

Mercury Bakeoff: Technology Comparison for the Treatment of Mixed Waste Mercury Contaminated Soils at BNL

P.D. Kalb¹, J.W. Adams¹, L.W. Milian¹, G. Penny², J. Brower¹, A. Lockwood³

¹ Brookhaven National Laboratory

² U.S. Department of Energy Brookhaven Group

³ CDM Federal Programs Corp.

Environmental Sciences Department

**Brookhaven National Laboratory
Brookhaven Science Associates
Upton, Long Island New York 11973**

Under Contract No. DE-AC02-98CH10886 with the

UNITED STATES DEPARTMENT OF ENERGY

Mercury Bakeoff: Technology Comparison for the Treatment of Mixed Waste Mercury Contaminated Soils at BNL*

P.D. Kalb¹, J.W. Adams¹, L.W. Milian¹, G. Penny², J. Brower¹, A. Lockwood³

¹ Brookhaven National Laboratory

² U.S. Department of Energy Brookhaven Group

³ CDM Federal Programs Corp.

ABSTRACT

Over 440 yd³ of radioactively contaminated soil containing toxic mercury was generated during a Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) removal action at Brookhaven National Laboratory (BNL). The U.S. Department of Energy's (DOE) Office of Science and Technology Mixed Waste Focus Area (DOE MWFA) is sponsoring a comparison of several technologies that may be used to treat these wastes and similar wastes at BNL and other sites across the DOE complex. Challenges associated with treating these wastes are discussed and the results of pilot-scale treatment using the Sulfur Polymer Stabilization/Solidification (SPSS) process are described in detail. This technology, recently developed at BNL, chemically stabilizes the mercury to reduce vapor pressure and leachability and physically encapsulates the waste in a solid to eliminate dispersion and provide long-term durability. Two 55-gal. drums of mixed waste soil containing high concentrations of mercury were successfully treated. Waste loadings of 60 wt% soil were achieved without resulting in any increase in waste volume. Preliminary Toxicity Characteristic Leaching Procedure (TCLP) analyses indicate the final waste form products pass current Environmental Protection Agency (EPA) allowable TCLP concentrations as well as the more stringent proposed Universal Treatment Standards.

BACKGROUND

Remedial excavation of the Animal/Chemical Pits and Glass Holes was conducted at BNL in the summer of 1997 in compliance with CERCLA and New York State regulations. Following removal of wastes, debris, and contaminated soil from a total of 55 separate waste pits, the materials were sorted, segregated, characterized, and either securely stored on-site or shipped for offsite disposal. One pile of approximately 440 yd³ of soil has been identified as mixed waste, since composite samples failed TCLP for mercury. A smaller volume of approximately 100 ft³ was segregated into two partially filled B-25 boxes because it contained higher concentrations, i.e., >260 ppm of mercury. The DOE MWFA is sponsoring a comparison of several technologies for the treatment of this high concentration mercury contaminated mixed waste soil.

The 260 ppm mercury concentration criteria is based on EPA Land Disposal Restriction (LDR) treatment standards. For wastes containing <260 ppm mercury, the EPA specific treatment standard is stabilization. Above 260 ppm mercury, the EPA specific treatment standard is RMERC (retorting

*This work was performed under the auspices of the U.S. Department of Energy

or roasting with recovery of the mercury for reuse). Demonstration of the baseline RMERC treatment for the BNL soil is scheduled to be conducted by Raduce, Inc. (Spring 1999) using their high vacuum rotary kiln separation process (1). However, EPA treatment standards were originally conceived for non-radiologically contaminated hazardous mercury. Separation of mercury from mixed waste soils results in generation of two waste streams for treatment/disposal. Recovered mercury would likely still be radiologically contaminated, prohibiting its recycle or reuse as elemental mercury. The elemental mercury would require further treatment prior to disposal. In reviewing and approving a request for Determination of Equivalent Treatment (2), EPA agreed that "RMERC is not appropriate for this waste"(3). Thus, several alternative treatment technologies that directly stabilize the mixed waste soil are being examined. Pilot-scale treatment of the soil using the BNL SPSS process has been completed and is reported here. Testing of several other stabilization technologies (final selections have not been made) is expected in FY 1999. Although this project is focusing on mercury soil exceeding 260 ppm, data can be used to evaluate treatment alternatives for other soils with lesser mercury and radionuclide concentrations.

