ppm Mercury

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Nuclear Science and Technology Division

**Demonstration of New Technologies Required
for the Treatment of Mixed Waste
Contaminated with ≥ 260 ppm Mercury**

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ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AMLGM	amalgamation (mercury treatment)
ATG	Allied Technology Group, Inc.
BNL	Brookhaven National Laboratory
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DET	determination of equivalent treatment
DOE	U.S. Department of Energy
DTC	dithiocarbamate
EPA	U.S. Environmental Protection Agency
HgWG	Mercury Working Group (of TMFA)
IMERC	incineration of mercury (waste treatment)
INEEL	Idaho National Engineering and Environmental Laboratory
ITSR	Innovative Technology Summary Report
LDR	land disposal restriction
LLW	low-level radioactive waste
MACT	maximum achievable control technology
MWFA	Mixed Waste Focus Area (DOE)
NFS	Nuclear Fuel Services, Inc.
NIOSH	National Institute for Occupational Safety and Health
NRC	U.S. Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
REL	recommended exposure limit
RMERC	retorting of mercury (waste treatment)
TLV	threshold limit value
SNS	Spallation Neutron Source (ORNL)
SOW	statement of work
SPC	sulfur polymer cement
SPSS	sulfur polymer solidification/stabilization
TCLP	toxicity characteristic leaching procedure (RCRA)
TDRD	technology development requirement document
TMFA	Transuranic and Mixed Waste Focus Area (DOE)
TRU	transuranic
UTS	universal treatment standard
WAC	waste acceptance criteria

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1. INTRODUCTION

1.1 BACKGROUND

The Resource Conservation and Recovery Act (RCRA)¹ defines several categories of mercury wastes, each of which has a defined technology or concentration-based treatment standard, or universal treatment standard (UTS). RCRA defines mercury hazardous wastes as any waste that has a TCLP value for mercury of 0.2 mg/L or greater. Three of these categories, all nonwastewaters, fall within the scope of this report on new technologies to treat mercury-contaminated wastes:

- wastes as elemental mercury,
- hazardous wastes with less than 260 mg/kg [parts per million (ppm)] mercury, and
- hazardous wastes with 260 ppm or more of mercury.

While this report deals specifically with the last category—hazardous wastes with 260 ppm or more of mercury—the other two categories will be discussed briefly so that the full range of mercury treatment challenges can be understood. The treatment methods for these three categories are as follows:

Waste as elemental mercury—RCRA identifies amalgamation (AMLGM) as the treatment standard for radioactive elemental mercury. However, radioactive mercury condensates from retorting (RMERC) processes also require amalgamation. In addition, incineration (IMERC) and RMERC processes that produce residues with >260 ppm of radioactive mercury contamination and that fail the RCRA toxicity characteristic leaching procedure (TCLP)² limit for mercury (0.20 mg/L) require RMERC, followed by AMLGM of the condensate.

Waste with <260 ppm mercury—No specific treatment method is specified for hazardous wastes containing <260 ppm. However, RCRA regulations require that such wastes (other than RMERC residues) that exceed a TCLP mercury concentration of 0.20 mg/L be treated by a suitable method to meet the TCLP limit for mercury of 0.025 mg/L. RMERC residues must meet the TCLP value of ≥0.20 mg/L, or be stabilized and meet the ≥0.025 mg/L limit.

Waste with ≥260 ppm mercury—For hazardous wastes with mercury contaminant concentrations ≥260 ppm *and* RCRA-regulated organic contaminants (other than incinerator residues), incineration or retorting (IMERC or RMERC) is the treatment standard. For wastes with mercury contaminant concentrations ≥260 ppm that are inorganic, including incinerator and retort residues, RMERC is the treatment standard. Mercury hazardous waste contaminated with ≥260 ppm mercury is the primary focus of this report.

1.2 WASTE INVENTORIES

Mercury-contaminated wastes in many forms are present at virtually every U.S. Department of Energy (DOE) facility in the United States (see Fig. 1.1). In addition to elemental mercury, these waste streams include sludges, soils, and debris waste, with mercury concentrations ranging from <2 ppm to >50,000 ppm. Estimates of the inventories of mercury-contaminated, mixed low-level, and transuranic

¹ 40 CFR 268.40

² This procedure is described in Method 1311 of U.S. Environmental Protection Agency (EPA) Publication SW-846.

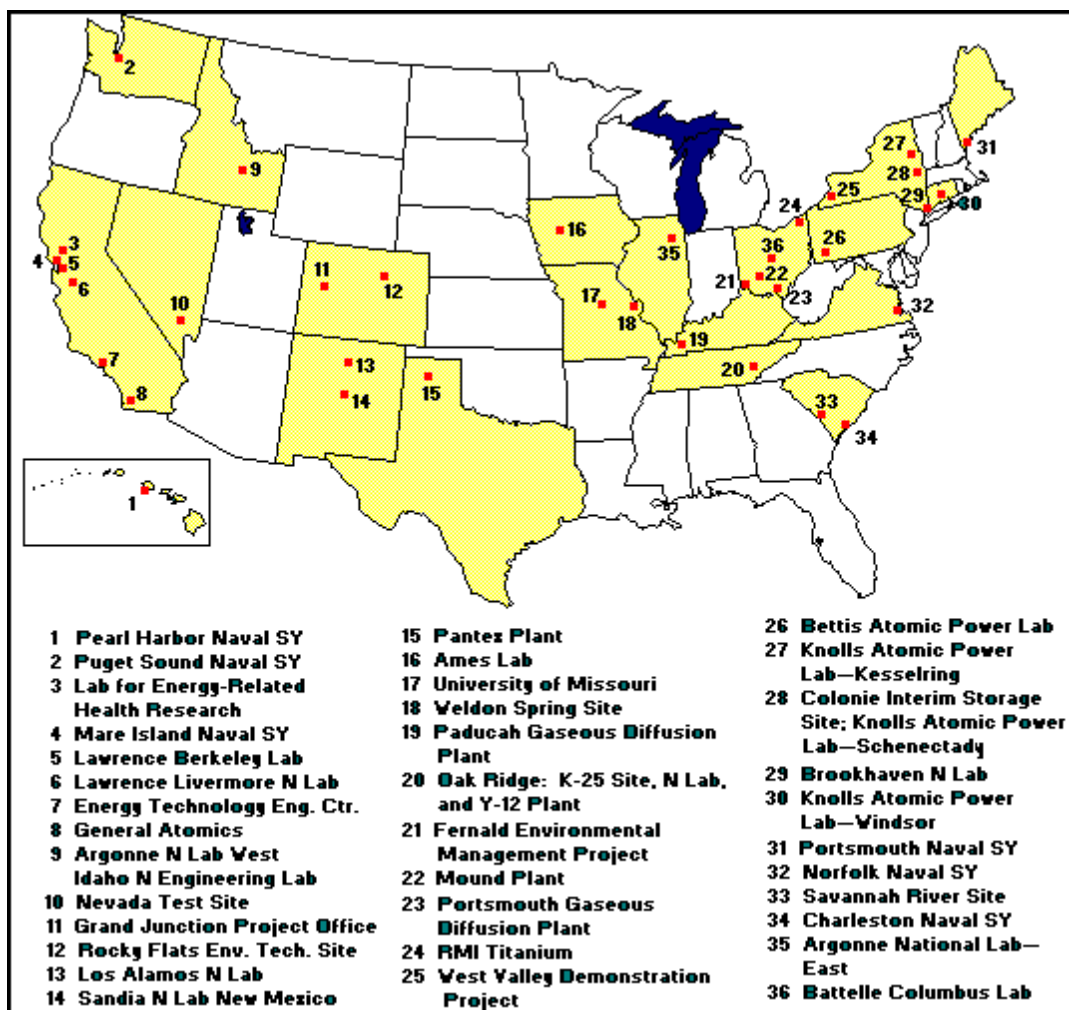


Fig. 1.1. Locations of facilities and sites throughout the DOE Complex.

(TRU) wastes in the DOE complex, based on efforts led by the TRU and Mixed Waste Focus Area (TMFA) and its Mercury Working Group (HgWG), are as follows (Conley et al. 1998):

- approximately 6 m³ of liquid elemental mercury,
- approximately 6000 m³ of mercury wastes contaminated with <260 ppm mercury,
- approximately 38,000 m³ contaminated with ≥260 ppm mercury and with radionuclides.

Additional inventories of elemental mercury will be generated at planned facilities such as the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL), the Defense Waste Processing Facility at the Savannah River Site and the Advanced Mixed Waste Treatment Facility at the Idaho National Environmental Engineering Laboratory (INEEL). In addition, treatment of other mercury wastes (e.g., soil, debris) through IMERC and retort RMERC will result in additional volumes of elemental mercury requiring stabilization.

1.3 TECHNOLOGY DEFICIENCIES

In 1997, TMFA (then known as the Mixed Waste Focus Area, or MWFA) examined the status of technologies available to treat mercury-contaminated mixed wastes and reported technology deficiencies in a series of technology development requirement documents (TDRDs) for amalgamation (MWFA 1997a), wastes with <260 ppm mercury (MWFA 1997b), and wastes with ≥260 ppm mercury (MWFA 1997c). Technology deficiencies were found to exist for mercury stabilization, separation/ removal, and amalgamation. The specific technology needs established for mercury and mercury-containing waste were (1) verification of mercury stabilization technology, (2) development of new technology for chemically or physically removing mercury contamination for separate stabilization, and (3) development of methods and equipment designs for amalgamating bulk nonrecyclable mercury. These three deficiencies are summarized in Table 1.1.

Table 1.1 Prioritized list of technology deficiencies for mercury and mercury-contaminated wastes

Technology deficiency	Description
1. Mercury stabilization	Toxic metal contaminants (regulated under RCRA) contained in mixed wastes require removal or stabilization to control solubility under TCLP conditions before disposal of the wastes is allowed. Under RCRA regulations, waste at contamination levels of <260 ppm mercury (≥260 ppm requires retorting) requires stabilization to control mercury solubility to <0.2 ppm. ^a Verification of treatment (penetrating the entire matrix and stabilizing essentially all of the mercury in the system) is required.
2. Mercury separation/ removal	The presence of mercury complicates the design of off-gas systems, the stabilization of residuals, and the monitoring of effluents from thermal systems. Removing the mercury as a pretreatment to simplify downstream operations may be advantageous. New techniques must be developed to remove (physically or chemically) the mercury for separate stabilization. Waste matrices from which mercury separation may be required include soil, all types of process residues or sludges and particulate materials, and debris. Processing methods must ensure adequate removal and must include measuring and monitoring methods to control and verify the process.
3. Mercury amalgamation	Elemental mercury may be derived as a product of retorting waste containing high mercury levels (≥260 ppm) or recovered from the off-gas of a thermal treatment unit, adding to the elemental mercury streams already in inventory. Radioactive mercury probably cannot be completely purified and verified for recycle. Disposal of the mercury will require amalgamation to form a stable, insoluble product. Methods and equipment designs are required for amalgamating bulk nonrecyclable mercury.

^a Subsequently changed to 0.025 ppm.

Efforts to develop the technology needed to meet the deficiencies identified in the TDRDs were laid out in a technology development plan, leading to the execution of three technology demonstration campaigns:

- MER01—Demonstration of the Amalgamation Process for Treatment of Radioactively Contaminated Elemental Mercury Wastes
- MER02—Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Mercury (<260 ppm) Wastes
- MER03—Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Mercury (≥260 ppm) Wastes

TMFA issued solicitations to industry for the MER01 demonstration campaign in November 1996, for MER02 in January 1998, and for MER03 in February 1999 to identify vendors with technologies that could be used to overcome the deficiencies shown in Table 1.1. The goal of the three campaigns is to demonstrate the effectiveness of newly developed technologies that can achieve the following:

- ensure adequate treatment via amalgamation, stabilization, or thermal treatment;
- include measuring and monitoring methods to control and verify the process;
- minimize worker exposure;
- minimize secondary waste generation; and
- maximize operational flexibility and radionuclide containment.

1.4 TREATMENT CHALLENGES

Because of mercury's unique characteristics—its mobility, volatility, toxicity, and tendency to complex with the waste matrix—the mercury wastes at DOE sites present significant challenges in developing effective and safe treatment technologies. Because mercury is a highly toxic metal, it is stringently regulated. Environmental Protection Agency (EPA) regulations contained in 40 CFR 261 restrict allowable concentrations of leachable mercury to very low levels (0.2 mg/L, or 200 ppb). Newer, more stringent UTS limits restrict leachable mercury from nonwastewater sources to 0.025 mg/L (25 ppb). Occupational Safety and Health Administration (OSHA) regulations restrict worker exposure to mercury vapors to a low threshold limit value (TLV) of 0.05 mg/m³.

The very nature of mercury contamination in wastes presents a challenge because it exists in various media, as well as in different chemical species of mercury. Many mercury-bearing DOE wastes are sludges, soils, absorbed liquids, partially or fully stabilized sludges, or debris. The mercury may be chemically bound to a matrix constituent such as vermiculite, Portland cement, or clay, or it may be trapped in a waste lattice structure. The mercury in these wastes is not readily accessible to leachants or retorting; and successful removal of mercury, at a rate practical for full-scale processing, is considered difficult.

Many DOE wastes contain other contaminants in addition to mercury, and additional treatment may be required. The presence of mercury complicates the design of off-gas systems, the stabilization of residuals, and the monitoring of all effluents. As a further difficulty, conventional solidification systems such as hydraulic cement are not effective in containing mercury or mercury salts, and high concentrations of organic compounds can make stabilization impracticable (Connor 1990).

Technology applications should be practicable for full-scale, fully regulated mixed waste treatment. There may be an advantage to use of a pretreatment to remove mercury to simplify downstream operations, regardless of the initial mercury concentration. However, the recovered mercury constitutes a secondary waste stream that must be treated by amalgamation. In addition, knowledge of the impacts that speciation, or the existence of mercury in the form of different chemical species, will have on technology performance is crucial. For this reason, TMFA issued a statement of work (SOW) within the scope of MER02, and three vendors were chosen to perform a series of bench-scale tests to identify and quantify the effects of varying the type of mercury species on the stabilization of surrogate wastes. The findings and results of these tests are reported elsewhere (Osborne-Lee et al. 1999).

The MER01, MER02, and MER03 solicitations target the most promising potential treatment technologies for mercury-contaminated wastes. Stabilization is of interest for radioactively contaminated mercury waste (<260 ppm mercury) because of its success with particular wastes, such

as soils, and its promise of applicability to a broad range of wastes. For the same reasons, stabilization is also of interest for waste with higher contamination levels (≥ 260 ppm mercury) as a possible alternative to the thermal treatment technologies currently prescribed by law. In either case, however, stabilization methods must be proven to be adequate to meet treatment standards. They must also be proven feasible in terms of economics, operability, and safety. At the time of the solicitations, no standard method of stabilization had been developed and proven for such varying waste types as those within the DOE complex.

TMFA is also interested in improved mercury removal and separation processes that would chemically, physically, or thermally extract mercury for separate stabilization from the complex sludges, stabilized wastes, soils, and debris in the DOE mixed waste inventory. Processing methods must ensure adequate removal of mercury and include measuring and monitoring methods to control and verify the process. Proposed technologies should include systems to minimize worker exposure and secondary waste generation while maximizing operational flexibility and radionuclide containment.

1.5 PURPOSE AND SCOPE

Currently, the EPA technology-based treatment standards for mercury-contaminated wastes are RMERC for wastes containing ≥ 260 ppm mercury and IMERC for wastes containing organics and ≥ 260 ppm mercury. RMERC requires retorting or roasting in a thermal processing unit, while IMERC specifies incineration. Both of these standards are based on the premise of recovering the mercury for recycle.

In the case of radioactively contaminated mercury, recovered mercury is still radioactive after RMERC or IMERC treatment and therefore cannot be recycled. EPA requires that this recovered radioactively contaminated mercury undergo additional treatment—amalgamation—prior to disposal. TMFA and its consulting mercury experts are working with EPA to validate equivalent technologies that would treat radioactively contaminated mercury wastes containing ≥ 260 ppm mercury directly, without the need for a thermal treatment that cannot recover recyclable elemental mercury, as originally intended by the regulation.

In addition, concern over fugitive emissions from retorting and roasting operations has raised the question of whether such processing is environmentally sound. Thus, EPA's emphasis on recycling has diminished. A change to the regulation to allow stabilization and disposal would reduce the overall environmental threat if the stabilization process can create a stable, nonleaching waste form.

