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DEMONSTRATION OF A STABILIZATION PROCESS FOR THE TREATMENT OF RADIOACTIVELY CONTAMINATED WASTES CONTAINING MERCURY AT CONCENTRATIONS GREATER THAN 260 PPM (1)

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ABSTRACT

In an earlier demonstration of an innovative mercury stabilization technology for the Department of Energy, ATG's full-scale process stabilized mercury in wastes that initially contained less than 260 ppm Hg (DOE, 1999b). The treated waste satisfied the applicable leaching standards for mercury and qualified for land disposal. This paper describes the extension of that work to demonstrate a full-scale process for the stabilization of a mixed waste that contained more than 260 ppm of Hg. Mixed waste contains both radioactive and chemically hazardous constituents.

The full-scale demonstrations described here produced a stabilized waste that satisfied the leaching standards applicable to wastes containing less than 260 ppm of mercury. This demonstration provides strong support for the designation of stabilization as a BDAT (Best Demonstrated and Available Technology) for wastes containing more than 260 ppm mercury. Such a designation would allow these wastes to be stabilized and disposed of in a permitted land disposal unit.

Full-scale demonstrations with two different formulations reduced the mercury concentrations in soil extracts 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). These formulations were based on dithiocarbamate (DTC) and liquid sulfide reagents. The full-scale DTC formulation reduced the concentration to about one-half the UTS limit, or 0.013 mg/l, and the full-scale liquid sulfide formulation to less than one-tenth of the limit, or 0.0025 mg/l. The volume increase resulting from the stabilization treatment was small, less than 20%. The DTC formulation immobilized the mercury within one hour. The liquid sulfide formulation required several hours and more tightly immobilized the mercury. The sulfide mercury stabilization was more sensitive to the degree of aeration and mixing than the DTC stabilization. The demonstration showed that aeration and mixing of the sulfide reagent can be modeled on the full-scale with lab-scale treatability studies.

INTRODUCTION

Currently the Department of Energy has few options for the treatment and disposal of mixed waste containing more than 260 ppm Hg. According to a Technology Development Requirements Document (TDRD) for Mercury Stabilization (DOE, 1996) many DOE sites, especially the Oak Ridge National Laboratory and the Idaho National Engineering Laboratory, contain debris and sludges that are contaminated with mercury in many forms.

The standards for treating wastes containing mercury prior to land disposal have become more stringent. The current Universal Treatment Standard (UTS) for the total concentration of mercury in the leachate generated by the Toxicity Characteristic Leaching Procedure (TCLP) is 0.025 mg/L, nearly 10 times less than the previous standard of 0.20 mg/L. According to Conner (Conner, 1990), many commercial-scale and laboratory-scale tests have satisfied the stricter standard, but most wastes had less than 5 mg/kg of total mercury and all but one had less than 20 mg/kg of total mercury.

The ATG team and others have developed several formulations that stabilize the most common mercury species for initial mercury concentrations in waste approaching 260 ppm. The development and performance of these formulations is described in previous reports (DOE, 1999a, 1999b, 1999c and 1999d). This demonstration test showed that bench-scale tests adequately predict full-scale stabilization performance for mercury stabilization of DOE wastes containing concentrations of mercury greater than 260 ppm by weight.

Previous bench-scale tests conducted by members of the ATG team showed that the degree of mixing and aeration is a very important aspect of the stabilization process, especially for liquid sulfides, which bind mercury more tightly than any other reagents tested. Entraining air into a sulfide formulation is necessary to stimulate the formation of active sulfides for the stabilization reaction. Entrainment of air into the paste-like stabilization mixtures is difficult to do on a large-scale. Therefore this study modified commercially available equipment to increase the air entrained.

The dynamics of the reactions with liquid sulfide reagents are complex and depend not only on the degree of aeration, but also on the degree of mixing. The degree of aeration and mixing differed between bench and full-scale systems. Despite these differences, the performance and operating parameters of the full-scale system were adequately modeled by bench scale tests.

In bench-scale tests 11 formulations reproducibly stabilized over 99.9 percent of the mercury initially present in the soil and met the UTS limit. One formulation reduced mercury concentrations in soil extracts over 300-fold, to levels 30-times less than the UTS limit.

The untreated soil received from Brookhaven National Laboratories (BNL) contained approximately 4,000 mg/kg of total mercury, and leachable mercury concentrations exceeded the UTS limit by more than 10-fold. The volume increase resulting from stabilization treatment was small, less than 20%, for both formulations demonstrated. Some of the successful bench scale formulations had no volume increase at all. The formulations also stabilized cadmium and lead, which were present in TCLP extracts above the UTS limits in the untreated soil.

