

The SepraDyne™ - Radsuce System for Recovery of Mercury From Mixed Waste

TRU and Mixed Waste Focus Area



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The SepraDyneTM- Raduce System for Recovery of Mercury From Mixed Waste

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TRU & Mixed Waste Focus Area

Demonstrated at
Brookhaven National Laboratory
Upton, New York

INNOVATIVE TECHNOLOGY

Summary Report

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://www.em.doe.gov/ost> under "Publications."

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SECTION 1 SUMMARY

Technology Description

Mercury contaminated wastes are present in many forms at DOE sites. Efforts led by the Transuranic (TRU) and Mixed Waste Focus Area (TMFA) and its Mercury Working Group (HgWG) identified inventories of mixed and hazardous wastes contaminated with mercury stored at various DOE sites and storage repositories. Extraction methods such as retorting are required to treat hazardous and mixed wastes containing mercury at levels greater than 260 ppm.

SepraDyne™, through its subsidiary Rадuce, has successfully demonstrated a process for vacuum thermal desorption capable of removing mercury to levels below 10 ppm. Bench-scale tests produced residues well below the TCLP standard, with leach concentrations at 8 µg/L or less. Pilot and full-scale demonstrations produced residues with equivalent results. This performance also meets the UTS of 0.025 mg/L for removal of mercury. Thus, the Maximum Achievable Control Technology (MACT) standard of 40 µg/M³ was met for all tests conducted. In the majority of cases and usually throughout an entire process run, mercury readings were typically nondetectable to less than 10 µg/M³. In all cases, mercury emissions did not exceed 29 µg/M³. More detailed mercury emissions results showing the peak and average values for each batch are presented later (Table 8).

Mercury contamination in wastes at DOE sites presents a challenge because various species of mercury exist in a multitude of waste forms such as soils, sludges, and debris. The effectiveness of the SepraDyne™-Raduce process showed no dependency on initial mixed waste physical form or mercury contaminant concentration. This flexibility reduces the need to chemically characterize the waste or perform treatability studies prior to processing.

The SepraDyne™-Raduce process is a simple and unique separation technology that removes volatiles from non-volatile matrices using high vacuum rotary retort. The contaminated water removed in the process must be processed to meet site discharge limits, while the small volume of toxic organics can be oxidized to nontoxic end products or collected for subsequent disposal. Because of potential radionuclide content, nearly pure mercury recovered from the process must be amalgamated to meet disposal requirements. The radioactive nonvolatile solids are suitable for super compaction to maximize volume reduction prior to disposal. The process is shown as a trailer mounted system in Figure 1.

The major concern regarding thermal desorption systems currently available on the market is the potential release of mercury, radionuclides, and toxic substances to the atmosphere. The SepraDyne™-Raduce process is expected to reduce the concern. The combination of indirect heating and high vacuum eliminates the need for noncondensable sweep gases. This is desirable since the movement of non-condensable gases through air pollution control equipment increases the chance of releasing toxic substances. Conversely, eliminating non-condensable gases from the system reduces that risk and facilitates condensation of all vapors and collection of any particulates in the off-gas treatment system.

SepraDyne™ has operated a full-scale unit to remove and recover mercury from mining operation sludges containing several thousand ppm mercury and from various forms of mixed waste with mercury concentrations ranging from 800-6,000 ppm.

This report summarizes the findings from the high vacuum high temperature rotary retort technology demonstration conducted by SepraDyne™-Raduce at the Brookhaven National Laboratory (BNL) under TMFA sponsorship (SepraDyne™ 2001).



Figure 1. Photograph of the SepraDyne™-Raduce trailer mounted rotary retort system.

Demonstration Summary

The Transuranic and Mixed Focus Area (TMFA) is investigating possible treatment methods for mercury-contaminated mixed waste streams and has funded demonstrations of several technologies on a variety of waste streams (MWFA 1999a-e). The Technology Development Requirements Document (TDRD), developed by the TMFA, requires that the effectiveness of newly developed technologies be proven (MWFA 1997). New technologies for mercury removal or stabilization must meet applicable treatment standards and must provide measuring and monitoring methods to verify the process. In addition, the new processes should:

- Minimize worker exposure
- Minimize volume of waste destined for long-term storage
- Minimize secondary waste generation
- Maximize operational flexibility and radionuclide containment.

Four participants, Brookhaven National Laboratory (BNL), Nuclear Fuel Services, Inc. (NFS), Allied Technology Group (ATG), and the SepraDyne Corporation (through its subsidiary Raduce, Inc.) conducted demonstrations of their respective technologies in response to the MER03 Request for Proposal (RFP).¹

¹ A solicitation to industry (February 26, 1999) entitled, "Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Wastes Containing >260 ppm Mercury."

BNL demonstrated its Sulfur Polymer Stabilization/Solidification (SPSS) process. NFS demonstrated their DeHg process. ATG demonstrated the use of chemical stabilization with their proprietary formulations. SepraDyne™-Raduce demonstrated their retort technology for vacuum thermal treatment. The first three participants demonstrated the stabilization of mixed waste containing total mercury greater than 260 ppm to provide data on the applicability of stabilization to high mercury content waste. Each of the three participants was successful in their respective demonstration. The vacuum thermal process was intended to demonstrate an improved form of the baseline technology, retort/roast, on which the EPA regulations are based. The SepraDyne™-Raduce technology demonstrated removal of mercury from mixed waste sources with concentrations up to 6,000 ppm Hg. The final residuals from the process had total mercury levels substantially below 10 ppm Hg and leachable mercury levels below 0.025 mg/L.

SepraDyne™-Raduce demonstrated two high-vacuum, high-temperature rotary retort systems at BNL. The focus of the treatment campaign centered primarily on mixed waste soils; however, several other waste streams were treated as illustrated in Section 4. Several goals were outlined with each demonstration: (1) One goal of each demonstration was to remove and recover mercury, where applicable, from a mixed waste matrix and provide a treated product with concentrations below 10 ppm total mercury and below 0.025 mg/L leachable mercury, while reducing mercury emissions to well below the maximum achievable control technology (MACT) standard. (2) In addition to mercury removal and recovery operations, another goal of the demonstration was to provide maximum volume and weight reduction efficiencies for the treated product. (3) A third objective of the projects was to demonstrate that the vacuum thermal desorption process can efficiently remove and capture, or completely pyrolyze any hazardous organic materials that may be present.

The demonstration results showed the SepraDyne™-Raduce process removed total mercury to levels ranging from 2-8 ppm and leachable mercury to 0.008 mg/L or less. Emission of mercury to the atmosphere was below the MACT standard at all times. In addition, because of the very low total volume of gases emitted, the total mass of mercury emitted to the atmosphere during the demonstrations was negligible.

Key Results

The key results of the demonstration are as follows:

- SepraDyne™-Raduce succeeded in demonstrating a process to remove and recover mercury from mixed waste that resulted in a final dry product containing less than 10 ppm of total mercury and less than 0.025 mg/L leachable mercury (8 µg/L or less) based on TCLP tests
- SepraDyne™-Raduce produced a final waste form with volume reductions typically in the 25%–40% range
- SepraDyne™-Raduce produced a final product in the form of a dry granular material regardless of the feed matrix. Pretreatment may be needed for the purpose of size reduction
- Process effectiveness was found for the wastes treated to be independent of initial waste form and mercury concentration
- Secondary waste generated from equipment consumables and operator personal protective equipment (PPE) were pyrolyzed or volume reduced in the high vacuum high temperature rotary retort.

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SECTION 2 TECHNOLOGY DESCRIPTION

Overview of Process

The HgWG has identified over 30,000 M³ of mercury-contaminated mixed low-level and transuranic (TRU) wastes in the DOE complex (Conley, Morris, Osborne-Lee and Hulet 1998). In addition to elemental mercury, these waste streams include sludges, soils, debris, and other wastes with mercury concentrations ranging from less than 2 ppm to greater than 50,000 ppm. Of this volume, approximately 6,000 M³ contain less than 260-ppm total mercury and do not require best demonstrated available technology (BDAT), such as retorting, to remove and recover the mercury. However, RCRA regulations do require that the remaining mercury waste containing in excess of 260 ppm Hg be processed by a technology that meets the criteria of EPA's BDAT. The recovered mercury may then be rendered insoluble by amalgamation. Residues from treatment must meet the TCLP standards of 0.2 mg/L for mercury. TMFA has set more stringent goals for the technologies it is developing for mercury-contaminated mixed-waste treatment, so that all treated mercury wastes must contain less than the UTS standard of 0.025 mg/L leachable mercury as determined by TCLP tests before disposal.