The MER03 campaign had three major objectives. The first objective was to evaluate alternative processes to RMERC and IMERC for DOE's legacy mixed waste. To that end, the processes were to treat the wastes to meet a mercury treatment goal of 0.025 mg/L or less in the TCLP leachate. The results of the studies will then be used by EPA to grant a determination of equivalent treatment (DET) so that the treated wastes from these studies can be disposed of at Envirocare of Utah. Additionally, a permanent DET will be sought for the process to allow treatment of other similar wastes. The second objective was to provide EPA with data to compare proposed new analytical protocols to the standard TCLP methodology. EPA will use these comparisons in its efforts to rewrite the mercury-related RCRA regulations. Finally, TMFA wanted to evaluate an improved retort process in comparison with the stabilization process.

The purpose of this report is to document findings from the MER03 campaigns. Results of the MER01 and MER02 demonstrations have been reported elsewhere (MWFA 1999a–e) in the form of

Innovative Technology Summary Reports (ITSRs) and other reports (Osborne-Lee et al. 1999). ITSRs have also been prepared for some of the MER03 work (TMFA 2001).

Technology requirements are further detailed in the next section. The technologies demonstrated, operations, and performance results are presented in Sect. 3. Section 4 analyzes the costs associated with each of the demonstrated technologies and presents cost comparisons. A summary of the MER03 achievements is presented in Sect. 5, followed by conclusions in Sect. 6.

2. TECHNOLOGY REQUIREMENTS

2.1 REGULATORY FRAMEWORK

Mixed waste is waste that contains both hazardous chemical components, subject to the requirements of RCRA, and radioactive components, subject to the requirements of the Atomic Energy Act. Mercury-contaminated low-level radioactive waste (LLW) is considered mixed waste and is therefore regulated by both EPA and the U.S. Nuclear Regulatory Commission (NRC). Given the combined restrictions of both EPA and NRC, there is no disposal path available for mixed waste. Since the radioactive characteristic cannot be eliminated, mixed wastes must be treated to eliminate the hazardous characteristic so that they may then be disposed of in accordance with NRC regulations.

Treatment requirements for radioactive mercury-contaminated LLW (D009 as designated by EPA) are governed by 40 CFR 268.40. The logic for accomplishing treatment of such wastes to satisfy the requirements of RCRA is summarized in Fig. 2.1. Inorganic waste containing ≥ 260 ppm non-elemental mercury must be treated by RMERC, and the recovered mercury must be amalgamated, as shown in Fig. 2.1. The residues may be disposed of as LLW if they meet the TCLP test limit for mercury (0.20 mg/L), provided that the original waste did not have another RCRA characteristic in addition to mercury. If other RCRA characteristic constituents were also originally present in the waste above TCLP limits, the waste must be treated to meet the UTS for those constituents, according to 40 CFR 268.48. In the event that the residue does not meet the TCLP limit, it must either be treated again by RMERC (if the residue contains ≥ 260 ppm mercury) to meet the TCLP limit or otherwise treated to meet the UTS (if the residue contains < 260 ppm mercury).

Wastes that originally contained < 260 ppm mercury must be treated to meet the UTS (0.025 mg/L for mercury) for all RCRA constituents, unless RMERC is used, in which case the residue must meet the TCLP limit of 0.20 mg/L for mercury. After treatment to 0.2 mg/L (RMERC residues where mercury is only RCRA constituent) or the UTS (all other situations), the waste may be disposed of as LLW.

Elemental mercury must be treated by amalgamation, after which it may be disposed of as LLW. This applies to original and secondary elemental waste streams.

2.2 DEMONSTRATION REQUIREMENTS

The participants in the MER03 demonstrations were required to demonstrate technologies that could process all DOE mixed waste containing > 260 ppm of mercury in a reasonable time period. Hence, each participant's system must be able to process in the range of 1000 lb/h of waste for soils and sludges or show that a pilot system demonstrated is scalable to this processing rate. Whether the process is continuous or batch-type, the system should also have defined alternative operating ranges such that it could be operated by individual sites at something less than the maximum processing rate.

Because the final waste form must be suitable for disposal, the participants were also required to provide chemical, physical, and engineering analyses, as well as any preliminary treatability studies, in addition to the demonstration needed to show that the process achieved the established performance targets and met the disposal facility's waste acceptance criteria (WAC). Participants were also required to provide for characterization, certification, transport, and disposal at Envirocare of Utah, including all treated wastes and secondary wastes generated from the demonstration.

Mercury RCRA Characteristic (D009) Radioactive Wastes Treatment Logic Diagram

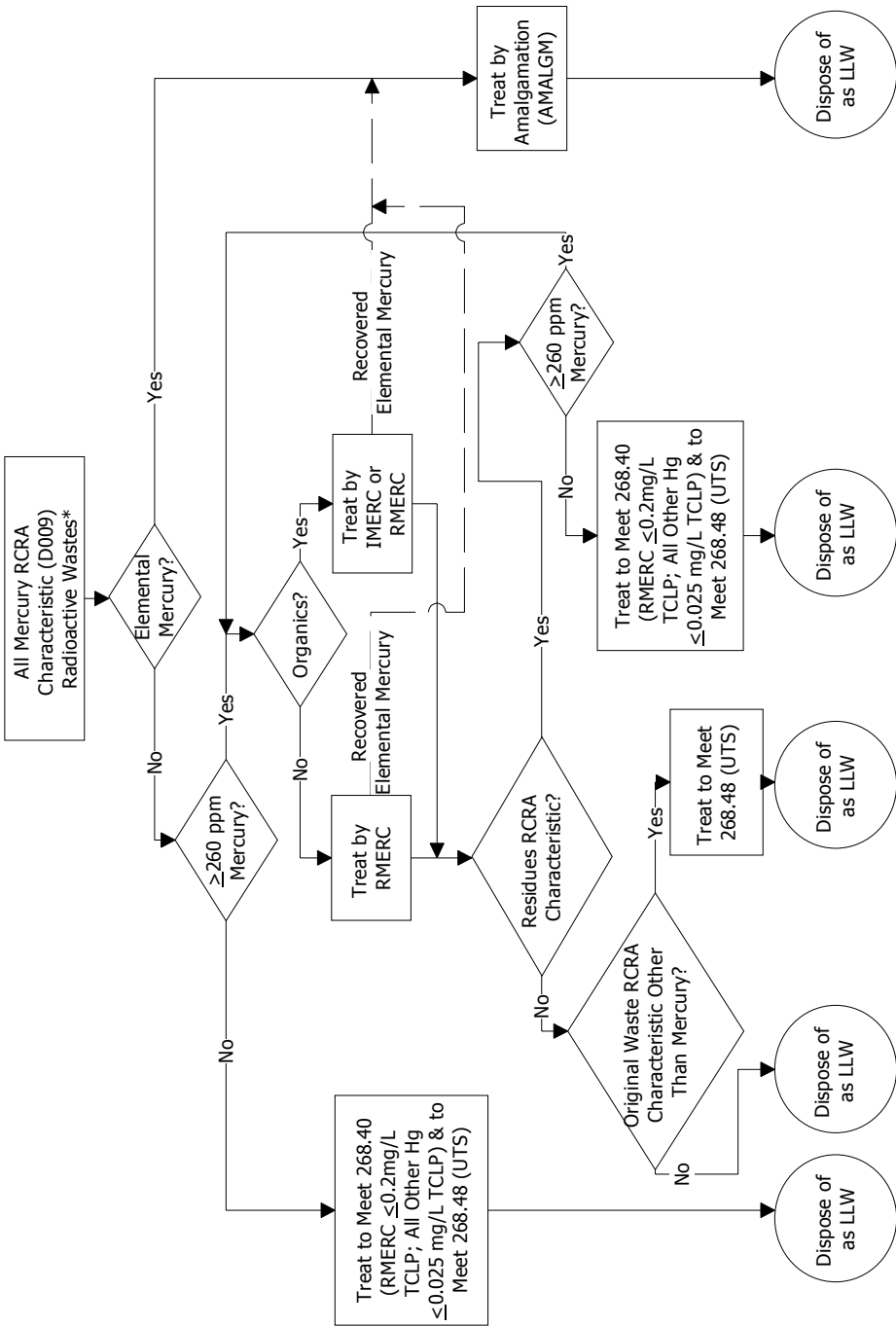


Fig. 2.1. Logic chart showing treatment and performance requirements needed to satisfy RCRA for mercury-contaminated radioactive wastes.

The performance goal for treatment by stabilization for the waste soils was to meet the UTS (0.025 mg/L mercury) for the category of “Mercury–All Other” wastes and the land disposal restriction (LDR). Other performance standards were as follows:

1. The mercury stabilization process had to stabilize mercury-containing wastes without removing the mercury from the waste matrix. Processes that involve separating the mercury from the waste matrix followed by amalgamation were not considered within the scope of the demonstration.
2. The mercury stabilization process had to stabilize all forms of mercury, including organic and halogenated mercury compounds, elemental mercury, mercury oxides, and mercury sulfates.
3. The mercury stabilization process should minimize secondary wastes. An increase in waste volume of the final waste form due to the stabilization process was also to be minimized.
4. If the stabilization process causes a chemical reaction that increases the temperature and releases undesired off-gases, the demonstration had to include control technology to ensure waste integrity and contain both mercury and organic emissions.
5. The stabilization process was required to accomplish mercury stabilization within the boundaries of worker and public exposure limits required by OSHA and local radiation control requirements. The process had to ensure that worker exposure to mercury vapors is below 0.05 g/m³.
6. The mercury stabilization technology had to be able to handle soils and sludges at a rate of approximately 1000 lb/h, based on current inventories and treatment schedules established by site treatment plans.

Additional requirements and specification details are published elsewhere (MWFA 1997c; TMFA 1999).

3. TECHNOLOGY DEMONSTRATIONS

3.1 OVERVIEW OF TECHNOLOGIES DEMONSTRATED

A campaign of demonstrations of treatment technologies on mercury-contaminated wastes has been completed. Four vendors were selected in response to the MER03 solicitation. These four vendors conducted demonstrations of their processes, which included three different stabilization technologies and one improved retort process. The vendors and their processes were as follows:

1. Brookhaven National Laboratory (BNL)—sulfur polymer stabilization/solidification (SPSS) process
2. Nuclear Fuel Services (NFS)—DeHg (de-merk') process
3. Allied Technology Group (ATG)—chemical stabilization
4. SeptraDyne-Raduce—vacuum thermal desorption

All four vendors were successful in performing the demonstrations, in that the demonstrations were on schedule, within budget, and met the treatment goals. The first three vendors demonstrated stabilization of mixed waste with a total mercury content >260 ppm to provide data on the applicability of stabilization to waste with a high mercury content. The vacuum thermal process demonstrated by the fourth vendor, SeptraDyne-Raduce, was intended to demonstrate an improved form of the baseline technology of retort. The SeptraDyne-Raduce technology demonstrated removal of mercury from mixed waste sources with mercury concentrations up to 6000 ppm.

3.1.1 Sulfur Polymer Solidification/Stabilization Demonstration

BNL demonstrated the application of a newly developed pilot-scale SPSS process on contaminated mixed-waste soils containing high concentrations (~5000 mg/L) of mercury and liquid elemental mercury (Kalb et al. 1999). The BNL process (patent pending) chemically stabilizes mercury to reduce vapor pressure and leachability and physically encapsulates the waste in a solid matrix to eliminate dispersion and provide long-term durability. Two 55-gal drums of mixed-waste soil containing high concentrations of mercury and about 62 kg (approximately 137 lb) of radioactively contaminated elemental mercury were successfully treated. Waste loadings of 60 wt % soil were achieved without an increase in waste volume, while elemental mercury was solidified at a waste loading of 33 wt % mercury. TCLP analyses indicate the final waste form products meet current EPA-allowable TCLP concentration requirements as well as the more stringent proposed UTS. Mass balance measurements show that 99.7% of the mercury treated was successfully retained within the waste form, while 0.3% was captured in the off-gas system.

3.1.2 DeHg Mercury Stabilization Demonstration

NFS demonstrated its DeHg mercury stabilization process on samples of the same soil that was treated by BNL (NFS 2000). The DeHg process operates at ambient temperature, chemically converting the mercury component in mixed waste to a nonhazardous LLW final waste form suitable for land disposal. The process was developed to address elemental, ionic, and complexed forms of mercury in mixed waste. Previously, the DeHg chemistry had been successfully applied over a wide variety of processing configurations for different waste matrices. NFS used a pilot-scale reactor, demonstrated previously for wastes containing <260 ppm Hg (MWFA 1999a), that was capable of handling up to 100 lb of soil, metering soil, and stabilizing reagents directly into the reactor. The soil samples were particle size, reduced prior to treatment to <1/8 in. in diameter. The demonstration consisted of seven batch runs that, on the average, resulted in final TCLP values ranging from <0.0006 to 0.0102 mg/L. Waste loadings of 85.5 wt % soil were achieved, with a volume increase of

13%. Mercury emissions were monitored with a Jerome mercury vapor analyzer; results indicated that mercury losses to the environment were negligible.

3.1.3 Chemical Stabilization Demonstration

ATG demonstrated its stabilization process on a one-drum sample of the same soil treated by BNL but used two different formulations to stabilize the waste (ATG 2000). The ATG process had been demonstrated previously at full scale for wastes containing < 260 ppm mercury (MWFA 1999b). The untreated soil received from BNL contained approximately 4000 mg/kg of total mercury, and leachable mercury concentrations exceeded the UTS limit by more than tenfold. Full-scale tests were conducted using a 7-ft³ mortar mixer with two different formulations that reduced the mercury concentrations in soil extracts below the UTS limit of 0.025 mg/L. The formulations were based on dithiocarbamate (DTC) and liquid sulfide reagents. The DTC formulation reduced the concentration to about one-half the UTS limit, or 0.013 mg/L, and the liquid sulfide formulation to less than one-tenth of the limit, or 0.0025 mg/L. Waste loadings averaged 72.2 wt %. The volume increase resulting from stabilization treatment was less than 20% for both formulations demonstrated. The formulations also stabilized cadmium and lead, which were present in TCLP extracts above the UTS limits in the untreated soil.

3.1.4 Vacuum Thermal Desorption Demonstration

SepraDyne-Raduce demonstrated its vacuum thermal desorption process on samples of the soil from BNL. The SepraDyne-Raduce high-vacuum rotary kiln thermal desorption process represents an improved version of the baseline treatment technology for wastes with high levels of mercury contamination. Four drums of the Brookhaven waste were treated as part of the SepraDyne-Raduce demonstration. In addition, a number of other problematic mercury-contaminated waste streams were treated, including radioactive, mercury-contaminated animal carcasses. The SepraDyne-Raduce process was highly successful in removing mercury from the waste streams treated, eliminating most of the small-volume mercury-contaminated BNL waste streams. The final product from the SepraDyne-Raduce process had total mercury levels substantially below 10 ppm mercury and leachable mercury levels below 0.025 mg/L. Readings of the Jerome Analyzer used to monitor for mercury in the air in the vicinity of the process were well below legal limits. Mercury removed from the waste and collected by the system was subsequently stabilized by BNL with the SPSS process. After secondary treatment, the final volume was 78% of the original.

3.2 CHARACTERISTICS OF SOIL USED IN MER03 DEMONSTRATIONS

BNL and the commercial vendors—SepraDyne, ATG, and NFS—each demonstrated their processes for the treatment of a mercury- and radioactively contaminated soil that had been excavated during a CERCLA removal action at BNL. During excavation of the BNL Chemical Holes, approximately 100 ft³ of soil, identified as potentially high in mercury, was removed and placed in two B-25 boxes, each about half full. Preliminary characterization showed the soil concentration of mercury in the two B-25 boxes, numbered 1 and 2, to be approximately 6750 mg/L and 18,000 mg/L, respectively. The primary radiological contaminants of concern were found to be ²⁴¹Am, ^{152/154}Eu, and ²²⁶Ra. Composite characterization data is summarized in Table 3.1.

The physical composition of the soil was mostly sand and silt, with a small percentage of gravel and approximately 5% debris (glass, metal, and plastic), most of which was removed during subsequent repackaging operations. During excavation, the soil was screened to particles of less than 1 in. Significant homogenization of the soil in the B-25 boxes occurred during the segregation/screening process. TCLP testing of representative samples of each waste bin showed mercury concentrations of

3.56 mg/L and 0.26 mg/L, respectively (above current limits of 0.2 mg/L), making the two drums subject to LDR treatment standards.

In addition to contaminated soils, 62 kg (approximately 137 lb) of liquid elemental mercury was also retrieved from the BNL Chemical Holes area. The mercury was buried and/or collected during remediation in 28 plastic and glass containers of different sizes. The radiological contaminants—identified as ^{235}U , ^{238}U , ^{226}Ra , ^{241}Am , ^{152}Eu , ^{137}Cs , and ^{60}Co —were present in very low concentrations.