WASTE DESCRIPTION

The subject waste consisted of approximately 4990 kg radioactively contaminated soil, originally contained in two B-25 boxes. The physical composition of the soil was mostly sand and silt with a small percentage of gravel and approximately 5 percent debris (glass, metal and plastic), most of which was removed during subsequent repackaging operations. During excavation, the soil was screened to less than 1 inch. Significant homogenization of the soil in the B-25s occurred during the segregation/screening process. Composite characterization data summarized in Table 1 indicate average total mercury concentrations of 6750 mg/kg and 18,000 mg/kg. Representative samples of each waste bin were TCLP tested yielding mercury concentrations of 3.56 mg/l and 0.26 mg/l, respectively, above current limits of 0.2 mg/l, making them subject to LDR treatment standards. In addition to varying levels of mercury, the two drums differed in isotopic mixture and concentrations. One contained relatively high concentrations of Am-241 and the other primarily Eu-152 and Ra-226.

Each B-25 box of soil was subdivided into seven 55-gal drums for eventual distribution to project participants. To ensure testing of comparable wastes, the soil was evenly divided when repackaged by manually shoveling small scoops into each drum in turn. The drums were assigned a unique identification number (A1 - A7 for the drums containing Am and E1 - E7 for the drums containing Eu) and sealed to ensure chain of custody. Composite samples taken from each drum will be analyzed to confirm equivalent source term composition of the waste. Large pieces of debris were manually removed while repackaging. Prior to processing using the SPSS process, the soil was re-sieved using a 3/8-in. screen, and a small quantity of stones removed.

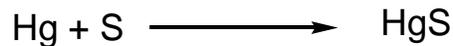
Table 1. Characterization Data for BNL Mixed Waste Soils

Parameter	B-25 Box 1	B-25 Box 2
Hg (total)	6750 mg/kg	18,000 mg/kg
Hg (TCLP)	3.56 mg/l	0.263 mg/l
Gross Alpha	4560 pCi/g	24.9 pCi/g
Gross Beta	525 pCi/g	35.9 pCi/g
Am ²⁴¹	7140 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
Ra ²²⁶	---	35.5 pCi/g

SULFUR POLYMER STABILIZATION/SOLIDIFICATION PROCESS

Sulfur Polymer Stabilization/Solidification (SPSS) is a new technology (patent pending) based on a patented mixed waste treatment technology previously developed at BNL (4). Sulfur Polymer Cement (SPC) consists of 95 wt% elemental sulfur reacted with 5 wt% of an organic modifier to enhance mechanical integrity and long-term durability. Previous testing conducted on sulfur polymer waste forms indicate excellent performance under anticipated disposal conditions (5),(6). Original development to apply the technology for treatment of elemental mercury was sponsored by the DOE MWFA as a “Quick Win” project (7).

SPSS mercury treatment is conducted in two stages. The first step is a reaction between mercury and powdered SPC, forming mercuric sulfide.



The reaction vessel is placed under inert gas atmosphere to prevent the formation of mercuric oxide (a water soluble and highly leachable compound), and a small quantity of additive is included to accelerate the reaction. The vessel is heated to ~ 40 °C during the stabilization phase to accelerate the sulfide formation reaction, and the materials are mixed until the mercury is completely reacted with the sulfur. Once the mercury is chemically stabilized, additional SPC is added, and the mixture is heated at about 130 °C until a homogeneous molten mixture is formed. It is then poured into a suitable mold where it cools to form a monolithic solid waste form.

SPSS processing was accomplished using a pilot-scale vertical cone blender/dryer (Ross Mixers, Hauppauge, NY) with a capacity of 1 ft³. A schematic diagram of the mixer is shown in Figure 1. Mixing is provided by an orbital helical screw, which both rotates and revolves drawing material upward from the base of the cone. Feed materials are charged to the unit through a 6-inch diameter port on the cone lid. A HEPA filtered ventilation system featuring a 10-inch diameter ventilation line and 1000-cfm blower prevents dispersion of particles during charging. A 2-inch heated ball valve at the base of the cone is used for product discharge. When mixing or drying, the system may be operated under vacuum through the use of a 14.6-cfm, 0.5-hp vacuum pump. Heat is provided to the jacketed cone by a 9kW circulating fluid heat transfer system (Mokon, Buffalo, NY). Off gas is collected/treated in multiple stages: first it passes through a shell and tube heat exchanger cooled by a 3 ton chiller (Mokon), followed by a liquid nitrogen cryogenic trap and finally through HEPA and activated charcoal filters before venting to the atmosphere. Condensate is collected at the heat exchanger in an off gas condensate vessel and at the cryogenic trap for analyses. A schematic diagram of the off gas system is shown in Figure 2.