The SepraDyne™-Raduce high-vacuum high-temperature rotary retort represents an advance in the baseline technology, roasting/retort. Demonstration of this advanced retort technology addresses concerns about fugitive emissions and better establishes the full capability of vacuum thermal desorption systems. The SepraDyne™-Raduce process removes mercury to very low levels (8 µg/L or less) while, in most cases, reducing the final volume of the waste form. Leachable mercury is reduced to levels below the UTS standards. However, mercury recovered from the process must also be treated by amalgamation, as required by RCRA, and disposed as an additional waste stream.

The HgWG selected participants for demonstrations of two categories of technology capable of reducing the soluble mercury to below 0.025 mg/L: stabilization and baseline treatment. At the time of this Request for Proposal (RFP), no studies beyond bench scale had been conducted on the stabilization of mercury mixed wastes. The SepraDyne™-Raduce process, which had previously-documented successes in the removal and recovery of mercury from nonradioactive solid wastes, was selected to participate in the TMFA full-scale demonstration with three stabilization technologies. Each of the participants was required to treat radioactive mercury-contaminated soil excavated during the BNL Chemical Holes cleanup effort. SepraDyne™-Raduce treated larger quantities of the soil than the other participants and, in addition, treated other mercury-contaminated BNL wastes.

Process Description

SepraDyne™-Raduce has developed, patented, and commercialized an indirectly heated rotary retort that operates at high vacuum and high temperature. The unique combination of these features produces an environment capable of volatilizing (1) water, (2) most organic compounds, and (3) low to moderate boiling point metals such as mercury, arsenic, selenium, and cadmium, with near zero toxic air emissions. The process has also been shown to volatilize and pyrolyze organic compounds (Adams, Kalb and Malkmus 2000). Depending on the waste matrix, it can also reduce the volume of the waste matrix during treatment. Because air and sweep gases are eliminated from the retort, combustion will not occur and total gas volume exhausted to the atmosphere is minimized. Only gases initially present and volatilized material will exit the retort, which substantially reduces the size of the off-gas treatment equipment required. The SepraDyne™-Raduce vacuum thermal desorption system provides the following advantages over traditional thermal processes:

- Air pollution is expected to be less, due to sweep gas elimination and rotary seal effectiveness
- 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 costs.

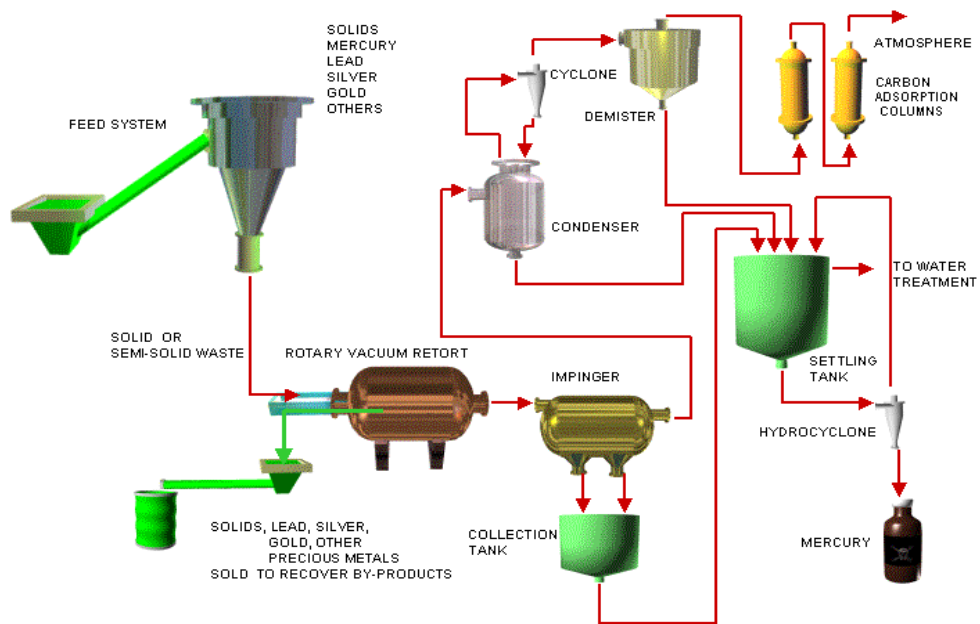
The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Fig. 2) are as follows. Mercury mixed with waste such as soil, sludge, PPE, and building materials are size reduced by a shredding and/or grinding process before being fed to the retort. Liquid or sludge can be pumped into the retort.

Once loaded, the retort is sealed and a vacuum of at least 25 inches of Hg 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, volatile 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 a cold-water impinger system. Due to the high vacuum environment, no sweep gases are needed. Thus, virtually all volatilized substances are readily condensed to liquid.

The temperature of the retort is held at a moderate temperature to allow water to be removed from the matrix. When the drying phase is complete, operators raise the retort temperature to a target value, typically in the range of 600-750°C, and hold it there for a predetermined period. During this period vacuum is kept at 20" of Hg or higher. 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 treated as required for the contaminants present.

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 trace hazardous 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.

Figure 2. Flow diagram depicting the SepraDyne separation process.



SECTION 3 PERFORMANCE

Background

Remedial excavation activities of the Animal/Chemical Pits and the Glass Holes were performed by BNL during the summer of 1997. The waste was removed from 55 specific pits and subsequently sorted, characterized, and stored, or shipped to a licensed disposal facility. Of the 440 cubic yards of soil that were identified as a mixed waste, 100 cubic feet of this material were segregated into two B-25 boxes due to its elevated concentration of mercury. Characterization (see Table 1) of the two boxes revealed that the soils had a total mercury concentration of 6,750 mg/kg and 18,000 mg/kg, respectively.

The TMFA sponsored demonstrations both to provide data on an alternative (stabilization) to the baseline technology for treatment of wastes with high mercury content (> 260 ppm) and to advance the state-of-the-art baseline technology (retort). SepraDyne™-Raduce was selected to demonstrate baseline technology advancement with its high vacuum rotary retort separation process. In addition to the soils, several other waste inventories were treated either on a bench-scale system or through a full-scale demonstration unit. In both cases, the process was able to demonstrate successful hazardous constituent removal and recovery, organic toxic waste destruction, and/or significant volume reduction.

Demonstrations

The full-scale demonstration and proof-of-principal bench-scale testing were conducted at Brookhaven National Laboratory in Upton, NY. Although the major focus of the effort was to treat mercury-contaminated soils retrieved from the Chemical Holes as part of the DOE full-scale demonstration project, several other significant and varied mixed waste streams were treated using the high-vacuum high-temperature rotary-retort process.

Bench-Scale Test

To establish process parameters for the BNL specific waste streams and to further demonstrate the effectiveness of their process on other waste forms, SepraDyne™-Raduce performed several proof of principle tests using a portable tabletop unit. Testing was conducted under the supervision of the Environmental and Waste Management Group (Environmental Research and Technology Division, Environmental Sciences Department, BNL) between April and July 1999.

Table 1. Characterization data for BNL mixed waste soils prior to treatment.

| Parameter | B-25 Box 1 | B-25 Box 2 |
|-----------------------|-------------|--------------|
| Hg (total) | 6,750 mg/kg | 18,000 mg/kg |
| Hg (TCLP) | 3.56 mg/L | 0.263 mg/L |
| Gross Alpha | 4,560 pCi/g | 24.9 pCi/g |
| Gross Beta | 525 pCi/g | 35.9 pCi/g |
| Am ²⁴¹ | 7,140 pCi/g | --- |
| Pu ²³⁸ | 72.6 pCi/g | --- |
| Pu ^{239/240} | 19.7 pCi/g | --- |
| Sr ⁹⁰ | 2.15 pCi/g | --- |
| U ^{233/234} | --- | 7.06 pCi/g |
| U ²³⁸ | --- | 5.87 pCi/g |
| Eu ^{152/154} | --- | 28.7 pCi/g |

The equipment used for protocol testing was similar in design and process-parameter capability to the larger units. The tabletop unit was capable of treating up to 2 pounds of material at batch process temperatures up to 815°C, under a vacuum as high as 28 inches of mercury. The complete batch process, excluding cool-down time, typically required 3-4 hours to complete. The following surrogate and actual waste streams were used to verify process parameters and treatment methodologies:

- Yard soils
- Americium / Mercury-contaminated soil
- Europium / Mercury-contaminated soil
- Chicken portions
- Waste Experimental Reduction Facility (WERF) fly ash.

