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Technologies for Immobilizing High Mercury Subcategory Wastes

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I. Introduction

Industry and commerce are using less mercury because of the high toxicity and environmental mobility of elemental mercury and its compounds. The alkyl mercury compounds are especially dangerous, as they can form from reactions with other mercury compounds released to the environment. Elemental mercury is also potentially dangerous, as it is hard to control during use because it is a liquid, it is volatile, and it can be absorbed through the skin.

EPA's policy, consistent with the philosophy of sustainable industrial growth, has been to encourage the recovery and reuse of mercury. The technologies for recovering this mercury have primarily been thermal (i.e., roasting, retorting, and incineration). However, the unintentional releases of mercury during these thermal recovery processes may be significant, despite carefully designed and implemented offgas capture and treatment. As is the case with any industrial process, leaks are hard to detect and prevent.

EPA is assessing the feasibility of immobilizing mercury wastes rather than using thermal processes to recover the mercury. To satisfy Land Disposal Restriction (LDR) requirements, EPA has allowed industry to use stabilization technologies only in the treatment of mercury wastes containing less than 260 mg/kg of total mercury. The LDR program currently requires thermal recovery of the mercury in wastes with total mercury contents greater than or equal to 260 mg/kg total mercury (i.e., high mercury subcategory wastes).

Mercury is one of the most difficult waste contaminants to stabilize. A study cited in EPA's Technical Background Document for Mercury Wastes indicated that cementitious stabilizing agents actually increased, rather than decreased, the leachability of mercury from wastes in some instances. Hot stabilization processes are difficult or impractical because of the high volatility of elemental mercury and its alkyl organic compounds, and because of the tendency of inorganic and organic mercury salts to decompose or sublime at low temperatures. The solubility of mercury salts at high pH tends to make cementitious stabilization problematic. Nevertheless, researchers are continuing to investigate stabilization technologies to treat mercury wastes.

A. Definitions

The following are definitions of key terms as used in this report. In the published literature on waste immobilization, many of the terms are used interchangeably. We have chosen more narrow definitions to help in distinguishing among the wide variety of options for mercury waste immobilization.

- Amalgamation - a physical immobilization technology unique to elemental mercury, in which another metal forms a semisolid alloy ("amalgam") with mercury. Mercury dissolves in the solid metal, forming a solid solution. The process is reversible, since mercury at the surface of the amalgam can evaporate, or react to form water soluble compounds. Amalgamation is a subset of solidification technologies, and it does not involve a chemical reaction.

- Immobilization - rendering a waste constituent stationary in the environment (i.e., not likely to move by vaporization into the air, or by leaching into surface water bodies or groundwater). It includes stabilization, solidification, and encapsulation.
- Solidification - physical immobilization of hazardous constituents, producing a final waste form that is consolidated to reduce the surface area of the waste available for vaporization or leaching. The final form may be porous.
- Stabilization - chemical immobilization of hazardous constituents, through chemical bonds to an immobile matrix, or chemical conversion to an immobile species, thereby reducing vaporization or leaching to the environment. Used in this report as a synonym for “chemical fixation,” precipitation of mercury as the very insoluble sulfide is an example of stabilization without solidification, while synthetic mineral immobilization is both stabilization and solidification
- Encapsulation - physical immobilization of hazardous constituents by enveloping a waste in a non-porous, impermeable material. If a waste is fine-grained and well dispersed throughout the encapsulation matrix so that each particle is separately encapsulated, it is “microencapsulated.” If clumps of waste matrix or bulk waste are enclosed within the encapsulating material, the waste is “macroencapsulated.” In this report, encapsulation technologies form a subset of solidification technologies

B. Purpose of Report

This report will accomplish three tasks:

(1) it will evaluate and compare immobilization technologies for high mercury category wastes, including the following major technologies that are applicable to mercury wastes.

- Stabilization - immobilization by chemical fixation
- Amalgamation - immobilization by dissolution in metals
- Encapsulation - immobilization by wrapping in an inert solid.

(2) it will assess the applicability of immobilization technologies for specific waste forms and waste matrices of mercury based on the following criteria.

- Effectiveness in reducing Toxicity Characteristic Leaching Procedure (TCLP) concentrations in treated waste, as compared to untreated waste
- Effectiveness in reducing mercury vaporization from the waste
- Treated waste strength and durability
- Long-term maintenance of non-mobile valence states of mercury.

