Solidification/stabilization of hazardous waste: Evidence of physical encapsulation

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Solidification/Stabilization of Hazardous Waste: Evidence of Physical Encapsulation

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■ A synthetic electroplating sludge was solidified/stabilized in ordinary portland cement. The microstructure and microchemistry were studied by scanning and transmission electron microscopy, optical microscopy, energy-dispersive X-ray microanalysis, and X-ray diffractometry. The sludge contained 86.6 mg/g Ni, 84.8 mg/g Cr, 18.8 mg/g Cd, and 0.137 mg/g Hg. The water to cement ratio was 1.43, and the cement to sludge (dry) ratio was 1.2. An ordinary portland cement sample with a similar water to cement ratio, but without sludge, was also prepared for comparison. The sludge consisted of submicrometer-sized particles of complex heavy metal salts, calcium hydroxide, and calcium carbonate. Ellipsoidal particles of sludge, hundreds of micrometers long, were found in the cement matrix of solidified/stabilized material. Large concentrations of waste elements were found in the sludge particles, and low levels were also present in the matrix. The solidified/stabilized waste was a mechanical mixture of sludge and binder.

Introduction

Solidification/stabilization (S/S) is an economical process for the disposal of many types of hazardous wastes (1, 2). The method involves mixing liquid or semisolid wastes with binders to produce a solid which is structurally sound and relatively impermeable. Binders often consist of Type I portland cement (ordinary portland cement, OPC) or OPC plus fly ash, kiln dust, other pozzolanic and industrial byproducts. Sometimes polymers, by themselves or in various combinations, are used (3).

The mechanisms of S/S are very incompletely understood (1, 4). The process usually involves addition of a heavy metal waste to a cementitious binder, with or without pretreatment with lime. At the resulting high pH, heavy metals are expected to precipitate as their respective insoluble hydroxides since many heavy metals reach their lowest solubility at ca. pH 10 (5). The hydroxides are subsequently immobilized in the dense matrix of binder, where ionic transport is decreased as the porosity and permeability are reduced (6). Leaching studies by Côté (7) however indicate that the leaching from S/S binders cannot be explained on the basis of the solubility characteristics of simple hydroxide species of the heavy metals involved. Observed leachate concentrations from solidified metal salts are either greater or smaller than that expected for the pure hydroxide and vary with the nature of the metal and with pH.

Most studies of S/S in OPC have concentrated on the mechanical properties (such as unconfined compressive strength) and leaching behavior of the treated products (2, 7, 8). Very few detailed microstructural and microchemical studies of OPC with complex wastes exist, and the waste itself has been investigated even less. The present research examines the nature of a synthetic electroplating waste (EPA classification F006, 40 CFR 261.31) and its S/S mechanisms by investigating the microscopic morphologies and microchemistries of the S/S products.

Experimental Methods

The sample preparation procedure has been discussed in detail by Cullinane et al. (9). The heavy metals were precipitated as their respective insoluble hydroxides by the addition of lime to a solution containing the nitrates. The precipitate was concentrated to ca. 25% solids, yielding heavy metal concentrations of 86.6 mg/g Ni, 84.8 mg/g Cr, 18.8 mg/g Cd, and 0.137 mg/g Hg. OPC was added to the sludge to attain a final mixture with a cement to water ratio 1.43 and a cement to sludge (dry) ratio of 1.2. A sample of portland cement with the same water to cement
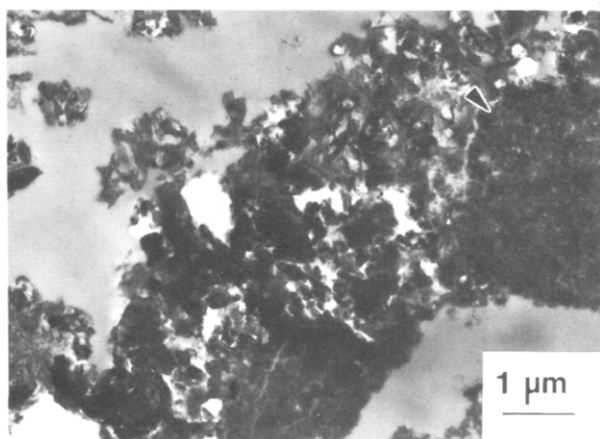
Figure 1. TEM photomicrograph of a sludge particle.

ratio but without waste was also prepared for comparison.