The yard 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 (1,200°F) and held under constant vacuum of at least 26" Hg for 30 minutes. Once the unit was verified to be in proper working order, two batches of mercury-laden Americium and Europium contaminated soils were treated. Tests were performed in similar fashion to the yard soil, providing the basis for the operating parameters chosen for the full-scale demonstration. The mercury concentration in the feed material for these Americium and Europium contaminated soil samples was analyzed to be 5,570 and 4,190 ppm, respectively.

When 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. Tests were performed using chicken carcasses; one test was performed with only chicken carcasses, while the second test used a mixture of chicken and mixed waste soils similar to what was expected during the full-scale demonstration.

A final series of tests were performed on mixed waste incinerator fly ash from the Waste Experimental Reduction Facility at the Idaho National Engineering and Environmental Laboratory (INEEL). The goal was to demonstrate the SepraDyne™-Raduce technology's effectiveness in treating materials containing high levels of furans and dioxins. The objective of this effort was to pyrolytically decompose the dioxins and furans to levels below 1 ppb by the vacuum thermal desorption process.

Bench Scale Results

In each series of tests performed, the SepraDyne™-Raduce process successfully achieved all of the proposed treatment goals. Results of specific demonstration trials are shown in Appendix C, Tables 1 and 2. In all cases, significant volume (40-92%) and weight (11-93%) reductions were observed. The tumbling action of the retort during operations reduced all treated material to a fine powder form. Results showed that the final soil matrix was typically reduced in volume by 40% or greater. Even the incinerator fly ash samples were significantly volume reduced (45-64%) when treated with this process at the bench scale.

The leachable mercury concentrations in the Americium and Europium contaminated soils were reduced to levels near the new UTS limit, with one post-process sample (0.0353 mg/L) above and one (0.0183 mg/L) below 0.025 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.

Pre- and post-treatment composite samples of the fly ash were sent to an independent laboratory for furan and dioxin analysis. Dioxin homologue concentration in the feed stream was 565 ppb, while the furan homologue concentration was 267 ppb. After analysis of most of the post samples, it was determined that the dioxin/furan concentrations were nondetectable. The highest dioxin concentration in the treated stream

was reported as 0.067 ppb, while the highest furan concentration recorded was 0.051 ppb. The results of these efforts are reported elsewhere (Adams, Kalb, and Malkmus 2000).

Full Scale Demonstration

As part of the full-scale mercury treatment demonstration, a larger, 200-pound-per-batch unit was relocated to the BNL site. For the study, 7 drums (approximately 3,004 lbs) of radioactively contaminated soil and sludge 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 in addition to the soil 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 is listed below:

- 3,004 lb soil – 7 drums of the original soil
- 4,471 lb soil – 8 additional drums of soil
- 170 lb mixed waste animal carcasses
- 360 lb mixed dry activated waste
- 42 lb spent resin
- 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 significantly homogenized, a large majority of the drums apparently were not sealed properly, or were defective. Of the original 15 drums, the soil in 12 of the drums was found to be extremely moist, sludgy or had at least 2" of standing water. Composite characterization of soil in the B-25 boxes has been summarized above in Table 1; and the total mercury concentration was found to be 6,750 mg/kg and 18,000 mg/kg, respectively. Representative bin samples were also analyzed by TCLP methods and exhibited mercury concentrations of 3.56 mg/L and 0.26 mg/L, respectively. Due to the elevated concentrations of mercury, the waste fell under the requirements for Land Disposal Restrictions (LDR) treatment standards. In addition to the mercury, the two boxes were segregated based on the predominant radioactive isotopes (Am-241 or Eu-152).

The animal carcasses were transported to the demonstration site and reduced 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 similar to 3" by 6" 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 in Table 2.

Table 2. Biological Waste Radiological Data.

| Parameter | Concentration pCi/g |
|-------------------|------------------------|
| Gross alpha | 21.1 |
| Gross beta | 186 |
| Plutonium-239/240 | 4.17 |
| Americium-241 | 4.23 |
| Strontium-90 | 59.9 |
| Carbon-14 | 3.06 |

The dry active waste consisted of three separate inventories. One lot of mixed dry active waste (approximately 100 pounds) consisted of liners and plastics used as the original containers for the animal carcasses and for the follow-up carcass size-reduction efforts. The second inventory (approximately 55 pounds) consisted mostly of mixed waste plastic and cardboard pieces that were collected and segregated during the BNL soil excavation process. The remaining 200 pounds of material consisted largely of consumable materials (filters, resin, and protective clothing) that were used during the monitoring and operation of the treatment process.

Demonstration Results

As part of the TMFA demonstration, SepraDyne™-Raduce treated seven drums of soils in 18 batch processing runs. Three of the treated drums, A-1, A-3, and A-5, contained mercury-contaminated soils having elevated concentrations of Americium (see Table 1). The remaining drums, E-3 to E-6 also contained elevated levels of mercury but exhibited high concentrations of the Europium radionuclide. Each test was performed in similar fashion to and under the same general operating conditions as the tests previously performed during the lab bench scale studies. Each batch was heated to a 650-700°C temperature level and was held under a vacuum between 26-29" Hg. Once these optimum parameters were established, each batch was held at these conditions for an elapsed time of 10 to 20 minutes. The processed material was then allowed to cool to below 400°F prior to unloading operations.

As the demonstration progressed, plant 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 (A-1/5, E-4/6) drums in a similar fashion to the above protocol. Approximately 100 lb of animal carcasses and plastic wrapping were treated in the remaining 350 lb of A-5 / E-6 inventory.

Quantitatively, 3,050 pounds 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 2,360 lbs. The data show that the vacuum thermal desorption process was able to provide a final product with a 23% weight reduction. Based on visual inspection, the volume reduction was estimated at approximately 40-50%.

There were no visible traces of the animal carcasses or dry active waste in the final product. The total mercury concentration was reduced from initial levels in the feed material as high as 5,510 ppm to levels in the residues below the demonstration goal of 10 ppm. TCLP levels were reduced from typical values in the range of 0.2-1.4 mg/L in the incoming feed stream to nondetectable levels in most cases with the highest post process level being 0.0084 mg/L. Results of the pilot-scale demonstration are provided in Tables 3 and 4.

Table 3. Pilot-scale Americium/Mercury Contaminated Soil Results.

| Parameter | Drum A-1 | Drum A-3 | Drum A-5 |
|------------------------------|------------------------------|------------------------------|------------------------------|
| Preprocess wt. (lbs) | 550 soil 31 carcasses | 470 soil | 541 soil 28 carcasses |
| Postprocess wt. (lbs) | 400 | 415 | 370 |
| % Wt. Reduction | 31.2 | 11.7 | 35.0 |
| Preprocess Hg (mg/kg) | 4040 | 2310 | |
| Postprocess Hg (mg/kg) | 1.8 | 1.0 | 3.4 |
| % Hg Removal | 99.96 | 99.96 | --- |
| Preprocess TCLP Hg (mg/L) | 0.868 | 1.390 | --- |
| Postprocess TCLP Hg (mg/L) | <0.0006 | <0.0006 | 0.008 |
| % TCLP Hg Removal | >99.93 | >99.96 | --- |
| Total Process Time (minutes) | 3 Batches @ 240 min/batch | 3 Batches @ 318 min/batch | 3 Batches @ 237 min/batch |
| Maximum Process Temp (°C) | 670 | 660 | 655 |

Table 4. Pilot-scale Europium/Mercury Demonstration Results.