(3) it will assess and discuss management practices that minimize mercury air emissions during handling and treatment, and the optimum long-term storage conditions for waste forms that minimize mercury mobilization.

II. Stabilization Technologies

Currently, treaters of mercury waste can only stabilize low mercury subcategory wastes. EPA's policy for high mercury subcategory wastes has been to encourage the recovery and reuse of mercury and its compounds through the use of thermal technologies.

Although cementitious stabilization technologies have been widely used for mercury wastes, there is a belief that these technologies do not directly stabilize mercury or its salts (U.S. DOE, 1998).

A. Stabilization of Mercury as an Insoluble Compound

Mercury can be precipitated from aqueous solution by oxidation to the mercuric (+2) state and precipitation as mercuric sulfide using sodium sulfide, Na_2S , or sodium hydrogen sulfide, NaHS (A. T. Kearney, 1997, Sec. 4.7). Mercuric sulfide is very insoluble in water (see Table 1), and is therefore a superior final waste form relative to other mercury compounds. Potassium sulfide and calcium polysulfides are also used to precipitate mercury salts from alkaline solution. Excess alkali or alkaline sulfide will increase the solubility of the mercuric sulfide, so only a small excess of soluble sulfide salt is used for precipitation.

Table 1: Solubility Data for Common Industrial Mercury Compounds

Compounds	Formula	Solubility (mg/L)	Reference
Mercuric sulfide	HgS	0.0125	Kirk-Othmer, 1995, V16, 241
Mercurous chloride	Hg_2Cl_2	2	Kirk-Othmer, 1995, V16, 231
Mercuric chloride	HgCl_2	7000	Kirk-Othmer, 1995, V16, 232
Mercurous sulfate	Hg_2SO_4	500 mg/kg	Kirk-Othmer, 1995, V16, 235

Mercuric sulfide generation, by mixing mercury metal with sulfur to form a semi-solid “amalgam,” is one of the options listed under amalgamation technologies in 40 CFR 268.42. When first mixed with sulfur, a mixture initially forms, then the mercury reacts to form the sulfide. Since an amalgam is really a solid solution (alloy) of mercury in another metal and does not involve a chemical reaction, mercury plus sulfur does not form a true amalgam.

Mercuric sulfide precipitation can be performed in a batch or continuous process. Thorough mixing is required to obtain a complete conversion of all dissolved mercury forms to the sulfide. A flocculent is added to help settle the very fine precipitate, and settling may be performed by gravity in a large tank or using a circular clarifier or an inclined separator. Filtration may be used for final polishing. The cost for mercuric sulfide precipitation is about \$100 to \$200 per ton of waste (A.T. Kearney, 1997). The mercury removal efficiency is ninety-five percent. Pretreatment is typically needed to get all mercury into solution from solid wastes, and to convert all mercury to the mercuric (+2) oxidation state for best process efficiency.

1. Full-Scale Commercial Technologies

Precipitation of Mercury from Scrubber Waters with Trimercapto-s-triazine

The trisodium salt of trimercapto-s-triazine (TMT) has been used for years in European industrial operations to remove mercury from scrubber water in offgas treatment systems (Roland, 1998). Its full-scale commercial use for mercury precipitation is established. Its insolubility in

water is similar to that of mercuric sulfide (Solujic, et al., 1996), and therefore it is a relatively stable final waste form.

Precipitation of Mercury from Acidic Waste Streams Using Hydrogen Sulfide

The Sachtleben-Lurgi process has been used in Duisburg, Germany for precipitation of arsenic and other heavy metals, including mercury, from acidic scrubber waters (ICF Kaiser, 1994). The wastewaters are generated by scrubbing offgas from smelting of metal ores. The process includes the addition of small amounts of a soluble hydrosulfide salt to provide the hydrosulfide ion (HS^-) to the reaction, assuring more complete heavy metal removal.

