

**DEVELOPMENT AND SELECTION OF TECHNOLOGIES FOR
MERCURY MANAGEMENT ON U.S. DEPARTMENT OF ENERGY SITES:
THE MER01–MER04 AND MERCURY SPECIATION DEMONSTRATIONS**

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ABSTRACT

The U.S. Department of Energy's (DOE's) Transuranic and Mixed Waste Focus Area (TMFA), funded from fiscal year (FY) 1996 through FY 2002, was tasked with finding solutions for the mixed waste treatment problems of the DOE complex. During TMFA's initial technical baseline development process, three of the top four technology deficiencies identified were the need for amalgamation, stabilization, and separation/removal technologies for the treatment of mercury-contaminated mixed waste. The Mercury Working Group (HgWG), a selected group of representatives from DOE sites with significant mercury waste inventories, assisted TMFA in soliciting, identifying, initiating, and managing efforts to address these areas. Solicitations and contract awards were made to the private sector to demonstrate both the amalgamation and stabilization processes using both actual mixed wastes and surrogate samples. The goal was to develop separation and removal processes that will meet DOE's needs. This paper discusses the technology selection process, development activities, and the accomplishments of TMFA through these various activities.

INTRODUCTION

Mercury is a big problem for the U.S. government. Virtually every U.S. Department of Energy (DOE) facility in the United States has mercury-contaminated wastes. DOE's Transuranic and Mixed Waste Focus Area (TMFA) estimated that the following quantities exist on the more than 70 DOE sites (1):

- approximately 16 m³ of liquid elemental mercury,
- approximately 6000 m³ of mercury wastes contaminated with <260 ppm mercury, and
- approximately 38,000 m³ contaminated with ≥260 ppm mercury and with radionuclides.

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. 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.

Mercury-contaminated low-level radioactive waste (LLW) is considered mixed waste—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)—and it is therefore regulated by both the U.S. Environmental Protection Agency (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 requirements for treatment of such wastes to satisfy the requirements of RCRA are summarized in Fig. 1. Specifically:

Waste as elemental mercury—RCRA identifies amalgamation as the treatment standard for elemental mercury contaminated with radioactive materials. This is also the required treatment for radioactively contaminated mercury condensates from retorting processes. In addition, incineration and retorting processes that produce residues with >260 ppm of radioactively contaminated mercury and that fail the RCRA toxicity characteristic leaching procedure (TCLP) limit for mercury (0.025 mg/L beginning in the year 2000) require retorting, followed by amalgamation of the condensate (2).

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 retorting 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. Retort 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—Incineration or retorting is the treatment standard for hazardous wastes with mercury contaminant concentrations ≥ 260 ppm and RCRA-regulated organic contaminants (other than incinerator residues). Inorganic wastes containing mercury concentrations ≥ 260 ppm, including incinerator and retort residues, are to be treated by retorting. If waste containing ≥ 260 ppm mercury is also radioactive (i.e., mixed waste), the recovered elemental mercury cannot be recycled and must therefore be amalgamated prior to disposal.