| Parameter | Drum E-3 | Drum E-4 | Drum E-5 | Drum E-6 |
|----------------------------|------------------------------|------------------------------|------------------------------|---|
| Preprocess weight (lbs) | 367 Soil | 375 Soil 23 carcasses | 342 soil | 329 soil 30 E-4 soil 20 carcasses |
| Postprocess weight (lbs) | 333 | 180 | 300 | 360 |
| % Weight reduction | 9.3 | 54.8 | 12.3 | 5.0 |
| Preprocess Hg (mg/kg) | 4880 | 5510 | --- | --- |
| Postprocess Hg (mg/kg) | 0.55 | 4.21 | 0.41 | 8.1 |
| % Hg removal | 99.99 | 99.92 | --- | --- |
| Preprocess TCLP Hg (mg/L) | 0.191 | 0.212 | --- | --- |
| Postprocess TCLP Hg (mg/L) | <0.0006 | 0.002 | <0.0006 | <0.0006 |
| % TCLP Hg removal | 99.69 | 99.06 | --- | --- |
| Total process time (min) | 2 Batches @ 240 min/batch | 2 Batches @ 175 min/batch | 3 Batches @ 220 min/batch | 2 Batches @ 180 min/batch |
| Maximum process temp (°C) | 730 | 690 | 700 | 690 |
| Minimum vacuum (in. Hg) | 26 | 26 | 26 | 26 |

In summary, the SeptraDyne™-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 (Appendix C, Tables 1 and 2). A fine dry granular product was produced, and the worst-case mercury emissions ($29 \mu\text{g}/\text{m}^3$) were below the 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 volume reduced to a few percent of its original volume in subsequent batch processes.

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 runs were performed which treated an additional 5,032 lbs of soils, carcasses and dry active waste. These inventories with their analytical results are listed in Appendix C, Table 3.

Mercury Emission Data

The SeptraDyne™-Raduce demonstration unit contained an emissions monitor (Arizona Instruments model JEROME X431) installed on the process off-gas line 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 set point of $40 \mu\text{g}/\text{M}^3$. Mercury emissions were recorded at 15-minute intervals for every process run. Optimum conditions for volatilization of mercury were predicted based on observations of the system temperature screens during processing. During the 46 batches, emissions monitor readings at the optimum mercury volatilization stage averaged in the range of $1\text{-}14 \mu\text{g}/\text{m}^3$. In the majority of cases and usually throughout an entire process run, mercury readings were typically nondetectable to less than $10 \mu\text{g}/\text{m}^3$. The highest emissions level recorded during the demonstration was $29 \mu\text{g}/\text{m}^3$, which was still within the current MACT

emission criteria. A mercury emissions summary showing the peak and average values for each batch has been provided in Appendix C, Table 4.

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

SECTION 4 TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Baseline Technologies

While roasting or retorting of mercury-bearing hazardous wastes (RMERC) has been used to address mercury waste (without organics) at concentrations exceeding 260 ppm, there has been relatively little work on the treatment of >260-ppm mercury waste by other means. Interest in alternative technologies for high mercury waste is considerable, since much of the appeal of retorting exists in the potential to recycle recovered elemental mercury. Recycling is not a feasible option for radioactively contaminated waste; the recovered mercury must be amalgamated and sent to a disposal site.

In an effort to develop data showing whether high mercury waste can be safely stabilized, the TMFA has sponsored stabilization technology demonstrations as an alternative approach to the prescribed baseline of retorting. Hence, the SepraDyne™-Raduce high-vacuum high-temperature rotary retort should be compared to two relevant categories of technologies: conventional retort (baseline technology) and stabilization (alternative technology). In such comparisons, the SepraDyne™-Raduce process represents an improvement to conventional baseline technology. However, only recent efforts sponsored by the TMFA have had the goal of meeting waste form TCLP performance levels such as the new UTS of 0.025 mg/L by TCLP. Hence, data from demonstrations of baseline retort processes with this performance goal are not available.

Four stabilization technologies were evaluated in the MER03 Scope of Work:

1. ATG demonstrated chemical stabilization (ATG 2000)
2. BNL demonstrated its SPSS process (Kalb, Adams and Milian 2001)
3. NFS demonstrated the DeHg process (NFS 2000)
4. SepraDyne™-Raduce demonstrated its improved vacuum retort technology (SepraDyne 2001).

These four technologies are compared in the following section on the basis of results obtained in the TMFA sponsored demonstrations. An important complication to be considered is that of mercury speciation. A recent study, funded by the TMFA and reported elsewhere, explored the impact of speciation on the effectiveness of stabilization technologies (Osborne-Lee, Conley, Morris, and Hulet 1999).

Technology Comparisons

Four stabilization technologies demonstrated under the TMFA treatment technology development program (ATG, GTS Duratek, NFS, and BNL) are summarized in comparison with the SepraDyne™-Raduce vacuum thermal treatment process in Table 5. Currently, there are no thermal technology demonstrations available for comparison. All technologies compared were tolerant of moisture (small amounts of water). No additional hazards, or safety or regulatory issues were found for the processes compared.

In the stabilization demonstrations, chemicals were added to convert the mercury present into an insoluble species. Because chemical reactions are required for the new insoluble species to be formed, stabilization technologies face the following challenges:

- Volume is increased in achieving the final waste form

- Mercury is not removed from the waste and so must be immobilized in the waste form
- Thorough chemical characterization of the waste may be required
- Treatability studies are required for each waste stream for appropriate stabilization formulation
- High levels of organic compounds can make stabilization difficult or unachievable (Connor 1990)
- Questions remain concerning the long-term stability of the final waste form.

The high vacuum high temperature rotary retort technology faces the following challenges.

- Mercury is removed from the waste and so must be amalgamated
- Volume reductions for residue are partly diminished by amalgamation of recovered mercury
- Toxicity characteristic (RCRA) metals not recovered may require stabilization of residue.

Stabilization methods can be used to convert the soluble mercury into insoluble mercury compounds. These methods (1) do not remove mercury, (2) may increase final waste volumes, and (3) raise questions regarding waste stability and the potential for release over long periods of time. For the latter reason, removing the mercury to very low levels may be better. However, recovered mercury must be treated by amalgamation, as required by RCRA, and disposed as an additional waste stream in the same disposal site. Non-volatile RCRA metals remaining in the residue after retorting could present a problem in meeting TCLP standards; such species were not tested in the demonstrations reported here. These metals would require stabilization prior to disposal.

The SepraDyne™-Raduce process can successfully treat some types of waste, preparing it for disposal. Leachable mercury is reduced to levels below the UTS because mercury compounds are volatile at high temperatures under vacuum. Also, significant volume reductions were achieved, based on comparisons of the final residue to the original waste. However, the recovered mercury stream does not account for the reported volume reduction achievements. Other materials besides mercury and water were vaporized or pyrolyzed in the matrices to reach the volume reductions reported. Amalgamation would be expected to produce a volume increase lowering the overall reduction. Based on previously reported waste loadings (MWFA 1999d, 1999e), the volume increase from amalgamation would be expected to be equivalent to the mercury volume multiplied by a factor of 2-5.

The SepraDyne™-Raduce process compares well with the competing technologies, yielding an effective, low-cost waste form with some additional advantages. It has eliminated the one major drawback to thermal processing, the emission of mercury and radioactive substances to the atmosphere. Indirectly heating a rotating retort under high vacuum and eliminating the use of any non-condensable sweep gas make this possible. Vapors diffuse from the retort into the off-gas treatment train. The result is the production of an easily condensable controlled vapor flow from the retort. Without added non-condensable gases passing through the off-gas system, there is very little motive force to transport particulates or vapors past the condensers and adsorbents. Volatilized mercury and radioactive substances are thus captured in a relatively compact off-gas treatment system which prevents their release to the atmosphere.

