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Title: **DEMONSTRATIONS TO SUPPORT CHANGE TO THE >260 PPM MERCURY TREATMENT REGULATIONS**

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ABSTRACT

The U.S. Department of Energy (DOE) and the U. S. Environmental Protection Agency (EPA) are working together to justify a change in the Land Disposal Restriction for High Mercury (>260 ppm mercury) waste. The present regulation that requires roasting or retorting is based on recovering and recycling the mercury in the waste. However, most of DOE's High Mercury waste is radioactively contaminated, eliminating the possibility of its recycle. The radioactive mercury recovered must be amalgamated and disposed. In addition, concern over fugitive emissions from retorting and roasting operations has raised the question of whether such processing is environmentally sound. A change to the regulation to allow stabilization and disposal would reduce the overall environmental threat, if the stabilization process can reduce the leachability of the mercury to regulatory levels. Demonstrations are underway to gather data showing that the High Mercury waste can be safely stabilized. At the same time, comparison tests are being conducted using an improved form of the baseline retorting technology to better quantify the fugitive emission problem and determine the full capability of thermal desorption systems.

A first round of demonstrations stabilizing mercury in soil from Brookhaven National Laboratory (BNL) has been completed. Four groups demonstrated their process on the waste: 1) BNL demonstrated its Sulfur Polymer Stabilization/Solidification process; 2) Nuclear Fuel Services used their DeHg (de-merk) process, 3) Allied Technology Group used chemical stabilization, and 4) Sepradyne demonstrated their vacuum thermal desorption system. All groups were successful in their tests, reaching regulatory levels for mercury leachability. Data for each group will be presented.

DOE, EPA, and the University of Cincinnati are presently working on another series of tests involving treatment of surrogate sludge and soil by commercial vendors. Protocols that better determine the waste form's ability to withstand leaching are being used to analyze the stabilized surrogates. Results of these and the previous demonstrations will be used to determine whether the High Mercury treatment regulation can be safely changed.

INTRODUCTION

The Department of Energy's (DOE) TRU and Mixed Waste Focus Area (TMFA) and the Environmental Protection Agency's Office of Solid Waste (OSW) and Office of

Research and Development (ORD) are working together to determine whether regulations governing the treatment of High Mercury waste could be changed without adversely affecting the environment. The two agencies have established a memorandum of understanding to cooperate on research with environmental significance to leverage scarce research dollars and to ensure that treatment alternatives developed will meet current and future regulations. This paper summarizes mercury waste treatment research that had been completed as of November 2000 and describes work that will be performed during the federal fiscal year 2001 (FY2001).

Background

High Mercury wastes contain greater than 260 ppm mercury. Present regulations require that these wastes be treated by roasting or retorting (RMERC) if they are primarily inorganic or by incineration if they are primarily organic (IMERC). In each case, the treatment system is required to collect the mercury given off for subsequent recycle. Mercury collected from the treatment of DOE's radioactive waste cannot be recycled, because the mercury is still considered radioactive. Mercury's natural shielding properties for radiation make verifying the mercury free of radioactivity nearly impossible. Therefore, returning the mercury to the marketplace would pose a significant risk to the public and the environment. Many of DOE's waste streams still require stabilization after the mercury has been removed because of other contaminants present. DOE would benefit greatly if its High Mercury waste streams could be directly stabilized.

A second factor that has reduced the desirability of RMERC and IMERC regulations is the increase in attention given to the potential for fugitive mercury emissions from thermal processes. Requiring that mercury be put into a gaseous phase and then trying to recollect it is hard to justify if some of the mercury is lost to the environment in the process. Modern thermal processes used for RMERC and IMERC activities are now very good at controlling mercury emissions, and will get better as new regulations requiring maximum achievable control technologies are implemented. However, to meet these regulations, some mercury-contaminated streams will not be accepted for treatment, while others will be mixed with non- or low-mercury feedstock to dilute the quantity of mercury coming through the process.

Because of the concerns over fugitive emissions and the desire to keep mercury out of the commercial sector, EPA is examining other possible approaches to replace RMERC and IMERC. Stabilization promises to provide an environmentally safe option for treating High Mercury waste, especially if the resulting waste form is stable over a wide pH range that would represent possible disposal scenarios. EPA is collecting data that support a possible change in the regulations to allow stabilization of High Mercury waste. EPA and DOE are co-funding research aimed at demonstrating the capabilities of commercial stabilization system, some of which has already been completed. Successful validated performances by the vendors would open the way for the regulations to be changed.