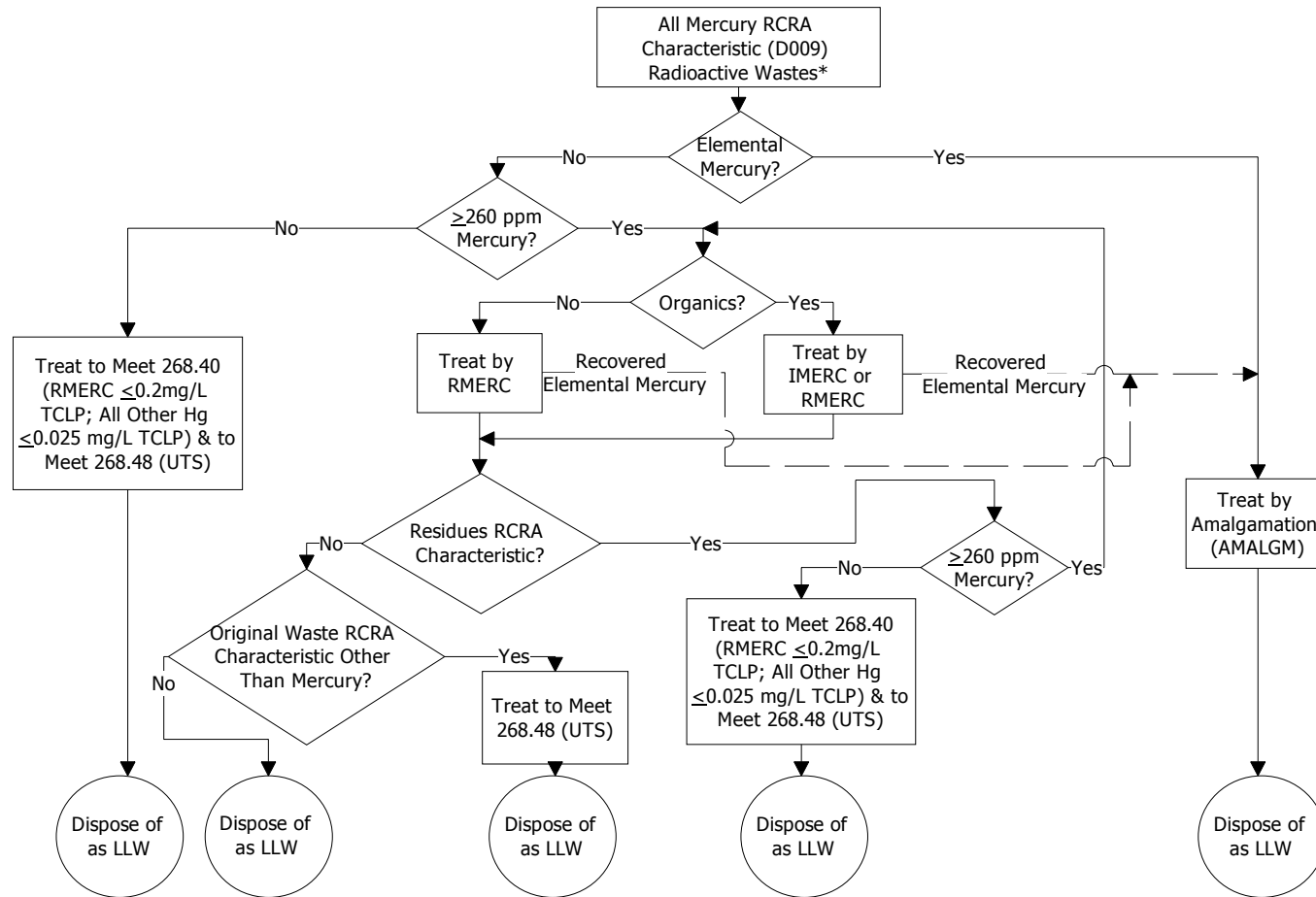
DOE'S MER CAMPAIGN

In 1996, DOE's TMFA (then known as the Mixed Waste Focus Area, or MWFA) examined the status of technologies available to treat mercury-contaminated mixed wastes. TMFA found technology deficiencies in all the treatment techniques (amalgamation, mercury stabilization, and separation/removal). As a result, TMFA, in conjunction with EPA, initiated four technology demonstration campaigns with the goal of demonstrating the effectiveness of newly developed technologies:

- 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
- MER04—Demonstration of the stabilization process for treatment of surrogate mercury sludge wastes containing >260 ppm mercury

TMFA issued solicitations to industry for the MER01 demonstration campaign in November 1996, for MER02 in January 1998, for MER03 in February 1999, and for MER04 in January 2001 to identify vendors with technologies that could be used to overcome the deficiencies in existing treatment

Mercury RCRA Characteristic (D009) Radioactive Wastes Treatment Logic Diagram



UTS: Universal Treatment Standards

RMERC: Technology standard retort or roasting

IMERC: Technology standard incineration for wastes containing organics

*Excluding hydraulic oils and high level waste from processing fuel rods.

Fig. 1. Logic chart showing treatment and performance requirements needed to satisfy RCRA for mercury-contaminated radioactive wastes.

approaches. The goal of the campaigns was 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.