2. Bench-Scale and Pilot-Scale Developmental Technologies

Simultaneous Precipitation and Froth Flotation of Mercuric Sulfide

One of the difficulties with the precipitation of heavy metals as sulfides is the very fine particles that form. These particles are hard to separate from the reaction solution and dewater. In one study, a bench-scale demonstration of simultaneous precipitation with hydrogen sulfide gas and froth flotation in a continuously operated flotation column was performed (Nesbitt and Davis, 1993). The pH was kept very acidic at about 0.7 to prevent precipitation of arsenic, iron, and zinc, and the Eh was maintained at about +350 millivolts. American Cyanamide's S-7151 nonionic collector was used to promote coagulation of the precipitate particles, and Dowfroth 1263 frother was used to promote formation of numerous fine bubbles to float the precipitate. In a test with mercury, 50 percent of the precipitate that formed was collected in the froth overflow. The conversion of the mercury to sulfide was only 56 percent, blamed on inadequate sulfide ion concentration. Sulfide ion concentration was intentionally minimized in all tests to allow fewer and larger metal sulfide precipitate particles to form. Further development of the technology modification was apparently needed. Conversion to sulfide was nearly complete in tests with lead, and flotation was over 80 percent for copper and 96 percent for cadmium.

Precipitation of Mercury from Precious Metals Extraction Wastes with Trimercapto-s-triazine

The trisodium salt of trimercapto-s-triazine (TMT) has been tested for precipitation of mercury from cyanide-containing wastewaters from the precious metals extraction process (Solujic, et al., 1996). TMT competes with the cyanide complexes of mercury to form a precipitate with a solubility product similar to that of metal sulfides.

In bench-scale tests using equimolar amounts of TMT alone, the most effective removal of mercury from a 10.0 ppm solution of mercuric cyanide occurred from solutions at pH 12. At a pH of 10, all of the mercury-TMT complex remained in colloidal suspension and did not precipitate. At pH 12, the removal efficiency was about 98 percent, with the balance remaining in colloidal suspension.

With ferrous sulfate as a coagulant and Superfloc® 16 polyacrylamide as a flocculent (to assure rapid coagulation and settling), the removal efficiencies were greatly improved, as shown in Table 2.

Table 2: Precipitation of Mercury With TMT: Removal Efficiency vs. pH

Solution pH	Percent Removal of Mercury - TMT Only	Percent Removal of Mercury - TMT + FeSO ₄ + Superfloc®
10	0	99.93
11	~30	99.85
12	98	99.30

No information was provided by Solujić and coworkers (1996) on the leachability of the mercury-TMT complex or on the stability of the complex toward microbial reactions that could biodegrade the TMT, mobilizing the mercury.

B. Stabilization of Mercury in an Inert Matrix

Stabilization using cementitious materials have been used to treat mercury-bearing wastes. Research has continued on other innovative technologies that show promise as long-term stable final forms for mercury.

Kiln dust and fly ash are examples of pozzolanic materials. Pozzolans are materials having hydraulic cementitious properties when mixed with free lime. They tend to be high in oxides of silicon, aluminum, and/or iron. Other examples include certain volcanic rocks and industrial byproducts, such as granulated blast furnace slag and silica fume. Pozzolanic cements, including blends with Portland cement, can have performance advantages over straight Portland cements for certain applications.

A synthetic mineral called Xtaltite™ has been developed to stabilize heavy metal wastes; and DOE laboratories are also developing a combination of organic monolayers on ceramic substrates for mercury stabilization. These two innovative approaches are also described in this subsection.

1. Full-Scale Commercial Technologies

Portland cement and lime-pozzolan combinations have been widely used for stabilization and solidification of mercury-containing nonwastewaters (Biennial Reporting System (BRS) System Code M111 - Stabilization/chemical fixation using cementitious and/or pozzolanic materials). The 1993 EPA BRS data for mercury waste shows that over 119,000 megagrams (Mg, or metric tons) of mercury-containing waste was treated by methods included in BRS System Code M111 (A.T. Kearney, 1997). The 1995 BRS data, summarized in a draft report prepared for EPA under this project (U.S. EPA, 1998), shows more than 124,000 Mg of mercury waste stabilized by technologies falling under System Code M111. Comparison of these two volumes indicates a similar extent of use.

A booklet provided by the Portland Cement Association states “substantial reduction in mercury leachability is easily accomplished in most stabilization processes,” but it does not speak to its effectiveness on wastes containing greater than 260 ppm total mercury. The booklet also mentions that elemental mercury and organomercury compounds present stabilization difficulties.