PROTOCOLS

EPA is currently evaluating new sets of protocols to replace the often-criticized Toxicity Characteristic Leaching Procedure (TCLP) presently in service for the determination of the hazardous nature of waste. DOE, working with the EPA, is examining the protocols to determine how they would affect waste-treatment operations and to better evaluate candidate technologies for DOE waste treatment. Establishing waste-form performance for a given process helps DOE determine its long-term risk and liability.

Vanderbilt Protocols

Dr. Kosson of Vanderbilt University has developed a set of protocols for extended evaluation of waste forms. These protocols involve a series of tests on the waste or treated waste forms evaluating the intrinsic leaching characteristics as measured by constituent availability, solubility as a function of pH, and mass transfer rate. These protocols are designed to

- Provide a conservative but more realistic estimate of leaching over a wide range of pHs
- Use testing approaches that can be carried out using standard laboratory practices in a reasonable time frame
- Provide release limits and estimates that consider site-specific conditions
- Encourage improvements in waste management practices (assuming that the TCLP results are, at times, misleading)
- Provide flexibility to allow level of evaluation (and, hence, degree of over conservatism) to be based on the user's requirements.

EPA has funded Dr. Kosson to use his protocols to evaluate the effectiveness of the four vendor produced waste forms as compared to the raw waste from the BNL demonstration described previously (1,2,3). Because these samples were radioactive, Dr. Kosson did not have facilities with the appropriate licenses and permits to be able to perform the testing. Thus, Vanderbilt University through the Work for Others (WFO) Program contracted ORNL to perform the testing. This testing is currently on-going. When completed, the results of sample analysis will be provided to Dr. Kosson along with supporting quality assurance/quality control results and a summary of all laboratory observations and notes, including any modifications to the procedures. Dr. Kosson and his team will interpret the data and prepare the final report for use and support to EPA. ORNL is also restricted from releasing any of the data or results without consent from Vanderbilt University. The testing is scheduled to be completed by the end of FY-2001. Preliminary reports indicate that waste forms from some processes that have met LDR standards leach significant concentrations of mercury at pH values that could be encountered in a landfill (4). The data from the application of the Vanderbilt protocols to stabilized DOE waste will be published by Vanderbilt.

University of Cincinnati Leaching Protocols

University of Cincinnati (UC), under contract to the EPA, developed leaching procedures to assess the stability of treated wastes. These leaching tests include TCLP, variable mass leaching, and UC constant pH leaching. The tests provide an approach that is simpler than the Vanderbilt protocols for determining the behavior of a waste form in a variety of disposal scenarios. The following paragraphs discuss the leaching tests.

Toxicity Characteristic Leaching Procedure

TCLP is a standard regulatory test intended to determine the potential mobility of contaminants in a liquid or solid under simulated landfill conditions. Tests are run in duplicate and analyzed for, in this case, mercury. Important aspects of the test include

- An extraction fluid of buffered acetic acid at pH 4.93 (or 2.88 for highly alkaline waste)
- A prescribed liquid/solid ration of 20:1
- Particle size reduction to 9.5 mm
- Agitation of the ground-waste/extraction-fluid mixture for 18 hours

UC Constant pH Based Leaching

The UC constant pH leaching tests, developed by UC, are a means to determine the effect pH has on the stability of a waste. Separate project-specific pH leaching procedures are provided for untreated and treated surrogate. Samples are leached in a constant pH solution that is adjusted to the desired pH end point. The constant-pH leaching test is typically run on 6 pH values between 2 and 12. Duplicates are run for three pH values. Two experimental blanks are included. The pH is maintained by automated systems for a 10-day period prior to leachate sampling. All pH experiments are duplicated. The test includes an experimental blank. All extracted samples are filtered and analyzed for mercury content.

DEMONSTRATIONS

<260 ppm Mercury Demonstrations

The DOE Mercury Working Group conducted a series of demonstrations to ensure that the private sector could safely stabilize waste contaminated with less than 260 ppm mercury. First, three vendors, Allied Technology Group (ATG), International Technologies, Inc. and Nuclear Fuel Services (NFS), conducted surrogate studies at bench scale that determined whether their process could handle five different species of mercury in a soil matrix (4,5,6). Each vendor successfully stabilized the surrogates to meet the Universal Treatment Standard, 0.025 mg/L in the TCLP leachate. The organo-mercury compound included posed the greatest difficulty for the vendors.

