



Project Summary

The Morphology and Microchemistry of Solidified/Stabilized Hazardous Waste Systems

F. K. Cartledge, H. C. Eaton, M. E. Tittlebaum

A study was carried out to gather data that can be interpreted in terms of the mechanisms operating during cementitious solidification/stabilization of hazardous waste streams containing water-soluble organics. Most of the work was carried out with phenols and ethylene glycol as the model wastes and Type I Portland cement as the fixing agent. Solidified products containing from 2% to 50% by weight of organics (measured relative to cement) were studied at various cure time up to 1 year. The products were studied at various time intervals using extractions with solvents of varying polarity, optical microscopy, scanning electron microscopy and energy dispersive elemental analysis, transmission electron microscopy, x-ray powder diffraction, and several physical tests (setting times and unconfined compressive strength).

The report describes and interprets effects of the organics on the developing cement matrix and the nature of the interactions involved. The organics were not effectively immobilized toward water leaching. Depending on the chemical nature of the organic, the distribution of the model waste in the cement matrix was either homogeneous at the micron level or quite heterogeneous. Effects on the matrix were very concentration dependent and were much more dramatic with ethylene glycol than with the phenols. These effects ranged from microscopic changes in morphologies and compositions of

cement phases to macroscopic properties such as compressive strength. Although there was evidence of chemical reaction between the phenols and the fixing agents (specifically, salt formation), the reaction did not result in chemical fixation of the organic.

At low concentrations, the organics did not greatly alter the hydration chemistry of the cement system. The probable consequence of this would be little interference in immobilization of inorganics in cases in which mixed inorganic/organic waste streams are encountered. Specific experiments designed to test this conclusion, however, have not yet been carried out.

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

The report summarized here describes the first of three phases of work aimed at thoroughly characterizing wastes solidified in a cement matrix, or whatever. Phase I, the fundamental research aspect of the work is an effort to understand solidification mechanisms with the use of cement and several water-soluble organics. Phase II is an extension of Phase I and involves cooperation with the Waterways Experiment Station of the U.S. Army Corps of Engineers (WES) in a

project to characterize interferences by various inorganic and organic materials in solidification of metal sludges with the use of cement and fly ash fixing agents. Phase III of the work involves the use of x-ray diffraction (XRD) and scanning electron microscopy (SEM) to characterize vendor-produced samples of wastes solidified by processes, which are usually proprietary. Phase III is a part of the U.S. EPA/Environment Canada joint project to evaluate test methods for solidified products. Phases II and III are not completed and will be described in detail in a future report.

Solidification/stabilization is a common technology used to immobilize wastes before landfilling, roadbed construction, etc. The technology has been most commonly studied as a potential technique to immobilize toxic metal ions or radioactive waste. Complete detoxification of metals by chemical, biological, or other means is impossible short of elemental transformation; hence, methods that dilute and/or isolate the metals are necessary as part of waste management schemes. Although many vendors of solidification/stabilization technology have presented leaching data claiming the efficacy of various immobilization techniques, claims concerning the nature of chemical interactions between waste metal ions and fixing agents have remained unsubstantiated.

The aim of the Phase I research was to gain information about the mechanisms by which solidification/stabilization schemes operate and to define the nature of the interferences associated with the presence of various classes of compounds, both inorganic and organic. Conceptually, there are two broad classes of mechanisms; namely, physical entrapment and chemical interaction. Physical tests, spectroscopy, and microscopy all were used to gain information about the interactions of various compounds with typical solidification/stabilization matrices.

The two principal constituents of most commercial fixing agents are cementitious materials (Portland cement, fly ash, etc.) and soluble silicates. A limitation often cited is that the processes are incompatible with organics, but details about the types of organics that interfere or the concentrations at which interference is detrimental are not available. The same is true with many inorganic materials. A potential concern is that interferences, even in small amounts, can alter the process sufficiently to substantially decrease the ability of the fixing agents to immobilize metal ions. Indeed,

it is well known that admixtures can alter the setting characteristics of Portland cement. It is not clear whether, and at what concentrations, various materials commonly present in waste streams interfere with the complex setting reactions and result in a significantly altered cement matrix. The question is of obvious interest with respect to solidification/stabilization technology, since complex mixed inorganic/organic waste streams are commonly encountered.