Table 5. Comparison of the SepraDyne™-Raduce vacuum thermal process with competing stabilization technologies.

| Comparison factor | SeptraDyne™-Raduce Vacuum thermal Treatment Process | Allied Technology Group (ATG) Stabilization Process | Nuclear Fuel Services (NFS) DeHg™ Stabilization Process | Brookhaven National Lab Stabilization/ Solidification Process |
|---|--|---|--|--|
| Waste type tested | Soils, fly ash, and animal carcasses, plus DAW (clothing, cleaning materials) and system consumables (spent resins, filters) | Soil from BNL containing 4,000 mg/kg Hg, plus leachable Cd and Pb | Soil from BNL containing 4,400 mg/kg Hg (principally elemental) | Soil and elemental mercury from BNL restoration activities |
| Process mechanism | High temperature high vacuum rotary retort | Modified mortar mixer with capacity of 7 ft ³ in a hazardous materials enclosure equipped with an air treatment system | DeHg reactor with 45 kg capacity for soil and reagents housed in ventilated structure | Chemical stabilization and physical encapsulation based in a 1ft ³ blender/ dryer with screw mixing |
| Scale of bench test | <1 kg bench tests performed | 1.0 kg bench tests performed | None were needed due to prior experience | Bench scale testing completed previously |
| Scale of demonstration | 90 kg batches | 60-80 kg batches | 25 kg batches | 25-50 kg batches |
| Final waste form performance | Removes Hg to below 10 ppm; meets UTS for Hg | UTS met for Hg and other RCRA metals present initially above UTS | Passes UTS for mercury; other RCRA metals not characterized initially | Successfully stabilized/ encapsulated soils at waste loadings of 60% |
| Volume Reduction Factor ($V_{Final}/V_{Initial}$) | 0.36-0.60 | < 1.20 | < 1.12 | 1.67 |
| Stabilization process (as applicable) | Amalgamation of elemental Hg recovered during processing; not part of SeptraDyne™-Raduce capability | Uses either dithiocarbamates or a liquid sulfide in proprietary formulations | Uses proprietary formulation of additives and EPA-prescribed agents | Patented process uses sulfur and polymer to produce an amalgam encapsulated in a solid matrix |
| Effect of contaminants on the process | Removes all volatiles and pyrolyzes organic compounds, independent of contaminant level | H ₂ O used in bench-scale (21%) tests and demonstrations (7-10%); other contamination not addressed | No adverse effects reported; H ₂ O not a problem as process has been applied to wastewaters | Drying to remove excess H ₂ O is a normal step in processing; other contaminants not addressed |
| Throughput | 1,000 lb/h at full scale (not demonstrated on mixed waste) | 1,200 lb/hr at full scale (not demonstrated) | 1,000 lb/hr | Not evaluated |
| Cost | \$2.00/kg at 1,000 lb/hr or \$2.50-\$10.00/kg at 100 lb/hr | \$0.40/kg at 1,200 lb/hr or \$2.40/kg at 100 lb/hr; not inclusive of transportation, disposal, or permitting costs | \$6.00/kg at 1,000 lb/hr or \$37.00/kg at 100 lb/hr | Not determined |
| Waste acceptance criteria | Mercury is removed, but other RCRA metals must be stabilized to meet disposal WAC | Waste form meets current WAC at Envirocare | Waste form meets current WAC at Envirocare | Waste form meets current WAC at Envirocare |
| Physical characteristics | Fine, leach resistant, fixable powder (except recovered mercury) | Low slump soil/cement | Cake-like with no standing water | Solid monolithic puck |
| Summary Assessment | Effective, economical removal and recovery process, avoids volume increase, secondary wastes, and emissions | Effective stabilization process; achieves higher waste loadings, less secondary waste, and fewer proprietary reagents | Effective stabilization process; less costly, better leach performance for more UHCs; formulations proprietary | Effective stabilization process with undetermined cost |

Technology Applicability

The vacuum-thermal-desorption process demonstrated by SepraDyne™-Raduce has the potential to treat many of the mercury contaminated DOE waste streams, including sludges and slurries containing mercury at any concentration, even those below the 260 ppm RMERC standard. Because oxygen is eliminated from the process, even extremely flammable wastes can be processed (normally at reduced temperature). In addition to removal of the mercury, the process can remove toxic organics, water, elemental sulfur, and volatile metals. Therefore, waste streams do not have to be thoroughly chemically characterized prior to processing. If the waste is held under high vacuum at a temperature around 650°C for a sufficient period of time, usually less than 30 minutes, all mercury forms will volatilize and separate from the nonvolatile waste matrix.

Process effectiveness and parameter control is independent of the waste matrix to be treated as well as forms and concentrations of mercury and organics present. PPE such as Tyvek suits and rubber gloves, waste disposal containers such as plastic bags and carboys, and typical waste processing consumables such as ion exchange media and filters are pyrolyzed to carbon and the hydrocarbons are captured in the off-gas system. The process has also been demonstrated at BNL to volume reduce contaminated animal carcasses. Wastewater generated from the moisture content of treated materials can be reused in the off-gas cooling system or can be processed by conventional water treatment technologies such as filters, carbon, and ion exchange media.

The processing equipment is skid mounted (see Figure 1); thus, it can be quickly and easily mobilized and placed in operation to process relatively small volumes of waste. The equipment can be sized to process inventories at a 55-gallon drum rate, or can be scaled up to process several tons per batch (see Section 5). Emissions are well below standard exemption levels, so SepraDyne/Raduce anticipates that air control and Department of Health and Environmental Control (DHEC) permits will be more easily obtained.

SECTION 5 COST

Methodology

The following cost estimate is based on a 1,000 lb/hr automated commercial vacuum thermal desorption unit complete with the 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 1,000-kg scale and a forklift to move drums.

Vendor operating costs are estimated to be \$90 per hour. The costs include two operators, health and safety oversight, and management support. The life cycle and cost basis are summarized in Table 6. Site oversight and support would have to be added to these costs.

Table 6. Summary of cost basis information for the SeptraDyne™-Raduce process.

| Parameter | Design and Cost Basis |
|-----------------------|--|
| Plant Life | 10 years |
| Operations | 250 days/year, 5 days/week, 8 hrs/day |
| Throughput | 1000 lbs/hr |
| Treatment Process | High vacuum rotary retort |
| Capital Costs | Processing equipment, air pollution control equipment, scale and forklift |
| Operating Cost | Laborers, oversight and management support and electricity |
| Disposal Costs | \$1000/M ³ for solids, \$ 0.10/gal for wastewater, \$ 25/gal for organics |
| Decommissioning Costs | Not included |
| PPE | Purchase and disposal costs |
| Transportation | Shipping costs to disposal site |

Taking the capital costs of \$1,500,000, 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 per kg.

Decontamination and decommissioning costs are not included. Capital costs are amortized over the life of the facility. The processed solids produced in the SeptraDyne™-Raduce process are dry and therefore suitable for super compaction, which can further reduce the final waste form volume sent for disposal.

To have a similar basis for cost comparison costs elements not included in the sum of the unit costs shown in Table 9 should be considered. They include the following:

- Chemical characterization of the waste streams, where needed
- Treatability studies to determine stabilization formula, where applicable, including leach testing
- Treatment and disposal of secondary wastes
- Added labor costs due to 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
- Permitting.

The areas where the SepraDyne™-Raduce process is less expensive than stabilization processes are as follows:

- Reduction in the amount of chemical characterization required for each waste stream
- Reduction in the amount of treatability testing required
- Reduction in the volume of solid waste sent for disposal
- Reduction in the volume of PPE generated because all PPE can be reduced to a few percent of its original volume in the high vacuum rotary retort
- Cost of stabilization chemicals is eliminated, although cost of amalgamation chemical offsets this gain to some extent.

The areas where the SepraDyne™-Raduce process is more expensive than stabilization processes are as follows:

- Capital costs
- Electricity costs
- Permitting
- Secondary waste stream treatment and disposal (elemental mercury requiring amalgamation)
- Testing and possible treatment for non-volatile RCRA metals.

Cost Conclusions

For the 1,000 pounds per hour processing rate specified in the original Statement of Work (SOW), the cost is estimated at \$2.00/kg regardless of the waste form. The cost is not expected to increase significantly due to the varying amounts of toxic organics or mercury. Also, the SepraDyne™-Raduce process can treat other volatile RCRA metals.

These cost estimates were based on the demonstration results and SepraDyne™-Raduce's commercial operation experience. Actual costs will increase if the waste is exceptionally wet due to increased processing time, electrical costs and production of wastewater. However, worst case cost estimates range only up to \$2.50/kg at processing rates near 1,000 pounds per hour.

SECTION 6

OCCUPATIONAL SAFETY AND HEALTH

Advantages of Safer Technologies

The Office of Science and Technology requires compliance with applicable quality assurance, safety, and health orders issued by DOE, as well as other appropriate requirements. Accordingly, technology development and demonstration activities are carried out in a manner to ensure that:

- Technology development work is performed in a manner that is safe for the workers and the public, and protects the environment, and
- The technologies resulting from OST program funding are deployed and implemented in a safe and environmentally satisfactory manner.