2. Bench-Scale and Pilot-Scale Developmental Technologies

Mercury Stabilization in Portland Cement and Lime-Pozzolan Matrices

Bhatty and West (1996) conducted tests of Portland cement stabilization of mercuric oxide, as well as several other metals including cadmium and lead. Cement pastes of ASTM Type I and ASTM Type V Portland cement, each containing heavy metal oxides, were cured for 28 days. TCLP results for mercury, cadmium and lead are provided in Table 3, together with their relative leachabilities expressed as a ratio of the concentration of the metal oxide in the cement to the metal in the TCLP leachate.

Mercury was clearly the most leachable and did not pass the TCLP, in spite of a very low mass loading (0.33 g/kg = 330 ppm by weight). By comparison, lead and cadmium, both of which are similar to mercury in that they become more mobile at strongly alkaline pH values, leached to a much lesser degree in the TCLP. Portland cement Types I and V are both adequate for stabilization of lead and cadmium at these waste loadings, but not for mercury. The regulatory levels for cadmium, lead are 1.0, 5.0, respectively, while the mercury regulatory level is 0.20 mg/L for retort residues, and 0.025 mg/L for non-retort residues.

Table 3: Leachability Comparison for Metals Stabilized in Portland Cement

Heavy Metal and Portland Cement Type	Waste Loading (g/kg)	TCLP (mg/L)	Leachability (mg/L per g/kg)
Mercuric oxide in Type I cement	0.33	1.71	5.2
Mercuric oxide in Type V cement	0.33	2.02	6.1
Lead oxide in Type I cement	7.3	1.21	0.17
Lead oxide in Type V cement	38	3.24	0.085
Cadmium oxide in Type I cement	5.8	0.0007	0.00012
Cadmium oxide in Type V cement	12.6	0.007	0.00056

Work conducted by the U.S. Army Corps of Engineers Waterways Experiment Station (WES) at Vicksburg, Mississippi, showed similar results when Portland cement, kiln dust, and lime/fly ash mixture were all tested for stabilizing K106 mercury cell process wastewater treatment sludge (Keenan and Berlow, 1988). Stabilizer/waste ratios were selected to assure an unconfined compressive strength in the stabilized material of at least 50 pounds per square inch (psi) after 28 days of curing. The waste contained the following constituents in these approximate percentages: mercuric sulfide, 3 percent; other metal sulfides, 2 percent; other solids (e.g., diatomite), 35 percent; and water, 60 percent.

The binder-to-waste ratios, mean unconfined compressive strengths, and binder-waste mixture pH for the K106 waste samples stabilized with the three types of binders are summarized in Table 4. (Note that the mass of the waste included water - the waste was moist enough that no water needed to be added to stabilize the waste.)

Table 4: Binder-to-Waste Ratios, Compressive Strength, and pH for Stabilized K106 Waste

Stabilizing Binder	Binder-to-Waste Ratio	Mean 28-Day Unconfined Compressive Strength (psi)	pH of Binder-Waste Mixture
Portland cement	0.1	105	12.00 - 12.05
Kiln dust	0.5	83	12.20 - 12.25
Lime/fly ash	0.1/0.1	58	12.45 - 12.50

Table 5 presents the mercury leachability results for the untreated K106 waste and for the K106 waste stabilized with each of three types of binder material.

Table 5: Mercury Leachability Comparison for K106 Waste Stabilized with Different Binders

Stabilizing Binder	Untreated Waste -Total (Hg, g/kg)	Untreated Waste - TCLP (Hg, mg/L)	Treated Waste TCLP - Set #1 (Hg, mg/L)	Treated Waste TCLP - Set #2 (Hg, mg/L)	Treated Waste TCLP - Set #3 (Hg, mg/L)	EPA TCLP Regulatory Limit (Hg, mg/L)
Portland cement	25.9	0.01	4.13	31.7	49.9	0.02
Kiln dust	25.9	0.01	0.0096	0.023	0.0093	0.02
Lime/fly ash	25.9	0.01	3.4	13.1	3.44	0.02

The leachability of mercury from the Portland cement stabilized waste *increased* by about 400 to 5000-fold. The lime/fly ash mixture was not much more effective, with leachability increasing by about 300 to 1300-fold. Only the kiln dust stabilized waste had acceptable mercury leachability, causing no significant increase or decrease in leaching of mercury. The data suggest that no cement- or lime-based stabilizing binder is effective for stabilizing mercury, at least when the binder is at the minimum ratio to achieve acceptable physical (unconfined compressive) strength.

