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MERCURY STABILIZATION IN CHEMICALLY BONDED PHOSPHATE CERAMICS*

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DISCLAIMER

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Abstract

Mercury stabilization and solidification is a significant challenge for conventional stabilization technologies. This is because of the stringent regulatory limits on leaching of its stabilized products. In a conventional cement stabilization process, Hg is converted at high pH to its hydroxide, which is not a very insoluble compound; hence the preferred route for Hg sulfidation to convert it into insoluble cinnabar (HgS). Unfortunately, efficient formation of this compound is pH-dependent. At a high pH, one obtains a more soluble Hg sulfate, in a very low pH range, insufficient immobilization occurs because of the escape of hydrogen sulfide, while efficient formation of HgS occurs only in a moderately acidic region. Thus, the pH range of 4 to 8 is where stabilization with Chemically Bonded Phosphate Ceramics (CBPC) is carried out.

This paper will discuss our experience on bench-scale stabilization of various U.S. Department of Energy (DOE) waste streams containing Hg in the CBPC process. This process was developed to treat DOE's mixed waste streams. It is a room-temperature-setting process based on an acid-base reaction between magnesium oxide and monopotassium phosphate solution that forms a dense ceramic within hours. For Hg stabilization, addition of a small amount (<1 wt.%) of Na_2S or K_2S is sufficient in the binder composition.

Here the Toxicity Characteristic Leaching Procedure (TCLP) results on CBPC waste forms of surrogate waste streams representing secondary Hg containing wastes such as combustion residues and Delphi "DETOX^{SM}" residues are presented. The results show that although the current limit on leaching of Hg is 0.2 mg/L, the results from the CBPC waste forms are at least one order lower than this stringent limit. Encouraged by these results on surrogate wastes, we treated actual low-level Hg-containing mixed waste from our facility at Idaho. TCLP results on this waste are presented here. The efficient stabilization in all these cases is attributed to chemical immobilization as both a sulfide (cinnabar) and a phosphate, followed by its physical encapsulation in a dense matrix of the ceramic.

Using this process, Argonne-West has eliminated Hg-contaminated light bulbs from its inventory. These bulbs were slightly contaminated radioactively, and hence this was a typical mixed waste stream. This presentation will provide a brief review on this work as an example of disposal of Hg-contaminated actual waste.

Introduction

Technology development for nonthermal stabilization and solidification of low-level mixed wastes containing volatile contaminants has been a major effort in the EM-50 program of the U.S. Department of Energy (DOE). Among the hazardous contaminants that need to be immobilized, mercury (Hg) has a high priority for DOE mixed wastes. This is because many Hg-bearing DOE wastes are nonaqueous and partially stabilized sludges, adsorbed liquids, and contaminated soils. Hg from these wastes is not easily accessible to leaching agents or thermal desorption, but is leachable in excess of the prescribed limits. Therefore, a suitable technology is needed to stabilize Hg from these wastes. In our study, we have explored a room-temperature-setting, chemically bonded phosphate ceramic (CBPC) process to address this need.

CBPCs are formed by the reaction of MgO and KH_2PO_4 in solution [1-2]. Solid or liquid waste streams are added during mixing of the two. Once these components are thoroughly mixed, the slurry is allowed to set. Setting occurs in approximately 2 h and a ceramic waste form of high strength and low open porosity is formed. During the reaction, contaminants such as Pb, Cr, and Cd react with the acid solution to form their respective phosphate or hydrophosphate salts that are chemically insoluble in groundwater. They are further encapsulated physically in the dense ceramic matrix. We have demonstrated superior stabilization of several contaminants by using this method [2].