We began our development of the formulations with surrogate soils, then bench-scale studies with BNL soils and finally refined the processing conditions during the full-scale demonstration with the BNL soils. After the full-scale demonstration, we conducted additional bench-scale studies to determine the degree to which bench-scale testing could model the complex full-scale process.

MATERIALS AND METHODS

Possible formulations for the full-scale demonstration were first screened with bench-scale testing. Laboratory equipment used for formulation development included two 4-liter Kitchen-Aide mixers, a large magnetic stir plate, pH meter, and scales. The commercial Essick mortar mixer used for the demonstrations is shown in Figure 1. Mercury concentrations were monitored with a Jerome Mercury monitor from Arizona Instruments. A Ludlum Model 2221 portable rate-scale meter was used to measure radioactivity. Mercury, metals, and TCLP analyses were performed by Mountain States Analytical, Inc., an EPA-certified laboratory. Methods described in this section include those for bench-scale tests, full-scale demonstration tests, and mixing tests.

Fig. 1. Commercial Mortar Mixer Used for Demonstrations

Materials

The full-scale demonstration tests, and supporting bench-scale tests, were conducted on mercury (Hg) contaminated soil supplied to ATG by Brookhaven National Labs (BNL). ATG received a 100 kg. sample of contaminated soil from BNL, which contained an average total Hg concentration of 4,200 mg/kg. Mercury, cadmium and lead all leached from the soil at concentrations exceeding the respective UTS limit.

As can be seen from the close agreement between mercury concentrations in the six samples reported in Table I, the soil was well mixed and homogeneous. The relative standard deviation of six different soil samples was less than 20% of the average concentration. The soil is derived from a larger waste stream in storage at BNL.

Table I. Distribution of Mercury in BNL Soil

	Total Hg Mg/kg
	3,600
	3,760
	3,690
	4,590
	4,350
	5,410
Average	**4,233**
Rel. Std. Dev.	**17%**

The soil was dark brown in color with a sandy texture. The soil had a sandy consistency with only a small amount of debris material. Debris consisted of pieces of plastic sheeting and shards of glass. Less than

5% of the soil was small rock with a diameter of minus ½ inch or larger. About 2 gallons of water had condensed behind the plastic drum liner. After this water was thoroughly mixed back into the soil, the total moisture content of the soil was 21.2%.

Analyses were performed to quantify anions associated with ionic forms of mercury such as chlorides, fluorides, and sulfates in the waste. Ion chromatography results showed that these anions were present, but not in quantities sufficient to bind all mercury. Thus the speciation of most of the mercury is unknown.

The soil contained a total 13.6 pCi/g of Europium 152 and 154. The activities of other radionuclides were less. The soil is a mixed waste that contains both radioactive and chemically hazardous constituents.

Generic reagents used in screened formulations included sodium thiosulfate, tetrathiocarbonate (TTC), calcium polysulfide, sulfuric acid, natural zeolite, and Portland Cement. The proprietary reagents tested included a dithiocarbamate (DTC) and inorganic sulfur compounds. Based on the results of the bench-scale tests conducted on 1,000 gm samples of the waste, two primary formulations were selected for the full-scale demonstration test. The base components of the two formulations selected for the full-scale demonstrations are identified in Table II.

Recipes for the two proprietary formulations selected are logged in laboratory notebooks. A DTC formulation consists of 1) water, 2) magnesium oxide, a mild buffering agent used when pH adjustment is required, and 3) a proprietary DTC liquid mixture. A proprietary liquid sulfide formulation consists of varying amounts of a 1) powdered initiator, 2) liquid sulfide, 3) promoter, 4) solidification agent, and 5) flow enhancer.

Except for a lower water content, the full-scale formulations were identical to the corresponding bench-scale formulations. Full-scale DTC formulation F-1 contained one-half as much water per kg of waste as the corresponding bench-scale formulation. Similarly, the full-scale liquid sulfide formulation F-2 contained about one-third as much water per kg of waste as the corresponding bench-scale formulation. For DTC formulations, all water was added prior to mixing. Water was periodically added to the liquid sulfide formulation to maintain a good consistency for mixing.

Table II. Base Components of Full-Scale Formulations

Formulation	**Reagent**		
	Sulfide	DTC	Portland Cement
F-1	X		X
F-2		X	X

Bench-Scale Tests

A total of 27 formulations were bench-tested on samples of waste. Between 1 and 1,000 grams of treatment reagents were mixed with 1,000-gram samples of waste. The order of addition for each treatment component and its corresponding mix time was carefully controlled and recorded.

For formulations based on liquid sulfides, a proprietary powdered reagent was added first to the mercury-containing soils to scavenge the mercury compounds. Tests have shown that the powdered reagent is necessary, no matter the form of mercury. A proprietary liquid sulfide reagent was then introduced to the soil mixture. The soil mixture was aerated to facilitate the formation of active sulfides. Once formed, the active sulfides react with the mercury compounds associated with the powdered reagent to form insoluble mercury sulfide. Different types of agitators provided different degrees of mixing.

