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SPECTROSCOPIC AND LEACHING STUDIES OF SOLIDIFIED TOXIC METALS*

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Summary

Portland cement samples containing the soluble nitrates of the priority pollutant metals chromium, lead, barium, mercury, cadmium, and zinc are being investigated using thermogravimetric (TGA) and fourier transform infrared techniques (FTIR). The major vibrational bands of the carbonate, sulfate, silicate, water, and nitrate species are tabulated and discussed in comparison to uncontaminated cement. In addition, results of leaching studies on the above samples containing sulfide and phosphate additives are reported.

Introduction

The disposal of hazardous substances is a pressing issue at the present time and safe, cost-efficient methods are urgently needed. The objective of this research is to develop chemical technology to render toxic and hazardous substances harmless by fixation and solidification methods. Our research program will also help alleviate the critical shortage of personnel in hazardous waste science by hiring and training graduate, undergraduate, and postdoctoral students. Our approach to help solve the difficult and complex problems of hazardous waste containment involves collaborative efforts of scientists and engineers with expertise in various fields, including surface chemistry; organic, inorganic, and coordination chemistry; and both civil and environmental engineering.

Results of recent research

Our recent research efforts [1–4] have provided a better understanding of the chemical environment and binding of several priority pollutant metals solidified in portland cement. The following results have been obtained: (1) We

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have established, for example, that mercury(II) reacts in the basic cement environment to form nearly linear polymeric mercuric oxide (HgO), a relatively soluble and volatile mercury salt. (2) Fourier transform infrared analysis strongly suggests that barium forms the insoluble sulfate, $BaSO_4$. This is a significant result since gypsum ($CaSO_4$) is added to cement to prevent "flash set" by retarding the hydration of tricalcium aluminate. Rapid hydration of this aluminate results in precipitates which have very little strength and weaken the solidified concrete. Metal ions which react with sulfate would therefore negate the beneficial reactions of the added gypsum. (3) Zinc also has a detrimental effect on the ability of water to hydrate the di- and tri-calcium silicates. These two silicates are primarily responsible for the strength and hardness of solidified concrete. (4) Also, lead retards cement setting by forming insoluble compounds which coat the silicates. It appears to be a kinetic effect that is overcome with additional setting time. Additional information for chromium and cadmium has also been collected. (5) Carbonate formation is greatly enhanced by the presence of metal ions in portland cement. (6) Recent leaching results indicate that cadmium stabilization is enhanced by sulfide additives, while lead stabilization is enhanced by phosphate additives.

Discussion

Portland cement samples containing the priority pollutant metals chromium, lead, mercury, cadmium, zinc, and barium (2, 5, 10, and 20 weight% metal nitrate salt) are being evaluated using the U.S. Environmental Protection Agency standard and modified versions of the EP (extraction procedure) and TCLP (toxicity characteristic leaching procedure). The major purpose of these tests is to determine the stability and insolubility of the various toxic metals in the cement matrix. In addition to the numerous samples prepared above, we have also prepared mercury, lead, and cadmium samples in cement with additives such as sodium phosphate and sodium sulfide. The objective here was to determine the effect that these anions have on the leachability (insolubility) of the metal ions in the solidified cement matrix under the conditions of the EP and TCLP tests.

A modified version of the TCLP involves periodic additions of acetic acid to maintain the pH near 5.0. In an effort to circumvent the necessity of a continuous 24-hour monitoring of the pH, a sodium acetate–acetic acid buffer was prepared ($pH=5$) and used as the extraction fluid on a number of samples. The results were expected to be similar to the unbuffered acetic acid extractions with the benefit of not having to adjust the pH over a 24-hour period. However, dramatic differences in metal ion extractions were found. The results of these tests and possible explanations for the significant differences are currently being addressed (data in Table 1 compares these results).

