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Demonstration Results on the Effects of Mercury Speciation on the Stabilization of Wastes

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Chemical Technology Division

DEMONSTRATION RESULTS ON THE EFFECTS OF MERCURY SPECIATION ON THE STABILIZATION OF WASTES

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ACRONYMNS AND ABBREVIATIONS

ATG	Allied Technology Group
DeHg	A proprietary process by NFS for processing mercury mixed waste (pronounced de´-merk)
DOE	Department of Energy
DTC	dithiocarbamate
EPA	Environmental Protection Agency
GEMEP	General Electric Mercury Extraction Process
HgWG	Mercury Working Group, MWFA
IT	IT Corporation
ITSR	Innovative Technology Summary Report
LANL	Los Alamos National Laboratory
LDR	Land Disposal Restrictions
LLNL	Lawrence Livermore National Laboratory
MWFA	Mixed Waste Focus Area
NFS	Nuclear Fuel Services
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
SAMMS	Self-Assemble Monolayers on Monoporous Substrate
SOW	Statement of Work
TCLP	Toxicity Characteristic Leaching Procedure
TDRD	Technology Development Requirements Document
UTS	Universal Treatment Standard

ABSTRACT

Mercury-contaminated wastes are currently being stored at approximately 19 Department of Energy sites, the volume of which is estimated to be about 16 m^3. These wastes exist in various forms including soil, sludges, and debris, which present a particular challenge regarding possible mercury stabilization methods. This reports provides the test results of three vendors, Allied Technology Group, IT Corporation, and Nuclear Fuel Services, Inc., that demonstrate the effects of mercury speciation on the stabilization of the mercury wastes. Mercury present in concentrations that exceed 260 parts per million must be removed by extraction methods and requires stabilization to ensure that the final wasteforms leach less than 0.2 mg/L of mercury by the Toxicity Characteristic Leaching Procedure or 0.025 mg/L using the Universal Treatment Standard.

1. SUMMARY

1.1 Background and Objectives

Mercury-contaminated wastes in many forms are present at various Department of Energy (DOE) sites. Based on efforts led by the Mixed Waste Focus Area (MWFA) and its Mercury Working Group (HgWG), the inventory of bulk elemental mercury contaminated with radionuclides stored at various DOE sites is thought to be approximately 16 m^3 (Conley, Morris, Osborne-Lee, and Hulet 1998). At least 19 different DOE sites have this type of mixed low-level waste in their storage facilities. Extraction methods are required to remove mercury from waste containing >260 parts per million (ppm) levels but are not required for mercury levels <260 ppm. Mercury waste requires stabilization to ensure that all final wasteforms leach less than 0.2 mg/L of mercury by the Toxicity Characteristic Leaching Procedure (TCLP) of Resource Conservation and Recovery Act (RCRA), or 0.025 mg/L if the Universal Treatment Standard (UTS) is used. Amalgamation of elemental mercury waste and other stabilization methods for mercury waste containing less than 260 ppm Hg have been demonstrated under the sponsorship of the MWFA and the coordination of the HgWG (MWFA 1998a, MWFA 1998b, Simpson 1996, Simpson 1998). Mercury contamination in the wastes at DOE sites presents a challenge because the wastes exist in various forms, such as soil, sludges, and debris. The situation is particularly challenging in light of the uncertainties raised by the existence of mercury in a variety of chemical species. To date, no standard method of stabilization has been developed for such varying waste types and the impact of speciation has not been determined.

The MWFA is investigating possible stabilization methods for mercury-contaminated mixed waste streams. The Mercury Stabilization Technology Development Requirements Document (TDRD), developed by the MWFA, requires that the effectiveness of newly developed technologies be proven (MWFA 1996). New technology for mercury stabilization must adhere to the following:

1. ensure adequate stabilization,
2. include measuring and monitoring methods to control and verify the process,
3. minimize worker exposure,
4. minimize secondary waste generation,
5. maximize operational flexibility and radionuclide containment.