Demonstration Tests

The full-scale demonstrations were performed in an Essick mortar mixer with a mixing capacity of 7 ft^3. The commercial mixer was modified to superaerate one batch of the liquid sulfide formulation. The air flowed into the mixture, beneath the surface, through seven 3/32" inside diameter teflon tubes. These tubes were regularly spaced across the bottom of the mortar mixer and supplied with compressed air at 25 psi through a distribution manifold.

DTC Formulation F-1: Analogous to the bench-scale tests using 1-kg of BNL soil, approximately 60 kg of soil was simply blended with the DTC formulation, F-1, and mixed for one-hour in the mortar mixer. The mixture was then cured for 48 hours and sampled for TCLP analysis.

Liquid Sulfide Formulation F-2: Uncertainties about the scale-up of processes relying on the sulfide formulation led to an examination of mixing times and aeration methods for the full-scale process. Differing from the bench-scale testing, the blending operation for the liquid sulfide formulation, F-2, consisted of two stages separated by an intermediate setting period. The first stage blended all of the components of F-2 except for Portland Cement. The mixture then set for an extended period before the Portland Cement was added and the second stage blending commenced.

For the first blending stage, the BNL soil was split into equal batches, approximately 40 kg each. After all reagents in formulation F-2, except Portland Cement, were added, one of these two batches was superaerated during blending.

The processing sequence for formulation F-2 began with the addition of a powdered activating reagent to the soil in the mortar mixer. The formulation contained sufficient water to produce a free-flowing material with the consistency of wet cement. After one hour of mixing, the mixer was stopped and the appropriate amount of the liquid-sulfide and other reagents were added.

The mixer was then started again and allowed to mix for six hours. The effect of mix time was examined by taking samples of the mix after mixing for one, three, and six hours following the addition of the liquid-sulfur reagent. Mixing was then stopped and the intermediate curing period started.

At the conclusion of the intermediate curing period, and after sampling for TCLP analysis, the two 40 kg batches of soil treated with formulation F-2, one superaerated and the other simply aerated, were combined into one large 80 kg batch. Portland Cement was added and blended with the partially treated soil for 15 minutes. The final blend occupied approximately 2 cubic feet, or about one-third of the 7 cubic foot capacity mortar mixer. After a 48-hour cure, final samples were submitted for TCLP analysis.

Bench-Scale Mixing Tests

In these tests, performed at ADA's treatability laboratory in Littleton, Colorado, a 1-kg batch of surrogate soils with 2,500 ppm elemental mercury and 2,500 ppm mercuric chloride was stabilized with the liquid sulfide formulation F-2 in a manner similar to the full-scale mixes. Portland Cement was omitted from this bench-scale formulation.

The powdered reagent was added and mixed with the soil for one hour. The liquid-sulfur reagent was then added, and mixing continued for an additional six hours. Soil samples were taken every half-hour for the first two hours and every hour thereafter. After the 6-hour mixing period, the mix was covered and allowed to set for 4 hours. After the 4-hour setting period, a soil sample was taken from the bowl and the remaining treated soil mixed for an additional seven hours, sampling every hour.

RESULTS AND DISCUSSION

The bench-scale tests evaluated 27 formulations and identified 11 that reduced the leaching of mercury from the treated soil below the UTS limit of 0.025 mg/l. All 27 formulations increased the soil volume by less than 25%. pH and temperature changes were minimal for all formulations. The base components of the 2 formulations selected for the full-scale demonstration tests were indicated earlier in Table II. The most successful formulations contained Portland Cement. Reagents tried in unsuccessful formulations include sodium thiosulfate ($Na_2S_20_4$), TTC, and natural Zeolite.

The simplest to use of the two formulations demonstrated, F-1, is based on a dithiocarbamate. Dithiocarbamates are one of a series of water-soluble organic sulfide compounds made from the reaction of a secondary amine with carbon disulfide. Dithiocarbamates offer the advantage of the sulfide ion's strong reducing and metal-complexing power while minimizing the hazards, odor and competing reactions associated with the use of inorganic sulfide.

Formulation F-2, based on a liquid sulfide reagent, reduced leachable mercury nearly ten times more than the DTC formulation, F-1. The liquid sulfur reagent converts elemental and speciated mercury to mercury sulfide, a stable and leach resistant form of mercury.

Formulation Development

In the bench-scale tests, 1-kg of BNL soil was mixed with various stabilization reagents, that reacted with mercury in the soil to form stabilized compounds of mercury. The DTC and sulfide formulations selected for the full-scale demonstration tests had the lowest concentrations of mercury in TCLP leachate from treated soils. The concentrations of mercury in leachate from bench-scale treatment of the soil with formulations selected for the full-scale demonstrations are shown in Table III.