Sludge, OPC, and 10 samples of sludge solidified by OPC (OPC/sludge) were studied by scanning and transmission electron microscopy (SEM and TEM), energy-dispersive X-ray microanalysis (EDX), X-ray diffractometry (XRD), and optical microscopy (OM) using methods previously discussed (10, 11). The age of the samples ranged from 6 months to 1 year. For TEM, millimeter-sized particles were first impregnated with L. R. White resin in BEEM capsules and then sectioned to ca. 100-nm thickness with a microtome. The thin sections were mounted on copper grids and observed in a JOEL 100-CX transmission electron microscope. Scanning electron microscopy and energy-dispersive X-ray analysis were performed with an ISI 60A scanning electron microscope equipped with an EDAX 9100 energy dispersive X-ray spectrometer. Separate samples were prepared for SEM and EDX. The SEM samples were coated with gold, and the EDX samples with carbon. Optical microscopy was performed on standard petrographic thin sections prepared from samples impregnated with L. R. White resin. The use of Al_2O_3 and SiC as abrasives for thin-section polishing can cause some ambiguity when EDX data obtained from thin sections are interpreted, as Al and Si values are often unusually high. The magnitude of the effect on studies of S/S mechanisms has been discussed by Skipper et al. (11).

X-ray diffractograms were obtained from samples ground with a mortar and pestle and passed through a 100-mesh (ASTM) sieve; however, some samples were too moist for sieving. A copper tube in a Scintag PAD-V automated X-ray diffractometer was excited to 45 keV and operated at 35 mA. The slit widths before and after the sample were 2° and 4°, and 0.5° and 0.3°, respectively. The samples were scanned from 3 to 70° 2θ with 0.02° step-width and counting time of 3 s, or a minimum of 3000 counts. The sample holder was spun on its vertical axis to minimize the effect of preferred orientation, texture, and grain size. Synthetic corundum (<5 μm) was used in several samples as an internal standard for accurate measurement of d-spacings.

Results

In the SEM, at magnifications of tens to ten thousand times, untreated sludge appears dense and structureless. At magnifications of tens of thousands in the TEM, sludge is observed to be aggregates of small, submicrometer-sized particles, as shown by the arrow in Figure 1. The polycrystalline nature of these aggregates is evident from selected area electron diffraction (SAED). However, the individual phases could not be identified because of the complex electron diffraction pattern. Larger single crys-
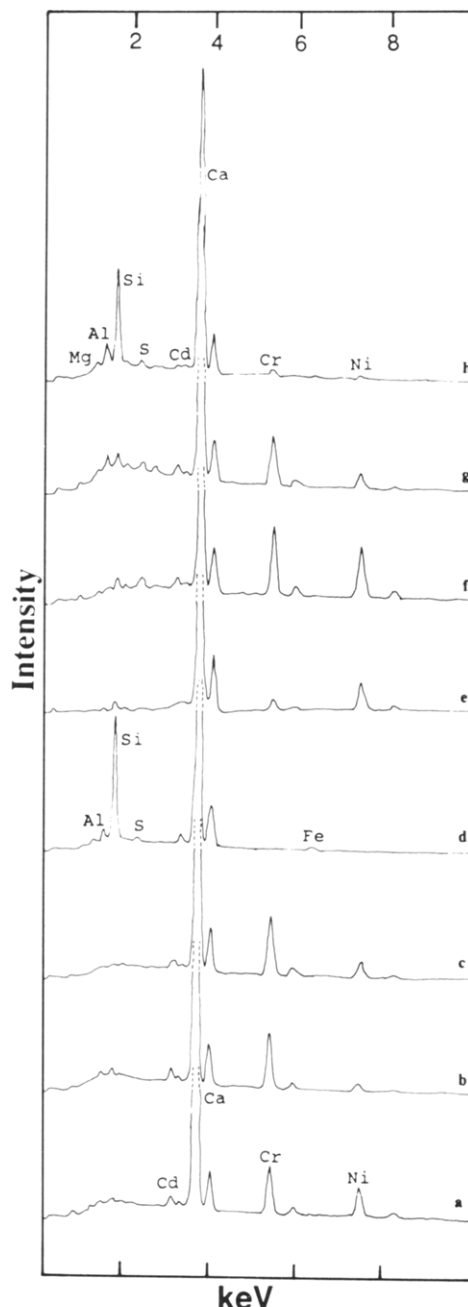
Figure 2. EDX spectra of (a–c) sludge, (d) OPC, (e) ellipsoidal particle in a freeze-fractured sludge-containing sample, (f, g) irregular cellular particle in thin sections of OPC/sludge sample, and (h) matrix (a few tenths of a millimeter away from one of the above particles).