Although the chemistry of amalgamation is well known, the practical engineering of a sizable amalgamation process had not been tested (3). 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, it 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.

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

Table I. Participants in DOE's MER Demonstrations

Vendor	MER01	MER02	MER03	MER04	Treatment process
ADA Technologies	X			X	Sulfur process
Allied Technology Group (ATG)		X	X	X	DTC formulation (02); DTC and liquid sulfide reagents (03); NaSH formulation (04)
Brookhaven National Laboratory (BNL)			X	X	Sulfur polymer stabilization / solidification (SPSS)
GTS Duratek		X			Cement-based grout
Nuclear Fuel Services (NFS)	X	X	X	X	DeHG process; different equipment in 01 demonstration
SepraDyne-Raduce			X		High-vacuum rotary kiln thermal desorption

Because the final waste form must be suitable for disposal, the participants were 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 the characterization, certification, transport, and disposal at Envirocare of Utah of all treated wastes and secondary wastes generated from the demonstration. Detailed findings and results of all four campaigns have been reported in Innovative Technology Summary Reports and other reports (4–11). The results of the four technology demonstrations are summarized in the sections that follow.

MER01 DEMONSTRATIONS: AMALGAMATION OF ELEMENTAL MERCURY

At least 19 DOE sites have bulk elemental mercury contaminated with radionuclides in their storage facilities. In previous years, several treatability studies and other development efforts related to amalgamation of mercury wastes have been performed throughout the DOE complex. These studies have used various materials to stabilize mercury. However, until the MER01 demonstration, no studies beyond bench scale had been conducted. Consequently, the primary technical issue associated with the amalgamation of mixed waste mercury was related to scale-up of the process to a cost-effective operations level.

After issuing the MER01 request for proposals to industry in November 1996, TWFA selected two vendors—ADA Technologies, Inc., and Nuclear Fuel Services, Inc. (NFS)—to demonstrate the technical feasibility of using amalgamation on a large scale. To eliminate the existing DOE inventory in a reasonable time frame, scalable equipment is needed that can

- produce waste forms that meet the EPA definition of amalgamation,
- produce waste forms that pass the EPA TCLP limit of 0.20 mg/L,
- limit mercury vapor concentrations during processing to less than the Occupational Safety and Health Administration's (OSHA's) 8-hour worker exposure limit for mercury ($50 \mu\text{g}/\text{m}^3$), and
- perform the above economically.

ADA Technologies Amalgamation Process

ADA Technologies and its subcontractors demonstrated a process for stabilizing radioactively contaminated elemental mercury with sulfur. The process combines and mixes waste mercury with sulfur in a commercially available pug mill to produce a stable mercury sulfide product. Initial testing was performed on surrogate waste, followed by demonstrations on two actual mixed waste streams.

ADA's treatment of liquid mercury involves adding powdered sulfur and mercury to the pug mill. As the mill continues to mix and reactions take place, additional chemicals are added. The temperature of the mixture is monitored, and samples are taken periodically and analyzed for free mercury. Processing is performed at ambient conditions without the addition of heat. Water vapor and heat are evolved during processing. Room air is swept over the pug mill and then filtered to remove mercury vapors from the mixing area. The pug mill is manually decontaminated after processing each waste stream.

ADA's sulfur treatment process was successfully demonstrated. By use of a proprietary additive mixture the process achieved a >99.9% completion of reaction and met vapor pressure requirements (12). The final waste product consistently achieved TCLP results below 0.1 mg/L. The pug mill was shown to be well-suited to the process because of its ability to adequately mix the components and control the residence time to ensure complete reaction. Moreover, the process demonstrated the use of a commercially available mixer. Radioactive contamination control requirements were readily implemented using the pug mill. This process is easily scalable to match the treatment needs at individual DOE sites. Finally, the product satisfies EPA's definition of an amalgam as given in 40 CFR 268.42, Table 1, meeting disposal requirements outlined in RCRA.

Details about the ADA demonstration of amalgamation are available in Ref. 4. The ADA process has now been installed at the Perma-Fix facility in Oak Ridge, Tennessee, and is being used to treat mixed waste containing elemental mercury.

