

MASS: Mercury Amalgamation Stabilization/Solidification

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ABSTRACT

Traditionally, cement has not stabilized mercury well. Mercury Amalgamation Stabilization/Solidification (MASS) overcomes this limitation through the use of a cement matrix capable of stabilizing soluble mercury compounds and amalgamating-stabilizing agents that also stabilize elemental mercury. The combination of this matrix and these agents not only stabilizes elemental mercury and its compounds but also suppresses the vapor pressure of elemental mercury. This paper presents the matrix and special agents tested for MASS, the resulting improvement in the Toxicity Characteristic Leaching Procedure results for soil spiked with mercury and pure mercury, and the effect of the MASS technique on surrogate sludge.

I. INTRODUCTION

Mercury is a toxic substance that can accumulate over time to toxic levels in the body. For these reasons, the Resource Conservation and Recovery Act (RCRA) regulates disposition and/or land disposal of mercury. The best demonstrated available technology for RCRA metals is stabilization/solidification (S/S). Traditionally, mercury has been one of the more difficult contaminants to stabilize in hazardous or mixed waste. Cement does not directly stabilize either elemental mercury or mercury salts, and high-temperature techniques, such as

incineration or vitrification, volatilize the mercury.

Unlike the case for many of the RCRA metals, high pH does not reduce mercury solubility to the low levels required for land disposal. Figure 1 illustrates the estimated mercury solubility as a function of pH using the published solubility data for HgO in aqueous solutions of various acids and bases.¹ Distribution into the cement matrix lowers the mercury concentration below the level of aqueous solubility illustrated in Figure 1, as it does for other RCRA metals; however, the mercury concentration at equilibrium still approaches the levels in Figure 1, which are well above regulatory limits.

This limitation in mercury pH control for standard cement matrices is overcome in Mercury Amalgamation S/S (MASS) by using a cement substitute — ground granulated blast furnace slag (slag) — capable of precipitating dissolved mercury compounds as HgS. Strong bases activate this glassy slag, which hydrates into a cement matrix. Mixing with standard cement ensures activation upon mixing with water or wet waste. Slags typically contain on the order of 1 wt % sulfide. Presumably, the stabilizing reaction is the conversion of the existing mercury compound into the less soluble HgS, as depicted in Eq. 1 for HgO.



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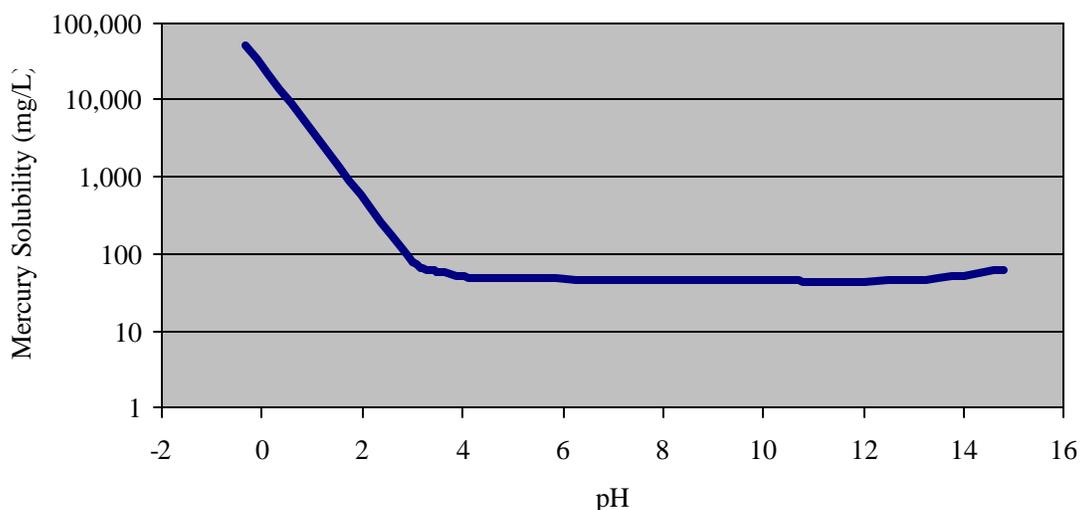


Figure 1. Plot of HgO solubility versus pH, using the data from reference 1.