Chemical Immobilization of Hg

Because phosphate formation of contaminants is the key to efficient chemical immobilization of contaminants in the CBPC process, some preliminary investigations were done to determine speciation of Hg compounds in a phosphoric acid solution. Our preliminary investigations showed that the major precipitation product is $Hg_3(PO_4)_2$. Because the reaction in the CBPC is in an aqueous solution, it is likely that hydrophosphates such as $HgHPO_4$ may also form. One may notice from Table 1 that the solubility of these phosphates is very low [3] and hence Hg from the waste form will not easily leach out into groundwater. To test this, we formed the CBPC waste forms of ash and ferric oxide wastes and tested leaching of Hg by using the Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) [4]. These initial tests showed that the leaching levels had dropped from 40 and 138 mg/L for untreated ash and ferric oxide, respectively, to 7.7 and 51 mg/L for the treated wastes. The actual regulatory limits for nonwaste water retort are 0.2 mg/L and 0.025 mg/L, respectively. This implies that while CBPC treatment reduces Hg leaching significantly, it may not be sufficient for treatment of a wide variety of wastes, particularly those characteristic wastes that must be subjected to retorting. This means that an additional stabilization mechanism is needed to immobilize Hg.

Table 1. Solubilities of metal sulfide and mercury phosphate

Species	K_{sp}	Solubility (mol/L)
HgS	2.0×10^{-49}	4.5×10^{-25}
$Hg_3(PO_4)_2$	7.9×10^{-46}	1.4×10^{-8}
$HgHPO_4$	7.9×10^{-14}	2.8×10^{-7}

This additional stabilization is provided by treatment of Hg-containing wastes with either hydrogen sulfide or more convenient salts such soluble alkali sulfides, the most common ones being Na_2S and NaHS [5]. This treatment converts Hg compounds into Hg sulfide, which has the lowest solubility shown in Table 1. Although a number of such sulfide stabilizers are available, because the CBPC binder is a potassium-based material, we used K_2S for stabilization in our system. The expected reaction between H_2S and Hg compounds such as HgO is given by

$$HgO + H_2S = HgS + H_2O \qquad (1)$$

Using the Gibb's free energy values ΔG for HgO, H_2S, HgS, and H_2O as -58.5kJ/mole, -33.4 kJ/mole, -50.6 kJ/mole, and -237.1 kJ/mole, respectively, we obtain the net change in Gibb's free energy for this reaction as -195.7 kJ/mole and the reaction constant of $\approx 10^{34}$, which is extremely high and thus implies that this reaction will occur spontaneously.

Conner [3] notes that addition of excess sulfide in fact leaches Hg. Our experience also has been the same in the CBPC process. If excess H_2S is added, it will reduce the redox potential of the system [6] by the reduction reaction

$$H_2S + 4H_2O = SO_4^{--} + 10H^+ + 8e^- \qquad (2)$$

The electrons released in this reaction will now will reduce $Hg(OH)_2$ by the reaction

$$2Hg(OH)_2 + 4H^+ + 2e^- = Hg_2^{++} + 4H_2O \qquad (3)$$

This reduced form of Hg_2^{++} will react with SO_4^{--} to form Hg_2SO_4 by the reaction

$$Hg_2^{++} + SO_4^{--} = Hg_2SO_4 \qquad (4)$$

The product Hg_2SO_4 has a solubility product constant of 7.99×10^{-7}, which indicates that it is much more soluble than HgS and hence will not stabilize Hg. This implies that one should not exceed the dose of sulfide to initiate the reduction reaction that may reduce the Hg compounds.

Our experience has shown that 0.5 wt.% of K_2S in the binder powder gives excellent results in Hg stabilization. K_2S is mixed with MgO and KH_2PO_4 powders to form one binder powder and thus pretreatment of Hg can be avoided in the process. In the conventional cement stabilization process, addition of excess sulfide affects setting of cement. This has also been our experience in the CBPC process. When the very small amount of sulfide is blended into the CBPC binder, Hg stabilization is very efficient. This was demonstrated in several surrogate waste streams and on one actual waste stream, as described below.

Treatability study on surrogate waste streams

Table 2 lists the four surrogate waste streams that were part of this treatability study. They represent either actual waste streams at DOE facilities, or secondary waste streams that may be generated during destruction of organics. For example, the DOE complex has stored several ash waste streams that were generated by destruction of combustibles. The surrogate ash waste given in Table 2 represents these waste streams [7]. On the other hand, secondary waste streams will be generated during destruction of organics in certain DOE waste streams by the DETOX^{SM} wet oxidation process developed by Delphi Research [8]. These secondary waste streams contain a mixture of ferric oxide and ferric chloride, or ferric phosphate, as the major components. The second and third waste streams in the table represent these. The soil, i.e., the last waste stream given in Table 2, represents waste from Argonne's inventory destined for treatment according to Argonne's site treatment plan.