NFS Amalgamation Process

NFS, located in Erwin, Tennessee, demonstrated its proprietary DeHg™ (de'-merk) process. The DeHg process is capable of converting mercury-containing mixed waste of various matrices and chemical species to nonhazardous final waste forms. DeHg was developed to treat mercury mixed waste containing not only elemental mercury, but also ionic and complexed forms of mercury. NFS received bulk elemental-mercury mixed waste streams from three different sites for the amalgamation demonstration.

The DeHg process as applied to elemental mercury consists of two steps. The amalgamation unit addresses the elemental forms of mercury within the waste. The second chemical processing unit is used, if necessary, to stabilize mercury compounds or complexed forms of mercury. The solid waste form produced by this treatment train is leach-tested and then either disposed of (if it passes TCLP) or passed back to the amalgamation step (if it does not). Any liquid remaining after stabilization is either recycled or treated before disposal. More information about the process has been reported elsewhere (13).

All the final waste forms produced through the DeHg process appeared to be acceptable for disposal. The new leaching standard for mercury (a Universal Treatment Standard [UTS] of 0.025 mg/L) was also met in many instances. The key results of the demonstration were as follows:

- The process met land disposal restriction requirements and, in some cases, the UTS for the radioactively contaminated mercury wastes processed.
- Mercury waste loadings of 20 to 25 wt % were achieved.
- Ambient-temperature processing was used to minimize the formation of mercuric oxide.
- The process is readily scalable to match the treatment needs at individual DOE sites.
- The final waste product satisfies EPA's definition of an amalgam (40 CFR 268.42, Table 1), meeting requirements outlined in RCRA.
- Because the process uses metal for amalgamation of elemental mercury, the vapor pressure was the same as for the elemental mercury before treatment.

Details about the NFS demonstration of amalgamation are available in Ref. 5.

MER02 DEMONSTRATIONS: STABILIZING MERCURY-CONTAMINATED (<260 PPM) MIXED WASTE

At least 26 DOE sites have mixed LLW containing <260 ppm mercury on site. While EPA does not require removal of the mercury from the waste at these levels of contamination, RCRA regulations require that leachate from such wastes not exceed a TCLP mercury concentration of 0.20 mg/L. If the mercury concentration in the leachate exceeds this level, steps must be taken to ensure that the treated waste does not leach mercury in excess of 0.025 mg/L. Thus, TMFA was interested in stabilization techniques for such wastes. Not only were these methods required to meet treatment standards, but they also had to be feasible in terms of economics, operability, and safety.

TMFA supported three demonstrations—by Allied Technology Group (ATG), GTS Duratek, and NFS—in response to the MER02 request for proposals, to determine commercial capabilities for stabilizing mercury-contaminated waste. ATG and NFS treated an ion exchange process stream from the DOE Portsmouth, Ohio, facility. GTS Duratek treated a waste stream consisting of sludge and laboratory residues from Los Alamos National Laboratory (LANL). The goal of the demonstrations was to demonstrate the effectiveness of these three technologies in stabilizing mercury and other RCRA metals in the mixed waste specimen to UTS limits.

ATG Stabilization Process (<260 ppm Mercury)

Building on the results of a companion bench-scale study (14), ATG conducted a demonstration with full-scale stabilization equipment at Mountain States Analytical Laboratory in Salt Lake City. The demonstration showed that a dithiocarbamate (DTC) formulation can produce a stabilized waste that satisfies the UTS limits for mercury. ATG performed seven bench-scale tests and then processed three full-scale batches. In these runs, DTC formulations reproducibly stabilized over 99% of the mercury initially present at 40 times the UTS limit. The volume increase resulting from stabilization was small (16% of the untreated waste volume). The DTC formulation also stabilized barium, cadmium, and chromium.

The full-scale demonstration showed that ATG's transportable stabilization and solidification system is suitable for on-site management of homogeneous streams of liquid, sludge, and solid wastes containing mercury. The process stabilized the mercury-contaminated mixed waste specimen to meet all UTS TCLP limits.