Additionally, knowledge of the impacts that speciation, or the existence of mercury in the form of different chemical species, will have on technology performance is crucial. For this reason, a Statement of Work (SOW) was issued and three vendors were chosen to perform a series of bench-scale tests to identify and quantify the effects of varying the type of mercury species on the stabilization of surrogate wastes.

1.2 Technology Description

Three vendors, Allied Technology Group (ATG), IT Corporation (IT), and Nuclear Fuel Services, Inc., (NFS), developed technologies to demonstrate the effects of mercury speciation on the stabilization of mercury waste. The stabilization technologies were to stabilize all forms of mercury specified in the SOW: elemental mercury, organic and halogenated mercury compounds, mercury oxides, and mercury sulfide. These mercury species are thought to be the most prevalent at stakeholder sites, based on HgWG investigations.

ATG successfully stabilized mercury waste using the stabilization reagent dithiocarbamate (DTC). However, the polysulfide and borohydride reagents tested by ATG proved to be unsuccessful as an immobilizing reagent for all five samples tested. In fact, the calcium polysulfide and sodium borohydride reagents each increased the leachability of the elemental mercury and mercury sulfide species, respectively, in the ATG tests. The DTC reagent resulted in minimal volume increase. Tests suggested that the DTC reagent reacted with the clay or the iron in the clay, causing it to deactivate and not stabilize the mercury. To increase DTC effectiveness, ATG suggests that future studies should use an inert sorbent instead of clay to minimize possible reaction, use buffers where pH would be increased, and use other reagents to tie up cations such as iron.

IT Corporation used a binding reagent, either TMT 15 (a 15% solution of 2,3,6 trimercapto-S-triazine trisodium salt) or calcium polysulfide, to treat each of the samples. Through concentration and pH adjustments, IT successfully stabilized mercury in all of the suggested waste forms. IT performed its work at its Technology Development Laboratory in Knoxville, Tennessee. Data Chem Laboratories (located in Salt Lake City, Utah) conducted the confirmation analyses. Sulfuric acid was used to lower the pH of the TMT 15 treated soils from 12 to 9 because the reagent has increased effectiveness to fixate mercury at lower pH values. The calcium polysulfide reagent was observed to be effective only when reacted with air. The air/calcium polysulfide mixture causes a chemical breakdown to thiosulfate and sulfide species, which are vital in mercury fixation agents.

NFS developed and demonstrated a process technology called DeHg^{SM} (de-merk). This is a two-step process in which a combination of amalgamation (conversion of liquid mercury to semisolid amalgam to reduce mercury emissions) of elemental mercury is followed by the stabilization of soluble mercury using the DeHg reagent. Upon stabilization, mercury residues are dewatered and packaged for land disposal. Testing was performed in the NFS Applied Technology Development Laboratories in Erwin, Tennessee. The NFS process was applied with success on seven of the eight samples prepared. The remaining sample passed TCLP without treatment.

1.3 Demonstration Summary

Bench-scale studies have been performed to prove that commercial stabilization processes can be used on a wide variety of mercury species. Following the directions provided in the SOW, each vendor assembled surrogate waste and spiked the "waste" with mercury species at levels below 260 ppm. The vendors stabilized samples of each mixture and analyzed 100 g of each final wasteform per the TCLP Hg protocol. The results of these analyses were compared against the UTS requirement of 0.025mg/L Hg in the leachate. IT treated the various surrogates with either TMT 15 or calcium polysulfide. After final TCLP testing, all residuals were below 0.025 mg/L. However, several pH, concentration, and surface area adjustments had to be made to achieve this goal. NFS successfully used the DeHg two-step process, including amalgamation, followed by treatment of waste with a proprietary reagent, which frees the mercury from soluble complexes and fixes it as a stable, nonleachable salt. ATG developed a DTC stabilization reagent, which successfully immobilizes the mercury in the wastes.

1.4 Key Results

The key results of the demonstration are as follows:

- With varying degrees of difficulty, each vendor was able to stabilize all mercury species present in surrogate waste, with no freestanding water.
- Volume increases ranged from modest (25% for IT and ATG) to large (90% for NFS).