As shown in Table III, and for other formulations not shown, concentrations of mercury in leachate from soil treated with liquid sulfide formulations were generally lower than those treated with DTC formulations. Formulations based on either DTC or liquid sulfide reagents that also included Portland Cement reduced mercury leaching the most. Several bench-scale formulations (not shown) were successful without the addition of Portland Cement. Formulations without Portland Cement exhibited no observable increase in volume.

Table III. Mercury in TCLP Leachate from Bench-Scale Treatment of Soil

Formulation Base	DTC	Liquid Sulfide
Mercury Concentration in TCLP Leachate (mg/l)	0.00696	0.000864
Increase in Weight as % of Initial Soil Wet Weight	59%	91%
Increase in Volume as % of Initial Soil Volume	15%	23%

Most of the weight and volume increase shown for both the DTC and the liquid sulfide formulations is attributable to Portland Cement and water. The weight of these two reagents added was 55% of the initial soil weight for the DTC formulation and 81% for the liquid sulfide formulation. Portland Cement and water likely accounted for all of the observed increase in volume shown in the table for both formulations.

Besides the RCRA metal mercury, the DTC and liquid sulfide formulation stabilized all other RCRA metals that leached from the untreated soil at concentrations above the UTS limits. Table IV presents the TCLP results for RCRA metals stabilized with the liquid sulfide formulation. The formulation reduced the concentration in TCLP leachate of all RCRA metals above the UTS limits by at least ten fold.

Table IV. Reduction in Metals Leachability After Bench-Scale Treatment with Liquid Sulfide

Metal	**Raw Waste Leaching (1)**	**UTS Leaching Limit**	**Treated Waste**		
			Leaching (3)	**Percent UTS**	**Percent Stabilized**
	TCLP mg/L	TCLP mg/L	TCLP mg/L	%	%
Sb	0.044	1.15	-	-	-
As / D004	<0.02	5	<0.02	<0.4%	(2)
Ba / D005	1.67	21	0.825	4%	51%
Be	0.00118	1.22	-	-	-
Cd / D006	***0.193***	0.11	<0.003	<3%	>98%
Cr / D007	<0.01	0.6	0.0957	16%	(2)
Pb / D008	***1.92***	0.75	0.131	17%	93%
Hg / D009	***0.282***	0.025	0.00211	8%	99%
Ni	0.105	11	-	-	-
Se / D010	<0.03	5.7	<0.03	<1%	(2)
Ag / D011	<0.004	0.14	<0.004	<3%	(2)
Tl	<0.02	0.2	-	-	(2)
V	<0.004	1.6	-	-	(2)
Zn	1.38	4.3	-	-	-

(1) Bold italicized figure in this column indicates raw waste failed to satisfy UTS treatment standard.

(2) Leaching from untreated waste near detection limits so no calculation of percent stabilized possible.

(3) Only the eight RCRA metals were analyzed in leachate from soil treated with this formulation, a formulation that contained no Portland Cement.

Leaching Performance of Soil Treated During Full-Scale Demonstration

Full-scale treatment of all soil batches treated with either the DTC or the liquid sulfide formulations met the UTS requirements for all metals, including mercury. A comparison of the points to consider in selecting either a DTC or a liquid sulfide formulation are summarized in Table V below.

These points, and other operational considerations, are discussed in the remainder of this section.

Table V. Points to Consider in Selecting a Formulation For Stabilizing Mercury

Point	**DTC**	**Liquid Sulfide**
Stabilization Performance	Satisfactory	Excellent
Throughput	Excellent	Low throughput demonstrated. More experience may allow significant increase.
Reliability of Scale-Up	Excellent	Must account for differences in mixing, aeration, and reaction chemistry.
Volume Increase	Satisfactory	Satisfactory
Weight Increase	Satisfactory	Satisfactory

As shown in Table VI, the mercury stabilization performance of the DTC formulation was satisfactory and that of the liquid sulfide formulation excellent. The DTC formulation applied at full-scale reduced the leachable mercury concentration from 10 times the UTS limit to about one-half of the UTS limit for mercury, for an overall 20-fold reduction in leachable mercury. The liquid sulfide formulation reduced the leachable mercury even more, to less than one-tenth of the UTS limit of 0.025 mg/l and an overall 100-fold reduction in leachable mercury.

Both formulations also stabilized the RCRA metals cadmium and lead that leached from the untreated soil at concentrations greater than the corresponding UTS limit shown in Table VII. Table VII also shows that the DTC formulation, F-1, stabilized over 98% of the leachable cadmium and over 99% of the leachable lead. The final treated soil satisfied all UTS leaching limits for metals.