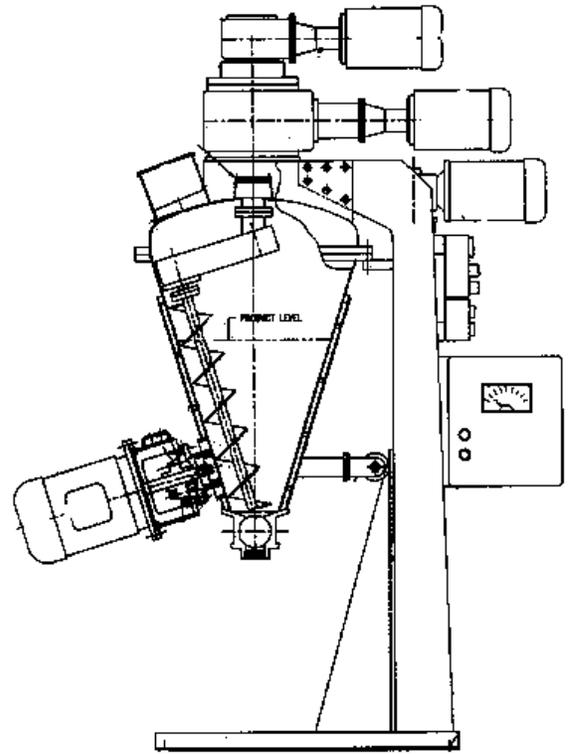


Figure 1. Schematic of 1 ft³ Cone Blender

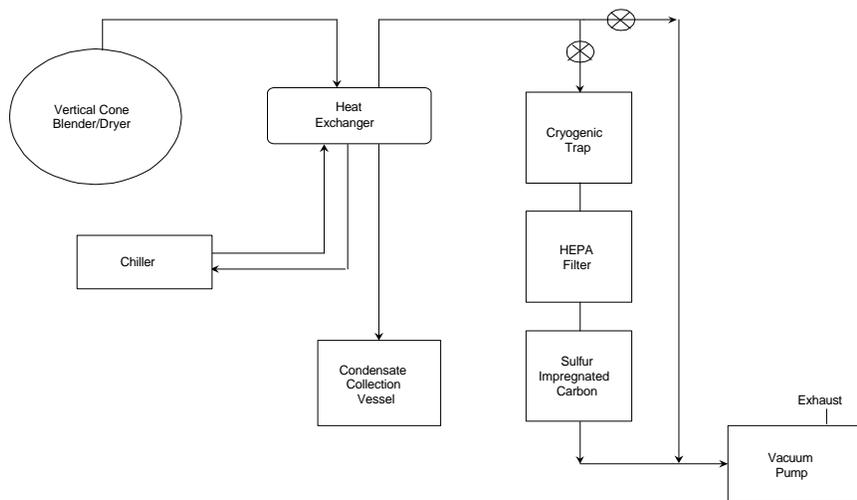


Figure 2. Schematic diagram of blender off gas system

Initial development work for the SPSS process demonstrated that as much as 33 wt% elemental mercury can be successfully encapsulated and still meet EPA TCLP leaching criteria (7). Although the soils tested in this study contained relatively high concentrations of mercury (up to 18,000 ppm), they contained far less mercury on a mass basis than the liquid mercury previously tested. Thus, physical processing parameters (e.g., viscosity of the mix) rather than mercury leachability represent the limiting constraint on maximum waste loading. Using the “off-the-shelf” vertical cone blender, mixtures containing up to 70 wt% soil were processed. However, when discharging the mixture at this waste loading, a layer of material tended to stick to the walls of the vessel and required manual scraping. When the waste loading was reduced to 60 wt% soil, the viscosity of the mixture was lower, and most of the mixture flowed easily out of the vessel into the collection container. At this waste loading, the volume of treated waste was virtually the same as the untreated waste, i.e., no increase in volume resulted. This is due to filling of void spaces in the soil by the molten sulfur polymer. Based on these results, modification of the mixer design to include a Teflon wiper blade in addition to the rotating mixing auger is suggested. This would result in the ability to successfully process increased waste loadings and higher viscosity wastes (e.g., sludges). Figure 3 is a photograph of the SPSS process showing discharge of treated mercury contaminated mixed waste soil.