One possible explanation for the inadequate performance of these binders, and the increased leachability of mercury may be the high pH of the binder-waste mixtures. Mercury is relatively mobile at these high pH values. The mercuric sulfide may be converted to the more soluble mercuric oxide, or a dihydroxy mercuric sulfide anion ($\text{HgS}(\text{OH})_2^-$) may have formed. Either form would contribute to the TCLP leaching of up to 49.9 mg/L of the mercury from the Portland cement stabilized waste.

Portland cement, the worst performing binder, actually formed the waste-binder mixture with the least alkaline pH (see Table 4). This suggests that some other factor was also important. Another possible factor was probably the lack of sufficient binder to chemically fix the mercury, in spite of achieving adequate compressive strength in the cured stabilized waste. The binder-waste mixture with the highest binder-to-waste ratio, the kiln dust stabilized waste (0.5, see Table 4), also had the best leachability results. The Portland cement mixture had a binder-to-waste ratio of 0.1, the lowest of the three, and also had the worst leachability performance. The kiln dust produced an alkaline binder-waste mixture (pH 12.20-12.25), but if this produced more soluble forms of mercury, it also bound those forms effectively in a stabilization matrix. The results with kiln dust are surprising, because Portland cement is a better binder than kiln dust, based on unconfined compressive strength results. Portland cement may also be a better stabilizer, if used in adequate ratios to the waste.

Based on the WES results, it may be possible to achieve an effective stabilization with any of the three cementitious binders if the waste loading is not excessive; or, inversely, if the binder-to-waste ratio is high enough. Additional work reported by WES in the same report (Keenan and Berlow, 1988) showed that a binder-to-waste ratio of 0.5 with Portland cement provided an unconfined compressive strength after 28 days of about 1500 psi. The mixture pH was 12.20 to 12.25, which was not any higher than for the kiln dust stabilized waste that showed no increased leachability in Table 5. TCLP tests were not conducted on the 0.5 binder-to-waste Portland cement specimens.

It is useful to compare the results obtained by Bhatta and West (1996) for stabilizing mercuric oxide with Portland cement, with the results obtained by Keenan and Berlow (1988) for stabilizing mercuric sulfide with kiln dust. Bhatta and West achieved poor stabilization performance (high leachability) when they stabilized mercuric oxide with Portland cement, even at a low waste loading (high binder content).

If the kiln dust results were due to the higher binder-to-waste ratio (0.5), then an equal ratio of Portland cement with waste might produce an even better leachability result. Also, the apparent better leachability results by Keenan and Berlow, even with Portland cement (leachability of mercury for the worst performing Set #3 was $49.9/25.9 = 2.0$ mg/L per g/kg), may have been because they were stabilizing the much less water soluble mercuric sulfide rather than the relatively water soluble mercuric oxide that Bhatta and West stabilized.

For the reasons discussed here, further research may be well justified to clarify the effects of the exact mercury compound and the binder-to-waste ratio on mercury leachability from cementitious stabilized wastes.

Stabilization of Mercury-Contaminated Soil with Portland Cement

Radian Corporation (1993) conducted bench scale treatability tests for stabilizing soil from the East Fork Poplar Creek (Oak Ridge, TN) area contaminated with 1000 mg/kg of mercury, mostly in the mercuric sulfide form. They used a 60 percent waste loading and 25 percent added water to prepare a 28-day cure stabilized sample with an unconfined compressive strength of 913 psi. They conducted an ASTM leaching test (ASTM Method D-2434) using deionized water as the leachant and detected 0.22 micrograms/L of mercury in the leachate. A separate laboratory (CompuChem) conducted total mercury analysis and TCLP on the stabilized material. The

mercury content was 406 mg/kg; their TCLP results showed less than 0.1 mg/L of mercury in the leachate. TCLP levels for the unstabilized soil by Radian and CompuChem were 0.0048 mg/L, and less than 0.1 mg/L, respectively.

Although the Radian results showed that they had stabilized a soil that would have passed the TCLP without treatment, the results also showed no increase in leaching of mercury following stabilization with Portland cement.