- Secondary water generation may occur due to equipment rinsing, as exhibited by NFS in its demonstration.
- Stabilizing agent formulations may be sensitive to concentration, pH, and particle surface area (as found by the IT demonstration).
- Interactions of some reagents with soil constituents may complicate the stabilization process, as found by ATG tests in which the DTC reagent may have been deactivated by the clay (or the iron in the clay) used in the demonstration.

2. TECHNOLOGY DESCRIPTION

2.1 Overview

Mercury is a ubiquitous hazardous contaminant often found in various wastes, such as soils, sludges, sediments, trash, debris, instruments, etc., including wastes located at sites in the DOE complex. The variety of matrices, chemical forms of mercury, and material-handling issues pose particular processing challenges for converting this waste into a final nonhazardous form. Recent technology demonstrations to address mercury waste treatment deficiencies have provided viable options for the stabilization of mercury waste. However, the effect of speciation on the performance of stabilization technology in treating mercury wastes has not been reported to any significant extent. This report supplements prior work on mercury waste stabilization by addressing the issue of speciation. Specifically, the findings of tests conducted by three different sources are reported.

IT Corporation, NFS, and ATG developed test procedures using stabilization technology to demonstrate the effects of mercury speciation on the stabilization of mercury waste. The stabilization technologies were to stabilize those forms of mercury specified in the SOW: elemental mercury, organic and halogenated mercury compounds, mercury oxides, and mercury sulfates. The three vendors followed individualized procedures, but were each compliant with the SOW. The overall process and system operations are described briefly below for each of the three demonstrations.

2.2 ATG Tests

2.2.1 Overall Process

ATG prepared surrogate waste by mixing reagent-grade mercuric compounds with Ottawa sand and distilled water. Surrogate samples were treated with the immobilizing reagents DTC, polysulfide/zeolite, or borohydride/zeolite. DTC was the only one of the three reagents successful in stabilizing all mercury species tested. Tests revealed that the DTC reagent can be deactivated by the clay, or the iron in the clay, used in the study. Because of these results, researchers at ATG concluded that some formulations used in their study could be unsuitable for field applications, particularly in waste matrices containing iron or other cations. Increased concentrations and pH, as well as changing from clay to an inert absorbent, are possible methods for increasing the performance of DTC.

2.2.2 System Operation

ATG tests successfully stabilized surrogate waste samples containing the various mercury contaminants. The surrogate waste samples were prepared using reagent-grade mercuric compounds, Ottawa sand, and 50 mL of distilled water (Table 1). The DTC reagent immobilized the mercury species and resulted in the smallest increase in volume. The volume increased directly proportionally to the mass of DTC and clay added to the mercury.

Table 1. Surrogate matrix used in the tests by Allied Technology Group, Inc.[a]

Compound	g/kg spiked soil			ppm
	Mercury Compound*	Dried Ottawa Sand	Added Water	
HgS	0.172	994.8	5.00	46.8
$HgCl_2$	0.157	994.8	5.00	36.6
HgO	0.135	994.9	5.00	36.1
Hg	0.220	994.8	5.00	63.2
C_6H_5HgCl	0.130	994.9	5.00	26.3

[a] Total Hg variation has a 95% confidence interval calculated with n = 5 and t = 2.77.

2.3 IT Tests

2.3.1 Overall Process

IT prepared multiple surrogates containing five different mercury species for TCLP analysis. Fluid type (TCLP Fluid 1 or 2) was determined for use in extraction. Three different stabilization formulations were tested on each of the surrogates. Either of two binding reagents (TMT 15 or calcium polysulfide) was used. Bottled samples were spiked with mercury and then treated with one of the two reagents. Sulfuric acid was used to lower the pH of the TMT 15–treated soils from 12 to 9 because the reagent has increased effectiveness to fixate mercury at lower pHs. The calcium polysulfide reagent must be reacted with air to be effective. The air-calcium polysulfide reaction causes a chemical breakdown of the polysulfide to thiosulfate and sulfide species, which are the mercury fixation agents.