Research Methods

The methods used in Phase I were adaptations of procedures used to characterize cement (or other inorganic) matrices, as well as common techniques to characterize solidified waste form. Samples were prepared using Type I Portland cement in a 0.4 water:cement ratio. The organic compounds were ethylene glycol (EG), *p*-bromophenol (pBP), and *p*-chlorophenol (pCP). The required amount of organic compound (0.2 g, 0.4 g, 1.0 g, or 2.0 g) was weighed out into a screw-cap vial, and 10.0 mL of Portland cement was added followed by 4.0 mL of deionized water. The mixture was stirred with a glass stirring rod, for 1 minute by hand. The vials were allowed to stand in the dark at room temperature for periods of from 12 hours to 1 year before being tested.

The test methods and the information they were expected to afford are briefly summarized here:

Extraction with Solvents of Varying Polarity

The samples containing various concentrations of organics were ground to a standard size and extracted with three solvents: dichloromethane (DCM), dimethyl sulfoxide (DMSO), and deionized water. The amount of organic compound recovered in the extractions was determined as a function of solvent polarity and time of cure for the sample. The data were used to reach qualitative conclusions concerning the environment of the organic compound in the cement structure, and trends in extractability were compared with qualitative differences in sample morphological composition observed by microscopy.

Microscopy (Optical and SEM) and Energy-Dispersive X-Ray Analysis (EDXA)

Optical and SEM observations of surfaces of solidified samples were made to characterize changes occurring as a

result of having added wastes to cement. Because numerous micrographs have been published for cements alone with various additives, a large amount of data are available for comparisons. EDXA can provide an elemental profile of a solid surface, with certain limitations. These methods in combination with the techniques described below can determine whether the waste has influenced the formation of the mineral phases characteristic of the matrix.

Transmission Electron Microscopy (TEM) and Selected Area Diffraction (SAD)

TEM has been used to study cement materials and minerals for the past several years, and several studies of cement have been reported. TEM, however, has not been applied to studies of solid hazardous chemical wastes. The major advantage of TEM is the high spatial resolution, which can exceed 0.2 nm. In addition, the SAD pattern can provide information about crystal structure and the orientation of crystalline phases. Some of these instrumental characteristics are important for waste research.

X-Ray Powder Diffraction (XRPD)

Powder diffraction analysis allows crystalline mineral constituents of the matrix to be identified by their characteristic set of diffraction lines. Many XRD studies of cements have been carried out. Although limitations associated with the complex nature of the formed solid matrix, some mineral constituents are easily identifiable. The presence or absence of specific mineral phases can be a function of admixture in the cement formulation; that is, presumably also be the case with wastes are the admixtures.

Physical Testing

Selected physical characteristics of solidified samples have been studied to define strength and practical workability of waste/cement mixes. Specific compressive strengths and setting times (initial and final) of cements containing organics were studied. The compressive strength test reflects the amount of applied loading the solidified wastes withstand before failure in a landfill. Setting time tests indicate the time needed for the solidified waste to become workable. In addition, these tests were conducted because they have been used by the cement industry as standard indicators of mechanical performance.

The Use of Polar Organics

Most of the Phase I studies involved relatively polar organic molecules, although some preliminary work with nonpolar organics is also reported. Because of their relatively high water solubility, polar organics are the ones most likely to be present in substantial concentrations in mixed aqueous waste streams that also contain metal ions. Thus, polar organics are good candidates as solidification/stabilization interferences. Glycols and phenols are typical of such species and are also major articles of commerce and, hence, constituents of waste streams. Apart from the fact that EG, pCP, and pBP are typical of real wastes, the reason for choosing halogenated phenols is that the presence of the heavy atoms enables elemental analysis by EDXA to locate the organic within the complex hydrated cement matrix.

These polyhydroxy compounds are, in fact, among the classes of organics that alter the setting characteristics of Portland cement. The polyhydroxy organic EG was chosen for several reasons. There is evidence in the literature that EG has profound effects on already set cement and the mineral constituents thereof. When hydrated cement of tricalcium silicate (C/S) is treated with EG, etching occurs, but it is unclear whether mainly calcium silicate hydrate gel (CSH) or calcium hydroxide (CH) is dissolved. A further consideration is that EG is completely miscible with water. Hence, cement pastes can be prepared with any concentration of EDG in water, and in all cases, a homogeneous liquid phase is being mixed with the unhydrated cement. The mixing problems are also minimized with the phenols, which are substantially water soluble. When the very water-in-soluble organic 1-decanol was solidified, as the right ratio of organic to cement varied from 50:1 to 1:1, the product of solidification varied from a solid, which was outwardly indistinguishable from hardened cement, to a two-phase system with hardened material and supernatant liquid (shown by gas chromatograph analysis to be pure 1-decanol). With the EG samples, there was great variation in the physical appearance of the mixes as functions of both concentration and time of cure.