tals, some tens of micrometers across, are also found, e.g., center of Figure 1. The aggregates contain few of the larger crystals.

Particle compositions analyzed by EDX (on an SEM) are shown in Figure 2a–c. The analyses show that the metal content in the sludge is ca. 80% Ca and 20% (Cr + Ni) by weight. Cd peaks are obvious, although Cd is a minor constituent, both in terms of the amount of Cd originally used for the sludge and the EDX spectral intensities. Considerable spatial variability in sludge composition is seen, as in Figure 2a–c, where variations in Ni and Cd concentrations are most obvious.

Figure 3 shows X-ray diffractograms of sludge, OPC, and OPC/sludge mixtures. Abbreviations used for the phases identified are given in Table I. In the X-ray diffractogram of sludge, shown in Figure 3a, the most intense peak is at 10.93° 2θ (0.8087 nm). A less intense peak (10.21° 2θ,
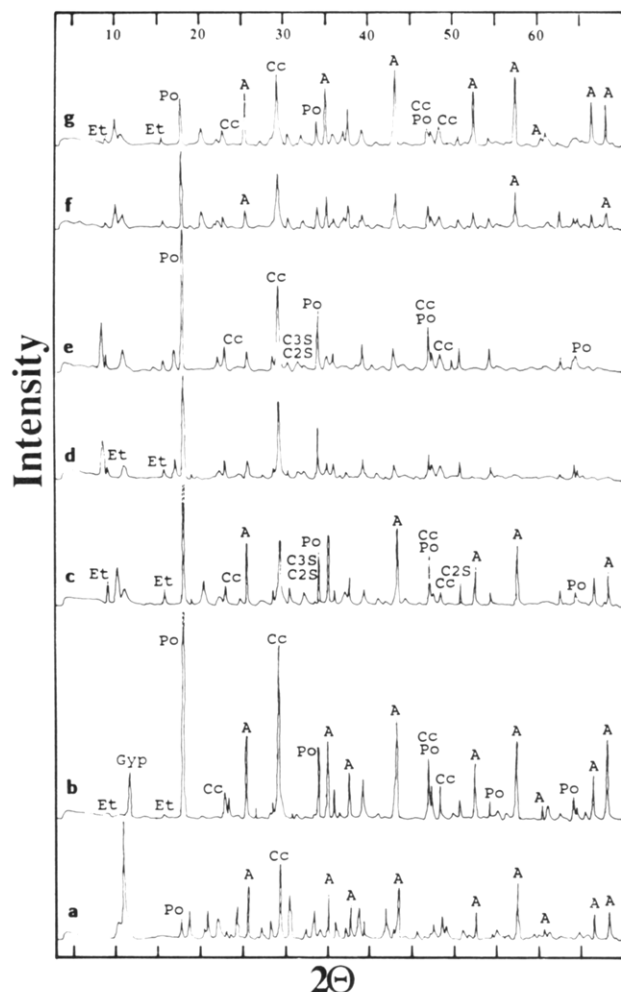
Figure 3. XRD patterns of (a) sludge, (b) OPC, and (c–g) sludge/OPC samples. Abbreviations for phases identified in XRD patterns are given in Table I.