This approach ensures that not only will the technologies developed and deployed perform the desired function, but also their adverse impacts on individuals and the environment will be minimized or eliminated.

Development and Demonstration Safety and Health Considerations

Before beginning any work, SeptraDyne™-Raduce was required to submit a Quality Assurance Plan representing their approach to ensuring that quality data are generated and that development and demonstration work is performed in a manner that protects the safety and health of the workers involved. With respect to safety, the plan was required to address how personnel are trained in laboratory analytical methods, quality control/QA procedures, and safety policies.

The SeptraDyne™-Raduce process demonstrated as part of the MER03 activities was developed prior to the MER03 call and so its development falls outside of the scope of this report. For the MER03 demonstrations, no additional hazards, safety, or regulatory issues were found for the processes compared.

Occupational Safety and Health Implications of the High Vacuum Rotary Retort

Technology users should understand the occupational safety and health implications of the technologies that they employ, particularly with respect to how the new technology compares with baseline or other alternatives. To make this clear, the several elements of risk are discussed below.

Health and Safety Risk to Operators

Retort processes pose conventional risks associated with elevated temperature processes including burn hazards and adverse health effects of fugitive emissions of harmful substances such as mercury. The latter is of particular concern. In addition, radiological exposure and the possibility of contamination raise concern since this process treats mixed waste. Based on the experience and results obtained in the MER03 demonstrations, these concerns may be answered as follows:

- The more conventional risks (such as burns) are well manageable within the scope of practical operations as demonstrated by SeptraDyne™-Raduce and by the large body of experience with the baseline technology for comparison—retorting.

- Fugitive emissions are very low and thus well manageable with the high vacuum rotary retort process based on the data reported herein.
- Radiological exposure and contamination risks were low and were well managed due to the very low activity levels and the effectiveness of standard radiation safety protocols properly applied.
- The risks to operators for the SepraDyne™-Raduce process are expected to be similar to those for alternative processes demonstrated as part of MER03; such stabilization processes pose less or no thermal hazards, but add particular, but manageable, chemical and mechanical hazards.

Overall, worker risk is considered as moderate to low. While mercury is a hazardous material of some concern and radioactive contamination has the potential to raise additional concern, mercury vapors and leaching appear to be well controlled by the process and radioactive contamination is low. The stability of the final waste form is key in isolating both mercury and radionuclides, thereby minimizing concerns over worker safety, public safety, and environmental protection. Nevertheless, as a high temperature process, there is some added concern.

Health and Safety Risk to Maintenance Workers

No particular source of added risk is expected for maintenance workers who service the SepraDyne™-Raduce high vacuum rotary retort process, compared to risks associated with the baseline technology or competing technologies. Thus, risk for maintenance workers from this technology is considered to be similar to that for operators.

Safety and Health Requirements

As a process that will treat waste material that is both hazardous (toxic) and radioactive, there are required safety and health measures for this technology to be used. Such measures include environmental or medical monitoring, personal protective equipment, safety and health training—that will be needed to implement this technology. These are all specified in the quality assurance plan submitted by SepraDyne™-Raduce. Potential users should note that these safety and health requirements are equivalent to those associated with implementation of the baseline technology (RMERC or IMERC) as well as the stabilization alternatives demonstrated as part of MER03. That is, all of these treatment technologies must protect the workers from exposure to mercury (and other toxic constituents in the waste) and radioactivity.

Lessons Learned

The demonstrations showed that the high vacuum rotary retort system is effective in managing health and safety concerns while also effectively treating wastes to produce a stable, disposal waste form. A particular concern as to whether effective mercury-emissions control could be achieved has been answered. The health and safety plan used was sufficient to effect a safe and successful demonstration of the SepraDyne™-Raduce high vacuum high temperature rotary retort process for treating high mercury mixed wastes.

SECTION 7 REGULATORY AND POLICY ISSUES

Regulatory Considerations

The regulatory goal of any end user deploying the high temperature high vacuum rotary retort process is to produce residue and amalgam waste forms that meet applicable RCRA LDR 40 CFR 268.40 treatment standards for land burial. As for the case of stabilization treatment of mixed waste, the vendor or site must know the characterization of the waste and final form, research the currently applicable treatment standards, and perform treatability studies as needed to ensure that all applicable treatment standards will be met. The following demonstrate the importance of this precept. The TCLP based treatment standards used in this study for cadmium, chromium, lead, and mercury have decreased significantly since the study, and may change again in the future. The mixed wastes to be treated may also contain additional toxic metals not tested in this study, but subject to RCRA LDR treatment standards, either as toxicity characteristics or as underlying hazardous constituents. In addition, NRC 10 CFR 61 waste form testing will be necessary if disposal is to be in an NRC licensed facility.

To treat mixed waste, any full-scale, high-temperature, high-vacuum, rotary-retort facility will require a Part B RCRA permit or a modification to an existing permit. An air emissions review should be performed to determine the applicability of requirements for emissions monitoring and air emissions permits under the Clean Air Act, including applicable National Emissions Standards for Hazardous Air Pollutants (NESHAP) and Prevention of Significant Deterioration requirements for ambient air quality. For commercial facilities, NRC or Agreement State licensing, or possibly license modification will be required for radioactive material handling. Additional requirements for applying the high-temperature, high-vacuum rotary-retort process at a federal facility include a National Environmental Policy Act (NEPA) review (a categorical exclusion is most likely to be applied).

If future development of the high-temperature, high-vacuum, rotary-retort process requires testing with actual waste streams at a federal facility, a NEPA approval through a categorical treatability study exclusion must be obtained. In addition, the state cognizant environmental agency in which the treatability study is to be performed must be notified 45 days before receiving archived samples for testing. In addition, the regional EPA must be notified.

Safety, Risks, Benefits, and Community Reaction

The HgWG, considering eight criteria for the level of risk as associated with > 260-ppm mercury waste treatment, as follows, evaluated various aspects of risk:

- Correctness (technical soundness)
- Cost (effectiveness of use)
- Permitability (ease of permitting)
- Safety
- Sponsorship (commitment by sponsors)
- Completeness (readiness for use)
- Acceptability (approval by stakeholders)

- Timeliness (scheduling soundness).

The risk values, established for the TMFA developed technology processes, have been derived from top-level requirements defined in the TMFA Systems Requirements Document. Evaluations of the technology and assignment of risk values were made by a team comprised of HgWG members, in consideration of the risk category definitions and performance observations from the demonstration experience. The assessments made are summarized below.

Correctness

This risk category is rated as very low. The targeted volume of waste seems to be suitable for treatment by this process. The fact that retort is required by law for wastes with greater than 260 ppm Hg reflects the fact that this type of technology is appropriate. The performance demonstrated by SepraDyne™-Raduce adequately addresses any concerns over the capability of their process to successfully treat mercury-contaminated mixed waste.

Cost

This risk category is rated as moderate to low. The targeted volume to be treated is sizable. Waste characteristics are diverse, but the treatment process appears flexible in the wastes it can handle. Complexation and speciation of mercury across various matrices are expected to add a minimal element of uncertainty. In addition, cost estimates provided by SepraDyne™-Raduce are relatively reliable, as they are based on commercial experience with similar processing activities. However, the potential impact of nonvolatile RCRA metals that initially exceed TCLP has not been addressed.

Permitability

This risk category is rated as low. The treatment process is simple and based on a well-proven best available demonstrated technology (BADT) for nonradioactive mercury waste. The volumes of emissions are low, compared with other thermal processes. Simplified permitting is expected because the SepraDyne™-Raduce process is classified as a recycling or resource recovery process, not incineration.

Safety

This risk category is rated as moderate to low. While mercury is a hazardous material of some concern and radioactive contamination has the potential to raise additional concern, mercury vapors and leaching appear to be well controlled by the process and radioactive contamination is low. The stability of the final waste form is key in isolating both mercury and radionuclides, thereby minimizing concerns over worker safety, public safety, and environmental protection. As a high temperature process, there is some added concern.

Sponsorship

This risk category is rated as moderate. While interest by the sites has been good, and programmatic support for technology development has also been good, capital costs are somewhat high, and potential for public concern though not high is still significant.

Completeness

This risk category is rated as low due to the established, proven nature of retort processes, and in consideration of the commercialized state of the SepraDyne™-Raduce process.