Table 2. Surrogate wastes and their formulation

Waste identification	Composition (wt.%)		Contaminants (wt.%)
DOE ash waste	Activated carbon	5	$HgCl_2$ added such that Hg level was 0.5
	Vermiculite	20	
	Class F fly ash	40	
	Coal bottom ash	33	
Delphi DETOX			
Oxide waste	Fe_2O_3	93.6	In both waste streams, $HgCl_2$, Ce_2O_3, and $Pb(NO_3)_2$ were 0.5 each
Chloride waste	$FeCl_2$	4.9	
Phosphate waste	$FePO_4$	98.5	
Soil	Topsoil from Argonne grounds		$HgCl_2$ added such that Hg level was 0.1; original waste had 2.7 ppm of Hg

To prepare the surrogates, components were mixed thoroughly for 24 h on a vibratory shaker. The resulting mixture was then added to the binder mixture. To prepare the reaction slurry, the powder mixtures were added to the stoichiometric or slightly higher amount of water and mixed thoroughly in a Hobart tabletop mixer for 30 min. The resulting slurry was a slightly viscous liquid that could be poured easily. Once poured in a mold, it set in ≈2 h into a hard and dense ceramic waste form. Using cylindrical polytethylene containers, we made samples of ≈100 g. The samples were stored for the next 3 weeks for good curing. Each sample was then crushed into a powder with a particle size of ≈0.5 mm or less and subjected to the TCLP test. We also performed the TCLP tests on the surrogate wastes. The results of these tests are given in Table 3.

Table 3. TCLP results on wastes and waste forms

Waste, EPA Limits	Result on waste (mg/L)	Result on waste form (mg/L)
Delphi DETOX		
Iron oxide	138	<0.00002
Iron phosphate	189	0.01
DOE ash waste	40	0.00085
Soil	2.27	0.00015
EPA limits	0.2	0.2 for noncharacteristic wastes and 0.025 for characteristic wastes

The TCLP results on the wastes themselves show that the leaching levels were well above the regulatory requirement limits and thus failed the test. Leaching levels of Hg from the waste forms, on the other hand, were well below the limits and below the UTS limit by at least one order of magnitude. This implies that one can use this process to treat even characteristic wastes for which the UTS limits are applicable. Considering that the original levels of Hg in the surrogate waste were very high and much above 260 ppm (the limit for waste destined for stabilization), immobilization of Hg in the phosphate ceramic waste forms, coupled with sulfide immobilization, has been very superior.

Long-Term Leaching Behavior

The TCLP test only qualifies the waste form for land disposal. However, to ensure that the waste form retains the contaminants in varying chemical environments of the landfill (indicated by its varying pH), it is necessary to demonstrate in a long-term leaching test that the contaminants are retained in the waste form. This was done by subjecting the samples to the American Nuclear Society ANS 16.1 test [9]. This test allows study of leaching behavior in an aqueous environment. Neutral water is used as the leachant, and monolithic samples of the waste forms are immersed in it for 90 days. Samples of the water are collected at prescribed periods and tested for chemical constituents and contaminant levels in the leachate water are determined for those periods. The data are then used to calculate the diffusion constant of the contaminant in the waste form. It is then expressed as the leaching index, which is a negative natural logarithm of the ratio of the diffusion constant.

We used this test to assess the waste forms for retention of the contaminants over 90 days. Samples of ≈20 g were used. The study was done for all four waste streams with neutral water. For ash waste, leaching levels were consistently below the detection limit of 0.025 μg of the measuring instrument, and thus we could not calculate the leaching index. For the rest of the waste forms, the data are given in Table 4.