Other key results of the demonstration were as follows:

- The waste form produced was a damp paste, with no freestanding water.
- Small but significant increases in volume were obtained, in most cases 10–25%.
- Secondary waste is expected to amount to 10–20 lb of dunnage per day of full-scale operation.
- Life cycle costs are estimated at less than \$2/kg, not including transportation and disposal of final waste. No significant decommissioning and site restoration costs are expected.

For wastes containing more than a few percentage points of water, improved water management presents the greatest potential for minimizing life cycle costs. Dewatering reduced the volume of stabilized ion exchange waste by 80%, with proportional reductions projected for the cost of treating, transporting, and disposing of the waste. A full description of the ATG stabilization demonstration can be found in Ref. 6.

GTS Duratek Stabilization Process (<260 ppm Mercury)

The GTS Duratek demonstration was performed on ~568 kg of sludge containing radionuclides, heavy metals, and RCRA-listed organic compounds from LANL. The study, conducted at the GTS Duratek facility in Oak Ridge, Tennessee, in 1997–98, evaluated the bench-scale performance of Portland cement–based grout to stabilize two different loadings of waste. The goal was to generate a disposable waste form that meets the Envirocare WAC and RCRA land disposal restrictions (LDR).

Solidification tests performed at low and high waste loadings resulted in stabilization of mercury to meet the UTS of 0.025 mg/L at the low loading and for two of the three runs at the high loading. The third high-loading run, however, had a TCLP of 0.0314 mg/L. In this run, levels of organic compounds, including some pesticides, were discovered to be much higher than originally reported—in some instances by an order of magnitude or more. Levels of some radionuclides were also much higher than initially reported.

These two important factors pose serious challenges to stabilization efforts, and pretreatment (for example, thermal pretreatment to remove or reduce organic compounds) is probably necessary for such wastes. Because of the initial characterization of the waste, the need for pretreatment was not anticipated. Although a formulation that will successfully treat higher radionuclide levels in the waste is feasible, the grout formulations developed for this demonstration were based on the initial, inaccurate characterization data.

Since the final waste form was not in compliance with Envirocare requirements, it could not be disposed of at Envirocare and was returned to LANL for long-term storage. Because of the need for further development to match treatment process with actual waste characteristics, volume increases, secondary waste expectations, and life-cycle costs were not estimated for the GTS Duratek process. A full description of the GTS Duratek stabilization demonstration can be found in Ref. 7.

NFS Stabilization Process (<260 ppm Mercury)

NFS demonstrated its DeHg process to stabilize mercury and other RCRA metals in the 30-kg mixed-waste specimen to meet UTS limits. Initial TCLP tests showed leachate mercury concentrations well above the UTS limit (0.49 mg/L). Scoping tests with 1-kg quantities of resin were conducted to identify optimal processing parameters. TCLP results for the scoping tests indicated that a mercury level of <0.005 mg/L could be achieved. Two demonstration runs with 14-kg quantities of resin were then performed. The first run met UTS criteria for all contaminants except for chromium, which was present in concentrations of 1.2 mg/L. The failure to meet the test criterion for chromium was attributed to the presence of chromium in the native resin water used to perform the tests. The second demonstration run used a modified method for stabilizing the chromium, and all UTS criteria were met.

NFS successfully stabilized the mercury-contaminated mixed waste specimen to meet all UTS TCLP limits. As with the ATG demonstration, the waste form produced was a damp paste, with no freestanding water. No significant volume increase was observed. A full description of the NFS stabilization demonstration can be found in Ref. 8.

MER03 DEMONSTRATIONS: STABILIZING MERCURY-CONTAMINATED (≥ 260 PPM) MIXED WASTE

The requirements for treating radioactive wastes containing ≥ 260 ppm of mercury are as follows:

- For hazardous wastes with mercury contaminant concentrations ≥ 260 ppm and RCRA-regulated organic contaminants (other than incinerator residues), incineration or retorting is the treatment standard.
- For inorganic wastes with mercury contaminant concentrations ≥ 260 ppm, including incinerator and retort residues, retorting is the treatment standard.