2.3.2 System Operation

The surrogate samples were prepared in amber glass bottles with Teflon lining and spiked with various mercury contamination species (Table 2). The material was chosen to prevent absorption, adsorption, or amalgamation of elemental or organic mercury.

Table 2. Surrogate matrix used in the tests by IT Corporation

Compound	g/kg spiked Ottawa Sand			ppm
	Mercury Compound	Dried Ottawa Sand	Added Water	
HgS	0.290	949.7	50.0	79.0
$HgCl_2$	0.339	949.7	50.0	79.0
HgO	0.270	949.7	50.0	72.3
Hg	0.250	949.8	50.0	71.7
C_6H_5HgCl	0.407	949.6	50.0	82.3

Note: These quantities were based on final added water content of 5 wt %. This was adjusted, as needed, by making changes in the added water and dried soil mass used to make the spiked soil.

All work was performed in a fume hood, and appropriate personal protective equipment was used to prevent worker contamination. Thorough mixing of the surrogate waste with the stabilization reagent was obtained by tumbling the sample bottle overnight. The compound mercury sulfide did not require any type of treatment to reach the TCLP goal; however, the other four samples spiked with different species did require treatment. Three species were stabilized using various concentrations of calcium polysulfide, pH adjustments, and Portland cement for increased surface area. The remaining sample (phenyl chloromercury) was stabilized by adjusting the pH and using six times the stoichiometric amount of TMT 15 reagent. IT suggests that it may be preferable to use the calcium polysulfide and cement formulation because it is less dependent on pH and can avoid potential precipitation problems that are caused in TMT 15 reagent when the stoichiometry is increased.

2.4 NFS Tests

2.4.1 Overall Process

NFS developed the DeHg process to convert wide varieties of mercury-contaminated wastes into a nonhazardous form. This is a two-step process involving amalgamation of elemental mercury in the compound followed by the treatment of the remaining soluble-mercury species with the proprietary DeHg reagent. The DeHg reagent is mixed for between 30 and 45 min with surrogate wastes to produce a damp paste. The DeHg reagent frees the mercury from soluble complexes and fixes it as a stable, nonleachable salt. After treatment, the residues are dewatered for burial. The dewatering process produces a reusable stream containing filtrates with a mercury concentration of <0.025 mg/L. The DeHg process was used to conduct stabilization tests on eight samples of surrogate mercury waste (Table 3). NFS performed three surrogate/species tests in addition to those specified in the SOW at no additional cost to the HgWG (see footnote, Table 3).

2.4.2 System Operation

The DeHg process functions at ambient temperature using a bench-scale batch mixer. A series of three tests were performed. Test one was an original TCLP analysis of the original 100-g spike surrogate waste. Of the eight samples tested (Table 3), only the mercuric sulfide–spiked sample passed the original test. A second test performed on the remaining seven samples stabilized 500-g surrogate specimens to determine optimum values for such processing parameters as chemical dosage, reaction time, and mixing technique. Six of the seven samples treated with the DeHg reagent were stabilized using the same formulation or "standard." Only the surrogate contaminated with elemental mercury required a combination of the DeHg reagent and a second amalgamation reagent. A third proving test was performed to verify the results from the second test. The DeHg reagent met the TCLP goal of 0.025 mg/L for all seven species, maximized waste loading, produced final residue with no freestanding solution, minimized secondary wastewater, and demonstrated a near-standard formulation for all mercury species.

Table 3. Surrogate matrix used in the tests by Nuclear Fuel Services, Inc.

Compound	g/kg spiked Ottawa Sand			ppm
	Mercury Compound	Dried Ottawa Sand	Added Water	
HgS	0.2900	949.7	50.0	79.0
$HgCl_2$	0.3384	949.7	50.0	78.9
HgO	0.2699	949.7	50.0	72.3
Hg (elemental)	0.2500	949.8	50.0	71.8
C_6H_5HgCl	0.3903	949.6	50.0	78.9
$Hg(SCN)_2$[a]	0.3948	949.6	50.0	78.9
$Hg(CN)_2$[a]	0.3148	949.7	50.0	78.9
HgI_2[a]	0.5663	949.4	50.0	78.8

[a] Surrogate samples tested by NFS in addition to those specified in the SOW.