Each B-25 box of soil was subdivided into seven 55-gal drums; these were distributed to the demonstration project participants. To ensure that comparable wastes were tested, the soil was evenly divided during repackaging by manually shoveling small scoops into each drum in turn. Large pieces of debris were manually removed during repackaging. The drums were assigned unique identification numbers (A1–A7 for the drums containing americium and E1–E7 for the drums containing europium) and sealed to ensure chain of custody. Composite samples taken from each drum were analyzed to confirm equivalent source term composition of the waste. Full TCLP metals analysis of samples from drums A1–A4 and E1–E4 were performed; results are shown in Tables 3.2 and 3.3, respectively. Total mercury measurements of the soils ranged from 2310 to 5570 mg/kg, with an average of just over 4000 mg/kg.

BNL demonstrated its SPSS process on two sample drums of the waste, drums A4 and E1 (Kalb et al. 1999). BNL also used this process to treat 400 lb of elemental mercury recovered from the same remediation project, meeting EPA’s amalgamation regulation. NFS processed one drum of the BNL soil (NFS 2000). Grab samples from each of the seven batch runs were submitted for analysis. ATG treated one drum of waste but split the contents of the drum and used two formulations to stabilize the waste (ATG 2000). SeptraDyne-Raduce treated seven drums of the BNL waste—four drums with mercury and europium contamination and three drums with mercury and americium contamination—as part of the demonstration, plus other contaminated BNL waste streams.

Table 3.1. Characterization data for B-25 boxes of mercury-contaminated mixed-waste soils

Parameter	B-25 Box 1	B-25 Box 2
Hg (total)	6750 mg/kg	18,000 mg/kg
Hg (TCLP)	3.56 mg/L	0.263 mg/L
Gross Alpha	4560 pCi/g	24.9 pCi/g
Gross Beta	525 pCi/g	35.9 pCi/g
^{241}Am	7140 pCi/g	—
^{238}Pu	72.6 pCi/g	—
$^{239/240}\text{Pu}$	19.7 pCi/g	—
^{90}Sr	2.15 pCi/g	—
$^{233/235}\text{U}^4$	—	7.06 pCi/g
^{238}U	—	5.87 pCi/g
$^{152/154}\text{Eu}$	—	28.7 pCi/g
^{226}Ra	—	35.5 pCi/g

3.3 BROOKHAVEN NATIONAL LABORATORY SPSS DEMONSTRATION

3.3.1 Technology Description

The sulfur polymer stabilization/solidification (SPSS) process is based on sulfur polymer microencapsulation, a mixed-waste treatment technology previously developed and patented at BNL (Colombo, Kalb, and Heiser 1997). The sulfur polymer cement (SPC) used in the process consists of 95 wt % elemental sulfur reacted with 5 wt % of an organic modifier to enhance mechanical integrity and long-term durability. Previous testing on sulfur polymer waste forms indicated excellent performance under anticipated disposal conditions (Kalb, Heiser, and Colombo 1991; Kalb et al. 1991).

Table 3.2. TCLP metals analysis for four drums of soil taken from B-25 box 1

Parameter	Box / drum ^a					Av. for A drums	TCLP limit	UTS limit
	B-25 box 1	A1	A2	A3	A4			
Total Hg (mg/kg)	6,750	4,040	4,190	2,310	5,570	4,028		
TCLP analysis (µg/L)								
As	<14.9	40.0	40.0	40.0	40.0	40.0	5,000	5,000
Ba	162	134	193	357	150	208	100,000	21,000
Cd	<1.04	11.4	11.4	11.4	11.4	11.4	1,000	110
Cr	<3.65	7.0	7.0	7.0	7.0	7.0	5,000	600
Pb	<3.39	15.0	21.6	26.3	15.0	19.5	5000	750
Hg	3,560	868	1,500	1,390	1,000	1,190	200	25
Se	<7.00	24.1	24.1	24.1	24.1	24.1	1,000	5,700
Ag	7.66	20.1	20.1	20.1	20.1	20.1	5,000	140

^a Soil in the drums was taken from the box, and the drums were then sampled for analysis.

Table 3.3. TCLP metals analysis for four drums of soil taken from B-25 box 2

Parameter	Box / drum ^a					Av. for E drums	TCLP limit	UTS limit
	B-25 box 2	E1	E2	E3	E4			
Total Hg (mg/kg)	18,000	4,190	3,100	4,880	5,510	4,420		
TCLP analysis (µg/L)								
As	<14.9	40.0	40.0	40.0	40.0	40.0	5,000	5,000
Ba	219	1,560	1,780	1,480	1,820	1,660	100,000	21,000
Cd	52.8	164	116	99.9	148	132	1,000	110
Cr	9.10	7.0	8.9	7.0	9.2	8.0	5,000	600
Pb	79.7	754	789	736	993	818	5,000	750
Hg	263	208	246	191	212	214	200	25
Se	<7.00	24.1	24.1	24.1	24.1	24.1	1,000	5,700
Ag	6.56	20.1	20.1	20.1	20.1	20.1	5,000	140

^a Soil in the drums was taken from the box, and the drums were then sampled for analysis.

SPSS mercury treatment is a two-stage process involving stabilization and solidification. In the first stage, mercury is reacted with powdered SPC, forming mercuric sulfide, as shown in Eq. 1:



Because the BNL SPSS process includes chemical stabilization of the mercury, yielding mercury sulfide, it meets EPA requirements for an amalgamation technology (AMLGM). To treat elemental mercury, equal masses of mercury and SPC were mixed in the reaction vessel, providing a sixfold molar excess of sulfur to mercury and facilitating a faster reaction of the mercury metal with sulfur.

For mercury-contaminated soil, waste loading was affected by mixability constraints as well as by the concentration of mercury in the waste. Prior to mixing, the reaction vessel was placed under an inert gas atmosphere to prevent the formation of mercuric oxide (a water-soluble and leachable compound), and a small quantity of additive was included to accelerate the reaction. The vessel was heated to about 40°C during the stabilization phase to accelerate the sulfide formation reaction. The materials were then mixed until the mercury was completely reacted with the sulfur.

Once the mercury is chemically stabilized, the waste is ready to be solidified. This is the second stage in the SPSS process. Additional SPC was added, and the mixture was heated at about 130°C to obtain a homogeneous molten mixture, which was then poured into a suitable mold, where it cooled to form a monolithic solid waste form.

SPSS processing was accomplished using a 1-ft³ pilot-scale vertical cone blender/dryer. Mixing action was provided by an orbital, helical screw, which rotated like an auger at 105 rpm. As the screw rotated, it also revolved around the wall of the vessel at 2.5 rpm, drawing material upward from the base of the cone. Feed materials were charged to the unit through a 6-in.-diam port on the cone lid. Photographs of the mixer and its mixing screw, respectively, are shown in Figs. 3.1 and 3.2.

When mixing or drying, the system could be operated under vacuum through the use of a vacuum pump, or under inert atmosphere, by connection to a regulated nitrogen gas supply. Heat was provided to the jacketed cone by a circulating fluid heat transfer system. The SPSS product was discharged through a 5-cm (2-in.) heated ball valve at the base of the cone. A HEPA-filtered ventilation system was used to prevent dispersion of particles during charging.

Off-gas was captured in multiple stages. First, the gas passed through a shell and a tube heat exchanger cooled by a 3-ton chiller. Next, the gas passed through a liquid nitrogen cryogenic trap. Finally, it passed through HEPA and activated charcoal filters before venting to the atmosphere. Condensate was collected at the heat exchanger in an off-gas condensate vessel and at the cryogenic trap, for analyses. A process flowchart of the off-gas system components is shown in Fig. 3.3.

3.3.2 Waste Treated by BNL

Two 55-gal drums of mixed waste soil and about 62 kg of radioactively contaminated elemental mercury were treated using the SPSS process. The two drums, E1 and A4, had net weights of 127 kg (280 lb) and 204 kg (450 lb), respectively. The drums were opened and sampled in a fully contained, HEPA-filtered hot cell. Air monitoring samples from these activities produced ²⁴¹Am levels of 2.3×10^{-2} µCi/g. Based on these results, the decision was made to transfer the soils into 1-gal containers to facilitate loading of the waste into the mixer. To remove large aggregate that could interfere with mixer operation, the soil was sieved to <9.5 mm (3/8 in.) during transfer to smaller

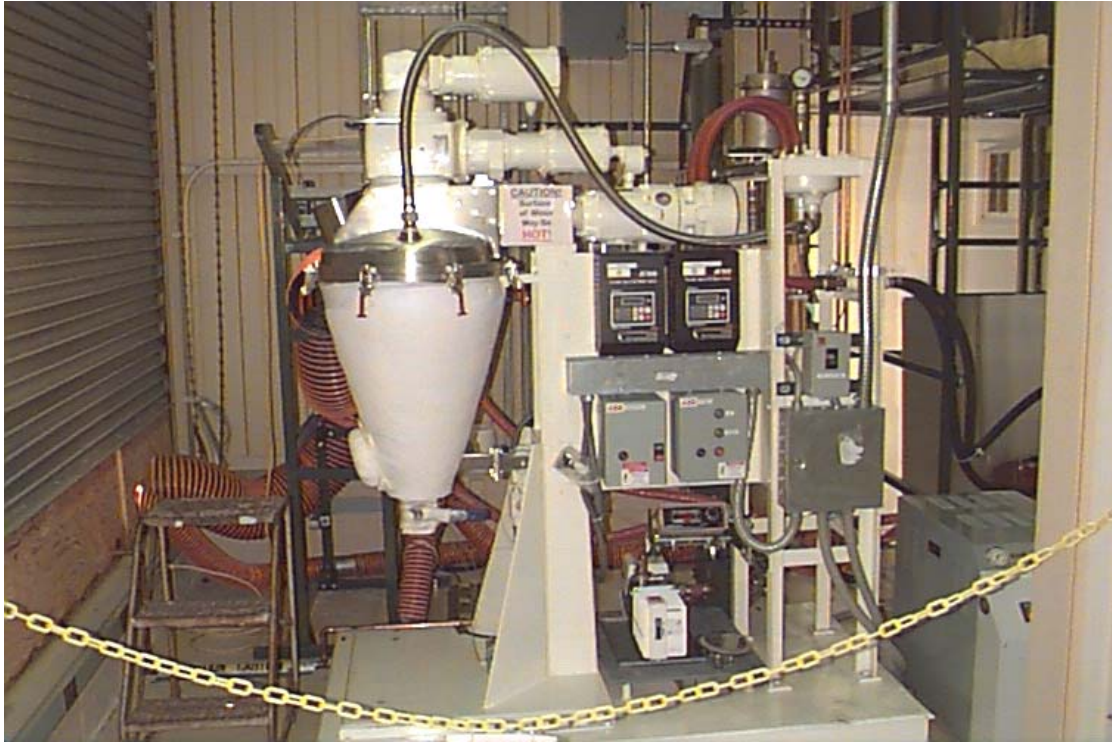


Fig. 3.1. SPSS mixer and process controls.



Fig. 3.2. View of inside of vertical cone mixer.

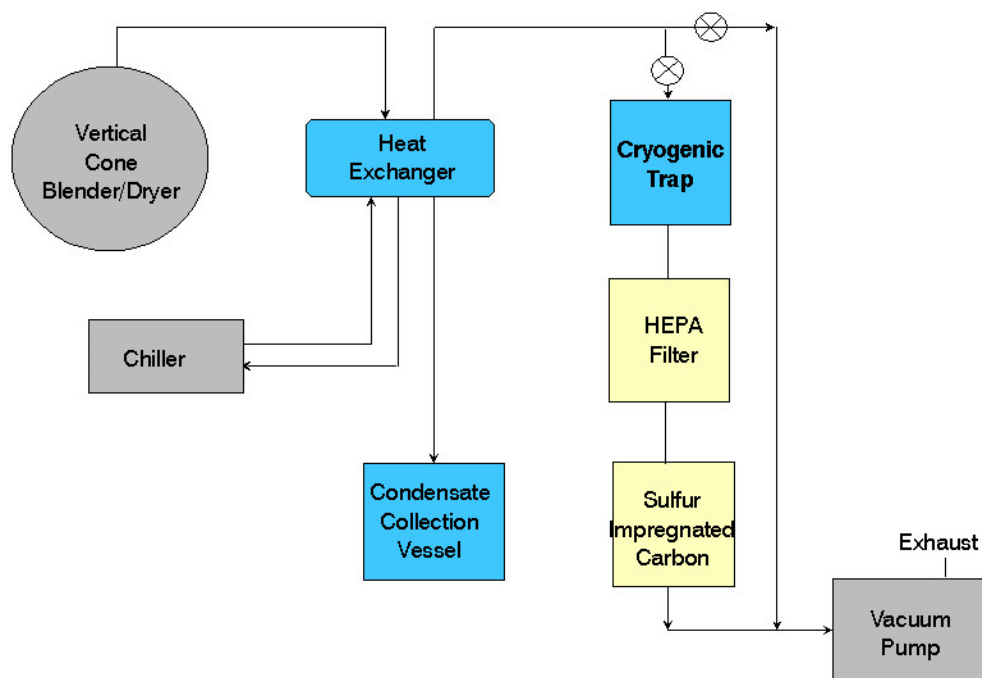


Fig. 3.3. Flowchart depicting SPSS off-gas treatment.

buckets. Gravel and small debris retrieved from each drum during sieving amounted to 14.6 kg for drum E1 and 10.9 kg for drum A4. The average moisture content of drum E1 was ~7.6 wt %, with little variation from top to bottom. Drum A4 was much wetter at the bottom (up to 14 wt % moisture) compared to the top (~7 wt % moisture), with an average moisture content of 8.4 wt %. Soil from the bottom third of drum A4 was air-dried to reduce moisture content to less than 2 wt % prior to SPSS processing.

In addition to mixed-waste soils, mixed-waste elemental mercury from the BNL Chemical Holes was also targeted for SPSS processing. A total of about 62 kg of liquid mercury waste was received for treatment. The inventory consisted of 28 individual containers (glass or plastic) of varying quantities and purity. Approximately a quarter of the inventory was positively identified to be radioactive after surveys indicated measurable activity, but all of the waste was treated as mixed waste, based on process knowledge.

3.3.3 Performance Results

Previous bench-scale development work for the SPSS process had shown that as much as 33 wt % elemental mercury could be successfully encapsulated and still meet TCLP criteria (Gorin, Leckey, and Nulf 1994), so this formulation was used to treat the BNL liquid mercury waste. Although the soils tested in this study contained relatively high concentrations of mercury (up to about 5000 mg/L), they contained far less mercury on a mass basis than the liquid mercury previously tested. Thus, physical processing parameters (e.g., viscosity of the mix), rather than mercury leachability, represented the limiting constraints on waste processing for mercury-contaminated soils.

Mercury-Contaminated, Mixed-Waste Soil

Trial process runs were first conducted by BNL using the vertical cone blender to determine optimum waste loading (mass of soil to mass of powdered SPC) based on dry mixing, melting, and discharging

of the molten mixture. When soil waste loadings of 70 wt % were processed, a layer of material tended to stick to the walls of the vessel during discharge, requiring manual scraping. When the waste loading was reduced to 60 wt % soil, the melt viscosity was lower, and most of the mixture flowed easily out of the vessel into the collection container. For the 60 wt % mixture, batch size was limited to 41 kg (90 lb). Because the mixing action tended to pull material high up the wall of the vessel, larger batch sizes tended to accumulate a ring of material on the wall that could not be incorporated into the melt. Both of these limitations are related to the design of the mixing vessel; such problems might be reduced with modifications to the mixer or selection of an alternate processing system.

The procedure for adding, mixing, and melting components in the cone blender was standardized to yield reproducible batch results. To “lubricate” the walls of the mixer and enhance discharge of material, powdered SPC was added first, followed by as-received soil, such that an SPC-rich layer would be created at the vessel wall. Next, the vessel was evacuated and purged with nitrogen gas. A slight overpressure of nitrogen gas, up to 5 psi, was maintained during mixing. The soil/SPC mixture was then reacted for a minimum of 4 h at $40 \pm 5^\circ\text{C}$, to ensure sufficient reaction between the mercury and sulfur. (For early process runs, samples were taken intermittently to determine reaction kinetics.)