Figure 2 shows the equilibrium species projected by the HSC 4.1 software (A. Roine, Outokumpu HSC Chemistry® for Windows, Version 4.1, 2000) for the addition of FeS to solid HgO in an aqueous environment. The combination of a sulfide-containing matrix and the encapsulation of the waste in this matrix stabilizes mercury compounds, even for wastes such as high pH sludges that are not amenable to the traditional wastewater treatment of using soluble sulfides to precipitate dissolved mercury compounds. Agents known to stabilize or complex mercury include soluble sulfides,²⁻⁴ sodium sulfide with iron sulfate,^{3,5,6} and cyanide.⁷ These agents were tested in MASS for enhancing stabilization of soluble mercury in the baseline slag-cement matrix.

Although slag enhances cement stabilization of mercury compounds, elemental mercury is, at best, only encapsulated. Elemental mercury is not very soluble in neutral or basic water, and the solid cement matrix helps retard solubilization to the extent that the treated waste can pass

regulatory testing. In addition, mercury is heavy, not miscible, and difficult to mix, making it problematic to ensure its encapsulation in the final waste form. Including amalgamating metals helps retain and encapsulate elemental mercury. Several metals are known to amalgamate with mercury, including precious metals, copper, and zinc. Amalgamating zinc with mercury makes it more susceptible to hydrolysis. Thus, copper metal was tested for MASS in the slag-cement matrix.

Sulfur is used to wet mercury into a paste for easier handling and to suppress the mercury vapor pressure. It is important to remember that the mercury vapor pressure above mercury metal amalgams approaches that of mercury metal alone. Thus, sulfur was tested for MASS in the slag-cement matrix. Figure 3 illustrates the equilibrium conversion of elemental mercury into HgS through the addition of sulfur, as calculated by HSC 4.1.

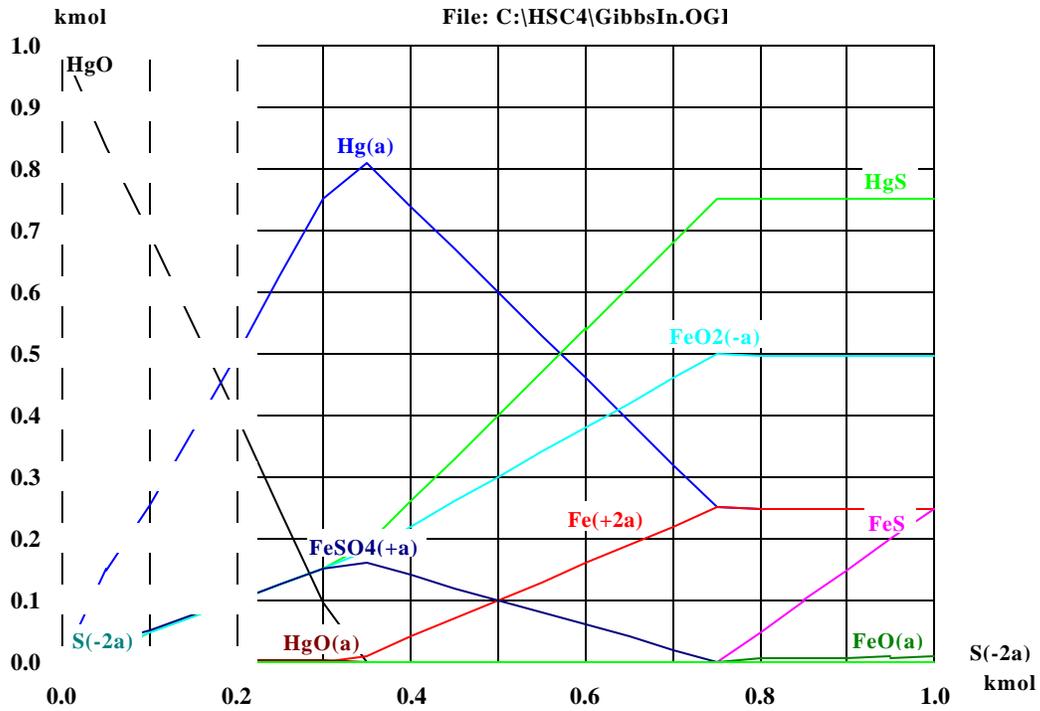


Figure 2. Projected equilibrium species calculated by HSC 4.1 for the addition of FeS to HgO in an aqueous environment.

