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Project Summary

An Evaluation of Factors Affecting the Stabilization/ Solidification of Heavy Metal Sludge

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Solidification/stabilization (S/S) of hazardous waste involves mixing the waste with a binder material to enhance the physical properties of the waste and to immobilize contaminants that may be detrimental to the environment. Many hazardous wastes contain materials that are known to inhibit the setting and strength development properties of cement and pozzolan binding agents commonly used in S/S processes.

The study summarizes the results of an evaluation of the effects of 10 interfering substances (oil, grease, lead, copper, zinc, sodium hydroxide, sodium sulfate, phenol, trichloroethylene, and hexachlorobenzene) on the physical and contaminant mobility properties of a solidified/stabilized heavy metal sludge. Three binder materials (Portland cement, CEM; lime/fly ash, LFA; and cement/fly ash, CFA) were used to solidify/stabilize a specially prepared sludge containing substantial concentrations of four metals (cadmium, chromium, nickel, and mercury). The effects of these interfering materials were evaluated using five physical tests (unconfined compressive strength, cone index, bulk density, wet/dry cycling, and permeability). Contaminant leaching properties were evaluated using the U.S. Environmental Protection Agency's (EPA) extraction procedure (EP) test. Microchemical/ micromorphological analyses were also performed on the samples.

Test results indicated that copper, lead, zinc, grease, oil, and phenol have a significant detrimental effect on the physical properties of the solidified/stabilized sludge. In contrast, the effects of hexachlorobenzene, trichloroethylene, and sodium sulfate on the physical properties were much less significant. The EP leaching test indicated that contaminant leaching, except for mercury, was highly dependent on the extraction solution's final pH. No definitive conclusions could be drawn from the microchemical/micromorphological examinations.

This research confirms the need for waste-binder specific studies before selecting a chemical S/S process for the treatment of hazardous waste.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

S/S is a process that involves mixing a hazardous waste with a binder material to enhance the physical and chemical properties of the waste and to chemically bind any free liquid. Several binder systems are currently available and widely used for the S/S of hazardous wastes.

Most common S/S techniques are built around either Portland cement or some type of pozzolan as the basic S/S reagent. CEM is widely available, relatively economical, and well known to the general public as producing a very durable product. Pozzolans are siliceous materials that, when added to a source of free lime, will go through a cementation process much like CEM but at a much lower rate. Fly ash and blast-furnace slags are common pozzolans that are generally considered as waste materials themselves.

Wastes most amenable to S/S treatment are water-based sludges. Most wastes are a complex and variable mixture of many precipitated and dissolved materials, some of which are expected to interfere with the S/S process and cause undesirable consequences. Effects that might be expected are a breakdown of the solidified matrix, flash or retarded set, or spalling and disintegration. Such reactions could cause contaminant loss to the environment.

Very few quantitative data are currently available concerning the effects of potential interfering compounds on particular S/S processes. This study was undertaken to help fill this data void. An earlier report from this study reviewed the literature and discussed theories and details of the effects of known interfering materials with cement, pozzolanic, and asphaltic S/S systems and products.[1]

General Approach to the Investigation

In Phase I of the study, an initial literature survey was conducted to identify any existing data describing the effects on materials that interfere with cementation or pozzolanic setting reactions.

In Phase II, a synthetic sludge containing four heavy metal contaminants was prepared with the use of lime precipitation. The lime sludge was then dewatered to produce the sludge used in this study.

In Phase III, after the metal sludge was produced, binding agents were added to solidify/stabilize the waste and immobilize the contaminants. Before setting, the sludge/binder mixture was divided into four portions. Selected interfering chemicals were mixed with three of the sludge/binder portions at three concentration levels. Molded specimens were prepared for the three interference/sludge/binder mixtures and for the sludge/binder mixture (control).

In Phase IV, an accepted testing regime was employed to evaluate the physical and contaminant release properties of the solidified/stabilized specimens.

Sludge Preparation

Laboratory jar tests were performed on the synthetic metal waste solution to determine the settling properties of the sludge and the calcium hydroxide dosage for maximum sludge formation. The synthetic metal solution was prepared by dissolving 23.1 g/L of $Cr(NO_3)_3 \cdot 9H_2O$, 14.9 g/L of $N_i(NO_3)_2 \cdot 6H_2O$, 1.6g/L of $Cd(NO_3)_2 \cdot 4H_2O$, and 0.02g/L of $Hg(NO_3)_2 \cdot H_2O$ in tap water.