Xtaltite™ Synthetic Mineral Immobilization of Mercury

Synthetic mineral immobilization technology (SMITE), which has been developed extensively for stabilization of high level radioactive waste, is also applicable to stabilization of heavy metal wastes. Xtaltite™ is the trade name for a technology that incorporates heavy metals (e.g., mercury, arsenic, cadmium, lead) into an apatite type of mineral crystal structure. Several of the characteristics of apatite make it ideal for SMITE applications:

- It is a stable geological entity that weathers slowly
- Many apatite end members form extensive solid solutions, allowing incorporation of a wide variety of metal species into the crystal lattice.

Apatite has the generic formula $A_5(BO_4)_3X$, where A = Ca, Cd, Hg, or Pb; B = P, As, Cr, V, C, or Se; and X = F, Cl, OH, or [vacant]. Mercury in the form of mercuric oxide can be incorporated into an apatite structure by mixing it in stoichiometric proportions with fluor spar (calcium fluoride) in dilute phosphoric acid for 1-2 hours. The solid product from this hydrometallurgical reaction, fluoromercuric calcium phosphate, contains some mercury apatite of low crystallinity. The formula may be $Hg_9Ca(PO_4)_6F_2$ or $Hg_4Ca_6(PO_4)_6F_2$, depending on the proportion of mercuric oxide used (and, presumably, requiring the addition of quicklime (CaO)). The latter form is simpler to synthesize, and has enhanced leach resistance; the weight percent of mercury is lower and therefore safer.

The initial hydrometallurgical product is filtered, dewatered, and then converted under pyrometallurgical conditions of 600°C for up to 12 hours to a stable, highly crystalline final waste form. When the initial rate of temperature increase is controlled to less than 150°C/hr, the mercury is not driven out of the product and an acceptable mercury apatite final form is obtained.

Mercury Stabilization with Self-Assembled Monolayers on Mesoporous Supports (SAMMS)

The U.S. Department of Energy (DOE) Mixed Waste Focus Area (MWFA) and Efficient Separations and Processing Crosscutting Program (ESP-CP) are jointly developing one example of a new class of materials at the Pacific Northwest National Laboratory (U.S. DOE, 1998). The new materials are known as self-assembled mercaptans on mesoporous silica (SAMMS), and are being designed specifically for mercury removal from wastewaters and long-term stabilization. SAMMS material consists of a monolayer of functional groups that aggregate on an active surface inside the pores of a stable oxide (i.e., SiO_2). The powdered form of SAMMS can be added to a liquid containing mercury and organics to remove the mercury. SAMMS has successfully removed mercury from organics. In an Oak Ridge National Laboratory sample, the mercury concentration was reduced from 1.6 mg/kg to less than 0.2 mg/kg.

III. Amalgamation Technologies

Currently the treatment standard for elemental mercury waste (i.e., nonwastewaters) contaminated with radioactive materials is amalgamation, which gives “a nonliquid, semi-solid amalgam” as the final form (40 CFR Section 268.42). Amalgamation has been selected as the technology-based standard because it reduces air emissions of elemental mercury vapor. The following are some of the metals that form an amalgam with mercury: copper, nickel, tin, zinc, gold, and silver.

Tin and zinc do not give an acceptable final waste form to meet DOE’s needs, but alloys of these two metals may (U.S. DOE, 1998). To improve on amalgamation alone, encapsulation of amalgamated mercury waste will further limit the volatilization and leaching of mercury.

Two generic processes are used for amalgamating mercury in wastes (Lopez and Rosengrant, 1991):

- Aqueous replacement (solution) process - a finely divided base metal such as zinc or copper is mixed well into a wastewater containing dissolved mercury salts; the base metal reduces mercuric and mercurous salts to elemental mercury, which dissolves in the metal to form a solid mercury-base metal alloy called an amalgam.
- Nonaqueous process - finely divided metal powders are used to contact waste liquid mercury; the mass solidifies into a solid amalgam.

The aqueous replacement process is not applicable to water-insoluble mercury compounds. The nonaqueous amalgamation process is useful for waste scrap elemental mercury only, including waste mercury contaminated with radioactive materials. If oils, greases, or emulsions are present, they may interfere with amalgam formation. Amalgamation does not significantly reduce the leachability of mercury, according to Lopez and Rosengrant (1991).