Following mixing, the system was evacuated (26 in. Hg) and the vessel temperature was increased to 100°C to drive moisture off the soil. Complete dryness, which usually occurred in less than 1 h, was indicated by visible dust in the vessel, followed by a rapid rise in the temperature of the mixture to the vessel setpoint. Following drying, the remaining SPC required by the formulation was added to the vessel (as SPC chips), and the temperature was increased to $135 \pm 5^\circ\text{C}$ to melt the SPC and encapsulate the chemically stabilized mercury waste. Melting occurred within 30 min, after which time the molten mixture was mixed another 15 min, prior to discharge into a metal 5-gal container. While the material was still molten, about 500 mL was ladled into a glass jar for subsequent analyses. The volume of the SPSS-treated waste, which nearly filled the 5-gal container, was virtually the same as the volume of the untreated waste. In the liquid state, the amount of SPC used for encapsulation is that volume required to fill interstitial void space in the soil; thus, no volume increase is observed. The lack of volume increase is depicted in a photograph of a simulated batch of soil, the reagents required for processing, and the stabilized/solidified waste form (Fig. 3.4). Note that the volume of the final waste form (the 5-gal container on the right) is nearly identical to the volume of the untreated waste (the 5-gal container on the left).

SPSS processing of mercury-contaminated, mixed-waste soil in drum E1 was completed first. Drum E1 waste was processed as five batches. The first two batches contained 25.8 and 25.4 kg of as-received soil; the last three batches each contained 26.0 kg of as-received soil. The dry weight of the soil in each batch was calculated on the basis of the moisture content of the individual buckets processed. For a batch composition of 60 wt % dry soil and 40 wt % SPC, the total batch weight and the weight of the SPC required were then calculated. For these batches, only one-quarter of the total SPC, in powdered form, was added to the as-received soil to chemically stabilize mercury in the waste. For a total batch weight of 40 kg, approximately 26 kg of as-received soil was processed (24 kg dry weight), with 4 kg and 12 kg of powdered and chip-form SPC, respectively.

Treatment of the second of two 55-gal drums (A4) containing mercury-contaminated, mixed-waste soil was similar, again with approximately 40-kg batches processed. Starting with the fourth batch, however, two significant changes were made. First, the amount of powdered SPC was increased (the ratio of powdered SPC to SPC chips changed from 1:3 to 3:1) to increase the surface area of SPC available to react with mercury droplets in the soil. Second, a small amount (0.5 wt %) of a proprietary ingredient was added to further enhance mercury stabilization. Seven batches of drum A4 soil were



Fig. 3.4. Volumetric comparison of SPSS batch components and final waste form (right).

processed, the final batch containing residuals from both drums (A4 and E1). Thus, 12 batches were required to complete pilot-scale treatment of the two 55-gal drums of waste.

TCLP samples were made by remelting the 500-mL subsample from each batch and pouring material into Teflon molds to create small pellets approximately 8 mm (5/16 in.) in diameter by 8 mm (5/16 in.) high, a size that meets the size requirement of the TCLP test while maintaining the integrity of the encapsulated product. Pelletized samples of the E-drum process batches were composited into a single 400-g sample (approximately 80 g from each of five batches). Similarly, a 400-g composite of A-drum process batches was created (approximately 60 g from each of seven batches). TCLP tests were done at BNL in accordance with EPA SW-846.3-3, Method 1311. All tests were conducted using extraction fluid #1 (pH 4.93 \pm 0.05). Filtered, acidified leach aliquots for individual batch samples and composite samples were shipped to Severn Trent Laboratories (Whippany, N.J.) for analysis. Composite pellet samples of the A4 and E1 soils were also sent for total mercury analysis.

Mercury analysis results for individual process batches and composite drum samples are summarized in Table 3.4. Except for the E1 composite sample, the data indicate a significant decrease in mercury leachability compared with untreated soils (208 and 914 $\mu\text{g/L}$, for drums E1 and A4, respectively). Considering that the TCLP concentrations for drums E1-1 through E1-5 varied between $<0.4 \mu\text{g/L}$

and 30 µg/L, the data for the E1 composite was considered anomalous by BNL. Significant improvements

were attained by processing drum A4 after optimization of the formulation; leaching was well below the more stringent UTS levels for mercury of 25 µg/L.

Mass balance between SPSS processed and unprocessed mixed-waste soil was performed to confirm that the mercury contamination in the soil was indeed stabilized in the final waste form. The volume and concentration of off-gas liquids, as well as the weight and concentration of the carbon trap, were determined so that the amount of mercury volatilized during processing could be calculated. Representative samples were taken from each of the components of the off-gas system (liquid condensate, cryogenic trap, and carbon filter) and analyzed for total mercury. As shown in Table 3.5, for 310 kg of E1 and A4 soil processed, only 0.3% of the mercury processed was captured in the off-gas, resulting in a capture efficiency of 99.7%. Approximately 90% of the moisture was accounted for in the chiller and cryogenic traps.

Liquid Mercury Mixed Waste

Although the elemental mercury waste was much denser than the soil waste, the total weights of SPSS/liquid mercury process batches were kept approximately the same as for the mercury-contaminated soil waste. Total batch volumes decreased only slightly, however, due to the increased volume of SPC used (all SPC was in powder form for these batches); reduced batch volumes were desired to enhance mixing action during the reaction phase. Bench-scale formulations were prepared

Table 3.4. TCLP results from BNL for SPSS-treated mercury-contaminated mixed-waste soils

SPSS batch ID	TCLP Hg (µg/L)
E1-1	7.4
E1-2	9.4
E1-3	33
E1-4	<0.40
E1-5	30
E1 SPSS composite ^a	147
E1 untreated soil	208
A4-1	0.50
A4-2	3.0
A4 composite ^b	0.50
A4 untreated soil	914

^a Composite sample containing equal weights of batches E1-1 through E1-5.

^b Composite sample containing equal weights of batches A4-1 through A4-7. Batches A4-4 through A4-7 contained 0.5 wt % of proprietary additive.

Table 3.5. Mass balance of condensates for SPSS-treated A4 and E1 waste streams

	Processed soil wt. (kg)	Moisture wt. (kg)	Hg wt. (g)
E1 process runs	154.36	10.58	679.75
A4 process runs	155.94	7.94	868.59
Total processed	310.30	18.51	1548.33
	Hg conc. (mg/L)	Condensate vol. (L)	Hg wt. (g)
Chiller trap (E1)	165	8.74	1.44
Cryogenic trap (E1)	676	0.74	0.50
Chiller trap (A4)	428	6.52	2.79
Cryogenic trap (A4)	420	0.54	0.23
Carbon trap (E1+A4) ^a	—	—	0.09
Total trapped		16.54	5.05
% trapped		89.4%	0.3%

^a Carbon trap contained 1.69 kg carbon with 52.6 ppm Hg.

with three levels of additive—1, 2, and 3 wt %—to confirm that treated waste would pass the treatment goal of 0.025 mg/L in TCLP leachate. At a waste loading of 33.3 wt % elemental mercury, all samples were indeed below EPA regulatory limits. To ensure optimal leaching results, 2 wt % additive was used for SPSS treatment of liquid mercury process batches. The total inventory of liquid mercury waste was treated in six batches—five 11.3-kg batches and one 5.4-kg batch. The total batch weights for the elemental mercury process runs were 34.0 kg (75 lb). Thus, a typical batch consisted of 11.3 kg of mercury, 0.7 kg of additive, and 22.0 kg of powdered SPC.

A procedure similar to that used for A-drum processing was used, with the exceptions that the total mass of powdered SPC was added initially and that the liquid mercury waste was added in small, approximately 20-mL additions. To enhance the dispersion of the liquid mercury, the waste was added while the screw was rotating, with the liquid added just prior to the advancing screw with each orbital rotation. With large and rapid addition of the liquid waste to the powder SPC, the dense liquid readily migrated and pooled at the bottom of the cone mixer, out of reach of the mixer screw and therefore not agitated and reacted with the powder. After addition of the liquid mercury, the ball valve at the bottom of the mixer was cracked open to catch any pooled waste; it was then reintroduced to the vessel. This process was repeated until there was no pooled mercury present at the base.

When the mixing was complete (>4 h), the powder had changed in color from bright yellow to dark gray-black, indicating that the reaction to mercuric sulfide had occurred. The vessel temperature was raised directly to the melt temperature, as no moisture was present in this waste. The sample volume of the molten product was approximately 4 gal. Archive samples of all process batches were collected, as previously described. For two batches, EM-5 and EM-6, samples were collected to determine whether stratification of the encapsulated SPSS material had occurred due to the high density of the amalgamated mercury phase. Approximately one-third of the batch was poured, a sample collected (labeled “bottom”), the second third of the batch poured (labeled “middle”), and the final third poured (labeled “top”).

Pellet samples were prepared from all batch archive samples for subsequent TCLP extraction. A certified laboratory was utilized to provide TCLP testing. The results from the certified lab TCLP tests, shown in Table 3.6, were all below UTS limits for mercury (25 µg/L).

Table 3.6. Certified laboratory TCLP results for SPSS-treated elemental mercury

SPSS batch ID	TCLP Hg (µg/L)
EM-1	<0.40
EM-2	<0.40
EM-3	<0.40
EM-4	0.70
EM-5T (top)	9.3
EM-5M (middle)	1.2
EM-5B (bottom)	<0.40
EM-6C (composite) ^a	4.9

^a Composite sample containing equal weights of top, middle, and bottom grab samples.

3.4 NUCLEAR FUEL SERVICES DeHg DEMONSTRATION

3.4.1 Technology Description

DeHg is an ambient temperature process that converts the mercury component in mixed waste (waste containing both hazardous and radioactive components) to a nonhazardous LLW form suitable for land disposal. It was developed to address elemental, ionic, and complexed forms of mercury in mixed waste. DeHg chemistry has also been successfully applied over a wide variety of processing configurations for different waste matrices including shreddable and nonshreddable debris, waste

waters, soils, organics, and sludge. The general DeHg process is shown in Fig. 3.5. The process, which

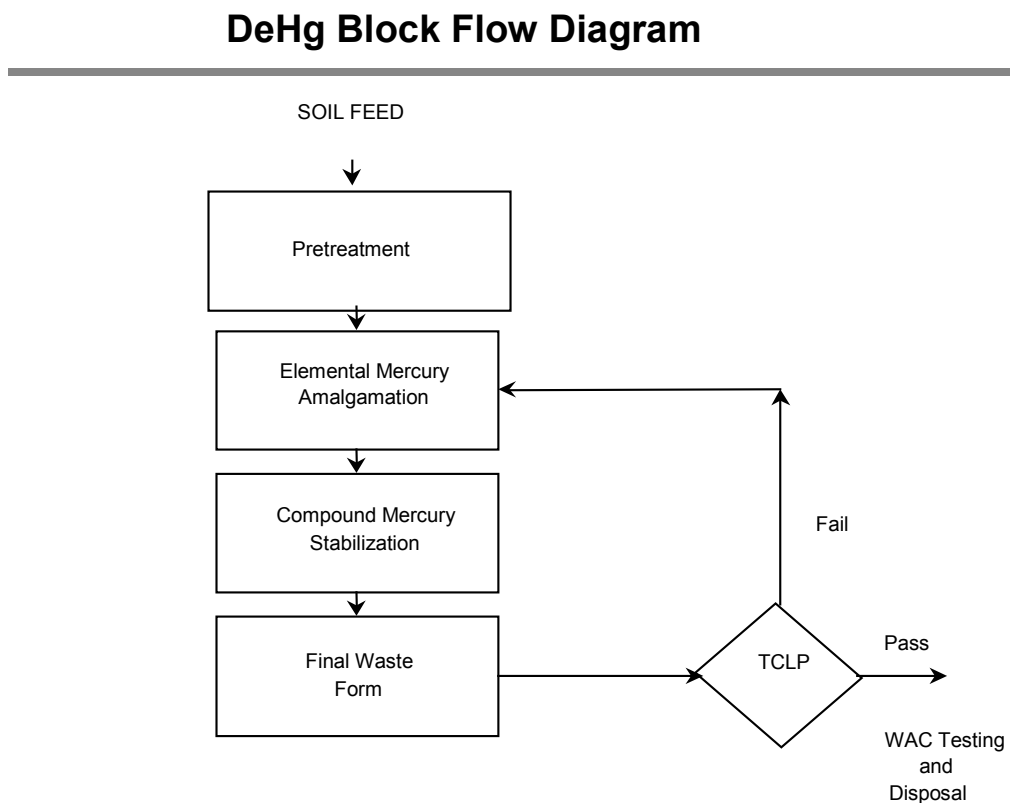


Fig. 3.5. Block flow diagram of the NFS treatment process.

uses standard equipment connected in typical fashion, has been applied in a number of different processing configurations.

The first stage of the process involves amalgamation of the elemental mercury component (if present). Prior to amalgamation, waste may need to be conditioned by shredding, grinding, and/or slurring it with water, depending on the capability of the mixing equipment to be used.

In the second stage, soluble mercury species are stabilized by use of the proprietary reagent. This reagent frees mercury from stable, soluble complexes and allows for its precipitation as a stable, nonleachable salt. The DeHg reagent was originally developed to treat solidified mercuric thiocyanate wastes when traditional mercury stabilization techniques failed to treat this difficult complex. Following treatment with the DeHg reagent(s), the residues are packaged for burial.

Demonstration testing was performed in the NFS Applied Technology Development Laboratories at the NFS site in Erwin, Tennessee, with a pilot-scale DeHg reactor capable of handling up to 45 kg (100 lb) of soil and reagents. The reactor system was housed in a ventilated structure constructed for

the purpose of demonstrating the DeHg process. The structure was approximately 300 ft² in area and 10 ft high and served as containment for all work activity. Typical scale-up systems will both meet and exceed the specified 1000-lb/h rate specified by HgWG for stabilization of mercury-bearing soils.

For full-scale operation, the greatest safety concerns with processing mercury mixed wastes are not only the radioactive components of the waste, but also the potential of mercury exposure to operating staff. The NFS facility utilizes a fully ventilated system designed to mitigate potential emission of radioactive particulates. The ventilation system also has mercury vapor removal capability. Since most of the process equipment is either contained or under ventilation, and the process is operated under ambient conditions, mercury emissions are minimized, if not practically eliminated.

3.4.2 Wastes Treated by NFS

NFS received approximately 176 kg (387 lb) of soil from BNL for this demonstration. This soil matrix was found to be mostly sandy and contaminated with elemental mercury, as determined by visual inspection. Table 3.7 summarizes initial soil characterization data provided by BNL prior to transport of this material to NFS.

Table 3.7. Characteristics of soil tested by NFS

Parameter	Concentration
Mercury (TCLP)	1.5 mg/L
²⁴¹ Am	10,300 pCi/g
¹³⁷ Cs	<0.1 pCi/g

3.4.3 Performance Results

NFS first sampled and assayed the waste materials to verify chemical and radiochemical attributes prior to demonstration runs. Upon inspection of the material, NFS found that the soil contained a number of rocks up to an inch in diameter. The entire soil specimen was submitted to a particle-reduction operation to ensure that no particle would exceed 1/8-in. diameter.

Because of prior experience in stabilization of mercury using DeHg, NFS proceeded directly to the demonstration phase without bench-scale runs. Seven batch runs were performed using DeHg chemistry on the material in aliquots of approximately 25 kg each. Runs 1, 2 and 3 were processed using different levels of amalgamation reagent. Runs 4, 5, 6, and 7 were processed using conditions similar to that of run 2. Each batch was mechanically discharged from the reactor when processing was completed.

After processing each batch, NFS acquired grab samples for process control and submitted these specimens to internal laboratories for mercury TCLP analysis. Batch mercury TCLP assays showed that the DeHg process produced stabilized waste forms that were below the UTS limit for mercury of 0.025 mg/L. Five of the seven runs indicated TCLP mercury levels of <0.005 mg/L; run 3 had a TCLP mercury level of 0.016 mg/L, and run 4, a level of 0.006 mg/L. All of these results were well below the 1 mg/L TCLP level of the raw waste and show that the DeHg process stabilized even the most leachable forms of mercury within soil matrices.

NFS sent specimens of the final waste form to an off-site Utah-certified laboratory for analysis. The Utah-certified laboratory results are in good agreement with the NFS internal assays. The results of the Utah profiling assays are provided in Table 3.8.