A lime dosage of 20 g/L produced a sludge with optimal settling characteristics and a supernatant with the lowest turbidity. This lime dosage was twice the calculated stoichiometric amount required for metal precipitation. The sludge produced using this lime dosage contained approximately 9% solids and had a density of 1.08 g/mL. The supernatant had a final pH of 11.5.

The maximum solid contents of the filter cake that could be achieved using vacuum filtration was 30% to 35%. Based on these preliminary test results and the fact that filtrate could be used to dilute the sludge, a 25% solid sludge was selected for use in this study. By using a constant sludge solids content, the water-to-binder ratio for the solidified/stabilized product could be tightly controlled. Analysis of this sludge indicated that it contained 18.1-mg/g of Cd, 81.3 mg/g of Cr, 1.39 mg/g Hg, and 81.1 mg/g Ni on a dry weight basis.

Sludge Treatment and Interference Addition

Binder-to-sludge ratios were formulated to produce a solidified/stabilized product that had a 28-day unconfined compressive strength (UCS) of at least 100 psi (690 kPa). For the three binder systems (Portland type I cement [CEM]; Portland type I cement and Class F fly ash [CFA]; and lime and Class C fly ash [LFA]), various sludge-to-binder ratios were prepared. Based on these results, the binder ratios shown in Table 1 were selected.

Table 1. Binder-to-Sludge Ratios Selected for Evaluation

Binder	*Binder/sludge ratio*	*Dilution factor**
CEM	*0.3:1 Cement:sludge*	*5.2*
LFA	*0.5:1 Fly ash:sludge*	*7.2*
CFA	*0.2:1 Cement:sludge 0.5:1 fly ash:sludge*	*6.8*

* *Weight of final mixture/weight of dry sludge.*

To limit variability, one interference chemical was evaluated for each batch of dewatered sludge prepared. Thus, for each batch of sludge, specimens were prepared for one binding agent in combination with one chemical at ratios (weight/weight) of 0, 0.02, 0.05, and 0.08. These specimens were subjected to physical and chemical evaluations after curing.

Chemical reagents were used to introduce the desired interference into the sludge/binder system. The desired interference, the interference reagent, and the weight correction factors are listed in Table 2. All specimens were cured in the molds at 23°C and 98% relative humidity until needed for testing.

Physical Testing

Five physical tests were performed on all solidified/stabilized samples: unconfined compressive strength (UCS), cone index (CI), bulk density (BD), weight/dry cycling durability (W/D), and permeability (PERM).

Unconfined Compressive Strength

The UCS test was used to determine the strength development characteristics of the various solidified/stabilized wastes. The UCS of the S/S wastes was determined using ASTM method C 109-86, Compressive Strength of Hydraulic Cement Mortars (using 2-in. or 50-mm cube specimens). The only deviation from this method was specimen vibration.

Cone Index

The CI test was used to evaluate the strength development characteristics of the solidified/stabilized materials during their initial strength development period. The CI measures the resistance of a material to the penetration of a 30-degree right circular cone. The method is specified in U.S. Army's "Materials Testing" Technical Manual 5-530. The CI is measured using a penetrometer.

Bulk Density

BD measurements were performed to evaluate density changes resulting from the added interfering chemicals. Although a standard method was not followed, the method used in this study was tailored after ASTM method D-558-82.

Wet/Dry Testing

Eleven cycles of W/D testing were performed to measure durability to cyclic weathering conditions and the effect of the interference chemicals on sample durability. A modified ASTM method 599-82

[1] Jones, L.W. 1989 Interference Mechanisms in Waste Solidification/Sabilization Processes. EPA/600/2-89/067 (NTIS No. PB90-156 209/AS). USEPA, Risk Reduction Engineering Laboratory.

Table 2. Interference Reagents Utilized

Desired Interference	Interference Reagent	Weight Correction Factor
Oil	30 weight motor oil	1.00
Grease	Axle grease	1.00
Phenol	Phenol	1.00
Sulfate	Sodium sulfate [Na_2SO_4]	1.48
Strong base	Sodium hydroxide [NaOH]	2.35
Degreaser	Trichloroethylene [TCE]	1.00
Pesticide	Hexachlorobenzene [HCB]	1.00
Lead	Lead nitrate [$Pb(NO_3)_2$]	1.60
Copper	Copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$]	3.80
Zinc	Zinc nitrate [$Zn(NO_3)_2 \cdot H_2O$]	4.55

was conducted on specimens after they had cured for 28 days.

