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MERCURY STABILIZATION IN CHEMICALLY BONDED PHOSPHATE CERAMICS*

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DISCLAIMER

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Abstract

We have investigated mercury stabilization in chemically bonded phosphate ceramic (CBPC) using four surrogate waste streams that represent U.S. Department of Energy (DOE) ash, soil, and two secondary waste streams resulting from the destruction of DOE's high-organic wastes by the DETOX^{SM} Wet Oxidation Process. Hg content in the waste streams was 0.1 to 0.5 wt.% (added as soluble salts). Sulfidation of Hg and its concurrent stabilization in the CBPC matrix yielded highly nonleachable waste forms. The Toxicity Characteristic Leaching Procedure showed that leaching levels were well below the U.S. Environmental Protection Agency's regulatory limits. The American Nuclear Society's ANS 16.1 immersion test also gave very high leaching indices, indicating excellent retention of the contaminants. In particular, leaching levels of Hg in the ash waste form were below the measurement detection limit in neutral and alkaline water, negligibly low but measurable in the first 72 h of leaching in acid water, and below the detection limit after that. These studies indicate that the waste forms are stable in a wide range of chemical environments during storage.

Introduction

Technology development for nonthermal stabilization and solidification of low-level mixed wastes containing volatile contaminants has been a major effort in the U.S. Department of Energy (DOE) EM-50 program. Among the hazardous contaminants that must be immobilized, mercury (Hg) in DOE mixed wastes has a high priority. 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 phosphate bonded ceramic (CBPC) process to address this need.

CBPCs are formed by 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. The contaminants 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. Using this method, we have demonstrated the superior stabilization of several contaminants [2].

Chemical Immobilization of Hg

Our preliminary investigations on the conversion of Hg compounds in the presence of phosphoric acid solution showed that the major product is $Hg_3(PO_4)_2$. Because the reaction in the CBPC is in an aqueous environment,

it is likely that hydrophosphates such as $HgHPO_4$ may also form. Table 1 indicates that the solubility of these phosphates is very low [3] and hence Hg from the waste form will not leach out easily into the groundwater. To test this, we fabricated CBPC waste forms of ash and ferric oxide wastes and tested the leaching of Hg by using the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure, or TCLP [4]. These initial tests showed that leaching levels had declined from 40 and 138 mg/L in untreated ash and ferric oxide, respectively, to 7.7 and 51 mg/L in the treated wastes. The actual regulatory limits for nonwastewater retort and other are 0.2 and 0.025 mg/L, respectively. This implies that while the CBPC treatment significantly reduces Hg leaching, it may not be sufficient for treating a wide variety of wastes, particularly those characteristic wastes that require retorting. This means that an additional stabilization mechanism is needed to immobilize Hg.

Table 1. Solubilities of mercuric sulfide and mercury phosphates [3]

Species	Solubility Product Constant (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 treating Hg-containing wastes with either hydrogen sulfide or one of the soluble alkali sulfides, the most common 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 CBPC

binder is a potassium-based material, we used K_2S for stabilization in our system.

K_2S powder formed an integral part of our process and was mixed with MgO and KH_2PO_4 powders to form one binder powder. It was added in a near-stoichiometric amount so that all of the Hg would be converted to HgS. Thus, no pretreatment step was needed. It has been reported that in the conventional cement stabilization process, addition of excess amount of sulfide affects the setting of cement [6]. This is partly because cement stabilization occurs at the high pH of ≈11. Therefore, acidic sulfides will affect stabilization at least locally in the cement matrix. On the other hand, because the CBPC process is based on an acid-base reaction, it is not sensitive to alteration of pH caused by addition of sulfides. The pH of the reaction slurry increases from its initial value of 4 to a more neutral 8 when the slurry sets, and chemical immobilization occurs in acidic to slightly above the neutral pH range. This more neutral environment, therefore, is very favorable for long-term storage of the chemically immobilized sulfide of Hg.

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 in storage 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 in Table 2 represents these waste streams [7]. On the other hand, secondary waste streams will be generated during destruction of

Table 2. Surrogate wastes and their formulations

Waste Identification	Composition (wt.%)		Contaminants (wt.%)
DOE ash waste	Activated carbon	5	$HgCl_2$ added to bring Hg level to 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.
	$FeCl_2$	4.9	
Phosphate waste			
	$FePO_4$	98.5	
Soil	Topsoil from Argonne grounds		$HgCl_2$ added to bring Hg level to 0.1. Original waste had 2.7 ppm of Hg.