Table I. Abbreviations Used in Phase Identification in XRD

A	alumina	CAH	calcium aluminum hydrate
Ettr	ettringite	Cc	calcium carbonate
C2S	dicalcium silicate	C3S	tricalcium silicate
Gyp	gypsum	Port	calcium hydroxide

0.8567 nm) is also present as a shoulder on the low-angle side of the 10.93° 2θ peak. Two phases could be identified unambiguously from the diffractogram: calcium hydroxide and calcium carbonate. An extensive computer search failed to match with certainty the remaining peaks with any well-characterized phases in the powder diffraction files (12), including hydroxides of the heavy metals. Among the possible matches, only $Ni_3O_2(OH)_4$ gives any close matches, but missing peaks and intensity differences preclude making positive identification. The inability to match simple hydroxides suggests that the heavy metals are most likely present as impure complex phases.

SEM of the OPC/sludge samples show considerable variation. A few of these samples contain abundant ellipsoidal particles, an example of which is shown by the arrow in Figure 4. The particles are usually separated from the surrounding matrix by a thin, void rim. Such structures are absent in OPC.

At low magnifications, under the optical microscope, the OPC/sludge samples are very fine-grained. Large particles, several hundreds of micrometers along the longest dimension, are present; some being translucent, and others
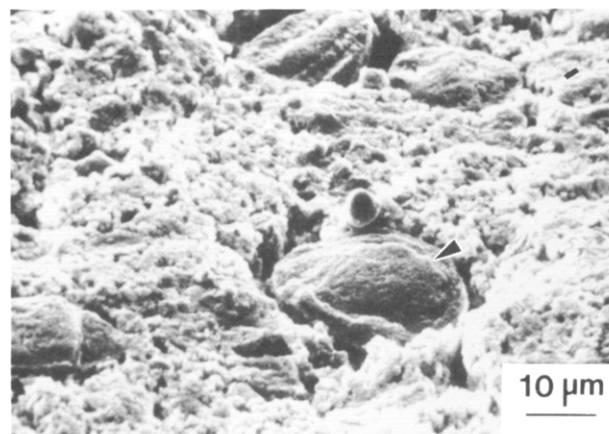

Figure 4. Discrete particles, several tens of micrometers across, in an OPC binder. The particles are of calcium silicate and sludge.
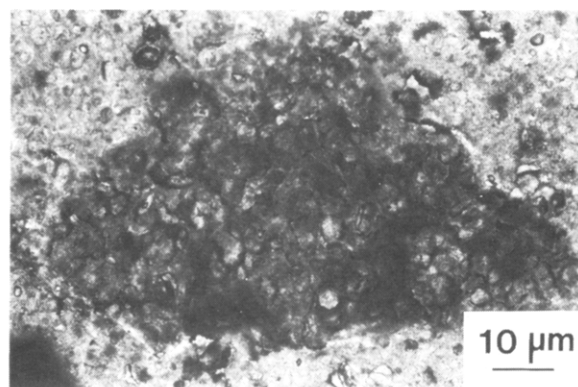

Figure 5. A translucent particle with an irregular cellular structure and bluish color, distinctly different from the surrounding matrix. The particle in the center is ca. 70 μm long.

transparent. The particles are blue in color and distinct from the surrounding matrix. Examples are shown in Figure 5. At higher magnifications, the transparent particles have an irregular cellular structure. They are distinguishable from the individual crystals of calcium silicates by a well-defined crystal outline and the optical properties of the latter.

A representative EDX analysis of OPC is shown in Figure 2d. The amount of Ca is high, and the Ca/Si ratio is typical of OPC. Minor amounts of Mg, Al, S, K, and Fe are also present. EDX of the treated sludge samples are shown in tracings e–h in Figure 2. An analysis of an ellipsoidal particle (Figure 2e), such as seen in Figure 4, indicates that its composition is similar to the composition of sludge. The large irregularly shaped particles seen in Figure 5 have also been analyzed. They are composed of Ca, Cr, and Ni, but exhibited considerable variation in Ni and Cr within a single particle (Figure 2f and g). Figure 2h shows an analysis from the matrix of the sample, several tenths of a millimeter from these large particles, where the same elements are observed but with the waste elements being present at much lower concentrations, while Al, Si, and S from the OPC matrix are prominent peaks.