Results and Discussion

The systems studied in Phase I represent the most thoroughly characterized

combinations of organics and cement pastes. In particular, the combinations included those with relatively high concentrations of organics—those typical of situations in which organics would constitute a large fraction of a waste mixture being solidified. Two questions concerning the Phase I study of organics are particularly relevant to solidification practice:

1. Do cementitious matrices have the ability to immobilize the organics themselves?
2. How do organics alter the cement matrix and thus affect immobilization of inorganic constituents?

The Phase I study has effectively demonstrated that cement alone is ineffective in immobilizing water-soluble organics such as EG or phenols. The second question is not completely answered to date. Although many effects of organics on the cement matrix at various concentrations have been documented. The leaching studies needed to determine whether the organics constitute interferences in inorganic immobilization remain to be carried out or interpreted. Phases II and III will report on some leaching studies at a later date.

The following paragraphs summarize the information obtained thus far.

EG/Cement

1. For ratios of up to 1:5 EG:cement, the same basic reaction chemistry went on during cement hydration in the presence or absence of EG. SEM/EDX analysis was able to identify phases apparently identical to those in hydrated cement alone (although not necessarily in the same proportions as in cement alone). At concentrations of 1:5 and greater, the samples did not effectively set even at 28 days or longer.
2. EG slowed the rate of hydration of cement, even in the 1:50 mixtures. At 1:5 ratios, final set was not reached.
3. There was a small percentage of strongly bound (although mostly reversibly bound) EG. Solvents in which EG is very soluble (DCM and DMSO) and that penetrate the cement matrix very effectively under our extraction conditions did not always give high recoveries of EG.
4. Despite the statements in the preceding paragraph, EG was not effectively immobilized toward water leaching even at low loadings of EG on cement. High percentage recover-

ies (up to 100% in a single extraction after grinding) were observed at all loadings of EG on cement at all times of cure.

5. The principal effect of EG on the microstructure of cement involved the CSH gel phase. There were noticeable effects on the morphology of this phase, particularly the presence of aggregates of small grains. EG also appeared to absorb to the surfaces of $\text{Ca}(\text{OH})_2$ crystals. Fine crystals with d-spacings uncharacteristic of common cement phases could be observed, but not identified by TEM.
6. Overall crystallinity of the matrix was diminished with increasing EG concentration, particularly above about 10% EG by weight.
7. Below 1:10 EG:cement, 28 day compressive strengths were comparable with those of cement pastes alone, but above 1:10 there were significant decreases in strength.
8. Increasing EG concentration increased porosity of the matrix, as judged qualitatively by SEM.

pCP/Cement

1. Unconfined compressive strength of pCP/cement was lower than for the control at 7 days but was approximately equal at 28 days.
2. Times for initial and final set were approximately doubled. pCP slowed the hydration of cement more than did pBP but less than did EG.
3. In 1:10 pCP:cement samples percent recovery in water extraction decreased with time of cure from 93% (12 hours) to 60% (90 days). There was no effective immobilization at any concentration or time of cure.
4. SEM showed significant morphological differences of pCP/cement when compared with cement pastes: more porous at 12 and 24 hours but less porous at 7 and 28 days.
5. EDX showed homogeneous distribution of Cl at the 10 μ level. pCP was not found in the CH phase, and it was not found in a separate phase as was pBP.
6. XRD showed new peaks, probably the Ca salt of pCP.
7. XRD showed significantly decreased crystallinity.
8. Despite the observations above, pCP allowed the basic reaction chemistry of setting cement to proceed, as shown by the presence of the normal cement mineral phases.

pBP/Cement

1. Unconfined compressive strength of pBP/cement was lower than was the control at 7 days but approximately equal at 28 days.
2. Time for initial set increased approximately 20%; time for final set increased approximately 75%.
3. In 1:10 pBP:cement samples, percent recovery in water extraction varied between 45% and 55% over the period from 12 hours to 90 days, but dropped to a low of 9% at 1 year. Again, effective immobilization was not achieved at any concentration or any time of cure.
4. Electron Probe Micro Analysis showed inhomogeneous distribution of Br at the 10 μ level. There were distinct Br-rich phases, presumably the Ca salt.
5. XRD showed new peaks, probably the Ca salt of pBP.
6. XRD showed significantly decreased crystallinity.
7. The presence of pBP allowed the basic reaction chemistry of setting cement to proceed.