The final waste form is best described as a cakelike product containing no freestanding water. Bulk density measurements made during the batch tests indicated that the stabilization adds 10–15% to the original volume of material. Weight is increased by about 15–20%. Vapor pressure and leach testing

Table 3.8. Summary of waste-profiling analyses by Utah-certified laboratory for NFS demonstration samples

Parameter	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	EPA limit
Metals (mg/L, TCLP)								
Arsenic	<0.0006	<0.0006	0.0009	<0.0006	<0.0006	<0.0006	<0.0006	5.0
Barium	0.409	0.35	0.295	0.250	0.291	0.340	0.173	21.0
Cadmium	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	0.11
Chromium	<0.002	0.032	<0.002	<0.002	<0.002	<0.002	0.049	0.60
Lead	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004	0.0104	0.75
Mercury	0.0102	<0.0006	0.005	0.006	0.002	0.007	0.001	0.025
Selenium	0.004	<0.002	<0.002	<0.002	<0.002	0.004	<0.002	5.7
Silver	<0.001	<0.001	0.001	0.001	<0.001	<0.001	<0.001	0.14
Zinc	0.109	0.106	0.227	0.102	0.179	0.099	0.095	4.3
Copper	0.024	0.009	0.007	0.003	0.029	<0.001	0.011	None
pH	9.73	9.82	9.64	9.69	9.59	9.85	9.88	>2 and <12
Paint filter	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Reactive sulfide, mg/kg	11	8	11	10	9	16	7	
Reactive cyanide, mg/kg	<3	<3	7	<3	<3	4	3	
Total organic halide (TOX), µg/L	<50	<50	<50	<50	<50	<50	<50	
Nuclides (pCi/g)								
^{233/234} U				<19				
^{235/236} U				<24				
²³⁸ U				<19				
²³⁰ Th				<40				
²³² Th				<50				
²³⁸ Pu				412				
^{239/240} Pu				54				
²⁴¹ Am				6140				

(Kosson protocols) of the NFS and other demonstration wastes were to be performed at ORNL. (On the Kosson protocols, see Sanchez et al. 2001.) The results of the ORNL tests will be reported separately.

During the course of the demonstration, NFS also monitored airborne mercury concentrations using a Jerome mercury vapor analyzer. These measurements permitted estimates to be made of mercury loss through vapor emissions during processing. The average mercury concentration measured in the contained work area was at all times less than federally mandated levels. These measurements and the federally mandated levels are summarized in Table 3.9. The higher airborne mercury levels during the processing of the early batches are ascribed to startup activities associated with initial handling of soils. Once processing reached a steady state, airborne mercury levels were very low, generally less than 0.005 mg/m³.

NFS used these measured airborne mercury levels to estimate the quantity of mercury evolved during processing. Using a conservative flow rate for the designated containment area, NFS estimated that a maximum of 0.05% of the initial inventory of mercury evolved during this demonstration. This is a negligible quantity relative to the quantity of mercury input for the demonstration. Approximately 99.95% of the mercury input to the process was retained within the processing system.

**Table 3.9. Regulatory limits for mercury vapor exposure and
NFS mercury measurements during processing**

Source of measurement	Mercury vapor level (mg/m ³)	Comment
<i>Regulatory agency limits</i>		
Occupational Safety and Health Administration (OSHA)	0.1	Permissible exposure limit (PEL); worker's exposure cannot exceed
National Institute for Occupational Safety and Health (NIOSH)	0.05	Recommended exposure limit (REL) for up to a 10-h workday and 40-h work week
American Conference of Governmental Industrial Hygienists (ACGIH)	0.025	Threshold limit value (TLV) for an 8-h workday and 40-h work week
<i>NFS measurements during processing by batch number</i>		
Batch 1	0.021	
Batch 2	0.023	
Batch 3	0.011	
Batch 4	0.005	
Batch 5	0.002	
Batch 6	0.002	
Batch 7	0.001	

3.5 ALLIED TECHNOLOGY GROUP CHEMICAL STABILIZATION DEMONSTRATION

3.5.1 Technology Description

ATG developed several commercial proprietary processes that have stabilized metals and organics in thousands of cubic yards of soils and sludges for a variety of commercial and government clients. Metals stabilized by ATG include lead, vanadium, nickel, chromium, chromium (VI), arsenic, copper, cadmium zinc, and mercury. Stabilized organics include polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol, dioxins, and furans as well as cyanide. ATG has also developed several formulations that stabilize the most common mercury species for initial mercury concentrations in waste approaching 260 ppm. The development and performance of these formulations is described in previous reports (Conley 1999; DOE 1999). DOE has a considerable volume of waste with mercury concentrations >260 mg/kg. This demonstration test examined the correlation between bench-scale tests and full-scale operations and evaluated the reliability of mercury stabilization for DOE wastes containing high concentrations of mercury.

Previous small-scale tests conducted by members of the ATG team have shown that the degree of mixing is a very important aspect of the stabilization process, especially for liquid sulfides, which bind mercury more tightly than any other reagents tested. Entraining air into a sulfide formulation is necessary to stimulate the formation of active sulfides for the stabilization reaction. Entrainment of air into the paste-like stabilization mixtures is difficult to do on a large scale. Therefore, this study modified commercially available equipment to increase the air entrained.

The dynamics of the reactions with liquid sulfide reagents are complex and depend not only on the degree of aeration, but also on the degree of mixing. Because aeration and mixing differ between

bench- and full-scale systems, the demonstration also addressed the question of whether the performance and operating parameters of a full-scale system could be adequately predicted from bench-scale tests. The ATG demonstration project included formulation development with bench-scale testing and then full-scale demonstrations. Two of the 27 formulations evaluated during the bench-scale testing were selected for the full-scale demonstrations.

Laboratory facilities and equipment used for formulation development are shown in Fig. 3.6. The commercial Essick mortar mixer used for the demonstrations is shown in Fig. 3.7. Mercury concentrations were monitored with a Jerome mercury monitor from Arizona Instruments not shown in the figure. A Ludlum Model 2221 portable rate-scale meter was used to measure radioactivity.



Fig. 3.6. Treatability study facilities used by ATG.

3.5.2 Wastes Treated by ATG

The full-scale demonstration tests with supporting bench-scale tests were conducted on mercury-contaminated soil supplied to ATG by BNL. The 220-lb (100-kg) sample of contaminated soil contained an average total mercury concentration of 4200 mg/kg. Mercury, cadmium, and lead all leached from the soil at concentrations exceeding the UTS limits. Of the six soil samples analyzed, the standard deviation was found to be 17%. Detailed analytical results are provided elsewhere (ATG 2000).

First inspection showed the soil to be well mixed and homogeneous. It was dark brown and had a sandy consistency, with only a small amount of debris consisting of pieces of plastic sheeting and shards of glass. A photograph of the soil as received from BNL is shown in Fig. 3.8. Less than 5% of the soil was small rock, with a diameter of 0.5 in. or larger. About 2 gal of water had condensed behind the plastic drum liner. This water was thoroughly mixed back into the soil to raise the total moisture content to 21.2%.



Fig. 3.7. Mortar mixer used for ATG demonstrations.



Fig. 3.8. BNL soil and original shipping container.

Analyses were performed to quantify anions associated with ionic forms of mercury such as chlorides, fluorides, and sulfates in the waste. Ion chromatography results showed that these anions were present; however, the quantities were not sufficient to bind all mercury. Thus, the speciation of most of the mercury is unknown.

The soil contained a total 13.6 pCi/g of $^{152/154}\text{Eu}$. The activities of other radionuclides were obtained by ATG from a third-party analytical laboratory; these are reported elsewhere (ATG 2000).

3.5.3 Performance Results

Bench-Scale Test Results

In the bench-scale tests, 1 kg of the soil obtained from BNL was mixed with various stabilization reagents, which reacted with mercury in the soil to form stabilized compounds of mercury. The dithiocarbamate (DTC) and sulfide formulations selected for the full-scale demonstration tests had the lowest concentrations of mercury in TCLP leachate from treated soils. The mercury concentrations in leachate from bench-scale treatment of the soil with formulations selected for the full-scale demonstrations are shown in Table 3.10.

As shown in Table 3.10, and for other formulations not shown, mercury concentrations in leachate from soil treated with liquid sulfide formulations were generally lower than those in soil treated with DTC formulations. Formulations based on either DTC or liquid sulfide reagents that also included Portland cement reduced mercury leaching the most. Several bench-scale formulations (not shown) were successful without the addition of Portland cement. Formulations without Portland cement exhibited no observable increase in volume.

Table 3.10. Performance of stabilization agents in bench-scale treatment of soil

	Formulation base	
	DTC	Liquid sulfide
Mercury concentration in TCLP leachate (mg/L)	0.00696	0.000864
Increase in weight as % of initial soil wet weight	59%	91%
Increase in volume as % of initial soil volume	15%	23%

Most of the weight and volume increase shown for both the DTC and the liquid sulfide formulations is attributable to Portland cement and water. The weight that these two reagents added was 55% of the initial soil weight for the DTC formulation and 81% for the liquid sulfide formulation. Portland cement and water probably accounted for all of the observed increase in volume shown in the table for both formulations.

Besides the RCRA metal mercury, the DTC and liquid sulfide formulation stabilized all other RCRA metals that leached from the untreated soil at concentrations above the UTS limits. Table 3.11 presents the TCLP results for RCRA metals stabilized with the liquid sulfide formulation. The formulation reduced the concentration in TCLP leachate of all RCRA metals that were above the UTS limits by at least tenfold.

Full-Scale Test Results

Full-scale treatment of all soil batches treated with both the DTC and liquid sulfide formulations met the UTS requirements for all metals, including mercury. A comparison of the points to consider in selecting either a DTC or a liquid sulfide formulation is given in Table 3.12. These points, and other operational considerations, are discussed in the remainder of this section.

Table 3.11. Reduction in metals leachability after bench-scale treatment with liquid sulfide

Metal	UTS leaching limit (TCLP mg/L)	Raw waste leaching (TCLP mg/L)	Treated waste		
			Leaching ^b (TCLP mg/L)	% of UTS	% stabilized
Sb	1.15	0.044	—	—	—
As/D004	5	<0.02	<0.02	<0.4	c
Ba/D005	21	1.67	0.825	4	51
Be	1.22	0.00118	—	—	—
Cd/D006	0.11	0.193 ^a	<0.003	<3	>98
Cr/D007	0.6	<0.01	0.0957	16	c
Pb/D008	0.75	1.92 ^a	0.131	17	93
Hg/D009	0.025	0.282 ^a	0.00211	8	99
Ni	11	0.105	—	—	—
Se/D010	5.7	<0.03	<0.03	<1	c
Ag/D011	0.14	<0.004	<0.004	<3	c
Tl	0.2	<0.02	—	—	c
V	1.6	<0.004	—	—	c
Zn	4.3	1.38	—	—	—

^a Raw waste failed to satisfy UTS treatment standard.

^b Only RCRA metals were analyzed in leachate from soil treated with this formulation, a formulation that contained no Portland cement.

^c Leaching from untreated waste was near detection limits; thus, no calculation of percent stabilized was possible.

Table 3.12. Performance of DTC and liquid sulfide for key performance characteristics

Characteristic	Performance of stabilization agent	
	DTC	Liquid sulfide
Stabilization performance	Satisfactory	Excellent
Throughput	Excellent	Low throughput demonstrated. More experience may allow significant increase.
Reliability of scale-up	Excellent	Must account for differences in mixing, aeration, and reaction chemistry.
Volume increase	Satisfactory	Satisfactory
Weight increase	Satisfactory	Satisfactory

As shown in Table 3.13, the mercury stabilization performance of the DTC formulation was satisfactory and that of the liquid sulfide formulation excellent. The DTC formulation applied at full scale reduced the leachable mercury concentration from 10 times the UTS limit to about one-half of the UTS limit for mercury, for an overall 20-fold reduction in leachable mercury. The liquid sulfide formulation reduced the leachable mercury even more, to less than one-tenth of the UTS limit of 0.025 mg/L, with an overall 100-fold reduction in leachable mercury. Volume increases resulting from treatment with the full-scale DTC and liquid sulfide formulations are shown in Table 3.13. The volume increases were 20% or less and very similar to volume increases observed in the bench-scale treatments.

Table 3.13. Performance of stabilization agents in full-scale treatment of soil

	Formulation base	
	DTC ^a	Liquid sulfide ^b
Mercury concentration in TCLP leachate (mg/L)	0.0139	0.0020
Weight increase as % of initial soil wet weight	33%	44%
Volume increase as % of initial soil volume	7%	20% ^c

^a Average of three samples of 0.0133, 0.0158, and 0.0126 µg/L.

^b Average of three samples of 0.000521, 0.00282, and 0.00274 µg/L.

^c Visual observations indicate a volume increase less than the 23% measured for bench-scale formulation. No actual measurements were performed.

Both formulations also stabilized the RCRA metals cadmium and lead, which leached from the untreated soil at concentrations greater than the corresponding UTS limit shown in Table 3.14. As this table indicates, the DTC formulation, batch F-1, stabilized more than 98% of the leachable cadmium and more than 99% of the leachable lead. The final treated soil satisfied all UTS leaching limits for metals.

Table 3.14. Reduction in leachability of metals after full-scale treatment with DTC

Metal	UTS leaching limit (TCLP mg/L)	Raw waste leaching (TCLP mg/L)	Treated waste ^b		
			Leaching (TCLP mg/L)	% of UTS	% stabilized
Sb	1.15	0.044	—	—	—
As/D004	5	<0.02	<0.02	<0.4%	c
Ba/D005	21	1.67	0.497 ^b	2%	70%
Be	1.22	0.00118	—	—	—
Cd/D006	0.11	0.193 ^a	<0.003	<3%	>98%
Cr/D007	0.6	<0.01	<0.01 ^b	<2%	c
Pb/D008	0.75	1.92 ^a	<0.02 ^b	<3%	>99%
Hg/D009	0.025	0.282 ^a	0.0139 ^b	56%	95%
Ni	11	0.105	—	—	—
Se/D010	5.7	<0.03	<0.03	<1%	c
Ag/D011	0.14	<0.004	<0.004	<3%	c
Tl	0.2	<0.02	—	—	c
V	1.6	<0.004	—	—	c
Zn	4.3	1.38	—	—	—

^a Raw waste failed to satisfy UTS treatment standard.

^b Values differ from values obtained in bench-scale treatment (see Table 3.11).

^c Leaching from untreated waste was near detection limits; thus, no calculation of percentage stabilized was possible.

Bench-scale testing suggests that smaller volume and weight increases may be achievable. Several successful formulations that omitted Portland cement produced a moderately dense monolith with a volume increase of less than 10%. Other formulations using Portland cement, including the two formulations used in the full-scale demonstration tests, set to a dense, concrete-like material that was easily granulated.

For all formulations with Portland cement, the volume increase was generally proportional to the mass of Portland cement added. Air trapped by the hydrated silicate matrix may also contribute to the volume increase.

Increases in volume were generally related to, but less than, increases in weight. For most reagents other than Portland cement, a weight increase of less than 10% resulted in no measurable volume increase. Portland cement and accompanying water accounted for most of the volume and weight increases of greater than 10%.

The only secondary wastes generated by the MER-03 tests were 51 lb (23 kg) of treated waste samples from the bench-scale tests and dunnage accumulated during the bench testing and full-scale demonstrations. The dunnage consisted of personal protective clothing, cloth wipes, plastic sheets, jars, and pails. Excluding empty waste containers, the demonstration test indicated that 10–20 lb (4.5–9 kg) of dunnage would be generated each day during full-scale operation.

3.6 SEPRADYNE-RADUCE VACUUM RETORT DEMONSTRATION

3.6.1 Technology Description

SeptraDyne-Raduce developed, patented, and commercialized an indirectly heated rotary retort that operates at a high vacuum and high temperature. The unique combination of these features produces an environment capable of volatilizing water, all organics, and metals with low to moderate boiling points (e.g., Hg, As, Se, and Cd) with near-zero toxic air emissions. The process has been shown to volatilize and pyrolyze organic compounds (Adams, Kalb, and Malkmus 2000). It also reduces feed material volume by 25–40%. Since air and sweep gases are eliminated from the retort, combustion will not occur and total gas volume exhausted to the atmosphere is minimized. Only volatilized material will exit the retort, and therefore, the off-gas equipment is drastically minimized in size. The SeptraDyne-Raduce vacuum thermal desorption system provides the following advantages over traditional thermal processes:

- Air pollution is expected to be less because of the elimination of sweep gas and the effectiveness of the rotary seal.
- The equipment is expected to be easier to site and permit because air pollution is reduced.
- Products of incomplete combustion such as dioxins and furans are not produced because of the reduced oxygen in the processing environment.
- Less off-gas treatment is required, decreasing capital and maintenance cost requirements.

The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Fig. 3.9) are as follows. Mercury mixed with waste such as soil, sludge, personal protective equipment, and building materials are reduced in size by a shredding and/or grinding process before being fed to the retort through a feed system. Any liquid and/or sludge inventory can be pumped into the retort.