Table VI. Mercury in TCLP Leachate from Full-Scale Treatment of Soil

Formulation Base	DTC (1)	Liquid Sulfide (2)
Mercury Concentration in TCLP Leachate (mg/l)	0.0139	0.0020
Increase in Weight as % of Initial Soil Wet Weight	33%	44%
Increase in Volume as % of Initial Soil Volume	7%	20% (3)

(1) Average of three samples of 0.0133, 0.0158, and 0.0126 mg/l.
(2) Average of three samples of 0.000521,0.00282, and 0.00274 mg/l.
(3) Visual observations indicate volume increase less than the 23% measured for bench-scale formulation.

Throughput

This demonstration did not attempt to demonstrate the maximum throughput for either the DTC or the liquid sulfide formulation. As demonstrated, the throughput of the DTC formulation was several times greater than that of the liquid sulfide formulation. The throughput varies almost linearly with the total mixing time required. The mixing time for the DTC reagent was one hour and that of the liquid sulfide reagent about ten hours. The throughput for a one-hour mixing time would be 1.3 cubic meters (45 cubic feet or six and one-half 55-gallon drums) for an eight-hour shift.

Table VII. Reduction in Leachability of Metals After Full-Scale Treatment with DTC

Metal	**Raw Waste Leaching (1)**	**UTS Leaching Limit**	**Treated Waste**		
			Leaching	**Percent UTS**	**Percent Stabilized**
	TCLP mg/L	TCLP mg/L	TCLP mg/L	%	%
Sb	0.044	1.15	-	-	-
As / D004	<0.02	5	<0.02	<0.4%	(2)
Ba / D005	1.67	21	0.497	2%	70%
Be	0.00118	1.22	-	-	-
Cd / D006	***0.193***	0.11	<0.003	<3%	>98%
Cr / D007	<0.01	0.6	<0.01	<2%	(2)
Pb / D008	***1.92***	0.75	<0.02	<3%	>99%
Hg / D009	***0.282***	0.025	0.0139	56%	95%
Ni	0.105	11	-	-	-
Se / D010	<0.03	5.7	<0.03	<1%	(2)
Ag / D011	<0.004	0.14	<0.004	<3%	(2)
Tl	<0.02	0.2	-	-	(2)
V	<0.004	1.6	-	-	(2)
Zn	1.38	4.3	-	-	-

(1) Bold italicized figure in this column indicates raw waste failed to satisfy UTS treatment standard.
(2) Leaching from untreated waste near detection limits so no calculation of percent stabilized possible.

Mixing times for both of these formulations can probably be substantially reduced. The mixing time for the DTC reagent apparently depends only on the time required to achieve physical homogeneity throughout the mix. The mixing time for the liquid sulfide reagent depends on the complex interaction between physical mixing, aeration, and competing sulfide reactions. Variations in the performance of the liquid sulfide reagent with mixing time were expected and tracked. Variations in the performance of the DTC reagent with mixing time were not expected and not tracked.

The concentration of leachable mercury in the first samples taken during the 6-hour mix cycle with the liquid sulfide reagent was low. The low concentration shortly after the addition of the liquid sulfides suggests that the addition of an agent, such as ferric sulfate, to oxidize excess sulfide shortly after addition of the liquid sulfides to prevent competing reactions would reduce the mixing time. The extended mixing time is required to oxidize excess sulfide. Excess sulfide promotes leaching of mercury from mercury sulfide (Biester, 1998). See additional discussion in the section titled "Time Dependence of Liquid Sulfide Stabilization".

Reliability of Scale-Up

Scale-up of DTC formulations has been much simpler than scale-up of liquid sulfide formulations. As discussed under throughput above, only differences in physical mixing must be considered when scaling up a DTC formulation. For liquid sulfide formulations, differences in aeration and reaction chemistry must also be considered.

Despite these additional complexities, the leaching performance of full-scale treatments with liquid sulfide formulations can be predicted based on the results of bench-scale testing. Two process parameters, required mixing times and aeration rates, must be determined in the full-scale system. General trends for mixing times and aeration rates can be established on the bench-scale, but not the actual mixing times and aeration rates required to efficiently operate full-scale systems employing liquid sulfide formulations.

Scaling-up the complex chemistry of liquid sulfides presents unusual challenges for developing full-scale formulations. Better mixing and aeration in the full-scale mixer allowed the sulfide reactions to proceed faster and revealed some time dependent reaction chemistry not observed in the initial bench-scale studies. An empirical understanding of the reaction chemistry resulted in a liquid sulfide formulation that is efficacious and stable.

The formulation is efficacious as the soil treated with the formulation leaches mercury at a concentration lower than any other formulation tested. The formula is stable because the team developed process conditions that oxidize the excess sulfide to sulfate. This oxidation prevents side reactions that slowly mobilize mercury when the treated material is stored. Once the excess sulfide is completely oxidized, the mercury is permanently immobilized.