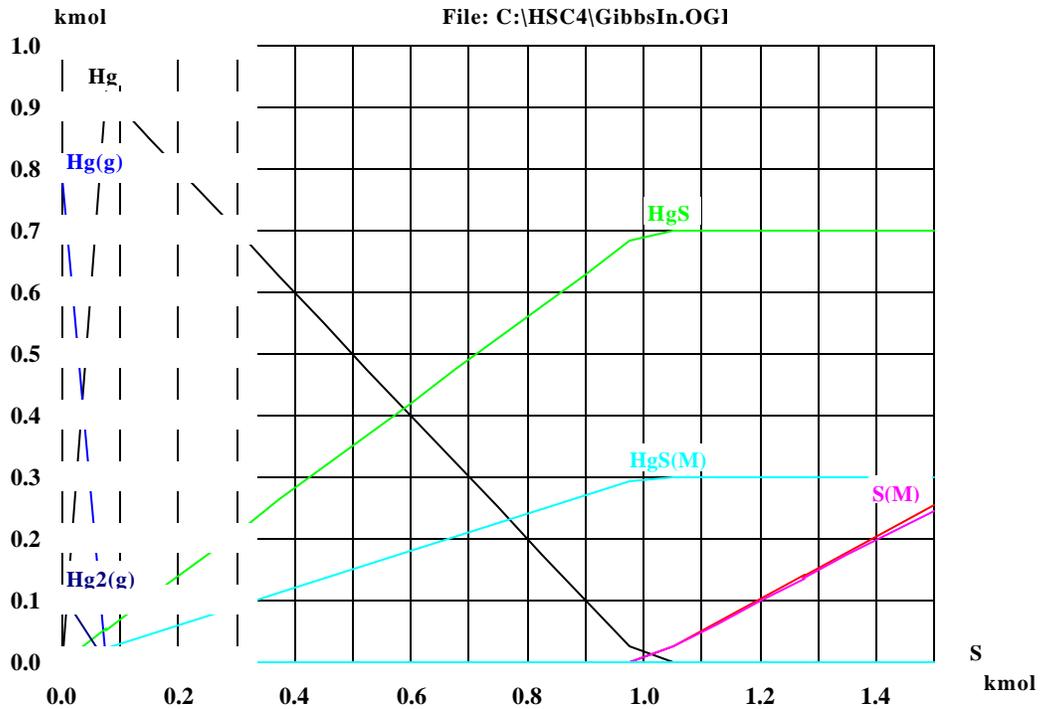


Figure 3. Equilibrium conversion of elemental mercury calculated by HSC 4.1 for the addition of sulfur.

II. WORK DESCRIPTION AND RESULTS

MASS treatment was tested on soil and surrogate sludge spiked with a mercury compound and/or elemental mercury at concentrations up to 10,000 mg/kg. In addition,

treatment of 100% mercury, pure elemental mercury or a simple mixture of elemental mercury and mercuric chloride, was tested. Various stabilizing agents were blended into the basic cementitious powders and then tested. Table I lists the Toxicity Characteristic Leaching Procedure (TCLP) extract concentrations of the treated and untreated surrogate wastes.