In addition to the modified extraction procedure described above, batch

TABLE 1

Weight % metal extracted by TCLP and buffer methods

Metal	TCLP	(Final pH)	Buffer
Cadmium	6.20	(7.7)	16.84
Chromium	0.12	(9.5)	62.99
Copper	4.36	(9.9)	92.43
Lead	0.004	(11.0)	69.35
Nickel	0.21	(9.9)	48.16
Zinc	3.16	(10.5)	48.44

leaching tests were performed on a selected number of samples including those containing the sodium phosphate and sulfide additives. After crushing the samples, the standard acetic acid (0.04 *N*) was added in a 50:1 solvent-to-solid ratio. The pH before and after a 24-hour extraction procedure was recorded and the remaining solid was then filtered. The leachate was saved for future analysis by atomic absorption. This procedure was repeated six times, using the remaining solid sample and replenishing the acetic acid extraction fluid. The results of these tests are portrayed in Table 2 and Figs. 1 and 2. From perusal of the data it is obvious that the addition of sulfide and phosphate to the cement samples containing cadmium and lead has significant effects on the amount of metal leached out.

Cadmium leaching results

Cement samples containing 10 wt.% cadmium nitrate (10% by weight) both with and without sodium sulfide were subjected to the leaching procedure as described above. Results indicate a substantial decrease in the amount of cadmium leached when sulfide is present. For example, after three extractions the values are 0.07% versus 2.74% in the total weight percent of cadmium leached out. After seven extractions the values are 21.95% versus 42.24%. It appears that the major reason for the enhanced stabilization when sulfide is present is due to the formation of the highly insoluble CdS.

Lead leaching results

Portland cement samples containing lead nitrate, lead nitrate plus sodium sulfide, and lead nitrate plus sodium phosphate (10 wt.%) were subjected to the leaching procedure as previously described. Results (see Fig. 2) indicate that lead–sulfide cement showed the poorest resistance to leaching (unlike the cadmium-sulfide sample), while the lead–phosphate sample showed the least solubility. The lead cement sample without additives was intermediate in its leaching behavior. Lead sulfide is soluble in acid, while lead phosphate is insoluble in acetic acid. The chemical nature and leaching mechanism of the lead and cadmium in these samples is currently under investigation.

TABLE 2

Batch leaching results with Pb and Cd (see also Figs. 1 and 2 resp.)

	Extraction No.						
	1	2	3	4	5	6	7
Pb-cement							
Final pH	11.5	10.9	7.0	6.4	6.0	5.4	4.9
Wt.% Extr.	0.07	0.07	0.13	0.38	0.75	2.95	6.75
Cumulative % Extr.	0.07	0.14	0.27	0.65	1.40	4.35	11.10
$Pb+S^{2-}$							
Final pH	11.2	8.4	6.8	6.3	5.9	5.2	4.7
Wt.% Extr.	0.06	0.08	0.13	0.39	1.18	4.58	8.59
Cumulative % Extr.	0.06	0.14	0.27	0.66	1.84	6.42	15.01
$Pb+PO_4^{3-}$							
Final pH	11.3	9.4	6.9	6.2	5.9	5.1	4.7
Wt.% Extr.	0.06	0.06	0.10	0.23	0.28	1.28	2.38
Cumulative % extracted	0.06	0.12	0.22	0.46	0.68	1.91	4.29
Cd-cement							
Final pH	11.5	9.9	6.8	6.2	5.8	5.2	4.8
Wt.% Extr.	0.01	0.03	2.70	6.41	9.35	11.43	12.31
Cumulative % Extr.	0.01	0.04	2.74	9.15	18.50	29.93	42.24
$Cd+S^{2-}$							
Final pH	11.3	9.1	6.8	6.5	6.0	5.6	5.1
Wt.% Extr.	0.01	0.02	0.04	2.66	6.61	5.81	6.80
Cumulative % Extr.	0.01	0.03	0.07	2.73	9.34	15.15	21.95

For solidified hazardous substances to be environmentally acceptable, they must be in a form deemed safe. This usually means, for example, that the toxic metal is in a form similar to that found in nature, i.e., mineral or rock-like. With the use of specific additives to the silicate matrix of cement we feel that this objective can be met (see Table 3).