Volume and Weight Increases

Volume increases resulting from treatment with the full-scale DTC and liquid sulfide formulations are shown in Table VI. The volume increases were 20% or less and very similar to volume increases observed in the bench-scale treatments.

Bench-scale testing suggests that smaller volume and weight increases may be achievable. Several successful formulations that omitted Portland Cement produced a moderately dense monolith with a volume increase of less than 10%. Other formulations using Portland Cement, including the two formulations used in the full-scale demonstration tests, set to a dense concrete-like material that was easily granulated.

For all formulations with Portland Cement, the volume increase was generally proportional to the mass of Portland Cement added. Air trapped by the hydrated silicate matrix may also contribute to the volume increase.

Increases in volume were generally related to, but less than increases in weight. For most reagents other than Portland Cement, a weight increase of less than 10% resulted in no measurable volume increase. Portland cement and accompanying water accounted for the bulk of most volume and weight increases of greater than 10%.

Operational Considerations

Other than an initial adjustment of pH to the proper range, no pH control was necessary. Mixing behavior must be closely monitored for all formulations, but especially for those containing liquid sulfide. As the observed temperature increases were small, less than 3 degrees Centigrade, temperature control was not required. Dust control was needed for the formulations since they included Portland Cement.

The pH of the waste is measured prior to treatment to determine if its pH is in the range of 4-10. If the pH is outside of that range, a mild buffering agent such as magnesium oxide will suffice to bring the pH in range. If the pH is in-range prior to treatment, it will not need to be monitored during full scale treatment of most wastes.

The mixing speed was constant at 66 rpm for all batches of each formulation. Both formulations mixed well in the mortar mixer. By carefully controlling the moisture content, the mixtures folded over smoothly when scraped by the mixer paddles with very little adhering to the sides of the mixer. Both mixtures of soil and reagents were originally a very dark green, even black, with little color change evident after mixing and curing.

Negligible quantities of mercury appear to have been lost by volatilization during mixing. Negligible loss by volatilization was expected as the mercury had been in the soil for years and volatile mercury would have migrated away and dispersed. Both undetectable mercury emissions and conservation of mercury in the waste before and after treatment indicate that insignificant quantities of mercury volatilized.

No mercury emissions from the mortar mixer were detected at levels greater than 0.01 mg/m3, the detection limit of the hand-held mercury monitor. At the beginning of a demonstration, mercury vapors were monitored every minute within the mortar mixer and were never detected. Also, mercury vapors were never detected when spot monitored during the remainder of a demonstration.

Closure of the mercury balance before and after processing the soil with the liquid sulfide formulation indicates that total mercury was conserved during treatment. The total mercury concentration in soil treated with the unaerated liquid sulfide, Formulation F-2, was 2,150 mg/kg as compared to a predicted value of 2,350 mg/kg. As shown by the 17% standard deviation for measurements of mercury concentration in untreated soils in Table I, these two values are well within the expected range of variability in total mercury measurements.

Small, but odiferous, quantities of ammonia were released when DTC reagents were added. When Portland Cement was added to formulations with DTC, the fishy smell disappeared. Similarly, when Portland Cement was added to the liquid sulfide formulations, the sulfur smell disappeared. Portland cement was the only reactive silicate used in any of the formulations.

Additives and water effectively shielded radioactivity within the waste. No radioactivity was observed with the portable scale rate-meter.

A plastic sheet covering the mixer sufficed to contain the small amount of material thrown off as the mixer blades rotated. When treatment was complete, most of the material readily dumped from the mixer and the remainder was easily scraped out with a flexible scraper. The final products, as shown in Figures 2 and 3, consisted of material that looked and worked like a low slump soil/cement.

The only secondary wastes generated by the MER-03 tests were 23 kg of treated waste samples from the bench-scale tests and dunnage accumulated during the bench testing and full-scale demonstrations. 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.

Fig. 2. BNL Soil Before and After Treatment with DTC

Time Dependence of Liquid Sulfide Stabilization

Many previous bench-scale tests have shown that mixing and aeration patterns are critical in determining the extent and rate of mercury immobilization by liquid sulfide formulations. As mixing and aeration patterns with the bench-scale kitchen mixer differed significantly from those with the full-scale mortar mixer, the progress of the sulfide reaction with time was monitored in the full-scale demonstration. Further, two different treatment processes were tried with the liquid sulfur formulation, aerated and superaerated. The aerated and superaerated batches, referred to as in-process batches in Table VIII, were combined before the Portland Cement was added to create the final formulation shown in the table for liquid sulfide.

Fig. 3. BNL Soil Before and After Treatment with Liquid Sulfide

The aerated and superaerated processes produced an in-process product that leached mercury at concentrations more than six and twenty times the UTS limit of 0.025 mg/l, respectively. Table VII shows that either curing the in-process batches or the addition of Portland Cement to make the final liquid sulfide formulation reduced mercury concentrations in the leachate from treated soils by over one-hundred fold.