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 mixtures. The soil composition, i.e., the last waste stream given in Table 2, represents waste from Argonne's inventory that is destined for treatment according to Argonne's site treatment plan.

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 poured easily. Once poured in a mold, it set in ≈2 h into a hard and dense ceramic waste form. Using cylindrical polyethylene containers, we made samples of ≈100 g.

The samples were stored for 3 weeks to ensure good curing. Each sample was then crushed into a powder with particle sizes of ≈0.5 mm or less and then subjected to the TCLP test. We also performed 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	Waste (mg/L)	Waste forms (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 (noncharacteristic wastes) 0.025 (characteristic wastes)

The TCLP results on the wastes themselves show that the leaching levels are well above the regulatory requirement limits and fail the test. The leaching levels of Hg from the waste forms, on the other hand, are well below the limits and at least one order of magnitude below the Universal Treatment Standard of the Environmental Protection Agency. This implies that the process can be used to treat even characteristic wastes for which the UTS limits are applicable. Considering that the original Hg levels in the surrogate waste were very high and much above 260 ppm that is 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 will form retain the contaminants within the various chemical environments of a landfill (indicated by different pH levels), it is necessary to demonstrate that the contaminants are retained in the waste form in a long-term leaching test. This was done by subjecting the samples to the American Nuclear Society's ANS 16.1 test [9], which allows us to study the leaching behavior in an aqueous environment. Neutral water is used as the leachant, and monolithic samples of the waste forms are immersed in the water for 90 days. Samples of the water are collected and tested for chemical constituents at prescribed periods, and contaminant levels in the leachate water are determined for those periods. The resulting data are then used to calculate the diffusion constant of the contaminant in the waste form which is then expressed as the leaching index that is the 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, the leaching levels were consistently below the measuring instrument's detection limit of 0.025 μg, 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

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 value of 6 found in cement systems [7]. This implies that Hg diffusion is lower than that in cement systems by 10 orders of magnitude. 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 leach resistance, we studied its leaching performance in both acidic and alkaline environments. The pH of the acidic solution was 3.5 and was obtained by adding acetic acid to the leachate water. The alkaline solution was that of an NaOH solution with a pH of 11. This study at low and high pH simulates extreme conditions in landfills or storage areas. In most cases, leaching levels were below the detection limits and hence the leaching indices could not be calculated. For this reason, we have presented in Table 5 the actual amount leached out during each measurement period.

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

	Time (h)					
Hg Leached	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 at all time intervals ---					

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 fall below the detection limit. This suggests that the waste form is very stable and can withstand a range of chemical environments from acidic to alkaline.

Discussion

Treatment of Hg-bearing mixed wastes is a difficult problem. This is because Hg in these wastes is not easily accessible to leaching agents or thermal desorption, and its successful removal has not been demonstrated. Therefore, stabilization of Hg becomes an important issue for DOE wastes. Coupled with this, many Hg-containing wastes are characteristic wastes for which the treatment standard requires that the TCLP limit be as low as 0.025 mg/L; this demands a superior stabilization technology. The data presented here indicate that CBPC technology may fulfill this need.

Because CBPC and Portland cement are both nonthermal technologies and use similar process steps, a comparison of the two is inevitable. The CBPC technology is based on an acid-base reaction, in which acidic to alkaline wastes can be incorporated. On the other hand, cement stabilization occurs only in an alkaline environment and the pH of the cement is ≈11 at the onset of setting. This limits its applications in waste management. Hg stabilization as HgS, although superior, may affect setting of the cement at least locally [6], but due to the acid-base nature of the CBPC binders, adding a component such as HgS does not affect the setting of

CBPC binders. In addition, waste loading in cement is comparatively low. In the CBPC matrix waste loading, can range from 50 wt.% for soil to 70 wt.% for ash, while a similar range for cement is 25 to 40 wt.%. The cost of the CBPC powders is slightly higher than that of cement, but the higher waste loading and shorter curing time offset these costs.

Acknowledgments

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