Acceptability

This risk category is rated as low. Retort is a process easily identifiable to the public because of its long-time status as a recommended treatment by law. The waste form stability, simplicity, and relatively small-scale nature that characterize the technology are expected to make for easy public acceptance.

Timeliness

This risk category is rated very low. Based on the success to date in demonstrating needed treatment technologies, some of which are commercially advanced, and in establishing national contracts for treatment of mercury contaminated wastes, there is high confidence that needed treatment technology will be available for the category of wastes that are the subject of this report.

Public Participation

The siting of a mixed waste treatment facility of any kind near communities will involve public input. Stakeholders are generally concerned about the type, toxicity, and amount of emissions to be discharged to the atmosphere and the disposal site for the final waste form.

The TMFA Tribal and Public Involvement Resource Team and HgWG initiated activities to involve and gather stakeholder issues, needs, and concerns about mercury treatment technologies. These activities included reviews, articles, and presentations. During November and December 1997, the chair of the HgWG addressed both the Oak Ridge Local Oversight Committee and the Site-Specific Advisory Board (SSAB). The purpose of the meetings on November 17–18, 1997, was to identify issues, needs, and concerns of various Oak Ridge stakeholders regarding technologies that may be applicable to Oak Ridge. The areas emphasized included continuous emission monitors, characterization, input to Technology Performance Reports (TPRs), and the HgWG. These meetings were interactive, where participants explored the issues and problem solved collectively. No formal presentations were made, but information was provided and progress on various TMFA projects was discussed. Participants included members of the local oversight committee, the Site Technology Coordination Group, and the general public.

The SSAB Environmental Technology Group meeting on December 10, 1997 involved providing stakeholder input into various technology development projects at Oak Ridge. Those they have expressed interest in addressing are:

- Transportable Vitrification System
- TSCA Test Bed for Continuous Emissions Monitors
- Mercury Working Group/Mercury Treatment Demonstrations
- Removal of Mercury from Liquid Wastes.

A short presentation on the status of each activity was given and the proposed future scopes were discussed.

The TMFA assembled a Technical Requirements Working Group (TRWG), which is a stakeholder group capable of representing varied tribal and public perspectives. The TRWG assisted TMFA technical staff in transforming or integrating site-specific issues, needs, and concerns into the TDRDs and in providing tribal and public perspectives to technical staff for identifying and resolving technical issues. The TRWG reviewed and provided recommendations to the TMFA on changes to the Mercury Removal/Extraction TDRD.

Lastly, the TMFA Resource Team facilitated tribal and public involvement by issuing an article in the quarterly, July 1997, newsletter highlighting mercury treatment and disposal.

The plan for a national contract for mercury waste treatment is consistent with minimizing concerns over siting for what would otherwise be multiple treatment facilities. While there are still transportation issues, these are expected to be routine and present no special concerns. No tribal issues are anticipated.

SECTION 8 LESSONS LEARNED

Implementation Considerations

The lessons learned from this process showed no surprises in waste handling or processing conditions required to adequately treat the waste.

Technology Limitations and Needs for Future Development

The high cost of treatment indicates a need for cost reduction measures, such as can be gained through the implementation of a national procurement contract. The need to treat recovered elemental mercury by amalgamation should be further considered and the impact of this secondary waste treatment should be evaluated.

There are still some unknowns about contaminants in commercial-scale treatment of mercury-contaminated mixed wastes. Likewise, there is a need to better define speciation.

Technology Selection Considerations

The process as demonstrated works well on mercury wastes. Once the process is located at a facility with a RCRA Part B permit, the primary consideration will be the extent of co-contamination of both RCRA substances and radionuclides.

APPENDIX A REFERENCES

- Adams, et. al. 2000. Adams, J. W.,* P. D. Kalb,* and D.B. Malkmus, "High Vacuum Thermal Process for Destruction of Dioxins in INEEL/WERF Fly Ash." Presented at: Waste Management 2000 Symposium, Tuscon, AZ, February 29, 2000.
- ATG. 2000. *MER03 – Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Wastes Containing > 260 ppm Mercury*. (Draft submitted to the TRU and Mixed Waste Focus Area, Mercury Working Group), Allied Technology Group, Inc., Fremont, California, July 2000.
- Conley, T. B., Morris, M. I., Osborne-Lee, I. W. and Hulet, G. A. "Mixed Waste Focus Area Mercury Working Group: An Integrated Approach To Mercury Waste Treatment and Disposal" presented at Waste Management '98, Tucson, AZ, March 1998.
- Connor, Jesse R. Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, New York, 1990.
- Kalb, P.D., J.W. Adams, and L.W. Milian. 2001. *Sulfur Polymer Stabilization/Solidification (SPSS) Treatment of Mixed-Waste Mercury Recovered from Environmental Restoration Activities at BNL*, Brookhaven National Laboratory, January 2001
- MWFA. 1999a. *Demonstration of GTS Duratek Process for Stabilizing Mercury Contaminated (<260 ppm) Mixed Wastes*, Mixed Waste Focus Area (MWFA), DOE/EM-0487 (OST #2409), 1999.
- MWFA. 1999b. *Demonstration of ATG Process for Stabilizing Mercury (<260 ppm) Contaminated Mixed Waste*, DOE/EM-0479 (OST #2407), 1999.
- MWFA. 1999c. *Demonstration of NFS DeHg Process for Stabilizing Mercury (<260 ppm) Contaminated Mixed Waste*, DOE/EM-0468 (OST #2229), 1999.
- MWFA. 1999d. *Mercury Contamination – Amalgamate (contract with NFS and ADA): Demonstration of DeHg Process*, DOE/EM-0471 (OST #1675), 1999.
- MWFA. 1999e. *Mercury Contamination – Amalgamate (contract with NFS and ADA): Stabilize Elemental Mercury Wastes*, DOE/EM-0472 (OST #1675-2), 1999.
- MWFA. 1997. *Mixed Waste Focus Area Technology Development Requirements Document*, Mercury Removal/Extraction, INEL/EXT-97-00317, March 1997, Revision 0.
- NFS. 2000. *Demonstration of the Nuclear Fuel Services, Inc. (NFS) DeHg[®] Stabilization Process for Treatment of Radioactively Contaminated Wastes Containing > 260 ppm Mercury (MER03)*. (Draft submitted to TRU and Mixed Waste Focus Area, Mercury Working Group), Nuclear Fuel Services, Inc., Erwin, Tennessee, September 2000.
- Osborne-Lee, I. W., T. B. Conley, M. I. Morris, and G. A. Hulet, *Demonstration Results on the Effect of Mercury Speciation on the Stabilization of Wastes*, ORNL/TM-1999/120, August 1999.
- SeptraDyne. 2001. *Demonstration Of SeptraDyne High Vacuum High Temperature Rotary Retort Process For The Removal And Recovery Of Mercury From Contaminated Mixed Waste*. (Draft submitted to Mixed Waste Focus Area Mercury Working Group), SeptraDyne, Inc., Denton, Texas, March 2001.

APPENDIX B ACRONYMS AND ABBREVIATIONS

| | |
|--------|---|
| ADA | ADA Technologies (Englewood, Colorado) |
| ARARs | Applicable or Relevant and Appropriate Requirements |
| BADT | best available demonstrated technology |
| CBD | <i>Commerce Business Daily</i> |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act |
| CFR | Code of Federal Regulations |
| DeHg | A proprietary process by NFS for processing mercury mixed waste (pronounced de'-merk) |
| DOE | Department of Energy |
| DOT | Department of Transportation |
| EPA | Environmental Protection Agency |
| HgWG | Mercury Working Group, MWFA |
| INEEL | Idaho National Engineering and Environmental Laboratory |
| ITSR | Innovative Technology Summary Report |
| LDR | Land Disposal Restrictions |
| MER02 | A solicitation to industry (September 1997) entitled, "Demonstration of the Stabilization |
| MER03 | Process for Treatment of Radioactively Contaminated Mercury (<260 ppm) Wastes |
| NEPA | National Environmental Policy Act |
| NESHAP | National Emissions Standard for Hazardous Air Pollutants |
| MWFA | Mixed Waste Focus Area |
| NFS | Nuclear Fuel Services, Incorporated (Erwin, Tennessee) |
| ORNL | Oak Ridge National Laboratory |
| OSHA | Occupational Safety and Health Administration |
| PPE | personal protection equipment |
| Ppm | parts per million |
| RCRA | Resource Conservation and Recovery Act |
| RFP | Request for Proposal |
| RI/ FS | Remedial Investigation/ Feasibility Study |
| RMERC | Roasting or Retorting of Mercury-Bearing Hazardous Wastes |
| SSAB | Site Specific Advisory Board |
| SOW | Statement of Work |
| SPSS | Sulfur Polymer Stabilization/Solidification |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TDRD | Technology Development Requirements Document |
| TMFA | TRU and Mixed Waste Focus Area |
| TRU | Transuranic |
| TRWG | Technical Requirements Working Group |
| UTS | Universal Treatment Standard |
| WAC | Waste Acceptance Criteria |