3. PERFORMANCE

3.1 ATG, Inc.

Tests were performed using three reagents: DTC; polysulfide, with zeolite; and borohydride, with zeolite. Test results are summarized in Table 4. Only DTC was successful in immobilizing all five mercury species tested. The organic mercury species was the most difficult to stabilize. The polysulfide and borohydride reagents increased the leachability of elemental mercury and of mercury sulfide. DTC also resulted in the smallest increase in volume for the treated wastes. Although DTC was successful in its applications, the reagent was believed to have reacted with the clay, or the iron in the clay. The clay was added as an absorbent to control freestanding water. Such a reaction would cause inactivity and decrease the potential for stabilizing the mercury. DTC may prove to be unsuitable for field applications where iron is present. To improve the formulation, ATG is considering using a higher concentration, switching to an inert absorbent, and/or adding buffers to lower the pH.

Table 4. Leach performance for ATG mercury waste stabilization tests

Mercury Species	Pretreatment TCLP Results (mg/kg)	Stabilization Reagent/Formulation	Post-Treatment TCLP Results[a] (mg/kg)
Mercury Sulfide	0.0407	Dithiocarbamate (NaDTC)	0.0092
		Polysulfide (CaS_x)	0.0089
		Borohydride ($NaBH_4$)	**1.73**
Mercury Chloride	18.3	NaDTC	0.0058
		CaS_x	0.0204
		$NaBH_4$	**0.0322**
Mercury Oxide	18.1	NaDTC	0.006
		CaS_x	0.0106
		$NaBH_4$	0.01
Elemental Mercury	0.0376	NaDTC	0.0041
		CaS_x	**1.28**
		$NaBH_4$	0.0091
Phenyl Mercury Chloride	12.4	NaDTC	0.022
		CaS_x	**1.53**
		$NaBH_4$	**6.92**

[a] Bold figures indicate that stabilization failed to meet the UTS standard of <0.025 mg/L in TCLP leachate.

3.2 IT Corporation

IT used the binding reagents TMT 15 and calcium polysulfide independently as stabilization formulations to treat five surrogate waste samples contaminated with 250 ppm mercury. Test results are summarized in Table 5. Initial TCLP analyses were used to test the reproducibility of the surrogate preparation procedure without the use of binding reagents. Mercury sulfide surrogate passed the initial test of leaching <0.025 mg/L, which is the performance goal of the UTS; therefore, mercury sulfide was not the subject of any further tests. The remaining four samples had TCLP mercury values ranging from 0.31 to 11 mg/L and thus required treatment. Calcium polysulfide was used to treat the mercury metal, while TMT 15 was used to treat all others. The TMT 15 soils were lowered in pH from 12 to 9 by adding sulfuric acid. This adjustment was made because TMT 15 has increased effectiveness to fixate mercury at lower pHs. Although the ideal pH values range from 4.5 to 6.0, the pH was not reduced to these levels because the pH reduction could cause precipitation of the TMT, leading to limited reactivity with the mercury species.

Unlike TMT, calcium polysulfide requires mixing with air to cause a chemical breakdown to thiosulfate and sulfide species, which are the mercury fixation agents. Results from the first tests indicated that TMT 15 and calcium polysulfide used alone were not adequate for complete stabilization.

IT performed follow-up tests using the calcium polysulfide formulation, because it is less dependent on pH and it does not pose the precipitation problems experienced with TMT. The test used surrogates contaminated with elemental mercury, phenyl mercury chloride, mercuric chloride, and mercuric oxide. IT lowered the pH to 5 and added a 5% Portland cement mixture and calcium polysulfide to achieve concentrations of 0.5 to 1.0% calcium polysulfide. This formulation was successful with all samples tested with the exception of phenyl mercury chloride. A formulation using TMT had to be used on this sample. The IT speciation study resulted in optimum formulations for each sample.