Permeability

The 2.8-in. specimens and a triaxial cylinder were used in all permeability measurements. Specimens were saturated using a back-pressure saturation technique following the method outlined in the U.S. Army's Corp of Engineers Manual 1110-2-1906. Triplicate permeability determinations were done on a single individual specimen that had cured a minimum of 28 days.

Chemical Testing

Extraction Procedure (EP) Toxicity Test

EPA method 1310 was followed, with the exception that all materials leached were ground to pass a 9.5-mm sieve.

Each waste/binder/interference mixture at each interference concentration was extracted in duplicate after the solidified/stabilized materials had cured for 28 days. The EP extracts were analyzed for Cadmium, Chromium, Mercury, Nickel, and the interference contaminant of interest.

Microchemical/ Micromorphological Characterization

The Louisiana State University (LSU) Hazardous Waste Research Center investigated the microchemical/micromorpho-logical characteristics of the solidified/stabilized materials to characterize the effects of the interference chemicals on microscopic properties of the samples. LSU employed three analytical techniques: scanning electron microscopy (SEM), SEM in conjunction with energy dispersive X-ray analysis (EDXRA), and X-ray diffraction (XRD).

Results

The levels of sludge metals contained in the raw waste were compared with EP results of the raw waste and specimens treated by each of the three binder systems without interferant addition in Table 3. The levels of metals found in the EP leachates were excellent, considering the high concentrations of metals contained in the sludge. All binders reduced the metal concentrations in the EP leachates by 3 to 5 orders of magnitude even though all the S/S products were ground before the EP. All three binder systems exhibited good containment characteristics for the metals in this sludge. Mercury levels in the EP leachates from the S/S products, however, are about the same as those from the raw sludge. All three binders were essentially ineffective at increasing the containment of the Hg in the sludge.

The results of this study conclusively show that common components of hazardous wastes interfere with the containment and strength characteristics of solidified/stabilized wastes. All measured parameters were affected by one or more of the interferant materials. Table 4 summarizes all the measured effects of the interferants on the binder systems used in the study. Each interferant was rated as to whether it produced a strong, moderate, or slight positive or negative effect on each of the test results on each binder system. PERM was not included in the summary table because of the high variability in the test results. BD was also omitted from the table because only slight differences were observed for this parameter, and these were not correlated with specimen physical or contaminant containment properties.

UCS, CI, and W/D

- The metals, grease and oil, and phenol were generally deleterious to all binder systems. The effects of these interferants generally increased with increasing concentration.
- Sulfate, hexachlorobenzene, and the chloroethylene had little measurable effect at any interference concentration.
- Sodium hydroxide had a mixed effect as it tended to increase early strength (CI) at the 2% and 5% interference addition, but decreased the early

Table 3. Comparison of the Solidified/Stabilized Extracts with Raw Waste Extracts

Parameter (units)	Cd	Cr	Hg	Ni
Sludge concentrations (mg/kg dry wt)	18,100	81,300	1,390	81,100
EP of raw sludge (mg/l leachate)	57.9	242	0.84	149
Median EP of CEM S/S controls (mg/l)	0.0021	0.010	0.95	0.083
Median EP of CFA S/S controls (mg/l)	0.028	0.078	0.29	0.068
Median EP of LFA S/S controls (mg/l)	0.0009	0.007	0.69	0.009

Table 4. Summary of the Effects of Interferants on the Solidified/Stabilized Samples

Binder	Interferant	UCS	CI	Wet/dry cycles	Final EP pH	EP Leachate Concentrations: Cd	Cr	Hg	Ni
CEM	Copper	+++*	--	---	--	---	---	+	BDL
CFA	Copper	---	ND	---	---	---	---	---	---
LFA	Copper	---	-	---	--	--	--	0	-
CEM	Lead	0	0	-	0	--	-	0	0
CFA	Lead	---	--	---	--	---	0	0	--
LFA	Lead	---	---	---	---	BDL	--	+	BDL
CEM	Zinc	--	---	---	-	-	---	+	--
CFA	Zinc	---	---	---	---	---	+	-	---
LFA	Zinc	---	---	---	---	BDL	--	+	BDL
CEM	Sulfate	-	-	0	0	-	---	0	BDL
CFA	Sulfate	0	0	0	--	---	--	+	0
LFA	Sulfate	+	++	+	--	BDL	---	+	BDL
CEM	NaOH	+	--	---	+	0	---	0	+
CFA	NaOH	-	++	0	++	--	---	+	0
LFA	NaOH	0	+++	-	0	-	--	0	+
CEM	Grease	--	---	---	0	BDL	0	0	0
CFA	Grease	--	--	0	+	++	+	+	+
LFA	Grease	--	-	--	0	--	0	0	0
CEM	Oil	--	--	---	0	-	0	+	0
CFA	Oil	-	-	---	0	-	-	+++	0
LFA	Oil	-	-	---	0	0	-	+++	0
CEM	HCB	0	0	-	0	++	+	0	0
CFA	HCB	0	0	0	0	+	+++	0	+
LFA	HCB	0	+	0	0	-	-	-	-
CEM	TCE	-	-	0	0	0	0	+	0
CFA	TCE	-	-	0	0	-	-	+	0
LFA	TCE	+	0	0	0	-	0	0	+
CEM	Phenol	-	---	---	-	-	0	+	0
CFA	Phenol	---	---	0	+	+	++	0	0
LFA	Phenol	---	---	---	0	+++	0	0	