Table VIII. Comparison of Full-Scale Mercury Stabilization by Different Stabilization Formulations and Treatment Processes

Formulation	**Formulation Base**	**Process**	**Mercury in TCLP Leachate (mg/l)**	
			In-Process	Final
F-1	DTC	Mix with aeration		0.0139 (1)
F-2	Liquid Sulfide	Mix with aeration	0.161	
		Mix with superaeration	0.574	
	Liquid Sulfide, then Portland Cement	Add F-2 and mix with or without superaeration, cure for 40 hours, add Portland Cement and mix again		0.00203 (2)
F-1 / F-2	All treated wastes	Composite sample of DTC (F-1) and liquid sulfide (F-2) treated wastes		0.00339

(1) Average of three samples of 0.0133, 0.0158, and 0.0126 mg/l.
(2) Average of three samples of 0.000521, 0.00282, and 0.00274 mg/l.

The concentration of mercury in the leachate is a strong function of mixing time and of degree of aeration, as is shown in Table IX. The liquid sulfide reagent first reduces the leachable mercury, then increases the leachable mercury to a level greater than that observed in the original waste (0.282 mg/l), and finally reduces the concentration once again. From the results shown in Table IX, it is unclear whether the peak in mercury concentrations for the superaerated in-process batch occurred before or after the last sampling point.

To determine if the observed dependence on mixing and aeration of the full-scale stabilization process with the liquid sulfide formulation could be duplicated in the lab, ADA conducted a laboratory experiment duplicating the mixing conditions used in the field tests. TCLP results from the mixing time trial are shown in Figure 4. TCLP results listed in Table IX for the unaerated 40-kg batch are shown for comparison. The initial lab, or in-process, mix cured for 40 hours before the Portland Cement was added to create the final mix. The mix time in the figure for the final mix is the number of hours after the Portland Cement was added to the final mix.

Figure 4 shows that the effect of mixing time on leachable mercury observed in the full-scale mixer can be approximated in bench-scale studies. As with the full-scale studies, the amount of leachable mercury was very low for short mix times, but increased abruptly after mixing the 40-kg batch for one hour and the bench-scale initial mix for four hours. The rapid increase in the amount of leachable mercury in both full- and bench-scale systems indicates that an abundance of sulfide ions suddenly became available to solubilize mercuric sulfide according to the equation below (Biester, 1998).

$$HgS + S^{-2} <=> HgS_2^{-2} \qquad \text{(Eq. 1)}$$

Table IX. Mercury Concentrations in TCLP Leachates from Soils Treated with a Liquid Sulfide Formulation as a Function of Mixing Time

Mixing Time After Addition of Liquid-Sulfur Reagent (hours)	Aerated Leachate Concentration(mg/l)	Superaerated TCLP Results (mg/l)
1	0.00255	0.055
3	0.937	0.272
6	0.161	0.574