Table 4. Leaching indices obtained in 90-day immersion tests

	Delphi DETOX		
Waste form	Iron oxide	Iron phosphate	Soil
Leaching index	16.34	16.33	16.42

The leaching indices in Table 4 are much higher than the 6 found with cement systems [7]. This implies the diffusion of Hg is by 10 orders lower than that in cement systems. This extremely superior retention is due to the very superior chemical immobilization of Hg and its microencapsulation in the dense phosphate ceramic matrix.

Because the ash waste form showed the best leaching resistance, we studied its leaching performance in both acidic and alkaline environments. The pH of the acidic solution was 3.5, which was obtained by adding acetic acid to the leachate water. The alkaline solution was that of NaOH solution with a pH of 11. This study at both low and high pH simulates extreme conditions in the landfill or storage area. In most cases, leaching levels were below the detection limits and hence leach indices could not be calculated. For this reason, we have presented the actual amount leached out during each measurement period.

The data in Table 5 show that, just as in the neutral aqueous environment, the leaching levels are undetectable in the alkaline environment. They are also extremely low and very close to the detection limit even in the acidic environment for the first 72 h of the measurement. After that, the leaching levels again fall below the detection limit. This suggests that the waste form is very stable and can sustain a range of chemical environments from acidic to alkaline.

Table 5. Leaching levels (μg) of Hg from ash waste forms in acidic and alkaline water

	Time (h)					
Level	2	7	24	48	72	96-2136
In acidic water	0.032	0.025	0.045	0.04	0.045	<0.025
In alkaline water	< 0.025 for all time intervals					

Tests on Actual Waste

The CBPC technology was deployed to treat and dispose Hg-contaminated crushed light bulbs, a low-level mixed waste, at Argonne's facility in Idaho (ANL-West) [10].

Visual inspection revealed that 90 vol.% of this waste was <60 mm in size; thus, it could not be classified as debris waste. Typical sizes of the crushed glass ranged from 2-3 cm long by 1-2 cm wide, down to fine particulates. Chemical analysis indicated Hg concentration at ≈2.5 ppm. In addition, emissions from isotopes of ^{60}Co, ^{137}Cs, and ^{154}Eu were 1.1 x 10^{-5} mCi/g, 4 x 10^{-4} mCi/g), and 4 x 10^{-6} mCi/g, respectively.

CBPC waste forms were fabricated at the 5-gal. size. Typical waste loadings were 35-40 wt.%. A small amount of K_2S was added to the binder mixture. After mixing for ≈30-35 min, the resulting slurry was allowed to set in the drum. Dense and hard ceramic waste forms were produced in this process.

The TCLP test results (Table 6) showed excellent stabilization of Hg in the waste forms. Hg levels of 0.05 ppb in the leachate were well below the EPA's Universal Treatment Standard (UTS) of 25 ppb, while for Pb, the level was < 0.1 ppm as compared to the UTS limit of 0.37 ppm. The principal advantage of this technology is that immobilization of contaminants results from both chemical stabilization and subsequent microencapsulation of the reaction products. In all, ≈22 kg of the waste was treated, removed from the inventory, and sent to the Radioactive Waste Management Complex (RWMC) at INEEL for storage.

Discussion

The data presented here demonstrate superior performance of the CBPC waste forms. Despite this success, robustness of this technology to treat Hg-containing wastes is yet to be established. This may be done by understanding the kinetics of stabilization of Hg in the phosphate systems, and by then testing Hg stabilization with a wide variety of Hg-containing wastes. This is particularly necessary because sulfidation is efficient only with a stoichiometric amount of added sulfides and with suitable pH control of the wastes. These parameters have not been established yet for the CBPC process. Such a study, however, is underway at this time.

Table 6. TCLP Results on CBPC Waste Forms

Waste Loading	Contaminant Concentration in Waste Form	TCLP on Waste	TCLP on Waste Form
40 wt.% Hg waste	Hg: 1000 ppb	24.4 ppb	0.05 ppb

However, our completed study establishes that Hg stabilization is not just a result of sulfidation, but is also due to chemical immobilzation of Hg as phosphates and then very efficient physical encapsulation in the dense CBPC matrix.

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