* Symbol	UCS and CI (number times the control)	Wet/Dry (cycles intact vs. control)	Final EP pH	EP Leachate Conc. (number times the control level)
+++	<2	+5	>+2	< 0.1
++	1.5 to 2.0	+2 to 5	+1 to 2	0.25 to 0.1
+	1.2 to 1.5	+1 to 2	+0.3 to 1	0.5 to 0.25
0	0.8 to 1.2	-1 to +1	-0.3 to 0.3	2 to 0.5
-	0.8 to 0.66	-1 to -2	-0.3 to -1	2 to 4
--	0.66 to 0.5	-2 to -5	-1 to -2	4 to 10
---	<0.5	-5	>-2	> 10

ND = not detected; BDL = below detection limit

strength at the 8% level. Sodium hydroxide also had less effect on long-term strength (UCS) and durability.

- The strength and durability of S/S products are strongly related, as might be expected.
- A highly significant correlation was found between the UCS and CI measurements.

Permeability

Because of their inherent variability, permeability measurements did not appear meaningful for evaluating solidified/stabilized solid samples. This information, however, is thought to be of basic importance for evaluating the leaching potential of S/S waste forms.

Bulk Density

Significant volume changes with increasing interference concentrations were observed for the phenol, sulfate, and copper interferences. Although these volume changes were significant, generally these changes were less than 10%.

EPA Extraction Procedure

- The changes in final EP leachate pH correlate with the EP leaching losses of cadmium and chromium, and to some extent with those of nickel. These metals were leached from the solidified/stabilized waste materials with an indirect relationship to the final EP leachate pH.
- The final pH values of the EP leachates were lowered appreciably by the metal nitrate and sulfate interferants. These interferants greatly increased the leaching rates of cadmium and chromium, and to a lesser extent that of nickel.
- Addition of sodium hydroxide raised the final pH as would be expected and caused an increased loss of chromium, and to some extent cadmium.
- The organic interferants had little effect upon the final EP pH. Generally the organic interferants did not appreciably affect the leaching of the metals, although hexachlorobenzene and phenol additions may have lowered the leaching rates of cadmium and chromium slightly.
- The mercury concentrations in the EP leachates were independent not only of the added interferants, but also of S/S treatment itself. Mercury was leached from the S/S products at about the same levels as from the raw sludge. Only the addition of oil as an interferant appeared to increase the concentration of mercury in the EP leachates.

Microchemical/ Micromorphological Examinations

No definitive conclusion can be drawn from the results of the microchemical/ micromorphological examinations. More work needs to be done to perfect these methods as a diagnostic tool for hazardous waste evaluation.

Recommendations

- Since the effect of waste constituents on the integrity of the final product cannot be predicted from current knowledge, tests of strength, durability, and leachability should be required of all S/S-treated wastes before disposal.
- CI measurements are recommended as a rapid and inexpensive method to estimate early strength of solidified/ stabilized waste. These measurements correlate well to 28-day unconfined compressive strengths. Longer term tests have not been evaluated.
- The variability associated with the permeability measurements needs to be addressed. Alternative measurements that address attributes such as connected pore volume or gas permeation may be of greater value for highly impermeable materials.
- Additional studies addressing long-term durability of solidified/stabilized materials must be conducted. These studies should include at least a small portion of the samples evaluated by this study. This will provide a basis for correlation of the short-term testing with long-term S/S treatment success.

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The complete report, entitled "An Evaluation of Factors Affecting the Stabiliztion/ Solidification of Heavy Metal Sludge," (Order No. ADA 264-128; Cost: $27.00, subject to change) will be available only from:

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