The MER03 campaign had three major objectives. The first was to evaluate alternative processes to retorting and incineration for DOE's legacy mixed waste. To that end, the processes were to treat the wastes to meet a treatment goal of ≤ 0.025 mg/L of mercury in the TCLP leachate. The second objective was to provide EPA with data to compare proposed new analytical protocols with the standard TCLP methodology. EPA will use these comparisons to rewrite the mercury-related RCRA regulations. Finally, TMFA wanted to evaluate an improved retort process in comparison with the stabilization process.

Four vendors were selected in response to the MER03 solicitation. These vendors and their processes were as follows:

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

All vendors performed testing on the same waste samples. The first three vendors demonstrated stabilization processes to provide data on the applicability of stabilization to waste with a high mercury content (> 260 ppm). The vacuum thermal desorption process demonstrated by the fourth vendor, SepraDyne-Raduce, was intended to demonstrate an improved form of the baseline technology of retort. The SepraDyne-Raduce technology demonstrated removal of mercury from mixed waste sources with mercury concentrations up to 6000 ppm. All four vendors were successful in performing the demonstrations, in that the demonstrations were on schedule, within budget, and met the treatment goals, as noted below. The MER03 technology demonstrations are described in detail in Ref. 15.

In addition to leach testing by the standard TCLP methodology, the final waste forms from the MER03 demonstration underwent vapor pressure and leach testing at ORNL according to the

Kosson analytical protocols. (The Kosson protocols are described in Ref. 16.) The results from the Kosson analyses differed from the results indicated in standard TCLP methods, as noted in Refs. 17 and 18.

ATG Stabilization Process (≥ 260 ppm Mercury)

ATG demonstrated its chemical stabilization process on a one-drum sample of contaminated mixed-waste soils containing high concentrations (~ 5000 ppm or mg/L) of mercury and liquid elemental mercury but used two different formulations to stabilize the waste (19). The untreated soil received from BNL contained ~ 4000 mg/kg of total mercury, and leachable mercury concentrations exceeded the UTS limit by more than tenfold. Full-scale tests were conducted with a 7-ft³ mortar mixer using 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. The average for waste loadings was 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 above UTS limits in TCLP extracts from the untreated soil. Life cycle costs were estimated at \$2.78/kg, a figure that includes disposal and transportation costs.

BNL Stabilization Process (≥ 260 ppm Mercury)

BNL demonstrated the application of a newly developed pilot-scale sulfur polymer stabilization/solidification (SPSS) process on the same soil treated by ATG (20). 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 (~ 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. Life cycle costs, including disposal and transportation, were estimated at \$2.88/kg.

NFS Stabilization Process (≥ 260 ppm Mercury)

NFS demonstrated its DeHg mercury stabilization process on samples of the same soil that was treated by BNL. 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. NFS used the pilot-scale reactor used previously for wastes containing < 260 ppm mercury; this reactor 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 < 0.125 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. Estimated life cycle costs, including disposal and transportation, were \$8.48/kg.

SepraDyne-Raduce Desorption Process (≥ 260 ppm Mercury)

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 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 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 from 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. Life cycle costs, including disposal and transportation, were estimated to be \$2.08/kg.

MER04 DEMONSTRATIONS: STABILIZING MERCURY-CONTAMINATED (>260 PPM) SURROGATE SLUDGE WASTES

The MER04 campaign was conducted to provide additional data on the treatment of mercury-contaminated soils and sludges, and focused on stabilization of a surrogate waste sludge with high levels of mercury contamination (~ 5000 mg/kg).

The MER04 demonstration had three major objectives. As in the MER03 campaign, the first objective was to evaluate alternatives to retorting and incineration, and the second was to treat a high-mercury waste to meet the TCLP treatment goal of 0.025 mg/L or less. The third objective was to provide EPA with treated waste forms that EPA would test to again compare the results from proposed new analytical protocols with those from the standard TCLP methodology. These comparisons will be used by EPA in its efforts to revise the LDR treatment standards for mercury-bearing hazardous wastes.

