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SOLUTION CHEMISTRY DURING CEMENT HYDRATION IN THE PRESENCE OF METAL HYDROXIDE WASTES

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ABSTRACT

Experiments were completed to compare the effects of 10% additions of Pb, Zn, and Cd hydroxide synthetic wastes on the early hydration of ordinary Portland cement, by analysing changes in the composition of solutions extracted during hydration, and using conduction calorimetry, and differential thermal analysis. Pb^{2+} was initially present at high concentrations, although this rapidly falls when the rate of heat evolution increases, despite the high pH environment. The Pb waste also delayed SO_4^{2-} removal from solution compared to OPC control data. Zn^{2+} was present in extracts at low concentrations but suppressed the heat evolution associated with normal cement hydration. SO_4^{2-} was rapidly removed from solution suggesting $CaZn_2(OH)_6.H_2O$ precipitates coat the surfaces of gypsum as well as cement clinker particles. Cd was present in the waste as crystalline $Cd(OH)_2$ and was not detected in solutions extracted from hydrating cement/Cd waste. © *1997 Elsevier Science Ltd*

Introduction

Stabilization/solidification is a pre-landfill waste treatment process which has been used for many types of industrial wastes, but is particularly suited to those containing heavy metals (1,2). The production of a solidified waste reduces the surface area available for leaching, and the highly alkaline environment produced by cementitious binders ensures that most heavy metals are effectively immobilized. Commercial solidification processes use cement or other readily available pozzolanic binders as solidification additives. The effects of wastes on the hydration reactions of the binders are important, as these influence the microstructure and therefore the performance of the treated product.

Commercial stabilization/solidification operators often accept solid and liquid wastes from a range of different industries. These are then chemically stabilized by controlling the pH of the mixed wastes to between 8 and 9.5. Most transition series elements and heavy metals are likely to precipitate under these conditions as insoluble hydroxides, although a

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range of other chemical forms of metals will exist in real wastes. The resulting slurry is then mixed with the solidification additives.

Recent studies have clearly demonstrated that retardation and in some cases inhibition of cement hydration reactions result from the addition of commercially stabilized wastes containing heavy metals (3,4,5,6,7,8). Although the mix may eventually set, reaction products are significantly different from those produced during normal cement hydration. These interference effects on cement hydration have, to some extent, limited the more widespread use of solidification technologies for industrial wastes.

The effects of Pb compounds on cement have been extensively studied. Additions of up to 4 wt% $Pb(NO_3)_2$ caused an increase in early heat liberation during cement hydration, followed by longer term retardation and rapid precipitation of gelatinous colloidal basic lead compounds (9). These coat the surfaces of cement grains, forming a low permeability layer which retarded hydration. Thermogravimetric analysis (TGA), Fourier transfer infrared spectroscopy (FTIR), and Si^{29} nuclear magnetic resonance (NMR) studies on $Pb(NO_3)_2$ doped cement suggested that retardation occurred through the solubilisation and reprecipitation of lead sulphate and its various basic forms on the surfaces of cement minerals (10,11). X-ray photoelectron spectroscopy (XPS) studies identified Pb at the surface of cement particles, supporting the gelatinous insoluble lead salt coating model for lead retardation (12).

The effects of adding a range of lead compounds, to Type 1 Portland cement have been studied (13), using the TCLP leach test (14) and X-ray diffraction (XRD). The form of lead salt significantly affected the interaction with the cement hydration process and lead nitrate was not found to be representative of lead compounds in general.

Solid state ^{27}Al and ^{29}Si NMR have also been used to study the effect of a "Pb hydroxide" sludge on the hydration of type 1 Portland cement (15). This resulted in a matrix with a much higher proportion of silicate chains containing Q^2 units (silicon-oxygen tetrahedra connected to two similar units) compared to normal cement.