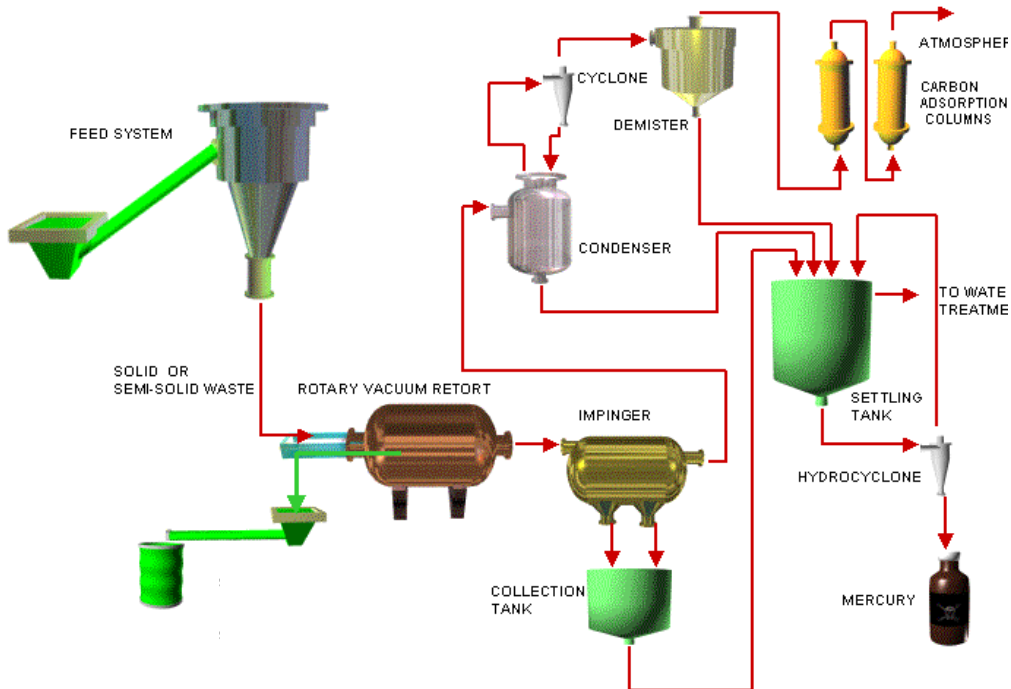


Fig. 3.9. Flow diagram depicting the SepraDyne separation process.

Once loaded, the retort is sealed and a vacuum of at least 25 in. of mercury is established. The retort is then set into rotation, and the burners are turned on to heat the outside of the retort. Heat is indirectly applied within an insulated firebox by an arrangement of burners fueled by natural gas, diesel oil, or propane. Electric heating can be employed in highly sensitive environmental settings. The waste is initially heated to remove the moisture. As the temperature of the mixed waste in the retort gradually increases, some of the substances present will volatilize. The lower-boiling-point substances will vaporize first as the temperature is increased. For instance, organics, water, sulfur, and then mercury will be sequentially transported out of the retort to the treatment and recovery system. The vapors diffuse out of the retort and are condensed in the cold-water impinger system. Because of the high-vacuum environment, no sweep gases are needed. Thus, virtually all volatilized substances are readily condensed to liquid.

Once the drying phase is complete, the retort temperature is raised to a target value, typically at temperatures in the range of 600 to 750°C, kept under a vacuum of at least 20 in. of mercury, and held at the target temperature for a set time. At this processing condition, any remaining organic compounds including heavy tars and all compounds of mercury are volatilized. Chemicals are separated from the condensed water through traditional wastewater treatment trains, and the water is discharged to an on-site water treatment system or sanitary sewer.

Combustion gases used to heat the outside of the retort are exhausted into the atmosphere. If electrical heating is employed, combustion gas emissions are eliminated. The activated carbon columns and subsequent HEPA filters remove any hazardous trace vapors that have passed through the impingers. Mercury is recovered from the impingers. The material in the retort is maintained for a predetermined process time at the target temperature until all of the contaminants of concern have been removed or

pyrolyzed. After the process sequence, the burners are turned off and the vacuum is released. The processed material is then unloaded into a receiving vessel.

3.6.2 Wastes Treated by SepraDyne

During remedial excavations of the Animal/Chemical Pits and the Glass Holes at BNL in the summer of 1997, waste was removed from 55 pits and subsequently sorted, characterized, and stored or shipped to a licensed disposal facility. Of the 440 yd³ of soil that was identified as a mixed waste, 100 ft³ was segregated into two B-25 boxes because it contained elevated concentrations of mercury. For the full-scale SepraDyne study, seven drums of radioactively contaminated soil and sludge (approximately 3004 lb) were treated. This material consisted of soils that were originally stored in the two B-25 boxes.

Although the major focus of the effort was to treat mercury-contaminated soils retrieved from the Chemical Holes as part of the DOE mercury treatment demonstration at BNL, several other mixed-waste streams were also treated using the vacuum thermal desorption process. These additional waste streams were chosen because BNL had not been able to find a company to process them or accept them for disposal.

The complete inventory of waste streams processed by SepraDyne (a total of 8057 lb) is listed below:

- 3004 lb soil—7 drums of soil for the demonstration,
- 4471 lb soil—8 additional drums of soil,
- 170 lb mixed-waste animal carcasses,
- 360 lb mixed, dry active waste,
- 42 lb spent resin, and
- 10 lb mixed-waste sand.

The physical composition of the soil was mostly sand and silt, with a small percentage of gravel and debris consisting of glass, metal, and plastic. Although the soils appeared to be significantly homogenized, a large majority of the drums were not sealed properly or were deemed defective. Of the original 15 drums, 12 of the drums contained soil that was extremely moist or sludgy or had at least 2 in. of standing water. As noted earlier, the composite characterization of the soil in the B-25 found total mercury concentrations of 6750 mg/kg and 18,000 mg/kg, respectively (see Table 3.1). Representative bin samples were also analyzed by TCLP methods and exhibited mercury concentrations of 3.56 mg/L and 0.26 mg/L, respectively. Because of the elevated mercury concentrations, the waste fell under the requirements for LDR treatment standards. In addition to the mercury, the two boxes were segregated on the basis of the predominant radioactive isotopes (²⁴¹Am or ¹⁵²Eu) that they contained.

The animal carcasses were also processed as part of the SepraDyne demonstration. These were transported to the demonstration site and reduced in volume to a size that could be readily fed into the retort. The carcasses were wrapped and sealed in plastic to prevent any spillage and cross contamination, and were typically shaped in a fashion similar to 3- by 6-in.-long sausages. Although a preprocess mercury analysis was not performed, the crushed animal bones and flesh contained much visible mercury. The radiological data pertaining to the animal carcasses is provided on Table 3.15.

The dry active waste consisted of three separate inventories. One lot of mixed dry active waste (approximately 100 lb) consisted of liners and plastics used as the original containers to contain the animal carcasses and for the follow-up carcass size-reduction efforts. The second inventory (approximately 55 lb) consisted mostly of mixed-waste plastic and cardboard pieces that were

collected and segregated during the BNL soil excavation process. The remaining 200 lb of material consisted largely of consumable materials (filters, resin, and protective clothing) that were used during the monitoring and operation of the treatment process.

3.6.3 Performance Results

The proof-of-principle bench-scale testing and the full-scale demonstration for the SepraDyne-Raduce process were conducted at BNL.

Bench-Scale Test

To establish process parameters for the BNL specific waste streams and to further demonstrate the effectiveness of its process on other waste forms, SepraDyne-Raduce performed several proof-of-principle testing protocols using a portable lab tabletop unit. The equipment used for protocol testing was similar in design and process parameter capability to the company's larger testing units. The tabletop unit was capable of treating up to 2 lb of material at batch process temperatures up to 815°C (1450°F), under a vacuum as high as 28 in. of mercury. The complete batch process, excluding cool-down time, typically required 3–4 h to complete. The following surrogate and actual waste streams were used to verify process parameters and treatment methodologies:

- uncontaminated test soil,
- chicken portions,
- americium- and mercury-contaminated soil, and
- europium- and mercury-contaminated soil.

The uncontaminated soils were initially treated to determine appropriate processing parameters for the treatment of the actual mixed-waste soils. This material was heated to a temperature of 650°C (1200°F) and held under a constant vacuum of at least 26 in. mercury for 30 min. Once the unit was verified to be in proper working order, two batches of mercury-laden americium- and europium-contaminated soils were treated. Tests of these soils were performed in similar fashion to those for the uncontaminated soil and provided the basis for the operating parameters chosen for the full-scale demonstration project. The mercury concentrations in the feed material for the americium- and europium-contaminated soil samples were found to be 5570 and 4190 ppm, respectively.

Once acceptable operating parameters were identified for the mercury-contaminated mixed-waste soils, SepraDyne-Raduce performed additional testing protocols for the potential treatment of animal carcasses. One test was performed with only chicken carcasses, while a second test used a mixture of chicken and mixed-waste soils similar to what was expected during the full-scale demonstration.

In each series of tests performed, the SepraDyne-Raduce process was able to achieve all of the proposed treatment goals. Results of specific demonstration trials are shown in Table 3.16. In all cases, significant reductions in the volume (40 to 92%) and weight (11 to 93%) of the final product were observed. The tumbling action of the retort during operations reduced all treated material to a fine powder. The final soil product was typically reduced in volume by 40% or greater.

Table 3.15. Radiological data for biological waste treated by SepraDyne-Raduce

Parameter	Concentration pCi/g
Gross alpha	21.1
Gross beta	186
^{239/240} Pu	4.17
²⁴¹ Am	4.23
⁹⁰ Sr	59.9
¹⁴ C	3.06

Table 3.16. Bench-scale test results for BNL wastes using SepraDyne-Raduce process

Parameter	BNL waste stream			
	Uncontaminated test soil	Chicken parts	Am/Hg soil	Eu/Hg soil
Pre-process weight (g)	272	98	990	995
Post-process weight (g)	241	6.7	890	881
% wt. reduction	11.2	93.2	10.9	11.5
Pre-process volume (mL)	250	250	800	800
Post-process volume (mL)	112	20	480	460
% vol. reduction	55	92	40	42.5
Pre-process total Hg (ppm)	—	—	5,570	4,190
Post-process total Hg (ppm)	—	—	7.77	3.3
% total Hg removal	—	—	99.86	99.92
Pre-process TCLP Hg (µg/L)	—	—	1,000	208
Post-process TCLP Hg (µg/L)	—	—	35.3	18.3
% TCLP Hg removal	—	—	96.4	91.2
% moisture	—	—	6.0	4.9
Total process time (min.)	135	55	455	310
Maximum process temp. (°C)	652	471	604	649
Minimum vacuum (in. Hg)	28	28	16.5	23.0

The leachable mercury concentrations in the americium- and europium-contaminated soils were reduced to levels near the new UTS (TCLP mercury levels below 0.025 mg/L), with one post-process sample above the UTS (at 0.0353 mg/L) and one below (0.0183 mg/L). Laboratory analysis confirmed that the total mercury removal efficiencies for these two soils averaged 99.89%. These results indicated that the UTS might be achievable; however, verification would be dependent on the large-scale demonstration results.

Full-Scale Demonstration

As part of the full-scale mercury treatment demonstration, the larger unit capable of processing 200-lb batches was relocated to the BNL site. For this demonstration, SepraDyne-Raduce treated seven drums of soils in 18 batch-processing runs. Three of the treated drums—A1, A3, and A5—contained mercury-contaminated soils having elevated concentrations of americium. The remaining drums—E3 to E6—also contained elevated levels of mercury but exhibited high concentrations of the europium isotopes $\text{Eu}^{152/154}$. Each test was performed in similar fashion to and under the same general operating conditions as the tests previously performed during the bench-scale studies. Each batch was heated to 650–700°C (1200–1292°F) and was held under a vacuum between 26 and 29 in. mercury. Once these optimum parameters were established, each batch was held at these conditions for an elapsed time of 10–20 min. The processed material was then allowed to cool to below 200°C (400°F) prior to unloading operations.

As the demonstration progressed, BNL officials permitted additional problematic waste material to be added to the soils. Mixed-waste animal carcasses were commingled and treated with soils from the

last four drums (A1, A5, E4, and E6) in a fashion similar to the demonstration protocol described above. Approximately 100 lb of animal carcasses and plastic wrapping were treated in the remaining 350 lb of the A5 and E6 inventory.

A total of 3050 lb of soils and waste carcasses were processed during the full-scale demonstration. All processed material and soils were reduced to a fine homogenous powder matrix, with a final product weight of approximately 2360 lb. The data show that the vacuum thermal desorption process was able to provide a final product with a 23% weight reduction. Through visual inspection, the reduction in the volume of the final product was estimated at approximately 40–50%.

The final waste form showed no visible traces of the animal carcasses or dry active waste. The total mercury concentration was reduced from initial levels in the feed material as high as 5510 ppm to levels in the residues below the demonstration goal of 10 ppm. TCLP levels were reduced from typical values in the range of 0.2 to 1.4 mg/L in the incoming feed stream to nondetectable levels in most cases, with the highest postprocess level being 0.0084 mg/L. Results of the pilot-scale demonstration are provided in Tables 3.17 and 3.18.

The SepraDyne-Raduce process met project goals established for this demonstration. Mercury was removed from each final product stream, with concentrations less than the proposed goals of 10 ppm total mercury and 0.025 mg/L of leachable mercury based on TCLP tests. Each final waste form exhibited a volume reduction of at least 25% in bench-scale testing (Table 3.16). A fine, dry granular product was produced, and even the worst-case mercury emissions ($29 \mu\text{g}/\text{m}^3$) were below the maximum achievable control technology (MACT) standard of $40 \mu\text{g}/\text{M}^3$. The secondary waste that was generated from equipment consumables (i.e., filters, cleaning equipment, and some protective clothing) was pyrolyzed and reduced in volume to a few percent of its original volume in subsequent batch processes.

Table 3.17. Pilot-scale test results for americium- and mercury-contaminated soil using the SepraDyne-Raduce process

Parameter	Drum A1	Drum A3	Drum A5
Total pre-process wt. (lb)	581	470	569
Soil	550	470	541
Carcasses	31	—	28
Post-process wt. (lb)	400	415	370
% wt. reduction	31.2	11.7	35.0
Pre-process Hg (mg/kg)	4040	2310	
Post-process Hg (mg/kg)	1.8	1.0	3.4
% Hg removal	99.96	99.96	—
Pre-process TCLP Hg (mg/L)	0.868	1.390	—
Post-process TCLP Hg (mg/L)	<0.0006	<0.0006	0.008
% TCLP Hg removal	>99.93	>99.96	—
Total process time (3 batches, min/batch)	240	318	237
Maximum process temp. (°C)	670	660	655
Minimum vacuum (in. Hg)	26	26	26

Table 3.18. Pilot-scale test results for europium- and mercury-contaminated soil using the SepraDyne-Raduce process

Parameter	Drum E3	Drum E4	Drum E5	Drum E6
Total pre-process wt. (lb)	367	398	342	379
Soil	367	375	342	329
E4 soil	—	—	—	30
Carcasses	—	23	—	20
Post-process wt. (lb)	333	180	300	360
% wt. reduction	9.3	54.8	12.3	5.0
Pre-process Hg (mg/kg)	4880	5510	—	—
Post-process Hg (mg/kg)	0.55	4.21	0.41	8.1
% Hg removal	99.99	99.92	—	—
Pre-process TCLP Hg (mg/L)	0.191	0.212	—	—
Post-process TCLP Hg (mg/L)	<0.0006	0.002	<0.0006	<0.0006
% TCLP Hg removal	99.69	99.06	—	—
Total process time (min/batch)	240 (2 batches)	175 (2 batches)	220 (3 batches)	180 (2 batches)
Maximum process temp. (°C)	730	690	700	690
Minimum vacuum (in. Hg)	26	26	26	26

Based on the results obtained from the full-scale demonstration, the remaining wastes, identified earlier, were then commingled (where appropriate) and treated. Thirty-one additional batch processes were performed to treat an additional 5032 lb of soils, carcasses, and dry active waste. These inventories, with their analytical results, are listed in Table 3.19.

Mercury Emission Data

The SepraDyne-Raduce demonstration unit contained an emissions monitor (Arizona Instruments model Jerome X431) installed on the process off-gas line and used to monitor mercury emissions during each batch operation. Furthermore, the system operations control program had an alarm function to notify the operator to shut down the system in its entirety if mercury emissions ever exceeded 75% of the allowed setpoint of 40 µg/m³. Mercury emissions were recorded at 15-min intervals for every process run. Optimum conditions for volatilization of mercury were predicted based on observations of the system temperature screens during processing. During processing of the 46 batches, emissions monitor readings at the optimum mercury volatilization stage averaged 1–14 µg/m³. In the majority of cases and usually throughout an entire process run, mercury readings were typically nondetectable to less than 10 µg/m³. The highest emissions level recorded during the demonstration was 29 µg/m³, which was still within the current MACT emission criteria. Table 3.20 summarizes mercury emissions, showing the peak and average values for each batch.