Table I. Testing the basic slag-cement matrix and different stabilizing agents for MASS

	Waste Loading (wt %)	TCLP Extract Hg Concentration (mg/L)
Spiked soil (10,000 mg/kg) — Elemental mercury		
Untreated	100.0	37
Slag-cement + sulfur	40.0	0.0014
Slag cement + copper	39.9	0.0113
Spiked soil (10,000 mg/kg) — Hg:HgCl₂ (50:50 molar)		
Untreated	100.0	34
Slag-cement	40.0	0.0157
Slag-cement + Na ₂ S	39.9	0.0027
Slag-cement + Na ₂ S + FeSO ₄	39.3	0.0130
Slag-cement + K ₃ Fe(CN) ₆	40.1	0.0032
Pure elemental Hg		
Untreated	100.0	43
Slag-cement + sulfur	28.0	17.74
Slag-cement + copper	13.2	0.052
Pure Hg:HgCl₂ (50:50 molar)		
Untreated	100.0	13,000
Slag-cement	40.6	124
Slag-cement + Na ₂ S (6 wt %)	35.8	76
Slag-cement + Na ₂ S (14 wt %)	36.0	19
Slag-cement + K ₃ Fe(CN) ₆	33.1	80

III. DISCUSSION

The TCLP results for metallic mercury in spiked soil were comparable to those for pure metallic mercury, 37 and 43 mg/L, respectively. The TCLP results for the mixture of pure mercury and mercuric chloride (50:50 molar)

was over two orders of magnitude higher (13,000 mg/L) than that for pure metallic mercury. The TCLP result (34 mg/L) for soil spiked with 10,000 mg/kg of mercury and mercuric chloride (50:50 molar) was comparable to that for the soil spiked with metallic mercury (37 mg/L).

MASS treatment of the soil spiked with metallic mercury was successful, with the TCLP extract concentration decreased by over four

orders of magnitude to a level well below the TCLP Universal Treatment Standards (UTS) limit of 0.025 mg/L. The addition of sulfur resulted in a TCLP extract concentration an order of magnitude lower than that for the addition of copper, 0.001 and 0.01 mg/L, respectively. The TCLP extract concentration obtained with the former additive was comparable to that for the soil grout blank.

On the other hand, the roles of these two agents were reversed for MASS treatment of pure metallic mercury. Sulfur reduced the TCLP extract concentration by a factor of 2.4, from 43 to 18 mg/L. By contrast, copper lowered the TCLP extract concentration of the MASS-treated pure metallic mercury by close to three orders of magnitude, from 43 to 0.05 mg/L, less than the TCLP RCRA hazardous limit (0.2 mg/L) but not less than the TCLP UTS limit (0.025 mg/L). The mercury loadings were 28.0 and 13.2 wt % for the added sulfur and added copper, respectively. It is likely that MASS treatment of pure metallic mercury can pass even the TCLP UTS limit with further development (for example, using lower mercury loading or smaller metal particle size). Thus, MASS treats metallic mercury contamination at concentrations well above those levels (>260 mg/kg) that are currently prohibited by the Resource Conservation and Recovery Act from treatment by S/S. This is especially important for mixed waste, where the elemental mercury recovered from retorting or incineration (the prescribed treatment for mercury concentrations >260 mg/kg) must then be amalgamated (the prescribed treatment for liquid mercury contaminated with radioactivity). Results for the spiked soil represent how effective MASS can be for actual waste contaminated with mercury. Results for the pure material are a measure of MASS stabilization of mercury. Both treatment agents were effective in treating the soil spiked with metallic mercury. However, it is not clear why the sulfur appears more effective for the spiked soil and the copper more effective for the pure metallic mercury, except for the obvious difference in loading for the pure elemental mercury.

For the soil spiked with the combination of metallic mercury and mercuric chloride, the slag-cement reduced the TCLP extract concentration by over three orders of magnitude, from 34 to 0.016 mg/L, below the TCLP UTS limit of 0.025 mg/L. The sodium sulfide-iron sulfate additive gave little assistance to the slag-cement, with a TCLP extract concentration of 0.013 mg/L.

Both the sodium sulfide and the cyanide reduced the TCLP extract concentration by about another order of magnitude below that of the slag-cement, from 0.016 to 0.003 mg/L. Thus, one can conclude that MASS treatment of mercury-contaminated wastes can be effective without special additives but that special additives do improve this efficiency.