In this demonstration, four vendors—ADA Technologies, Allied Technology Group (ATG), Brookhaven National Laboratory (BNL), and Nuclear Fuel Services (NFS)—treated a nonradioactive surrogate waste sludge. The nonradioactive surrogate eliminated the added cost and requirements for handling, treatment, and disposal of an actual radioactive mixed waste. The surrogate sludge contained 5000 mg/kg mercury in the form of five mercury species: elemental mercury, mercury chloride, mercury nitrate, mercury oxide, and organic phenyl mercury (Table II). Three of the four vendors were successful in performing the demonstrations: the demonstrations were on schedule, within budget, and met the treatment goals, as noted below. The fourth vendor performed the demonstration as a post-project effort at no cost to the project, but failed to meet the TCLP goal of 0.025 mg/L.

Table II. Composition of Mercury-Contaminated Surrogate Waste for MER04 Demonstrations

Mercury species components	Weight %	Mercury concentration (mg/kg)	Other components	Weight %
Mercury chloride	0.1	1,000	Diatomaceous earth	20
Mercury nitrate	0.1	1,000	Aluminum hydroxide	10
Mercury oxide	0.1	1,000	Ferric chloride	10
Mercury (elemental)	0.15	1,500	Sodium chloride	10
Phenyl mercury (organic)	0.05	500	Motor oil	1
Total Hg		5,000	Water	48.5

After treatment, each vendor was required to ship samples of the treated waste to the University of Cincinnati for additional analysis, as well as to Oak Ridge National Laboratory (ORNL) for mercury vapor testing. The results from the University of Cincinnati analyses (Rieser protocols) differed from the results indicated in standard TCLP methods, as noted in Ref. 21.

ADA Stabilization Process (>260 ppm Surrogate)

ADA Technologies used a three-step process to stabilize the surrogate. The first step (primary stabilization) involves reaction of the mercury contained in the bulk waste matrix to form a mercuric sulfide product that meets the TCLP UTS for mercury. The second stage involves addition of binders. In the third stage, coating agents are added to render a final waste form that is nominally spherical with a maximum diameter of 9.5 mm. Treatment results showed an average TCLP of 0.159 mg/L of mercury, which exceeded the 0.025 mg/L UTS.

ATG Stabilization Process (>260 ppm Surrogate)

ATG has developed several commercial proprietary processes that stabilize metals or organics in soils and sludges. On the basis of bench-scale tests, ATG selected a sodium hydrogen sulfide (NaSH) formulation for treatment of the contaminated sludge in the demonstration. Conversion of mercury to its sulfide salt is recognized as a means of stabilizing it in an essentially inert form. In the two large-batch tests, the NaSH formulation reduced the leaching of several mercury species present in the surrogate waste to TCLP leachate concentrations of 0.0027 mg/L and 0.011 mg/L, respectively—or one-tenth to one-half the UTS limit. During the first week after treatment, the consistency of the treated sludge was similar to that of a pliable clay, and the sludge had an internal temperature of ~85°C. After one week the material cooled and set to a very hard concrete. No airborne mercury was detected by a Jerome mercury monitor during treatment. The volume increase resulting from stabilization was small, 25% of the untreated waste volume. The weight increase was 50%. The waste loading on a dry basis was 25.4 wt %. The ATG demonstration is described in more detail in Ref. 9.

BNL Stabilization Process (>260 ppm Surrogate)

As in the MER03 demonstrations, BNL used its SPSS process, described earlier in this paper. Bench-scale treatability tests indicated that maximum waste loading of the dry sludge was limited to 30 wt %, based on physical mixability issues, not the leachability of mercury from the

final waste form product. Pilot-scale processing was performed on a surrogate waste containing no mercury and then on a surrogate containing 5000 ppm mercury. For the nonhazardous batch, mixing and dewatering were very well controlled, with 96 wt % of the added water recovered. For the mercury batch, a slightly lower observed yield of condensed vapor of 85 wt % was probably due to several vacuum pump shutdowns. The SPSS treatment successfully stabilized the mercury in the surrogate sludge, with a measured TCLP mercury concentration of <0.010 mg/L, well below the TCLP treatment goal of 0.025 mg/L. The final waste form showed a volume increase of 36% and had a waste loading of 30 wt %. The BNL demonstration is described in more detail in Ref. 10.