The SepraDyne demonstration achieved substantial reduction in mercury emissions over existing baseline processes, with emissions concentration levels below MACT. However, additional impact was obtained by the absence of a sweep gas, which resulted in much lower volumetric discharges than is typical for conventional, nonvacuum retort processes. SepraDyne-Raduce estimates that by mass, the total mercury emitted to the atmosphere during these tests is less than 0.05 lb of mercury per 10,000 tons of mercury-contaminated mixed waste processed.

Table 3.19. Processing results for additional problematic waste streams from the SepraDyne-Raduce demonstration

Drum ID	Waste stream	Weight (lb)		% wt. reduction	Post-process TCLP Hg (mg/L)	Post-process Hg (mg/kg) ^a
		Pre-process	Post-process			
A-6	Soil	525				
	Carcasses	27				
	DAW	<u>18</u>				
	Total	570	440	22.8	<0.0006	0.20
A-7	Soil	495				
	Carcasses	16				
	DAW	<u>18</u>				
	Total	529	350	33.8	0.0042	5.08
A-8	Soil	690				
	Carcasses	10				
	DAW	29				
	AE	<u>4</u>				
	Total	733	370	49.5	<0.0006	2.50
A-9	Soil	495				
	Carcasses	10				
	DAW	<u>10</u>				
	Total	515	—	—	<0.0006	1.14
E-7	Soil	245	225	8.2	<0.0006	2.06
RA2-090	Soil	990				
	AE	49				
	DAW	<u>24</u>				
	Total	1063	420	60.5	—	—
RA2-091	Soil	490				
	DAW	40				
	AE	<u>32</u>				
	Total	562	520	7.5	—	—
A-10	Soil	384				
	AE	18				
	Carcasses	5				
	DAW	18				
	RA2-091	<u>50</u>				
	soil	475	—	—	—	—
	Total					
Soil samples	Soil	157				
	DAW	35				
	Hg H ₂ O	<u>32</u>				
	Total	224	111	50.4	—	—
Mercury sludge	Sludge	302				
	DAW	61				
	Resin	42				
	Sand	<u>10</u>				
	Total	415	180	56.6	—	—

Table 3.19 (continued)

Drum ID	Waste stream	Weight (lb)		% wt. reduction	Post-process TCLP Hg (mg/L)	Post-process Hg (mg/kg) ^a
		Pre-process	Post-process			
All drums ^b	Soil	4471				
	Carcasses	68				
	DAW	253				
	Hg/H ₂ O	32				
	Resin	42				
	Sand	10				
	RA2-091	50				
	AE	103				
	Sludge	302				
	Total	5331	2616	39.7	—	—

Abbreviations: DAW = dry active weight; AE = americium or europium contamination.

^a Pre-process mercury analyses were not performed.

^b Only runs in which both pre- and post-processing weight data was obtained are included in the total weight reduction summary.

Table 3.20. Mercury emissions data from SepraDyne-Raduce demonstration

Drum	Batch	Hg concentration (μG/M ³)		Drum	Batch	Hg concentration (μG/M ³)	
		Av.	Max. ^b			Av.	Max. ^b
A1	1	8 (9)	28	E3	1	7 (6)	8
	2	10 (7)	19		2	7 (5)	11
	3	14 (6)	18	E4	1	12 (7)	16
A3	1	13 (8)	21		2	8 (8)	11
	2	14 (7)	29		3	8 (8)	10
	3	12 (10)	23	E6	1	8 (8)	14
A5	1	8 (9)	12		2	10 (9)	16
	2	13 (10)	16	E7	1	9 (6)	12
	3	9 (12)	12		2	8 (3)	9
A6	1	10 (6)	19	RA290	1	<1 (10)	4
	2	13 (9)	17		2	<1 (10)	4
	3	10 (12)	16		3	<1 (10)	3
A7	1	12 (10)	18		4	<1 (10)	3
	2	11 (6)	17	RA2 91	5	<1 (10)	5
	3	8 (3)	10		6	<1.0 (12)	<1
A8	1	<1 (10)	3		1	<1.0 (6)	<1
	2	<1 (10)	4		2	<1.0 (13)	<1
	3	<1 (12)	4		3	<1.0 (12)	<1
	4	<1 (10)	4	A10	1	<1 (8)	<1
A8/A9	1	5 (5)	7		2	<1 (10)	<1
	2	6 (9)	7		3	<1 (8)	<1

^a The mercury concentration is an average of all the data values obtained during the mercury volatilization phase. The numbers in parentheses indicate the number of data points. Values were obtained at 15-min intervals.

^b Maximum mercury concentrations occurred during the peak bake conditions.

4. COST ANALYSIS

All participants in the MER03 demonstrations were required by the SOW to submit a detailed life cycle cost analysis. The cost analysis was to be based on a full-scale treatment facility and was to include, at a minimum, the following elements:

- operating costs,
- capital costs,
- disposal costs,
- transportation costs, and
- material costs.

The cost analysis for each of the four vendors is presented and discussed below.

4.1 LIFE CYCLE COST ANALYSIS FROM VENDORS

4.1.1 BNL SPSS Process Costs

The 1-ft³ pilot-scale system tested by BNL can be operated as a fixed facility or deployed as a transportable process, depending on such issues as permitting, cost, and transportation risk. BNL plans to license the SPSS technology to a commercial vendor. Hence, potential processing locations are not known at this time. BNL expects that the technology could be implemented by a licensed vendor within 6 months to a year.

The pilot-scale unit is easily scaled up by a factor of 10, 32, 64, or 350. The 350-ft³ unit can provide the desired processing rate of 1000 lb/h. Capital costs depend on the size and number of process units deployed. For example, a unit with a capacity of 10 ft³ would cost about \$75,000, whereas a unit with a capacity of 350 ft³ would cost about \$250,000. Ancillary equipment (steam generator, chiller, feed system, off-gas system, monitoring, and controls) is an additional cost. Processing costs depend directly on reagent cost, which is approximately \$0.10/lb (\$200/T). One operator could operate the process; however, this cost analysis assumes two workers with oversight for added safety. The PPE required for operators is a negligible cost, consisting simply of gloves and lab coat.

Secondary waste costs are negligible because the approximately 0.3% mercury captured in off-gas condensate and activated charcoal can be recycled back through the process, so that ultimately, no secondary waste is generated. Table 4.1 summarizes the life cycle design and cost basis for the BNL process.

Table 4.1. Summary of life cycle design and cost basis for the BNL process

Parameter	Design and cost basis
Plant life	10 years
Operations	250 d/year, 5 d/week, 8 h/day
Throughput	1000 lb/h
Treatment process	SPSS
Capital costs	350-ft ³ -capacity unit, with ancillary equipment excluded
Operating costs	Reagents and materials; laborers, oversight, and management support
Disposal costs	\$1000/m ³ for solids
Decommissioning costs	\$30,000
Personal protective equipment	Negligible (purchase and disposal costs for gloves and lab coats)
Transportation	Not included

The estimated life cycle costs for the BNL process are \$2.30/kg, approximately 89% of which is for disposal of the final waste form. This cost excludes transportation costs, which are considered in Sect. 4.2 below.

4.1.2 NFS Stabilization Process Costs

NFS estimated life cycle unit costs for waste processed with a tiered approach. The tiered approach was based on four throughput rates, with 1000 lb/h as the maximum rate for treatment of mercury mixed waste. The life cycle design and cost basis are summarized in Table 4.2. Figure 4.1 illustrates the results of the life cycle model. The costs shown are estimates, which NFS believes to be conservative. Actual costs will depend on the homogeneity of the waste, the nature of the matrix being processed, and the presence of other hazardous constituents requiring treatment.

Table 4. 2. Summary of life cycle design and cost basis for the NFS process

Parameter	Design and cost basis
Plant life	10 years
Operations	250 d/year, 5 d/week, 8 h/d
Throughput	100, 250, 500, and 1000 lb/h
Treatment process	DeHg mercury stabilization
Capital costs	Engineering, equipment, construction, licensing, permitting, testing, and start-up
Operating costs	Labor, supplies, analytical, wastewater, utilities, depreciation, benefits, general and administrative, maintenance and repairs
Disposal costs	Not included
Decommissioning costs	Decontamination, decommissioning, waste disposition and required environmental restoration
Personal protective equipment	Negligible (purchase and disposal costs for gloves and lab coats)
Transportation	Not included

For the steady-state 1000 lb/h processing rate specified in the original solicitation for this work, the cost ranged from \$5.35 to \$6.93/kg for soils, sludges, and shreddable debris under 5 wt % in mercury concentration. These costs escalate to \$33–\$37/kg in the same mercury concentration range for processing rates averaging 10% of the specified steady state rate (100 lb/h). NFS also calculated costs for intermediate processing rates as well as for treatment of wastes containing differing concentrations of mercury. These costs estimates, which were produced by NFS, do not include either transportation or disposal of waste. Disposal costs are estimated to be an additional \$1.89/kg. Thus, for a 1000 lb/h facility processing soil-type wastes with less than 5 wt % mercury, the unit cost would be approximately \$8/kg, not including transportation costs.

4.1.3 ATG Stabilization Process Costs

The full-scale system tested by ATG is portable and well suited for homogeneous streams of liquid, sludge, or solid waste. Most waste streams of <50 m³ total volume can be processed by the mobile facility in 10 days or less by a crew of two.

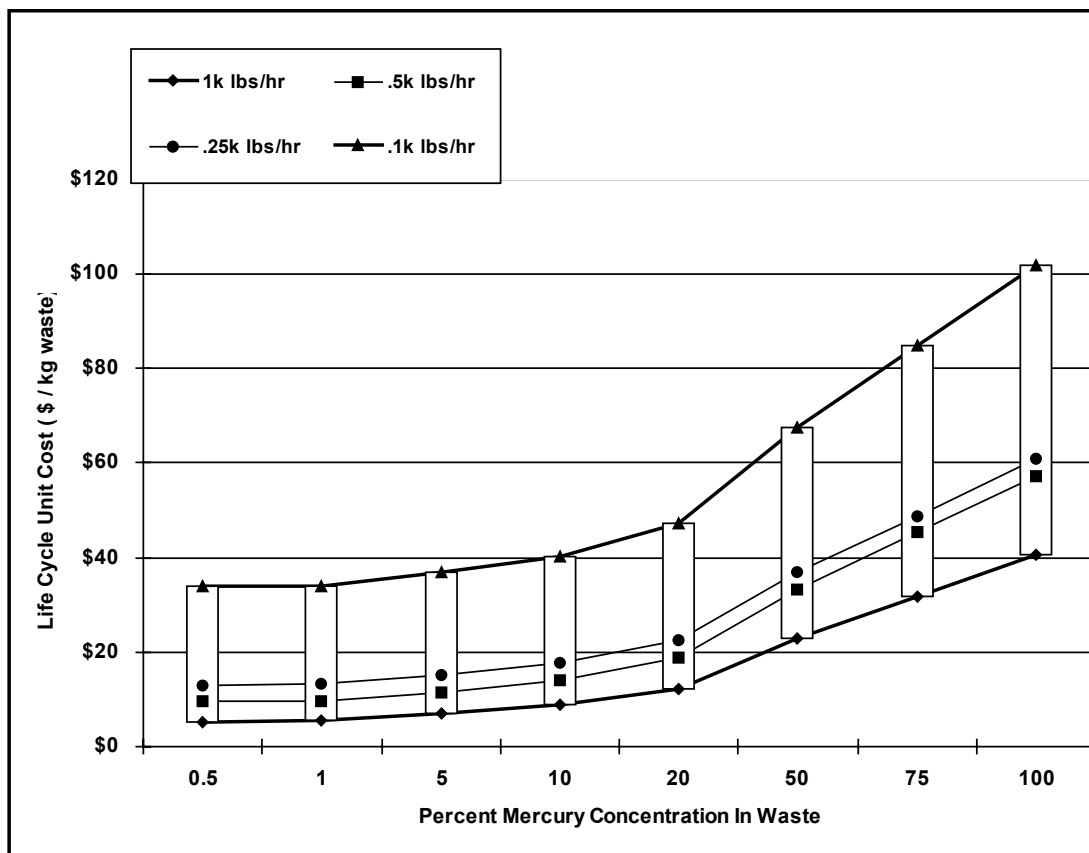


Fig. 4.1. Life cycle unit cost of treating mercury mixed waste.

ATG believes that no federal permitting is required for this transportable mercury stabilization system. Federal regulations allow on-site treatment of hazardous waste without a permit under certain conditions. Processing of lead-contaminated soils in a pug mill satisfied these conditions (EPA 1994), as should processing of mercury-contaminated mixed waste in a mortar mixer.

The small 7-ft³ mortar mixer used in the demonstration test is large enough for a full-scale (1000 lb/h) facility. A larger 9-ft³ mixer, however, would be more practical because of the reserve capacity it would provide. The 9-ft³ mixer also simplifies operational scheduling; thus, ATG prefers the larger mixer for a full-scale transportable facility.

In addition to the mixer, a transportable stabilization facility must also include a hazardous materials enclosure with an air treatment system and a hood. The air treatment system includes a HEPA filter and a carbon filter. The air treatment system and hazardous materials enclosure were described in a previous work plan (ATG 1997). The system described in that work plan also includes a separate hood and workbench for the conduct of treatability studies. Other required equipment items include a 1000-kg scale and a hand-operated forklift for raising and lowering drums. Total capital costs for the system are \$30,000.

Operating costs—which include two laborers, health and safety oversight, and management support—are in the range of \$100 per hour. Reagent and material costs are based on the concentration of mercury in the waste and are highly variable. The expected range is \$45–\$90 per ton for soil. This

cost estimate equates to \$0.40/kg at 1200 lb/h or \$2.40/kg at 100 lb/h, not inclusive of transportation, disposal, or permitting costs. Disposal costs are estimated to be \$1.91/kg. Thus, for a 1000 lb/h facility processing soil type waste, the unit cost would be approximately \$2.2/kg, not including transportation costs.

Table 4.3. Summary of life cycle design and cost basis for the ATG process

Parameter	Design and cost basis
Plant life	10 years
Operations	250 d/year, 5 d/week, 8 h/day
Throughput	1000 lb/h
Treatment process	Chemical stabilization
Capital costs	9-ft ³ mortar mixer, hazardous materials enclosure with air treatment system and hood, 1000-kg scale, hand-operated forklift
Operating costs	Reagent and materials; laborers, oversight, and management support
Disposal costs	\$1.91/kg
Decommissioning costs	Not included
Personal protective equipment	Negligible (purchase and disposal costs for gloves and lab coats)
Transportation	Not included

4.1.4 SepraDyne-Raduce Thermal Treatment Process Costs

The SepraDyne-Raduce cost estimate is based on a 1000 lb/h automated commercial vacuum thermal desorption unit complete with material load and unload equipment. In addition to the high-vacuum rotary retort and off-gas processing equipment, the unit also includes a hazardous materials enclosure, a 1000-kg scale, and a forklift to move drums.

Operating costs are estimated to be \$90 per hour. These costs include two operators, health and safety oversight, and management support. The life cycle and cost basis are summarized in Table 4.4.

Table 4.4. Summary of life cycle design and cost basis for the SepraDyne-Raduce process

Parameter	Design and cost basis
Plant life	10 years
Operations	250 d/year, 5 d/week, 8 h/day
Throughput	1000 lb/h
Treatment process	High-vacuum rotary retort
Capital costs	Processing equipment, air pollution control equipment, scale and forklift
Operating costs	Laborers, oversight, management support, and electricity
Disposal costs	Not included
Decommissioning costs	Not included
Personal protective equipment	Negligible (purchase and disposal costs for gloves and lab coats)
Transportation	Not included

Taking the capital costs of \$1.5 million, operating costs over 10 years at full operating capacity, and disposal costs of the associated waste streams, the life cycle cost is estimated to be \$2.00/kg, or

\$1.25/kg without waste disposal. Decontamination and decommissioning costs are not included. Capital costs are amortized over the life of the facility. The processed solids produced in the SepraDyne-Raduce process are dry and therefore suitable for supercompaction, which can further reduce the final waste volume sent for disposal.

For the 1000 lb/h processing rate specified in the original SOW, the cost is estimated at \$2.00/kg regardless of the waste form. The cost is not expected to increase significantly because of varying amounts, toxic organics, or mercury. In addition, the SepraDyne-Raduce process can treat other RCRA metals.