IV. Encapsulation Technologies

Sulfur polymer cement (SPC) can be used to convert mercury compounds to mercuric sulfide and encapsulate simultaneously (U.S. DOE, 1998). However, the encapsulation process temperatures can volatilize mercury (see Table 6), so the mercury vapor and oxide that forms must be captured and recycled in the process. SPC processing temperatures are much lower than mercury retorting temperatures, so good control is much more feasible.

Table 6: Data Indicating Relative Volatility of Mercury and Mercury Compounds

Compounds	Formula	Volatility Parameter	Reference
Mercury	Hg	bp. 357°C	Radian, 1993
Mercuric sulfide	HgS	sublimes 584°C	Radian, 1993
Mercurous chloride	Hg ₂ Cl ₂	bp. 320°C	Radian, 1993
Mercuric chloride	HgCl ₂	sublimes 300°C	Kirk-Othmer, 1995, V16, 232
Mercuric oxide	HgO	decomposes 332°C	Kirk-Othmer, 1995, V16, 234

Encapsulation of amalgamated elemental mercury will further limit the escape of mercury vapor, and also prevent leaching of mercury from amalgams. The following encapsulation

technologies are applicable directly to mercury nonwastewaters, to mercury amalgams, and to chemically fixed mercury (i.e., mercuric sulfide).

A. Sulfur Polymer Stabilization/Solidification

Brookhaven National Laboratory has been testing SPC for microencapsulation of elemental mercury in cooperation with the DOE Mixed Waste Focus Area's Mercury Working Group (INEL, 1997). A two-stage process is being used: first, elemental mercury is chemically stabilized using SPC (converting the mercury to mercuric sulfide); then, the stabilized mercuric sulfide is encapsulated in SPC and molded into a monolithic waste form. This process avoids the oxidation of the mercury to mercuric oxide and minimizes the amount of unreacted mercury.

Oak Ridge National Laboratory has been scaling up the SPC process for macroencapsulation of 204 kg of mercury contaminated lead pipes (ORNL, 1998). They report that SPC macroencapsulation successfully rendered the waste no longer D009 (TCLP characteristic for mercury). The final form is cast in a 5-gallon steel pail.

B. Sodium Sulfide Nonahydrate in Sulfur Polymer Cement

Darnell (1996) described the use of SPC cement for stabilization and microencapsulation of mercuric oxide. Sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) was added at 7 weight percent to the SPC mixture to enhance the conversion of mercuric oxide to mercuric sulfide. SPC melts at 115°C and pours at 135°C ; the recommended mixing temperature is $127\text{--}138^\circ\text{C}$. When a 5 weight percent loading of mercuric oxide was stabilized in this SPC mixture, the final waste form leached less than the EPA TCLP limit for mercury (0.2 mg/L).

SPC-stabilized waste achieves an unconfined compressive strength of about 4000 psi, immediately upon cooling. It contains no water and is resistant to acids and salts for years, under conditions that would deteriorate a hydraulic concrete in weeks to months. It is generally less permeable than hydraulic concrete; its porosity is about the same, but the pores are not connected, as they are in hydraulic concrete. It is less resistant to strong alkali (above 10 percent), strong oxidizers (e.g., hot chromic acid, sodium chlorate-hypochlorite), hot organic solvents, and some metal slimes like copper (Darnell, 1996).

C. Encapsulation of Mercury Waste in Emulsified Asphalt

The encapsulation of mercury wastes in hot-mix asphalt is not practical because of the volatility of elemental mercury and its compounds at the temperatures required (see Table 6). Cold-mix asphalt encapsulation, using emulsified asphalt or asphalt cut with hydrocarbon solvent, may be a practical technology because no heating is required to obtain a cured asphalt final form.

Radian Corporation (1993) reported performing microencapsulation treatability tests on mercury-contaminated soil (average 78 mg/kg) using coal tar emulsion (which is similar to emulsified asphalt); the material was marketed as a driveway sealer. The specimens with 20 percent coal tar achieved an unconfined compressive strength of 176 psi after only 7 days of curing. EPA's recommended minimum strength for stabilized waste is 50 psi. No leachability

tests were done, but further development and testing with emulsified asphalt or solvent-cut asphalt, using longer cure times, may show this to be a feasible encapsulation method.

V. References

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