The hydration products identified from the X-ray diffractograms shown in Figure 3b–f of the OPC/sludge samples are calcium hydroxide, ettringite, and varieties of calcium aluminum hydrates, all typical of phases found in OPC (Figure 3g). Unhydrated di- and tricalcium silicate (C_2S and C_3S) peaks are present in all samples but variable in intensity. Their intensities are higher compared to the OPC control sample with the same water-to-cement ratio (w/c), where the peaks were barely distinguishable from the background. On the basis of the remaining peaks, the

samples could be broadly divided into two mutually exclusive groups: the first group had strong peaks around 8.60° 2θ (d = 1.03 nm) and 17.16° 2θ (d = 0.518 nm) (Figure 3c–e), and the second group had strong peaks at 10.2° 2θ (d = 0.806 nm) and 11.1° 2θ (d = 0.795 nm) (Figure 3f and g). All of these XRD peaks are present in the sludge, although it was not apparent that the sludge itself consisted of two separate types.

Discussion

The efficacy of S/S for permanent treatment of hazardous wastes depends on the way the waste is present in the binder. There are two extreme possibilities: physical entrapment, when the chemical species remain unchanged and the waste is protected from percolating groundwater by a coating of the binder, or chemical entrapment, when the wastes react with the binder to form new, stable phases. If the waste is chemically entrapped in new phases, then the stability of these phases in different environments must be known in order to predict their long-term behavior. The formation of metastable species may lead to phase changes in the long term, which may make more waste elements available for leaching after long curing times. In contrast, if the entrapment is physical, the distribution of the waste and the degree of encapsulation will control leaching. In the real world, both mechanisms are expected to operate, but to different degrees in a particular S/S process.

In the last few years, there has been increasing research effort devoted to identifying the chemical forms of metal species solidified in portland cement (13). In almost all of those studies, a minor amount of a soluble metal salt (mostly about 10% by weight) is dissolved in water, combined with cement, allowed to cure. Since the metals are relatively minor constituents, it is reasonable to conclude that the environment is rather similar to that of portland cement, for instance, with respect to pore water composition, where the pH is often greater than 13. Under those conditions, it has been shown that most heavy metal ions give surface precipitates, often as Ca salts of metalate ions, such as $CaCd(OH)_4$ from Cd(II) (14), $CaZn_2(OH)_6 \cdot 2H_2O$ from Zn(II) (15), or $NaCaAsO_4 \cdot 7.5H_2O$ from As(V) (16). A notable exception is Cr(III), for which there is direct evidence that the metal ion becomes incorporated into the C-S-H, with alteration of the gel structure (17–19).

In the present study, however, the metal cations were precipitated first, dewatered, and then treated with cement. It is not clear that the conditions, although clearly very basic, are like those of the studies cited above. Certainly, precipitation of hydroxides of Cd (20, 21), Cr (21), and Ni (20, 21) could be expected during sludge formation. For Hg, the hydroxide is not appreciably stable and transforms to HgO, which is the only detectable Hg-containing species when $Hg(NO_3)_2$ is solidified in the presence of OPC (22). However, it is not surprising from the XRD studies of the sludge and the OPC/sludge mixtures that crystalline hydroxide salts could not be identified. The sludge was prepared from lime addition to a solution of nitrate salts and thus contains major amounts of nitrate, some carbonate from atmospheric CO_2, and probably other anions in smaller amounts. Precipitates formed from the addition of base to aqueous metal salts are notorious for producing many things other than binary, easily characterizable, crystalline metal hydroxides (20). Salts containing halide anions in addition to hydroxide are particularly well-known, but many examples of hydroxy nitrate salts are also known. The dewatered sludge is a very complex mixture, and metals can be present as noncrystalline hydroxide gels, as nonstoichiometric salts with more than one metal ion in the same lattice, as complex

salts with more than one anion, or as solid solutions. All of these effects make XRD identification difficult, even in the sludge prior to mixing with cement.

In this study, electron microscopy of sludge indicates that sludge particles, hundreds of micrometers in diameter, are themselves aggregates of submicrometer-sized particles. These particles are composed of Ca, Cr, and Ni, but they vary widely in composition. The EDX analyses are averages of the small submicrometer-sized crystallites seen in the TEM, as the electron beam diameter during EDX analysis is ca. 1 μm. XRD diffractograms show the continuing presence of some of the calcium hydroxide added for precipitation of heavy metals and a minor amount of calcium carbonate from atmospheric carbonation. However, despite the presence of many XRD peaks, no simple hydroxides of Cr, Ni, or Cd could be identified. They may in fact be present, perhaps in small amounts and obscured by peaks from complex and/or impure crystalline phases.