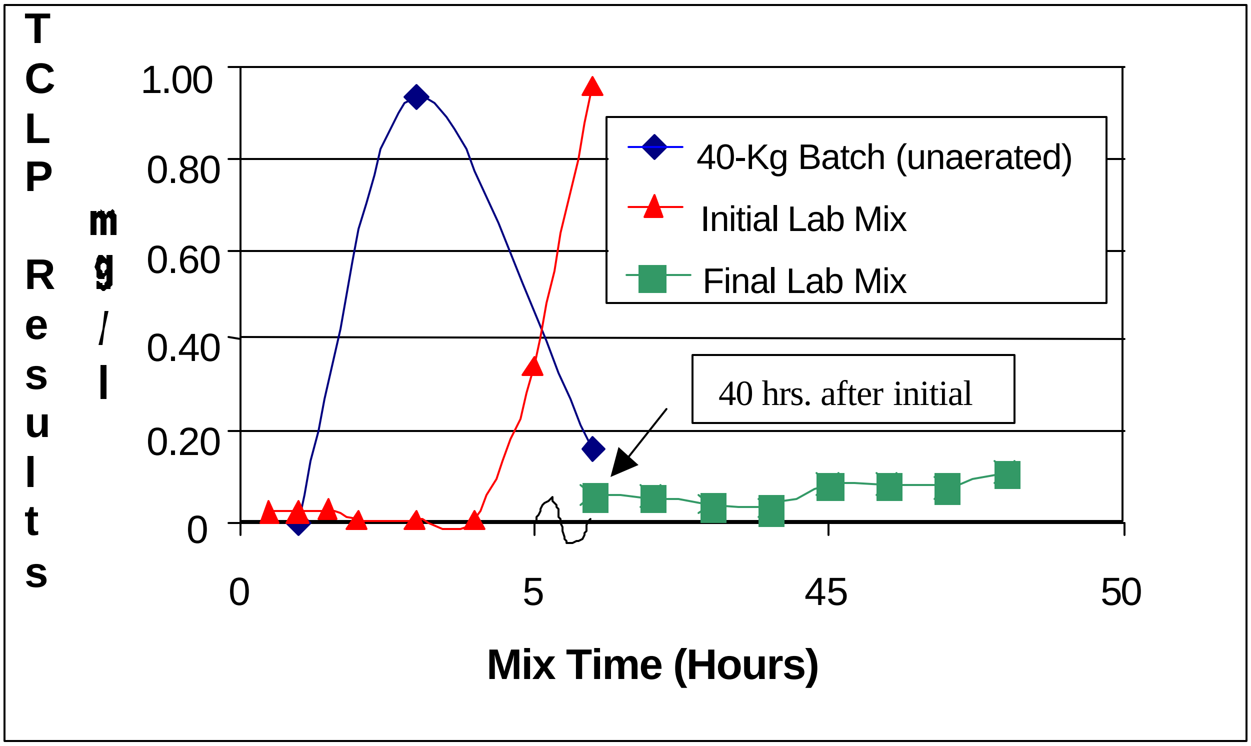

Fig. 4. Effect of Mix Time on Leachable Mercury

The reduced amount of leachable mercury at still longer mix times, indicates that the active sulfides were being oxidized to the inactive sulfate ion. Over time, the oxidation reaction proceeded to remove sufficient amounts of active sulfides and shifted the equilibrium to convert the mercury-polysulfides back to mercuric sulfide.

The concentrations of mercury in the TCLP leachate initially increased with mixing time for both 40-kg in-process batches, and later dropped to levels below those observed with the DTC reagent. The initial increase in leachable mercury indicates that simple entrainment of air into the mix as the mortar mixer turned provided adequate oxygen to form an excess of active sulfide ions from the start of the mixing process. As discussed above, an excess of sulfide ions actually promotes leaching of mercury.

The slower increase in leachable mercury concentrations for the super-aerated in-process batch suggests that competing reactions are involved in the stabilization process. To explain the observed mercury leaching data, the reaction rates for the production of sulfate ion, mercuric sulfide, and mercury-polysulfide must be investigated in detail. However, such an analysis of the stabilization process was beyond the scope of this full-scale demonstration.

Thus, the effect of aeration on the required reaction time is uncertain and must be established empirically. Efficient mixing will likely shorten the required reaction time. One promising aeration strategy would be to aerate slowly until the soil and formulation are well mixed. Then aerate at the maximum rate to rapidly convert the free sulfides to sulfates. This strategy should work if the mercury sulfide is stable when the mix is well aerated and all free sulfides have been converted to sulfates.

This demonstration has shown that leaching performance of full-scale treatments with liquid sulfide formulations can be predicted based on the results of bench-scale testing. Two process parameters, required mixing times and aeration rates, must be determined in the full-scale system. General trends for mixing times and aeration rates were modeled on the bench-scale, but not the actual mixing times and aeration rates required to efficiently operate full-scale systems.

Permitting

The full-scale system tested in this study is easily portable and well suited for homogeneous streams of liquid, sludge or solid waste. Most waste streams of less than 50 cubic meters total volume can be processed by the mortar mixer in ten days or less with a crew of two.

No federal permitting may be required for this transportable mercury stabilization system. Federal regulations allow on-site treatment of hazardous waste without a permit under certain conditions. Processing of lead contaminated soils in a pug mill satisfied these conditions (EPA, 1994) as should processing of mercury contaminated mixed waste in a mortar mixer.

CONCLUSIONS

The stabilization system demonstrated can potentially treat low-level waste streams containing more than 260 ppm of mercury to UTS standards. The DTC and liquid sulfide formulations have been demonstrated to be suitable for the full-scale treatment of at least one DOE waste stream, the soil received from BNL. Studies of the dosages of the reagents and mixing times required for other DOE waste streams would establish the suitability of DTC and liquid sulfide formulations for those streams as well.

The performance of full-scale treatment is reliably predicted by bench-scale tests for the DTC formulation. Differences in mixing between the bench-scale and full-scale systems must be accounted for to reliably predict the performance of full-scale treatment with liquid sulfide reagents from bench-scale tests. More experience with both DTC and liquid sulfide formulations, but especially with liquid sulfide formulations, will be required to determine their applicability to non-soil wastes. Non-soil wastes include paper, clothing, wood, and inorganic and organic debris.

This demonstration showed that stabilization of at least one waste containing mercury with concentrations greater than 260 ppm satisfied the technical requirements for listing as a Best Demonstrated and Available Technology (BDAT).

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