Results and discussion of infrared data

When Hg(II) salts are present in basic aqueous solutions the yellow form of mercuric hydroxide forms ($Hg(OH)_2$ is not known). In our mercury-containing cement samples the yellow form of HgO predominates at room temperature

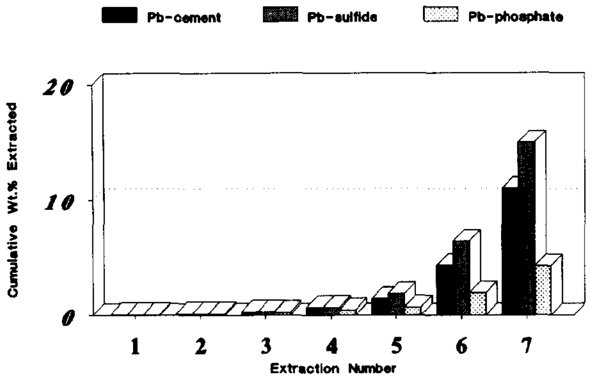

Fig. 1. Results of lead leaching (see Table 2) over a 24-h period.

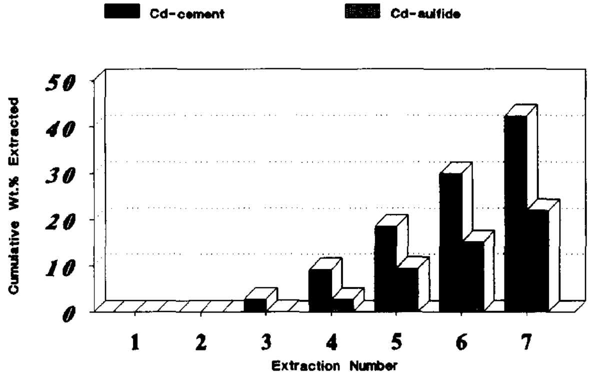

Fig. 2. Results of cadmium leaching (see Table 2) over a 24-h period.

TABLE 3

Priority pollutant metals and their natural mineral forms

Heavy metal	Mineral form
Arsenic	Various As sulfides, CoAs.
Barium	Barium sulfate (barite)
Zinc	found as sulfides. ZnS
Cadmium	CdS
Mercury	HgS
Chromium	Chromite ($FeCr_2O_4$), $PbCrO_4$, chromium(III) oxide.
Lead	Galena (PbS), lead sulfate, lead carbonate, $Pb_5(PO_4)_3Cl$

(the color is obvious) but changes to the red form at elevated temperatures. The difference in color is due to the HgO particle size. An important consequence of this oxide formation in the basic cement environment is its solubility. Although most mercury compounds are highly insoluble (one microgram/ liter for HgS) mercuric oxide is fairly soluble (10^{-3} to 10^{-4} *M*, depending on particle size). To prevent serious leaching problems, therefore, the oxide must be converted to a much less soluble species. Also, the Hg-cement loses considerably more weight between 300–500 °C when compared to the other samples. This additional loss of weight is no doubt due to the decomposition of HgO to form volatile elemental mercury and oxygen.

Carbonate

Fourier transform infrared (FTIR) spectra indicate enhanced carbonate formation in the metal doped cement samples. Both the aragonite and calcite forms of calcium carbonate are present. The metal-ion doped samples are all similar in this region of the spectrum where ν_2 and ν_3 vibration vary by only a few wavenumbers. When compared to the pure cement ν_2 is raised slightly in energy while ν_3 is lowered slightly. In the thermogravimetric (TGA) studies a weight loss near 310 °C corresponds to aragonite decomposition. At temperatures of 410 °C and higher the calcite peak diminishes in intensity relative to the aragonite band. These observations are probably due to conformational changes between the metastable orthorhombic form and the more stable rhombohedral (calcite) structure. The weight loss is due to the partial decomposition of the carbonate to yield CO_2 and oxide. However, at temperatures as high as 700 °C some carbonate is still detectable in all samples.

Sulfate

The ν_3 vibration of the sulphate ion in the metal–cement samples is found between 1,112–1,116 cm^{-1} and 1,121 cm^{-1} for pure portland cement. Since this triply degenerate mode is not split the sulfate environment is highly symmetrical (*Td* symmetry) and primarily ionic. Lowered symmetry causes splitting of the degenerate modes and is observed in only the barium sample. The three components of ν_3 for pure $BaSO_4$ (C_{2v}) are 1,090, 1,142, and 1,167 cm^{-1} and are almost identical with the three bands found in Ba-cement. Also, ν_4 exhibits two components at 634 and 612 cm^{-1} in both Ba-cement and pure $BaSO_4$.