EDX of OPC/sludge samples show ellipsoidal particles that are either calcium silicate clinker minerals coated with small amounts of Cr and Ni or sludge particles. The physical nature of S/S in the present case is further evident from optical microscopy, where transparent particles can be seen displaying an irregular cellular structure and bluish color, distinctly different from the surrounding matrix. These particles are mainly composed of Ca, Cr, and Ni, although considerable variation in Ni and Cr concentrations exists within a single particle, a variation which is not surprising since the sludge itself shows considerable heterogeneity. The waste metals in the OPC/sludge samples are mostly confined to the ellipsoidal to irregular-shaped particles. The matrix away from these particles also contains the heavy metals, but at much lower concentrations. The Cd peak is observable in the untreated sludge and in sludge particles in the treated samples, but not in the matrix of the S/S samples.

The presence of sludge affects the hydration of OPC, as the overall XRD intensities are lower and C_2S and C_3S peaks are higher compared to OPC. The observation of unreacted clinker minerals is somewhat unexpected, since a rather high w/c ratio was used to prepare the OPC/sludge samples. The control without sludge shows barely discernible peaks for C_2S and C_3S. However, the effect of sludge is not very drastic, since the same hydration products are observed in approximately the same proportions in OPC with and without sludge.

The complexity of the reactions that take place in heavy metal precipitation is apparent from the XRD and TEM. The presence of microscopic·sludge particles in the treated sludge samples is suggested by SEM and OM observations and confirmed by XRD and EDX. The XRD pattern of a treated sludge sample is the sum of the patterns of OPC and untreated sludge. The OPC/sludge samples are thus mechanical mixtures of sludge and OPC. However, the same sludge phases are not observed in each OPC/sludge sample. The sludge-containing OPC samples belong to two groups depending on sludge species, and the proportions of sludge species are also variable. This variability may reflect kinetics of precipitation of metastable chemical species as different samples were prepared at different times. The variability may also explain the 5-fold variation in unconfined compressive strength from 230 to 45 psi (9).

The present investigation indicates that entrapment is mainly physical, the waste being confined to large particles, hundreds of micrometers in diameter, embedded in the OPC matrix. The waste is also present in the matrix at low levels, but whether they are chemical species different from those in the sludge particles could not be determined

using the methods of this study.

It appears that cementitious S/S can involve either chemical transformations of wastes or microscopic encapsulation. A number of studies referred to earlier have shown that the chemical forms of metal ions within a cement matrix are different from the form present in the aqueous waste. The present results are the clearest evidence that microscopic encapsulation is important. It may be that the latter is the usual case when a preformed "hydroxide" sludge is solidified, but it is not yet clear whether the microencapsulation phenomenon is common. The two varieties of S/S should give different problems to the modelers who attempt to predict long-term leachability of wastes from cement matrices. The ultimate goal of modeling would be to predict release rates based on thermodynamic properties of the specific chemical species involved. Those, of course, will be different depending upon whether the waste/matrix interactions involve chemical change or only encapsulation. The latter may be most successfully modeled on the basis of the leachability of the sludge, with a minor correction for transport through the cement matrix. Whatever form the modeling ultimately takes, it is important to know whether chemical transformations of the waste take place during S/S or whether they do not.

Conclusions

The synthetic electroplating sludge, subject of the present study, was composed of impure, submicrometer-sized crystallites of heavy metal salts. Minor carbonation occurred. The metal composition of the sludge determined by EDX was ca. 80% Ca and 20% (Cr + Ni) with small amounts of Cd. The presence of sludge retarded hydration of OPC, but the hydration products were the same as those formed in its absence.

Morphologies observed in the OPC/sludge samples were distinctly different from those normally observed in hardened OPC. The samples often had ellipsoidal to irregularly shaped particles, a few hundreds of micrometers in diameter. The heavy metals were mostly confined to these particles, although they were present in the matrix at much lower concentrations. Physical encapsulation on a microscopic scale was the principal mechanism of stabilization.

Acknowledgments

Registry No. Cr, 7440-47-3; Ni, 7440-02-0; Cd, 7440-43-9.

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