Three vendors, ATG, GTS Duratek, and NFS performed larger-scale demonstrations on actual radioactive mercury wastes. ATG and NFS stabilized ion exchange resin contaminated with mercury (5,6), while GTS Duratek (7) stabilized sludge contaminated with heavy metals, including mercury, and RCRA-listed organic compounds. The mercury and metals were successfully stabilized in each case.

> 260 ppm Mercury in Soil Demonstrations

In 1996 the HgWG and the EPA began discussions of the problems of applying the current treatment standards to mixed waste. The HgWG proposed stabilization demonstrations on >260 ppm mercury waste as a follow-on to the <260 ppm mercury that that were being planned. These discussions laid the groundwork for demonstrations that started in 1998. Three commercial vendors, SeptraDyne, ATG and NFS, and Brookhaven National Laboratory (BNL) each demonstrated their respective process for the treatment of a mercury-contaminated soil from BNL (8,9). The soil, excavated as part of an environmental remediation project, was contaminated with approximately 4000 ppm mercury. The sample drums used for the demonstrations came from two B-25 boxes of soil that were different mainly in their concentration of specific radionuclides, Americium (A drums) and Europium (E drums). Each sample drum was a carefully mixed portion of a single box. Initially the A and E drums were expected to have radically different mercury concentrations, but sampling that followed the division of the box contents into drums showed the concentrations to be similar.

Sulfur Polymer Solidification/Stabilization Demonstration

BNL demonstrated their Sulfur Polymer Solidification/Stabilization process on two sample drums of the waste, drums A4 and E1 (9). In addition BNL used the SPSS process to treat 400 pounds of elemental mercury recovered from the same remediation project, meeting the EPA's amalgamation regulation. BNL successfully treated each of the waste types, though BNL was forced to adjust process chemistry to be able to meet the UTS limit. Table I contains a summary of the data generated by BNL. BNL monitored for mercury vapor in the work area and from the process offgas system and found none. TMFA will issue an Integrated Technology Summary Report describing the technology.

Table I. Sulfur polymer solidification/stabilization >260 ppm mercury stabilization test data.

Drum ID	Pre-Wt (Lb)	Pre-TCLP (mg/L)	Pre-Total Hg (mg/kg)	Wt Change	Post-TCLP (mg/L)
A-4	450	0.914	5570	+53%	0.0005
E-1	280	0.208	4190	+54%	0.00147

Nuclear Fuel Services Stabilization Demonstration

NFS demonstrated its DeHg mercury stabilization process on one drum of the BNL soil (10). NFS used a pilot-scale DeHg reactor capable of handling up to 100 pounds of soil, metering soil and stabilizing reagents directly into the reactor. The soil samples were

particle size reduced to ensure that feed particles did not exceed 1/8 inch in diameter. The demonstration consisted of seven batch runs, with grab samples from each being submitted for analysis. An average of the results is shown in Table II with the final TCLP results ranging from <0.0006 to 0.0102 mg/L TCLP. NFS monitored for mercury emissions with a Jerome mercury vapor analyzer and determined that mercury losses to the environment were negligible.

Table II. Nuclear Fuel Services DeHg process >260 ppm mercury stabilization test data.

Drum ID	Pre-Wt (Lb)	Pre-TCLP (mg/L)	Pre-Total Hg (mg/kg)	Wt Change	Post-TCLP (mg/L)
A-2	387	1.5	4400	+17%	0.0045*

Note: *Average of six batches.

Allied Technology Group Stabilization Demonstration

ATG treated one drum of waste, but split the contents of the drum and used two formulations to stabilize the waste (11). Bench- and pilot-scale tests indicated that both dithiocarbamate-based and liquid sulfide formulations coupled with Portland Cement could effectively stabilize the soil. Full-scale tests were conducted using a seven-cubic-foot Essick mortar mixer. The mixer was modified to include aeration. ATG is presenting the details of the work as part of the Waste Management 2001 conference. Table III contains a summary of the full-scale test data generated by ATG.

Table III. Allied Technology Group >260 ppm mercury stabilization test data.

Drum ID	Treatment	Pre-Wt (Lb)	Pre-TCLP (mg/L)	Pre-Total Hg (mg/kg)	Wt Change	Post-TCLP (mg/L)
E-2*	DTC	220*	0.282	4233	+33%	0.0139
E-2*	Sulfide	220*	0.282	4233	+44%	0.0020

Note: * ATG split drum E-2 and treated with two different chemicals.

