STABILIZATION OF A MIXED WASTE SLUDGE SURROGATE CONTAINING MORE THAN 260 PPM MERCURY (1)

William J. Smith
Jacobs Engineering Group Inc.
2822 Bayview Drive, Alameda, CA 94501

Fred Feizollahi and Richard Brimley
ATG Inc.
2025 Battelle Blvd., Richland, WA 99352

ABSTRACT

In an earlier demonstration of an innovative mercury stabilization technology for the Department of Energy, ATG's full-scale process stabilized mercury in soils that initially contained more than 260 ppm of mercury of unknown speciation. The treated waste satisfied the leaching standards for mercury that qualify wastes containing less than 260 ppm for land disposal. This paper describes the extension of that work to demonstrate a full-scale process for the stabilization of a representative sludge that contained more than 260 ppm of Hg of several mercury species.

RCRA (Resource Conservation and Recovery Act) regulations now require the recovery of mercury from any waste containing more than 260 ppm of mercury, usually with thermal retorts. The results of this work with a surrogate sludge, and of the previous work with an actual soil, support a proposal now before the U.S. EPA (Environmental Protection Agency) to allow such wastes to be stabilized without retorting.

The full-scale demonstration with a sulfide reagent reduced the mercury concentrations in extracts of treated sludge below the relevant leaching standard, a Universal Treatment Standard (UTS) limit of 0.025 mg mercury per liter of leachate generated by the Toxicity Characteristic Leaching Procedure (TCLP). The sulfide formulation reduced the concentration to about one-half the UTS limit.

INTRODUCTION

Building on the results of companion demonstrations with ion exchange resin and soil (1-5), this paper describes the stabilization of a variety of mercury species in a synthetic sludge provided by the University of Cincinnati. The stabilized sludge satisfied the Universal Treatment Standards, which are the technical requirements for disposal of waste containing less than 260 ppm of mercury in a landfill. Although the stabilized sludge satisfied these technical requirements for land disposal, the treated material is legally ineligible for land disposal on a commercial scale. The various mercury species were present at concentrations greater than 260 ppm and current regulations require that the mercury be recovered from such high mercury wastes prior to land disposal.

Although mercury from hazardous wastes is recovered and recycled, recovered mercury from mixed waste is potentially radioactive, and recyclers will not accept mercury recovered from mixed waste. Mixed waste contains both hazardous chemicals and radioactive constituents. Instead, mercury recovered from mixed waste is amalgamated and disposed of in a landfill along with the matrix, such as soil, from which the mercury was recovered.

(1) Demonstration Sponsored by DOE Mixed Waste Focus Area

The stabilization of mercury reported in this paper supports the elimination of the mercury recovery step for mixed waste. The single step process used here immobilized mercury within the original matrix and produced a treated waste form that satisfied the Universal Treatment Standards. The Universal Treatment Standards currently govern the land disposal of wastes containing less than 260 ppm mercury.
Additional characterization of this, and other treated materials by the University of Cincinnati to be reported elsewhere, will be used by the U.S. EPA to determine if a change in regulations to permit the stabilization of mixed waste containing greater than 260 ppm of mercury is warranted. Such a change in regulations would allow the industry to treat hundreds of cubic meters of mixed waste with a one-step process rather than the multi-step process currently required.

EXPERIMENTAL MATERIALS AND METHODS

Using a synthetic sludge containing a variety of mercury species, ATG conducted bench-scale tests with 3 different formulations. The best formulation was chosen for the demonstration.

The demonstration test and supporting bench-scale tests were conducted with a surrogate material supplied by the University of Cincinnati. ATG received sufficient premeasured materials to make up two 50 lb batches of surrogate material. Figure 1 shows several of the colorful mercury species added to the surrogate sludge. Excellent dispersion of elemental mercury was achieved by mixing the elemental mercury separately with a small quantity of dry ingredients and then mixing the dry mixture into the sludge.

Fig. 1. Unmixed Sludge After Adding All Mercury Additives

The three reagents used as the basis for the three different formulations tested included 1) a proprietary dithiocarbamate (DTC), 2) sodium tetrathiocarbonate, and 3) sodium hydrogen sulfide (NaHS). A clay (AquaSet 2-H) supplied by FluidTech of Las Vegas, Nevada, was used to solidify the treated material.

The bench-scale tests were conducted with 600 gm samples of waste. Based on the results of standard TCLP tests conducted with samples of the treated wastes, the NaHS formulation was selected for the demonstration. As the small 50-pound batch was near the minimum size required for the powered mortar mixer described in the work plan, ATG used a smaller manual mixer for this demonstration. Standard TCLP tests assess the degree of leaching of mercury from a solid matrix.