APPENDIX C DATA TABLES

Table 1. Bench-Scale Test Results.

| Parameter | Yard Soil | Chicken Parts | AM/Hg Soil | EU/Hg Soil |
|-------------------------------|-----------|---------------|------------|------------|
| Date | 4/22/99 | 4/23/99 | 5/11/99 | 5/14/99 |
| 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 |
| % Volume Reduction | 55 | 92 | 40 | 42.5 |
| % Moisture | --- | --- | 6.0 | 4.9 |
| Total Process Time (Minutes) | 135 | 55 | 455 | 310 |
| Maximum Process Temp. (°C) | 652 | 471 | 604 | 649 |
| Minimum Vacuum (Inches of Hg) | 28 | 28 | 16.5 | 23.0 |
| 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 |

Table 2. WERF Bench Scale Test Results.

| WERF Sample | 9904-07-4-2 | 9904-07-4-2 | 9904-7-4-1 | 9904-7-4-4 | 9904-7-4-4 |
|---|-------------|-------------|------------|------------|------------|
| Date | 5/14/99 | 5/27/99 | 5/28/99 | 6/21/99 | 6/21/99 |
| Pre-process weight (g) | 91.9 | 59.2 | 73.6 | 114 | 90.75 |
| Post-process weight (g) | 50.5 | 42.9 | 53.6 | 83.4 | 53 |
| Pre-process volume (ml) | 250 | 150 | 200 | 250 | 250 |
| Post-process volume (ml) | 90 | 80 | 100 | 120 | 90 |
| % Weight reduction | 45.0 | 27.5 | 27.2 | 26.8 | 41.6 |
| % Volume reduction | 64 | 47 | 50 | 52 | 64 |
| Pre-process dioxins ² (ppb) | 565 | 565 | 565 | 565 | 565 |
| Post-process dioxins ^a (ppb) | 0.067 | 0.067 | 0.067 | 0.016 | 0.016 |
| % Dioxin removal | 99.98 | 99.98 | 99.98 | 99.98 | 99.98 |
| Pre-process furans ^a (ppb) | 267 | 267 | 267 | 267 | 267 |
| Post-process furans ³ (ppb) | 0.051 | 0.051 | 0.051 | <0.006 | <0.006 |
| % Furan removal | 99.981 | 99.981 | 99.98 | 99.989 | 99.989 |
| % Moisture | 7.3 | 8.3 | 1.91 | 8.4 | 8.15 |

² WERF waste samples were combined as a composite sample before analysis to reduce testing costs. Post-processing WERF samples 99407-4-1 and 99407-4-2 were combined before analysis. Post processing WERF sample 99407-4-4 was analyzed separately.

³ Vacuum levels within the retort fluctuated from 1 to 27 inches of Hg vacuum.

| | | | | | |
|------------------------------|-----|-----|-----|-----|-----|
| Total process time (minutes) | 360 | 90 | 250 | 195 | 50 |
| Maximum process temp. (°C) | 680 | 730 | 760 | 480 | 450 |

Table 3. Additional Problematic Waste Steams Processing Results.

| Drum ID | Preprocess Weight (lbs) | Postprocess Weight (lbs) | % Weight Reduction | Postprocess TCLP Hg (mg/L) | Postprocess Hg (mg/kg) ⁴ |
|----------------|--|--------------------------|--------------------|----------------------------|-------------------------------------|
| A-6 | 525 Soil 27 Carcasses 18 DAW | 440 | 22.8 | <0.0006 | 0.20 |
| A-7 | 495 Soil 16 Carcasses 18 DAW | 350 | 33.8 | 0.0042 | 5.08 |
| A-8 | 690 Soil 10 Carcasses 29 DAW 4 AE1 | 370 | 49.5 | <0.0006 | 2.50 |
| A-9 | 495 Soil 10 Carcasses 10 DAW | --- | --- | <0.0006 | 1.14 |
| E-7 | 245 – Soil | 225 | 8.2 | <0.0006 | 2.06 |
| RA2-090 | 990 Soil 49 AE1 24 DAW | 420 | 60.5 | --- | --- |
| RA2-091 | 490 Soil 40 DAW 32 AE-2/3 | 520 | 7.5 | --- | --- |
| A-10 | 384 Soil 18 AE-1 5 Carcasses 18 DAW | --- | --- | --- | --- |
| Soil Samples | 50 RA291 soil 157 Soil 35 DAW 4 gals (32 lbs.) Hg water | 111 | 50.4 | --- | --- |
| Mercury Sludge | 302 Sludge 61 DAW 42 Resin 10 Sand | 180 | 56.6 | --- | --- |
| Total | 3591 Soil 53 Carcasses 225 DAW ⁵ 32 Hg/water 42 Resin 10 Sand 85 AE 302 Sludge | 2616 | 39.7 | --- | --- |

⁴ Preprocess Hg analyses were not performed.

⁵ Only runs in which both pre and post processing weight data was obtained are included in the total weight reduction summary.

Table 4. Mercury Emissions Data.

| Drum | Batch | Hg Concentration $\mu\text{g}/\text{M}^3$ | |
|-----------|-------|---|----------------------|
| | | Average ⁶ | Maximum ⁷ |
| A-1 | 1 | 8 (9) | 28 |
| | 2 | 10 (7) | 19 |
| | 3 | 14 (6) | 18 |
| A-3 | 1 | 13 (8) | 21 |
| | 2 | 14 (7) | 29 |
| | 3 | 12 (10) | 23 |
| A-5 | 1 | 8 (9) | 12 |
| | 2 | 13 (10) | 16 |
| | 3 | 9 (12) | 12 |
| A-6 | 1 | 10 (6) | 19 |
| | 2 | 13 (9) | 17 |
| | 3 | 10 (12) | 16 |
| A-7 | 1 | 12 (10) | 18 |
| | 2 | 11 (6) | 17 |
| | 3 | 8 (3) | 10 |
| A-8 | 1 | <1 (10) | 3 |
| | 2 | <1 (10) | 4 |
| | 3 | <1 (12) | 4 |
| | 4 | <1 (10) | 4 |
| A-8 / A-9 | 1 | 5 (5) | 7 |
| | 2 | 6 (9) | 7 |
| E-3 | 1 | 7 (6) | 8 |
| | 2 | 7 (5) | 11 |
| E-4 | 1 | 12 (7) | 16 |
| | 2 | 8 (8) | 11 |
| | 3 | 8 (8) | 10 |
| E-6 | 1 | 8 (8) | 14 |
| | 2 | 10 (9) | 16 |
| E-7 | 1 | 9 (6) | 12 |
| | 2 | 8 (3) | 9 |
| RA2-90 | 1 | <1 (10) | 4 |
| | 2 | <1 (10) | 4 |
| | 3 | <1 (10) | 3 |
| | 4 | <1 (10) | 3 |
| | 5 | <1 (10) | 5 |
| | 6 | <1.0 (12) | < 1 |
| RA2 -91 | 1 | <1.0 (6) | < 1 |
| | 2 | <1.0 (13) | < 1 |
| | 3 | <1.0 (12) | < 1 |
| A-10 | 1 | <1 (8) | <1 |
| | 2 | <1 (10) | <1 |
| | 3 | <1 (8) | <1 |

⁶ The mercury concentration is an average of all the data point values obtained during the mercury volatilization phase. The numbers in parenthesis relate to the number of data points. Each value was obtained at 15-minute intervals.

⁷ The maximum mercury concentrations occurred during the peak bake conditions