Table 5. Leaching performance for IT Corp. mercury waste stabilization tests

Mercury Species	Pretreatment TCLP Results (mg/kg)	Stabilization Reagent/Formulation	Post-Treatment TCLP Results[a] (mg/kg)
Mercury Sulfide	0.0016	N/A	N/A
Mercury Chloride	9.8	Surrogate pH adjusted to 5 0.5% calcium polysulfide 5% Portland cement	<0.00020
Mercury Oxide	10.	Surrogate pH adjusted to 5 0.5% calcium polysulfide 5% Portland cement	0.00030
Elemental Mercury	0.36	Surrogate pH adjusted to 5 1.0% calcium polysulfide 5% Portland cement	0.00055
Phenyl Mercury Chloride	11.	Surrogate pH adjusted to 9.5 1.21% TMT 15	0.029

[a] A temperature preservation nonconformance was reported by ITC, but is not expected to have appreciably impacted the results.

3.3 NFS Corporation

NFS used DeHg to treat eight surrogate samples spiked with various mercury species at 250 ppm. NFS prepared 32 samples (four of each mercury species). Two of the samples of each species would be tested in house, and the remaining two would be sent for off-site TCLP analysis. Test results are summarized in Table 6. The initial testing showed that all samples except mercuric sulfide did not meet the UTS performance goal of <0.025 mg/L Hg. Scoping tests were performed on 500-g surrogate wastes of the remaining seven samples. From the scoping test, the same formulation was determined for six of the seven mercury compounds using the DeHg reagent. Elemental mercury required another amalgamation reagent. All samples had a TCLP Hg reading of <0.013 mg/L. To verify the results from the scoping tests, NFS performed a series of proving tests. The results were positive, but because of some high variability between duplicate samples, three of the waste forms are being retested by Core Laboratories.

The DeHg treatment process increased the weight of the final waste residues by an average of 25%. Weight increases ranged from 20 to 32%. Volume increases averaged approximately 90%.

Table 6. Leaching performance for NFS mercury waste stabilization tests

Mercury Species	Pretreatment TCLP Results (mg/kg)	Stabilization Reagent/Formulation	Posttreatment TCLP Results (mg/kg)
Mercury Sulfide	0.024	N/A	N/A
Mercury Chloride	15.0	Proprietary chemical stabilization reagent	<0.005
Mercury Oxide	15.4	Proprietary chemical stabilization reagent	<0.005
Elemental Mercury	0.23	Proprietary chemical stabilization reagent, plus and amalgamation reagent	<0.005
Phenyl Mercury Chloride	15.4	Proprietary chemical stabilization reagent	<0.005
Mercuric Thiocyanate	15.1	Proprietary chemical stabilization reagent	0.006
Mercuric Cyanide	14.7	Proprietary chemical stabilization reagent	<0.005
Mercuric Iodide	14.5	Proprietary chemical stabilization reagent	0.006

4. TECHNOLOGY APPLICABILITY AND ALTERNATIVE TECHNOLOGIES

4.1 Baseline Technologies

Methods to stabilize mercury contamination in various waste matrices have been developed and demonstrated, but no universally applicable treatment process or technology is presently available. Commercially available processes must tailor their reagents to each wastestream, depending on the mercury species present. These processes typically use a sulfur-bearing compound to chemically react with the mercury to form insoluble salts and some form of grout or cement to help stabilize the waste matrix. Several commercial vendors advertise stabilization capabilities for mercury mixed waste, but for most of them, experience in the area has been limited to treatability studies.

Wastes with elemental mercury contamination can be treated with amalgamation processes as defined by the Environmental Protection Agency (EPA). These processes mix specified metals such as zinc or copper with the waste matrix to form a metal-mercury amalgam that reduces the mobility of the mercury in the environment. The EPA also includes sulfur as an acceptable reagent, although sulfur reacts chemically with the mercury to form a salt. If the mercury has reacted in the waste matrix to form another chemical compound, the sulfur may not react, leaving the mercury free to leach. Determining the species of mercury in a matrix is expensive, and the available analyses are of questionable accuracy, making amalgamation for mercury in complex matrices risky.