The effectiveness of special additives is illustrated by comparing the results from treating a mixture of pure metallic mercury and mercuric chloride. The slag-cement alone reduced the TCLP extract concentration by over two orders of magnitude, from 13,000 to 124 mg/L. The cyanide reduced the TCLP extract concentration by another third, from 124 to 80 mg/L. Sodium sulfide (6 wt %) also reduced the TCLP extract concentration by about a third, from 124 to 76 mg/L. However, increasing this additive to 14 wt % reduced the TCLP extract concentration by a factor of 6.5, from 124 to 19 mg/L. None of the TCLP extract concentrations for the samples containing pure mercury-mercuric chloride were below the TCLP characteristic limit of 0.2 mg/L, much less the UTS limit of 0.025 mg/L. Thus, if recycle is not an option for pure mercuric chloride, then more development is required for land disposal: for example, lower loading or chemical conversion such as that achieved by means of dissolving and then precipitating.

MASS also treated surrogate tank sludges to generate solid waste forms that met TCLP UTS limits.⁸⁻¹⁰ In an attempt to minimize the volume increase of the treated sludge, MASS treatment met TCLP UTS limits with sludge loadings >90 wt %. Such high sludge loadings resulted in weak waste forms, more like sludge than cement. Figure 5 illustrates the effect of final slag content on the fraction of mercury extraction during TCLP testing for these simulated tank sludges.

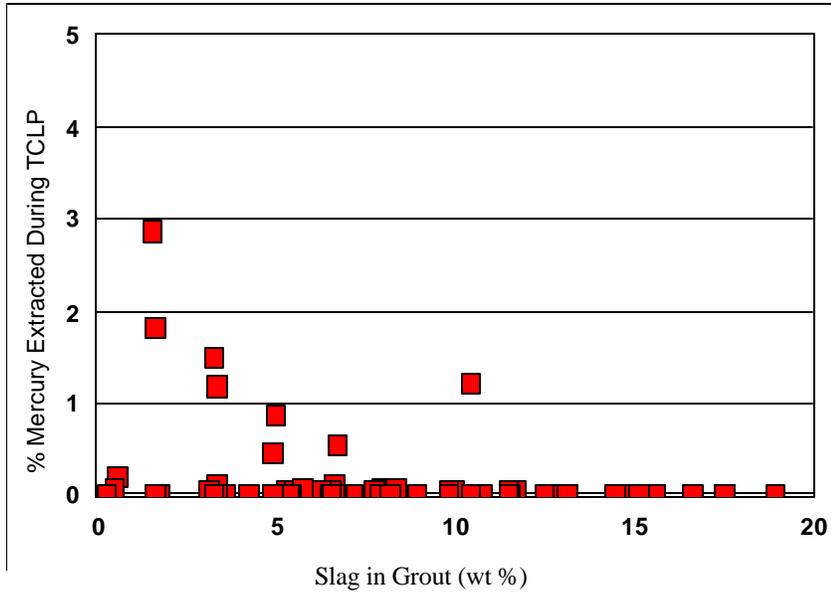


Figure 5. The percentage mercury extracted from treated surrogate sludges during TCLP as a function of slag content.

IV. CONCLUSIONS

MASS treats waste contaminated with mercury into a cementitious waste form in a single step, retaining the simplicity of traditional S/S and allowing in situ treatment of media contaminated with mercury. MASS reduces leaching of mercury into the environment several hundred fold compared with untreated waste, thereby reducing risk. MASS has proven successful in stabilizing mercury and mercury compounds to meet the UTS limit of 0.025 mg/L in the TCLP extract at concentrations in the waste well above the 260-mg/kg ceiling established by RCRA for stabilization. In addition to relatively pure mercury contaminated with radioactivity, the U.S. Department of Energy sites have many mixed waste streams and media contaminated with significant amounts of mercury that may be treated with this technique. MASS offers the following advantages:

- stabilizes both elemental mercury and soluble mercury compounds,
- minimizes the mercury vapor pressure inside the waste form,
- controls the oxygen potential inside the waste form to prevent oxidation of the amalgamating agents,

- solidifies the stabilized mercury, other RCRA metals, and radionuclides inside a cementitious waste form,
- stabilizes and solidifies by mixing the treatment agents with the waste in one step,
- utilizes readily available S/S and/or cement mixing and grouting equipment, and
- is amenable to in situ treatment of mercury and other contaminants.

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