Nitrate

X-ray photoelectron spectroscopic[1] (XPS) studies [4] show that potassium migrates to the surface when samples contain metal nitrates. To maintain electrical balance between the nitrate and metal ions, potassium is apparently ion-

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[1] XPS is synonymous to ESCA, electron spectroscopy for chemical analysis.

exchanged into solution as the doped metal ions are incorporated into the solidified cement structure. The nature of the nitrate environment, i.e., ionic, uni- or bi-dentate, may be determined by the magnitude of the splitting of the degenerate ν_3 and ν_4 vibrations [5]. However, due to the complexity of the spectra in this region definitive assignments are difficult although many ionic nitrates exhibit strong sharp bands near 800 cm^{-1} and 1,380 cm^{-1}. In our series of samples a sharp peak is located between 787–796 and another at 1,385 cm^{-1} suggesting the ionic nature of the nitrate ion in the cement. Like carbonate, the nitrate begins to thermally decompose between 400 and 500°C.

Water and calcium hydroxide

Between room temperature and 274°C all samples lose water (17–21.5 wt.%). Water loss above this temperature continues but at a much lower rate. The broad adsorption band between 3,200–3,600 cm^{-1} (symmetric and antisymmetric O–H stretching) contains a sharp spike at 3,644 cm^{-1}, which is due to the O–H stretching of $Ca(OH)_2$. The H–O–H bending mode is also obvious near 1,640 cm^{-1}.

Silicate

Hydration of portland cement constituents dicalcium silicate (belite) and tricalcium silicate results in the formation of a similar form of calcium silicate hydrate (C-S-H) [6,7]. The major infrared bands observed are the ν_3 (asymmetrical Si–O stretch) and ν_4 (out-of-plane bending) vibrations located near 1,000 cm^{-1} and 600 cm^{-1}, respectively. All of the above bands have similar shapes and shoulders are not obvious. The diffuse nature of the bands is indicative of the amorphous nature of these silicate hydration products. Although early setting is retarded by lead salts the final product (after 28 or more days) may not suffer strength loss. Indeed, there are reports that strength may be improved [8].

We have addressed the influence that lead salt has on cement setting and found, via XPS studies, that lead is present primarily on the surface [4]. In this study, FTIR diffuse reflectance measurements indicate a very intense sulfate band (1,170 cm^{-1}) also on the surface of the lead cement. This is consistent with the XPS results, suggesting that Pb is present as a sulfate or hydrosulfate species. The possibility of surface species such as multinuclear lead hydroxo cations–sulfate anions also exists [9,10]. The chromium doped samples, by contrast, show a much less intense surface sulfate absorption band and XPS studies show that Cr is not a surface species but is incorporated throughout the cement matrix. It appears also that Zn, Cd, and Hg may be covered by carbonate species [3,4]. Significantly, basic salts such as the Zn salt ($ZnCO_3 \cdot 2\ Zn(OH)_2 \cdot H_2O$) are known to precipitate from solution [11].

Since retardation of setting is usually associated with decreased strength, it is interesting to note that our samples containing 20% and 30% $Zn(NO_3)_2$, after curing over three months, can be crumbled with slight pressure between one's fingers, unlike the Pb-doped samples. Inspection of the FTIR spectra of changes in ν_3 and ν_4 of the dry, unhydrated cement and the hydrated uncontaminated cement and the 10, 20, and 30 percent $Zn(NO_3)_2$ samples if very informative. The 10 wt.% Zn-cement shows a broad diffuse ν_3 band located at 1,015 cm^{-1}. However, for zinc nitrate concentrations of 20–30% the silicate ν_3 and ν_4 regions are dramatically changed and are almost identical to the dry cement clinker spectra of C_2S and C_3S. The values for the dry clinker are: 994, 937, 883, 848, and 526 cm^{-1}; for 20 wt.% Zn-cement: 987, 935, 874, 844, and 544 cm^{-1}; and for 30 wt.% Zn-cement: 997, 927, 876, 838, and 526 cm^{-1}. Apparently these higher Zn ion concentrations inhibit substantially the condensation process thereby producing a solid product without strength that is easily broken down.

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