Conclusions

Clearly neither the phenols used in this study nor ethylene glycol was effectively immobilized by cement alone at any concentration studied. We assume that this will also be the case with other relatively water-soluble organics. The only evidence of reaction between the organics and the fixing medium was salt formation. Indeed, when salt formation occurred, as in the case of the phenols, the organic remained relatively water soluble and easily extractable from the solidified matrix. There appeared to be several distinguishable environments for the organics in the cement matrix:

1. a separate microscopically distinguishable phase, as with the Ca salt of pBP; as such, it was easily extractable.

2. an environment from which the organic was rather easily extracted by water but not by less polar solvents; probably involved hydrogen bonding by the organic hydroxy groups in interlayer spaces of CSH gel.
3. an environment in which the organic was quite loosely bound and easily extracted by any solvent in which it was moderately soluble; this environment may also have involved the CSH phase.

The idea that there is a definite number of binding sites in the cement matrix at which the organic may be effectively immobilized was not borne out by our work. Even at the lowest concentrations of organics in the cement matrix, water extracted the organics efficiently.

The cement matrix was affected in dramatic ways by the presence of organics. Presumably the ability of the matrix to contain other wastes, such as metal ions, will also be affected by the changes induced by the presence of organics. The matrix changes depended on the nature and the concentration of the organic. The changes in easily observable or measurable properties of the matrix were greatest with EG, less with pCP, and least with pBP. At or below a 1:10 ratio of organic to cement, the effects of all three organics on the easily measurable properties of the matrix were rather minor. All gave homogeneous matrices that looked like set cement; set times were affected to a significant degree by EG but not much by pCP and pBP; compressive strengths at 28 days were comparable to those of cement pastes without additives. Nevertheless, while SEM, TEM, and XRD indicated that some cement hydration reactions were taking place in the same way that they do in the absence of the organics, the situation was much more complex. New phases were formed; the usual phases appeared to undergo solid solution formation giving shifted XRD peaks; new morphologies appeared with increasing frequency and increasing con-

centration of organics. Although changes can be documented, the effect of such changes on some of the measurable properties, particularly compressive strength, were minor. The most important point would be whether changes affected the immobilizing ability of the matrix toward a variety of wastes. Some information of the latter kind should be available from the WES project; results of our participation in that project will be reported as Phase II of the project.

Nevertheless, additional work needs to be done to bridge the gap between the work done here and field application of solidification technology. Cementitious solidification/stabilization is most commonly used to immobilize metal ions. We are now investigating the effectiveness of immobilization, as measured by Toxicity Characteristic Leaching Procedure (TCLP), as various metal containing wastes are solidified, increasing waste-to-cement ratios gradually until failure occurs. At the same time, increasing amounts of organic in the wastes are being added. In addition to monitoring metal and organic concentration in TCLP leachates, the matrix changes are being monitored using techniques developed in this study. We can thus have a thorough characterization of the matrix in cases where immobilization is effective and can watch for changes in the matrix that occur as the system approaches failure. We can thereby identify what changes are associated with decreasing (or increasing) effectiveness of immobilization.

The full report was submitted in fulfillment of Contract No. CR 812318-01 by Louisiana State University under sponsorship of the U.S. Environmental Protection Agency.

F. K. Cartledge, H. C. Eaton, and M. E. Tittlebaum are with Louisiana State University, Baton Rouge, LA 70803.

Charles I. Mashni is the EPA Project Officer (see below).

The complete report, entitled "The Morphology and Microchemistry of Solidified/Stabilized Hazardous Waste Systems," (Order No. PB 90-134 156/AS; Cost: \$23.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use \$300

EPA/600/S2-89/056

000085956
JON GRAND
USEPA REGION V
230 S DEARBORN ST
CHICAGO IL 60604

130