SepraDyne/Raduce Vacuum Thermal Desorption Demonstration

SepraDyne/Raduce, Inc. demonstrated their vacuum thermal desorption process, an improved version of the High Mercury baseline waste treatment technology. SepraDyne treated four drums of the Brookhaven waste as part of the demonstration, along with a number of other problematic mercury-contaminated waste streams, which even included radioactive, mercury-contaminated animal carcasses. The SepraDyne process was highly successful in removing mercury from the waste streams treated, eliminating most of BNL's small-volume mercury waste streams. Readings of the Jerome Analyzer used to monitor for mercury in the air in the vicinity of the process were well below legal limits. Mercury removed from the waste and collected by the system was subsequently

stabilized by BNL with the sulfur polymer solidification/stabilization process. Table IV summarizes the data for the four drums of soil treated by SepraDyne.

Table IV. SepraDyne – Brookhaven National Laboratory demonstration unit results.

Drum ID	Pre-Wt (Lb)	Pre-TCLP (mg/L)	Pre-Total Hg (mg/kg)	Wt Change	Post-TCLP (mg/L)	Post-Total (mg/kg)
A-1	550	0.868	4040	-27%	Non-Detect	1.8
A-3	470	1.390	2310	-12%	Non-Detect	1.02
E-3	367	0.191	4880	-9%	Non-Detect	0.545
E-4	375	0.212	5510	-52%	0.002	4.21

Sludge Demonstrations

DOE and EPA agreed to conduct tests on another waste matrix besides soil to generate additional supporting data for a possible High Mercury regulation change. UC will construct surrogate mercury sludge for use in this evaluation. The surrogate will be subjected to physical and chemical characterization and leaching tests to provide a baseline for comparison after treatment. Vendors selected by the HgWG and EPA’s Office of Solid Waste through a competitive bidding process will treat two one-hundred-pound samples of the surrogate. UC will ship the surrogate as pre-measured components to be blended by the vendors. UC will make additional surrogate available to the vendors upon request for pre-treatment treatability testing. Following successful treatment of the two surrogate batches by the selected vendors, the vendors will ship the treated surrogate to UC for sampling and evaluation. Physical and chemical characterization and leaching tests will be performed on the baseline surrogate and on the vendor-stabilized materials.

The composition of the surrogate sludge is outlined in Table V. Mercury species as listed in Table V will be added only after the major constituents have been well blended. UC will analyze three random samples of surrogate prepared at UC to assess total mercury variability and leachability. The laboratory-scale surrogate will be characterized and leached to generate baseline data, against which the vendor treated samples can be compared. If the research team encounters difficulties in working with the surrogate, the team will adjust the surrogate composition to ensure that the demonstrations can be successfully completed.

Table V. Surrogate sludge composition.

Sludge Constituent	Weight Percentage %	Mercury Concentration ppm
Phenyl Mercury	0.05	500
Mercury Nitrate	0.1	1000
Elemental Mercury	0.15	1500
Mercury Oxide	0.1	1000
Mercury Chloride	0.1	1000
Diatomaceous Earth	20	
Aluminum Hydroxide	10	
Ferric Chloride	10	
Sodium Chloride	10	
Motor Oil (new)	1	
Water	48.5	
Total	100	5000

Samples of the baseline surrogate, and the vendor mixed surrogate will be analyzed for total mercury and subjected to the TCLP. Samples of the sludge and leachate will be submitted to a commercial analytical laboratory for mercury analysis. Samples of the baseline surrogate and treated surrogate will also be sent to a commercial laboratory for physical and chemical measurements, including bulk density, moisture content, percent organic matter, cation-exchange capacity, and particle-size distribution. The testing uses standard methods for soils, established by the USDA and the Soil Society of America.

Additional characterization of the baseline surrogate and vendor stabilized materials by UC will include alkalinity and acidity testing following one leaching procedure, and pH analysis on all samples. All characterization testing will be performed in duplicate.

CONCLUSION

Tests co-sponsored by EPA and DOE are building a case for a change to the regulations for treatment and disposal of waste containing >260 ppm mercury. TCLP results for the first set of demonstrations have indicated that stabilization of >260 ppm mercury waste could be environmentally safe. However, more detailed, exacting tests will provide a broader picture of how the stabilized waste will behave under a variety of conditions. These tests may show that the stabilized waste cannot be safely disposed in the relatively uncontrolled environment of a typical disposal site. Applying these tests to stabilized soil from BNL and stabilized surrogate sludge will indicate whether industry can safely stabilize and dispose High Mercury waste. EPA will have to weigh whether extra precautions would be required for disposal of the treated waste forms. Those additional measures could raise the treatment and disposal costs so much that retorting and roasting will become more cost effective.

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