NFS Stabilization Process (>260 ppm Surrogate)

NFS demonstrated the ability of its DeHg process to stabilize mercury in the surrogate waste sludge to concentrations of <0.025 mg/L mercury. Using a pilot-scale DeHg batch reactor capable of handling up to 45 kg of soil and reagents, NFS performed two batch runs with waste sludge aliquots of ~25 kg each. The DeHg process stabilized the contaminated waste to meet all UTS TCLP limits. The untreated material had a mercury TCLP of ~150 mg/L; the NFS process reduced the mercury TCLP to <0.01 mg/L. 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 <0.05% of the original mercury input to the process. Treatment of the surrogate waste resulted in ~60% weight increase, much greater than the 15–20% increase typically seen in the treatment of real soil. Waste loadings for the two batches were 44.9 and 47.0%, respectively. The NFS demonstration is described in more detail in Ref. 11.

MERCURY SPECIATION DEMONSTRATION

In addition to the MER01–04 demonstrations, TMFA identified three vendors—ATG, IT Corporation, and NFS—to demonstrate the effects of different mercury species on the stabilization of mercury waste. The stabilization technologies were to stabilize the forms of mercury thought to be most prevalent at DOE sites in surrogate waste spiked with individual, known mercury species.

ATG used three reagents: dithiocarbamate (DTC), polysulfide (with zeolite), and borohydride (with zeolite). Only DTC was successful in immobilizing all five mercury species tested. The organic mercury species were the most difficult to stabilize. IT used the binding reagents TMT 15 and calcium polysulfide. NFS used its DeHg process. A summary of the pre- and post-leaching results for all three vendors are shown in Table III. A detailed description of the demonstrations and the results can be found in Ref. 22.

Table III. Pre- and Post-Treatment Leaching of Mercury (mg/L) in Mercury Speciation Demonstrations

Species	ATG		IT		NFS	
	Pre	Post ^a	Pre	Post	Pre	Post
Mercury sulfide	0.0407	0.0089–0.0092	0.0016	NA ^b	0.024	NA ^b
Mercury chloride	18.3	0.0058–0.0204	9.8	<0.00020	15.0	<0.005
Mercury oxide	18.1	0.006–0.0106	10.0	0.00030	15.4	<0.005
Mercury (elemental)	0.0376	0.0041–0.0091	0.36	0.00055	0.23	<0.005
Phenyl mercury chloride	12.4	0.022	11.0	0.029	15.4	<0.005

^a ATC used three reagents. Range includes results that met TCLP. Post-treatment range does not include results that exceeded TCLP.

^b NA = Not applicable. Pretreatment leaching met TCLP, and thus, no treatment was necessary.

Source: Ref. 17.

The key results of the speciation demonstration were as follows:

- With varying degrees of difficulty, each vendor was able to stabilize all mercury species present in surrogate waste, with no freestanding water.
- Volume increases ranged from modest (25% for ATG and IT) to large (90% for NFS).
- Secondary water generation may occur as a result of equipment rinsing.
- Stabilizing agent formulations may be sensitive to concentration, pH, and particle surface area.
- Interactions of some reagents with soil constituents may complicate the stabilization process, since reagents may be deactivated.

CONCLUSIONS

Through the MER program, DOE's TMFA made considerable progress in its mission of identifying technologies that will allow DOE facilities and sites to effectively and safely dispose of their legacy mixed low-level and transuranic waste. In preparation for the demonstrations of mercury treatment technologies, TMFA and its Mercury Working Group (HgWG) identified and quantified all the different types of solid mercury mixed wastes—elemental, <260 ppm, and ≥260 ppm—in the DOE complex. TMFA then developed the MER program to determine the capabilities in the private sector for treatment of each of the different types of mercury wastes.

The pilot-scale and full-scale treatability studies to demonstrate these treatment technologies on surrogate and/or actual mixed wastes were successful in meeting the established treatment goals, along with meeting the regulatory requirements for each of the different waste types. For mixed wastes containing >260 ppm of mercury, the program not only demonstrated processes for meeting the regulatory requirements but also developed alternative technologies—namely, stabilization processes—which produced waste forms well below the 0.025 ppm TCLP for mercury. The deployment of these technologies will have a significant national impact in safely and cost-effectively moving mercury-contaminated wastes out of storage at DOE sites to final disposal.

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