Along with amalgamation, mercury can also be converted into a stable, inert sulfide salt by the use of sulfur polymer cement. This process has been marketed for soils, but applications may be limited because it may not adequately penetrate some matrices.

Thermal extraction could potentially remove the mercury from mixed waste but may not be able to reach the required levels of treatment. Thermal extraction is the specified treatment for wastes with >260 mg/L mercury. These processes heat the waste matrix, vaporizing the mercury, which is then collected from the off-gas system. Waste processors must amalgamate extracted mercury to prepare it for disposal. Some tests with storm sewer sediment from Oak Ridge resulted in residual mercury levels above the EPA 0.2-mg/kg limit. The UTS limit would have been exceeded by an even greater margin. In addition, the EPA is reviewing the use of thermal processes because of the risk of fugitive emissions of mercury vapor.

4.2 Competing Technologies

The DOE MWFA issued a Request for Information to determine what capabilities existed for mercury mixed waste treatment. Several vendors responded, and, based on their responses, the MWFA issued a Request for Proposal for mercury waste stabilization to those companies that indicated they had stabilization capabilities. The companies that submitted proposals for stabilization work represented the competing technologies at that time. Other companies have since developed stabilization capability, but the technologies described here are a cross section of the treatment processes competing in the stabilization arena.

The stabilization studies for mercury species came as an offshoot to the original SOW for the mercury waste treatment demonstrations. IT Corporation, NFS, Inc., and ATG used their respective treatment technologies to stabilize various species of mercury, thereby demonstrating the effects of mercury speciation on the stabilization of mercury waste. To be considered successful, a stabilization technology should stabilize all forms of mercury, including elemental mercury, organic, oxidized, and halogenated mercury compounds and mercury sulfates. The speciation studies reported herein were performed only at the bench scale.

ATG successfully stabilized mercury waste using the stabilization reagent DTC. Tests revealed that the DTC reagent can be deactivated by the clay, or the iron in the clay, used in the study. This deactivation reduces the performance of the process, possibly jeopardizing its ability to meet disposal standards. Through the series of tests, ATG demonstrated that their process could stabilize each of the mercury species required.

IT used the binding reagents TMT 15 or calcium polysulfide to treat surrogate waste samples contaminated with various mercury species. Through reagent concentration and pH adjustments, IT successfully stabilized mercury in all of the tested waste surrogates. Sulfuric acid was used to lower the pH of the TMT 15–treated soils from 12 to 9 because the reagent increased the effectiveness to fixate mercury at lower pHs. The calcium polysulfide reagent uses reaction with air to be effective. Air breaks down the calcium polysulfide to thiosulfate and sulfide species, which are vital in mercury fixation.

The NFS DeHg process converts wide varieties of mercury-contaminated wastes into nonhazardous form. The two-step process involves amalgamation of elemental mercury in the waste matrix and then the treatment of the remaining soluble mercury species with the DeHg reagent. This reagent frees the mercury from soluble complexes and fixes it as a stable, nonleachable salt.

Metcalf & Eddy, Inc., is marketing the General Electric Mercury Extraction Process (GEMEP) that uses a combination of potassium iodide and iodine to extract mercury from a waste matrix and stabilize it as an amalgam. The process is being used to clean up a mercury-contaminated Superfund site in Puerto Rico but, at last report, is experiencing problems in achieving the necessary level of treatment. The process is limited to wastestreams that will not react with iodine in the process. Otherwise, chemical costs make the process noncompetitive.

Pacific Northwest National Laboratory (PNNL) is developing Self-Assemble Monolayers on Mesoporous Substrates (SAMMS) material that will react with mercury that is in solution and create a stable wasteform that meets EPA requirements and resists biodegradation. The SAMMS material has been tested on a small scale, but no large-scale applications have been demonstrated. PNNL must engineer a system that can get mercury into solution to expose the mercury to the SAMMS material.

Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL) are developing processes to extract mercury with polymeric materials serving as the extractant. LANL has designed a pilot-scale system that appears capable of removing mercury from mixed waste matrices and stabilizing the extracted mercury as an amalgam. LLNL's process is still at a laboratory scale.