Figure 3. Discharge of treated mercury contaminated mixed waste soil using the pilot-scale BNL SPSS process.

A total of 12 batches of soil were processed to complete the pilot-scale treatment of the two 55-gal. drums of waste. Several hundred gram subsamples were taken from each batch to be used for performance evaluation. Approximately 20 g of treated material from each batch was prepared for composite TCLP analyses. Although these data are not yet available, preliminary TCLP testing was completed for two batches processed from Drum A4. Data summarized in Table 2 indicate extremely low leachability for mercury (0.5 and 3 ppb, respectively), compared with the untreated soil (914 ppb), the current TCLP limit (200 ppb), and the more stringent Universal Treatment Standard (25 ppb).

Table 2. Toxicity Characteristic Leaching Procedure (TCLP) Data for Mercury Contaminated Mixed Waste Soils

Sample	Mercury Concentration, ppb
Untreated soil (Drum A4)	914
SPSS treated soil, 60 wt% loading (A4-1)	0.5
SPSS treated soil, 60 wt% loading (A4-2)	3
TCLP maximum concentration	200
UTS maximum concentration	25

SUMMARY AND CONCLUSIONS

A large volume of mercury-contaminated mixed waste soil requiring treatment was generated at BNL as a result of recent environmental restoration activities. Current EPA treatment standards for mixed wastes containing >260 ppm mercury (retort) are not appropriate since the mercury cannot be recycled, and secondary wastes requiring further treatment are produced. Thus, direct stabilization for disposal of these high concentration mercury mixed wastes is sought, and DOE MWFA is supporting a comparison of several treatment options. Pilot-scale treatment using SPSS resulted in successful treatment of the soil at a waste loading of 60 wt% soil, with no increase in waste volume. Higher waste loadings may be possible but, due to viscosity limitations of the mixture, would require engineering modifications of the process equipment. Final characterization of the treated waste is not yet complete, but preliminary data indicate the waste form product easily meets both existing TCLP and more stringent UTS leaching criteria. Plans to demonstrate at full-scale and commercially license the SPSS technology are currently being discussed.

ACKNOWLEDGMENTS

This work was supported by the Mercury Working Group of the DOE Office of Science and Technology Mixed Waste Focus Area and the BNL Office of Environmental Restoration.

REFERENCES

1. R. AULBAUGH and G. G. HAWK, "Low Temperature High Vacuum Rotating Retort for the Removal and Recovery of Mercury from the East Fork Poplar Creek Soils in Oak Ridge, TN," Proceedings of the International Incineration Conference, May 1996.
2. U.S. DOE Brookhaven Group, "Request for Determination of Equivalent Treatment for Mercury Contaminated Wastes," Submitted to EPA July 1, 1998.
3. E.A. COTSWORTH, Acting Director of U.S. EPA Office of Solid Waste, Letter to G.J. Malosh, approving request for Determination of Equivalent Treatment, July 27, 1998.
4. P. COLOMBO, P.D. KALB, and J. H HEISER, "Process for the Encapsulation and Stabilization of Radioactive, Hazardous and Mixed Wastes," U.S. Patent 5,678,234, October 14, 1997.
5. P.D. KALB, J.H. HEISER, R. PIETRZAK, and P. COLOMBO, "Durability of Incinerator Ash Waste Encapsulated in Modified Sulfur Cement," Presented at the 1991 Incineration Conference: Thermal Treatment of Radioactive, Hazardous, Chemical, Mixed, and Medical Wastes, Knoxville, TN, May 1991.
6. P.D. KALB, J.H. HEISER, and P. COLOMBO, "Modified Sulfur Cement Encapsulation of Mixed Waste Contaminated Incinerator Fly Ash," *Waste Management*, Vol. 11, No. 3, pp. 147-153, Pergamon Press, 1991.
7. P.D. KALB, D. MELAMED, M. FUHRMANN, J.W. ADAMS, M. SAPANARA, and C. DETELLO, "Sulfur Polymer Stabilization/Solidification of Elemental Mercury Mixed Waste," Presented at 19th U.S. Department of Energy Low-Level Radioactive Waste Management Conference, Salt Lake City, UT, November 1998.