These cost estimates were based on the results of the demonstration and SepraDyne-Raduce's commercial operations experience. Actual costs will increase if the waste is exceptionally wet because increased processing time, electrical costs, and production of wastewater will be involved. However, worst-case cost estimates range up to \$2.50/kg at processing rates near 1000 lb/h or \$37.00/kg at 100 lb/h, inclusive of transportation costs.

4.2 COST ADJUSTMENTS FOR DISPOSAL AND TRANSPORTATION

As required by the SOW, each vendor provided estimates of the life cycle costs associated with use of their technology for treating the wastes in the demonstration. While similar bases were used to an extent, there were differences in the way cost calculations were made. Cost comparisons must be made on a similar basis; therefore, the cost estimations were normalized for a more accurate comparison. Cost elements that could be important but are not included in some of the unit costs noted in Sects. 4.1.1–4.1.4 are the following:

- chemical characterization of the waste streams, where needed;
- treatability studies to determine the stabilization formula, where applicable, including leach testing;
- treatment and disposal of secondary wastes;
- added labor costs due to a batch mode of operation;
- transportation of the waste to the disposal site;
- PPE procurement and disposal;
- dewatering the waste prior to stabilization, where necessary;
- wastewater treatment and disposal;
- utilities; and
- permitting.

Of these, the most important costs are likely to be transportation and disposal. Disposal costs vary depending on waste characteristics and the specific disposal site. However, an estimate of disposal costs can be made using a particular site, such as Envirocare of Utah, as a basis. Actual disposal cost rates might range between \$11 and \$33/ft³. For the purpose of comparing costs for the demonstrations reported here, a disposal cost rate of \$35/ft³ (nearly \$1000/m³) is assumed. Disposal cost projections were made to supplement the cost estimates provided by the vendor, where this information was not provided, based on the amount of final waste generated by a facility operating at 1200 lb/h.

Transportation costs are also variable, depending greatly on the distance of the treatment facility from the disposal site, the type of transport vehicle, and characteristics of the waste that determine how much can be shipped on each transport vehicle. For the transportation mode, we assumed shipment by truck. The cost per mile per truck is taken to be approximately \$2.00. Because none of the vendors

except ATG actually treat the waste at their facilities, the same distance (1000 miles) is assumed for each vendor.

Life cycle costs including disposal and transportation costs are shown in Table 4.5. The basis for the cost analysis shown in this table is as follows:

- system capacity: 545 kg/h (1200 lb/h)
- system runtime: 8 h/day, 5 days/week, for 10 years;
- total waste processed: 10.9×10^6 kg (24×10^6 lb)

As Table 4.5 indicates, the unit cost performance generally tracks transportation and disposal costs; however, capital and operating costs also have a significant effect. This behavior is summarized as follows:

- The life cycle per-unit cost is lowest for the SeptraDyne-Raduce high-vacuum rotary thermal process, which also includes stabilization of the secondary waste stream of elemental mercury. This is because the process has the largest volume reduction of the four technologies.
- The ATG stabilization process yields the next lowest unit cost, though its costs are only marginally lower than those for the next lowest vendor.
- The BNL SPSS process is next, with costs very close to those of ATG.
- The NFS stabilization process has transportation costs similar to those of BNL and ATG, and slightly lower disposal costs than ATG, but these factors are offset by substantially higher capital and operating costs.

Table 4.5 Life cycle costs for demonstrated technologies, including disposal and transportation costs

Vendor	Life cycle cost element (\$ millions)				Life cycle unit cost (\$/kg)
	Capital and operating ^a	Transportation ^b	Disposal ^c	Total ^d	
SeptraDyne-Raduce	3.83	3.26	15.61	22.70	2.08
ATG	2.86	4.75	22.76	30.37	2.78
BNL	4.82	4.60	22.00	31.42	2.88
NFS	65.38	4.70	22.46	92.54	8.48

^a Capital and operating costs are based on vendor-provided information.

^b Estimates of transportation costs are based on a shipping cost factor of \$2.00 per mile per truck. The number of trucks required was based on the volume of waste for disposal, which, in turn, depends on the amount of waste treated (assumed to be the same for all vendors) and the volume increase (or decrease) as a result of treatment. Distances are assumed to be the same for each vendor in this scenario.

^c Estimated disposal costs were based on a disposal cost factor of \$1,019/m³ at a facility such as Envirocare (Clive, Utah). The volume of waste for disposal was based on the amount of waste treated (assumed to be the same for all vendors), the volume change from treatment, and final waste form density. Pre- and post-process densities were calculated from vendor reports of volume and weight changes from processing of wastes.

^d The cost for D&D was estimated but appears to be an insignificant part of the total life cycle cost.

5. DISCUSSION OF RESULTS

5.1 PERFORMANCE

TMFA and HgWG are working with EPA to validate equivalent technologies for treatment of radioactively contaminated mercury wastes containing >260 ppm mercury that would treat this waste directly, as alternatives to RMERC and IMERC. A primary objective of the MER03 demonstrations was to evaluate alternative processes to RMERC and IMERC for DOE's legacy mixed waste. To that end, the BNL, NFS, ATG, and SepraDyne-Raduce processes were used to treat the wastes to meet a mercury TCLP treatment goal of 0.025 mg/L or less.

Table 5.1 summarizes the data generated by the four vendors. For SepraDyne-Raduce, the table summarizes the data for the four drums of soil treated.

Table 5.1. Summary of soil test data generated by four vendors

Drum ID	Pre-treatment			Post-treatment		
	Wt. (lb)	TCLP (mg/L)	Total Hg (mg/kg)	Wt. change (%)	TCLP (mg/L)	Total Hg (mg/kg)
<i>BNL SPSS process</i>						
A-4	450	0.914	5570	+53	0.0005	3640 ^a
E-1	280	0.208	4190	+54	0.00147	2720 ^a
<i>NFS DeHg process</i>						
A-2	387	1.5	4400	+17	0.0045 ^b	3760 ^a
<i>ATG stabilization process^c</i>						
E-2 ^d	220	0.282	4233	+33	0.0139	3170 ^a
E-2 ^e	220	0.282	4233	+44	0.0020	2940 ^a
<i>SepraDyne-Raduce vacuum thermal desorption process</i>						
A-1	550	0.868	4040	-27	Nondetect	1.8
A-3	470	1.390	2310	-12	Nondetect	1.02
E-3	367	0.191	4880	-9	Nondetect	0.545
E-4	375	0.212	5510	-52	0.002	4.21

^a Calculated on the assumption that no mercury is lost during the process.

^b Average of six batches.

^c ATG split drum E-2 and treated the soil with two different chemicals.

^d DTC treatment.

^e Sulfide treatment.

The demonstration results for the four vendors indicate that all are capable of meeting this treatment goal, as supported by the following findings.

BNL

- The pilot-scale SPSS system successfully treated soils at a waste loading of 60 wt % soils, with no increase in waste volume.
- While higher waste loadings may be possible, they would require engineering modifications of the process equipment due to viscosity limitations of the mixture.

- The waste forms produced easily meet both existing TCLP and more stringent UTS leaching criteria.
- According to BNL, results of an accelerated leach test (ASTM C-1308) for mixed-waste elemental mercury treated by the SPSS process indicated that diffusion is the predominant leaching mechanism. Extremely low leach rates were observed with diffusion coefficients ranging between 10^{-17} and 10^{-18} (11–12 orders of magnitude better than minimum leach rates recommended by NRC for radioactive contaminants).

NFS

- The DeHg process stabilized the mercury-contaminated mixed-waste BNL soils containing >260 ppm mercury to meet all UTS TCLP limits.
- The waste form produced was a damp, soil-like product with no freestanding water.
- Mercury lost through airborne evolution during the demonstration was estimated to be <0.06% of the original mercury input to the process.
- Treatment of the soil resulted in only about a 17% weight increase, with a corresponding volume increase of less than 12%.

ATG

- Bench-scale tests reproducibly stabilized >99.9% of the mercury initially present in the soil and met the UTS limit.
- Full-scale demonstrations reduced the mercury concentrations in soil extracts below the UTS limit of 0.025 mg/L with two different formulations. The DTC formulation achieved about one-half the UTS limit, or 0.013 mg/L, and the liquid sulfide formulation achieved less than one-tenth of the limit, or 0.0025 mg/L.
- The volume increase resulting from stabilization treatment was less than 20%. Some of the successful bench-scale formulations had no volume increase at all.
- The formulations also stabilized cadmium and lead, which were present in TCLP extracts above the UTS limits in the untreated soil.
- Full-scale demonstrations showed that a transportable stabilization and solidification system is suitable for on-site management of homogeneous streams of liquid, sludge, and solid wastes containing more than 260 ppm of mercury.

SepraDyne-Raduce

- The vacuum retort process used by SepraDyne removed and recovered mercury from mixed waste to produce a final dry product containing less than 10 ppm of total mercury and less than 0.025 mg/L leachable mercury (0.002 mg/L or less) based on TCLP tests.
- The final waste form was achieved with volume reduction efficiencies typically in the 25–40% range.
- The final product was in the form of a dry, granular material regardless of the feed matrix. Pretreatment may be needed for the purpose of size reduction.
- The effectiveness of the process was found to be independent of the initial waste form and the mercury concentration.
- The secondary waste generated from equipment consumables and operator PPE are pyrolyzed or volume-reduced in the high-vacuum high temperature rotary retort.

The successful demonstrations described here provide strong support for the designation of stabilization and high-vacuum rotary retort as the best demonstrated and available technologies (BDATs) for wastes containing >260 ppm mercury. Once these technologies are designated as BDAT

for these wastes, RCRA Part B permits should not be required to stabilize or retort mercury in mixed waste at the point of generation or long-term storage.

5.2 COST

Life cycle costs for the four technologies demonstrated were presented earlier in Table 4.5. With the exception of NFS, disposal costs were the most significant element of the life cycle cost, averaging 70% of the total life cycle cost. Capital and operating costs, together, and transportation costs made up the remainder, each accounting for approximately 15% of the total life cycle cost based on the transportation distance of 1000 miles. Decontamination and decommissioning costs are not shown, but they constituted less than 1% of the cost in each case.

As shown in Table 4.5, the unit cost performance follows the same trend as that for the volume change during processing, with one exception. As the transportation distance increases, so too does the significance of volume changes in affecting the overall costs. This behavior is summarized as follows:

- The SeptraDyne-Raduce high-vacuum rotary thermal process yields the lowest unit cost, with stabilization of secondary waste stream of elemental mercury accounted for.
- The ATG stabilization process is next, but only slightly better than the next vendor.
- The BNL SPSS process is next.
- The NFS stabilization process achieves the highest waste loadings of the stabilization processes, but this is offset by higher capital and operating costs.

6. SUMMARY AND CONCLUSIONS

Using similar wastes, the four vendors in the MER03 campaign demonstrated four different processes for treating mercury-contaminated wastes with mercury concentrations >260 ppm: three stabilization processes and a thermal treatment process. Experiments were conducted from bench scale (up to 1-kg batches) to pilot unit scale. All four processes performed satisfactorily in that achievement of the UTS was demonstrated with each process. Table 6.1 summarizes the demonstrations and findings for the four vendors.

Waste loadings ranged from 60 to 85%, with NFS achieving the highest waste loadings of the stabilization processes, with commensurate waste volume increases. The SeptraDyne-Raduce thermal treatment process removed mass during treatment that would require stabilization (amalgamation for elemental mercury), yet still achieved an overall reduction in the final waste volume generated. All four processes resulted in manageable waste forms, from dry or moist powder to a solid, monolithic puck, and are suitable for commercialization.

Cost estimates ranged from about \$2.08/kg to \$8.48/kg, with SeptraDyne-Raduce showing a cost advantage over the stabilization processes. These results are highly variable as a function of the distance that waste must be shipped for disposal (related to where the processing site is located) and the volume of waste generated. High capital costs, such as for processes that do not use conventional or off-the-shelf technology, can be a factor in the total cost of treatment.

These TMFA and HgWG demonstrations have produced instrumental data that EPA can use to validate equivalent technologies, as alternatives to RMERC and IMERC, for direct treatment of radioactively contaminated mercury wastes containing >260 ppm mercury. In addition, the demonstration was used to evaluate alternative processes to RMERC and IMERC for DOE's legacy mixed waste. Four alternative processes—those of BNL, NFS, ATG, and SeptraDyne-Raduce—are now available for treatment of wastes to meet a mercury TCLP treatment goal of 0.025 mg/L or less.

Table 6.1. Comparison of mercury treatment technologies

Comparison factor	BNL stabilization/ solidification process	NFS DeHg stabilization process	ATG stabilization process	SepraDyne-Raduce thermal treatment process
Waste type tested ^a	Soil and elemental Hg from BNL restoration activities	Soil from BNL	Soil from BNL	Soils and animal carcasses from BNL
Process mechanism	Chemical stabilization and physical encapsulation based in a 1-ft ³ (0.028 m ³) blender/dryer with screw mixing	DeHg reactor with 45-kg capacity for soil and reagents housed in ventilated structure	Modified mortar mixer with capacity of 7 ft ³ (0.20 m ³) in a hazardous materials enclosure equipped with an air treatment system	High-temperature high-vacuum rotary retort
Scale of bench test	Bench-scale testing completed previously	None needed because of prior experience	1.0-kg bench tests performed	1-kg bench tests performed
Scale of demonstration	25- to 50-kg batches	25-kg batches	60- to 80-kg batches	75-kg average batch size
Final waste form performance	Successfully stabilizes/encapsulates soils at waste loadings averaging 60%	Successfully stabilizes to pass TCLP and UTS for Hg at waste loadings of 85.5%	Successfully stabilizes to pass TCLP and UTS for Hg at waste loadings averaging 72.2%	Removes Hg to below 10 ppm; meets TCLP and UTS for Hg with mass removals of 9–52%
Volume reduction factor ($V_{\text{Final}}/V_{\text{Initial}}$)	1.0	1.13	1.14	0.78 ^b
$(W_{\text{Final}}/W_{\text{Initial}})$	1.54	1.17	1.39	1.22 ^b
Stabilization process (as applicable)	Patented process uses sulfur and polymer to produce an amalgam encapsulated in a solid matrix	Uses proprietary formulation of additives and EPA-prescribed agents	Uses either dithiocarbamates or a liquid sulfide in proprietary formulations	Amalgamation of elemental Hg recovered as secondary waste stream during thermal processing
Effect of contaminants on the process	Drying to remove excess H ₂ O is a normal step in processing; other contaminants not addressed	No adverse effects reported; H ₂ O not a problem as process has been applied to wastewaters	H ₂ O used in bench-scale (21%) tests and demonstrations (7–10%); other contamination not addressed	Removed all volatiles and pyrolyzes organic compounds, independent of contaminant level
Life cycle cost for a 1200 lb/hr (545 kg/hr) facility ^c	\$2.88/kg (\$ 3,500/m ³)	\$8.48/kg (\$10,300/m ³)	\$2.78/kg (\$ 3,400/m ³)	\$2.08/kg (\$ 2,540/m ³)

Table 6.1 (continued)

Comparison factor	BNL stabilization/ solidification process	NFS DeHg stabilization process	ATG stabilization process	SeptraDyne-Raduce thermal treatment process
Waste acceptance criteria, subject to meeting underlying hazardous constituent (UHC) EPA requirements	Previous testing of SPSS waste forms has indicated favorable performance under anticipated disposal conditions.	Waste form meets current WAC at Envirocare (subject to determination of equivalent treatment by EPA)	Waste form meets current WAC at Envirocare	Meets EPA disposal requirements for >260 ppm Hg wastes; meets WAC for Hg at Envirocare
Physical characteristic of final waste form	Solid, monolithic puck	Cakelike with no standing water	Low-slump soil/cement	Fine, leach-resistant, fixable powder (except recovered mercury)
Summary of assessment	Effective stabilization process with competitive cost characteristics	Effective stabilization process, but more costly than other processes compared here; leach performance successfully demonstrated for multiple UHCs; all formulations proprietary	Effective stabilization process; achieves high waste loadings with some small generation of secondary waste; uses some proprietary reagents	Effective, economical removal and recovery process; produces volume decrease; secondary treatment of recovered mercury required

^aSoils contained 4400 mg/kg Hg (principally elemental Hg), plus leachable Cd and Pb.

^bAfter secondary waste treatment.

^cUnit costs are based on pre-process weights and volumes. NFS achieved higher waste loadings than BNL and so generated less waste for final disposal, by weight. However, BNL achieved higher densities in the final waste form; thus, disposal costs (based on volumes) for BNL and NFS were similar. The higher capital and operating costs for the BNL process result in higher unit cost for BNL. The high capital and operating costs of the NFS process, as compared to that of the other processes, result in the highest unit cost. The lower waste volume generated by the SeptraDyne-Raduce process makes this process the most favorable by unit cost.

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