Bench-Scale Test: The three formulations indicated in the materials section above were bench-tested by adding each formulation to 600 grams of waste and mixing with a Kitchen-Aide Blender. The order of addition of the reagents for each formulation was carefully controlled.

Demonstration Test: After mixing the surrogate sludge as instructed by the University of Cincinnati, each 50-lb batch of surrogate material was treated with the NaHS formulation. 1-gallon of the NaHS solution was added to each sludge batch and mixed for 15 minutes. Then 50 pounds of the clay was added and mixed. Samples for testing were collected after the clay was mixed in. The samples were then cured for two weeks before they were submitted to the lab. The remainder of the treated material was poured into a 62-quart cooler lined with a plastic bag. The final treated material was a monolith with a volume of approximately 2 cubic feet.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the TCLP testing showed that the sodium sulfide formulation produced a stabilized material that satisfied the UTS (Universal Treatment Standard) treatment limits for mercury. In bench-scale tests and in two large batches, the formulations reduced the leaching of several mercury species present in the surrogate waste to concentrations one-tenth to one-half of the UTS limit.

Bench-Scale Test

The bench-scale test evaluated three formulations and identified one, the NaHS formulation, that reduced the leaching of mercury from the treated waste below the UTS limit. Temperature increases were observed for the NaHS formulation. As shown in Table I, the total concentration of mercury in the leachate was one-tenth of the UTS value of 0.025 mg/l for the NaHS compound. The concentrations of leachate were slightly greater than the UTS value for the dithiocarbamate and much greater for the tetrathiocarbamate.

Demonstration Test

The demonstration test showed that treatment with NaHS stabilized the mercury in the surrogate sludge to the UTS limit. Figures 2 and 3 show the sludge before and after treatment. The untreated sludge in Figure 2 is colored burnt orange by the iron oxide added to the sludge matrix. The treated material in Figure 3 is colored deep black by sulfide compounds.

Leaching: As shown in Table II, the total concentration of mercury in the leachate from the two batches of surrogate material treated with the NaHS formulation was approximately one-tenth and one-half of the UTS limit of 0.025 mg/l for Batches 1 and 2 respectively.

Table I
Mercury in TCLP Leachate from Bench Scale Tests

Formulation	Leachate mg/ml
Dithiocarbamate (DTC)	0.055
Sodium Tetrathiocarbamate (STTC)	0.400
Sodium Hydrogen Sulfide (NaHS)	0.002

Fig. 2. Untreated Sludge

Fig. 3. Treated Sludge

Table II
Mercury in TCLP Leachate from Sludge Surrogate Treated with NaHS

	Batch 1	**Batch 2**
Mercury Concentration in TCLP Leachate (mg/l)	0.0027	0.011
Increase in Weight as % of Initial Sludge Weight	50%	50%
Increase in Volume as % of Initial Sludge Volume	~100%	~100%

Operational Considerations: Approximately 30 minutes is required for a batch cycle: 5 minutes to pour the sludge into the mixer, 5 minutes to add and mix the NaHS, 15 minutes to add and mix the clay, and 5 minutes to pour the treated waste out of the mixer.

The consistency of the treated sludge was similar to a pliable clay for one week after treatment, during which the internal temperature remained at about 30°C. After 1-week the material cooled and set to a very hard concrete.

Temperature control is unlikely to be required during mixing. During curing, temperature control will be adequate if at least one linear dimension of the final waste form is less than 1.5 feet.

No airborne mercury was detected by a Jerome mercury monitor during treatment. Hydrogen sulfide concentrations did initially approach adminstrative control limits of 10 ppm in the room air and the odor was unpleasant. Placement of additional plastic sheeting over the mixer reduced room concentrations of hydrogen sulfide to less than 5 ppm and a tolerable odor. Good ventilation is required for this process to capture or disperse the hydrogen sulfide.

The only secondary wastes generated by the demonstration test were three 0.6-0.9 kg samples of treated waste (approximately 2 kg total) generated by the bench tests and dunnage. The dunnage consisted of personal protective clothing, cloth wipes, plastic sheets, jars, and pails. Excluding empty waste containers, the demonstration test indicated that 10 – 20 pounds of dunnage would be generated each day during full-scale operation.

CONCLUSION

The stabilization system demonstrated here has the potential to treat most of the low-level streams listed in Table 1 of the Mixed Waste Focus Area Requirements Document (4), including aqueous streams designated for the TSCA incinerator and the transportable vitrification system. The demonstration, which reduced the concentrations of mercury in leachate below the UTS limits, provides strong support for designation of stabilization as a treatment technology for wastes with mercury concentrations greater than 260 ppm.

REFERENCES

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