4.3 Technology Applicability

Each of the three vendors was able to modify their respective process to stabilize the subject mercury species. The final residues produced met the TCLP performance goals set by RCRA and UTS. IT developed optimum formulations for the samples tested. The formulations required two chemicals of various concentrations, pHs, and surface area adjustments. IT did not produce one general formulation that was effective on all the mercury surrogate waste. IT was unable to meet the UTS for the organomercury species tested. Based on the study, the calcium polysulfide reagent was favored over the TMT 15 because it is less dependent on pH and can avoid potential precipitation problems caused by increased stoichiometry.

The NFS DeHG process was able to stabilize all forms of mercury waste. This stabilization process maximized waste loading, produced no freestanding solution, and minimized wastewater. NFS stabilized all of the samples tested using the same amount of reagent, except for the case of elemental mercury, where an additional reagent was required.

ATG completed their speciation study using the stabilization reagent DTC. DTC successfully stabilized all mercury forms while resulting in a minimum volume increase. Test results suggested that the DTC reagent reacted with the clay or the iron in the clay causing it to deactivate and not stabilize the mercury. The ATG formulations would have to be changed significantly for matrices with a high concentration of the interfering chemical. To increase DTC effectiveness, ATG suggests that future studies should use an inert absorbent instead of clay to minimize possible reaction, buffers where pH would be increased, and other reagents to tie up cations.

5. LESSONS LEARNED

5.1 Implementation Considerations

The speciation studies summarized in this report provide insight into the impact that different mercury species have on the stabilization of mercury wastes. The test results reported have important implications for developing technologies, such as amalgamation and fixation technologies, and should be provided to and considered by stakeholders, including the developers and users of stabilization technologies. Further implementation considerations are not applicable to this work.

5.2 Technology Limitations and Needs for Future Development

This report confirms the importance of speciation on the effectiveness of stabilization technologies. The effectiveness of the reagents TMT 15 and calcium polysulfide, tested by IT Corporation, are found to be concentration-, pH-, and surface-area dependent. Reagents or formulations that are more universally effective are yet to be identified.

In addition, the presence of more than one species of mercury complicates the treatment process. NFS must add another reagent to treat elemental mercury. IT was unable to fully treat phenyl mercury chloride. Actual DOE wastes have, in some cases, been exposed to the environment, which through oxidation or biodegradation has produced additional species of mercury. One need for future development is refinement of mercury speciation analyses to make them more accurate and less expensive. Data generated by improved speciation analyses would allow those treating wastes to define the process required to process each wastestream, without the extensive preliminary tests presently required.

Furthermore, nonmercury constituents in the waste matrix can complicate stabilization technology performance. Using the DTC stabilization reagent, ATG found that interactions with the iron in clay could deactivate the stabilization reagent. Workers at ATG have suggested that future studies should use an inert absorbent instead of clay to minimize possible reaction, use buffers to adjust pH, and use other reagents to tie up cations. Based on the current experience, the ATG formulation may not be suitable for all field applications because it might not be effective on mercury-contaminated wastes that have iron present.

The EPA is considering allowing stabilization of mercury-contaminated waste with greater than 260 mg/kg mercury. Speciation tests should be conducted at higher concentrations of mercury to support this change to the regulations. If commercial processes are unable to stabilize certain species at the higher levels, those processes would require development work to make the necessary modifications.

5.3 Technology Selection Considerations

With the exception of IT's failure to meet the UTS limit with phenyl mercury chloride, each of the mercury species included in the speciation study was successfully stabilized. Each vendor was able to produce final residues that met the UTS of <0.025 mg/L, which is more stringent than the Land Disposal Restrictions (LDR) TCLP limit of <0.2 mg/L. IT was close to the UTS limit with the phenyl mercury chloride. Testing proved that a wide variety of mercury wastes could be stabilized using near-standard formulations of readily available reagents. Commercially available technologies should be able to stabilize DOE's mercury-contaminated wastes. Although the results were positive and provide valuable insight into mercury speciation technology, larger-scale studies should be performed to obtain more precise results.

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