The interfering effects of Zn and Cd on cement based stabilization/solidification have also been extensively studied using techniques such as FTIR, MAS-NMR, XRD and SEM (10,11,15,16). FTIR results confirm formation of $CaZn_2(OH)_6.H_2O$ and $CaCd_2(OH)_4$ on the hydrated surfaces of cement phases, and this has been explained by proposing a "Charge Dispersal Model" (17). In this, charge-controlled reactions lead to retardation of cement hydration and subsequent setting due to competition mainly between Ca^{2+} ions and metal hydroxy anions present in the system. In the case of Zn, the zinc hydroxy anions $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are reported to be present between pH 12 and 13. These are transformed into $CaZn_2(OH)_6.H_2O$, which completely covers the cement grains and passivates further hydration reactions.

The chemical composition of solutions separated from hydrating cement can provide important information on the mechanisms and processes occurring during hydration (18,19). It is a technique which has not been extensively used to study cement solidified wastes. In this work, solution chemistry data has been combined with XRD, conduction calorimetry and thermogravimetric analysis/differential thermal analysis (TG/DTA) to determine changes induced by synthetic metal waste additions containing Pb, Zn, and Cd on OPC hydration.

Experimental

Pb, Zn, and Cd were precipitated from 1M metal nitrate solutions by adding 10M NaOH to pH 9.5 (SLR grade Fisons plc). The sludges were vacuum filtered through a No.1 filter paper (Whatman Ltd.), dried overnight at 105°C, ground to <500µm, and stored in sealed glass bottles. The synthetic metal wastes and cement solidified wastes hydrated for 28 days were analyzed by X-ray diffraction (XRD) using a Philips PW 1820 System with Cu Kα radiation, to determine the major crystalline phases present.

Solution chemistry studies were completed by dry mixing 30g of OPC (Blue Circle (UK) plc.) with 3g of the selected synthetic wastes. Sufficient water was then added to give a water/cement (w/c) ratio of 3. The slurry was continually agitated for a range of predetermined times, after which the solution was separated by vacuum filtration through a No. 1 filter paper. The filtrate was then passed through an additional 0.45µm syringe filter and the pH measured, prior to either acidification to 10% HNO_3 (Aristar, BDH) for metals analysis by ICP-AES (ARL 3580) or dilution with RO water for Ion Chromatography (IC) analysis of SO_4^{2-} (Waters IC-Pak A Column Borate/Gluconate eluent, method #GABG-101). All mixing and filtering operations were completed under a N_2 atmosphere to exclude the effects of CO_2 from the experiments. Experiments were completed at least in duplicate to confirm the changes in ion concentrations reported.

The heat of hydration was determined for OPC and OPC plus 10% of dried "metal hydroxide" sludge using a Wexham Developments Isothermal Conduction Calorimeter operating at 20°C. Samples were thoroughly mixed in sealed plastic bags at a w/s ratio of 0.5 before placement in the calorimeter cell, and the rate of heat output monitored for 300 hours.

The development of $Ca(OH)_2$ in cement/metal waste samples was investigated using TG/DTA (Polymer Laboratories PL-STA) (22). Samples were prepared in a similar manner to those for calorimetry, and were cured for up to 90 days. 15mg sub-samples, ground to <150µm were heated to 600°C in alumina crucibles under a N_2 atmosphere at a rate of $5°Cmin^{-1}$. Under these conditions $Ca(OH)_2$ dehydrates in the temperature range between approximately 370 and 430°C. DTA data was calibrated by analyzing varying amounts of GPR grade $Ca(OH)_2$ mixed with Al_2O_3. This gave a linear relationship between the area under the DTA peak and the amount of $Ca(OH)_2$ in the mix.

Results

XRD Data. Precipitated hydroxides are rarely pure systems but form complex mixtures of hydroxide and counter anions from the soluble salt (21). The metals in the synthetic wastes used in these experiments were therefore not present as pure hydroxides. XRD data in Figure 1 indicates that the major crystalline phases in the lead hydroxide sludge were lead nitrate hydroxide [$Pb_3(NO_3)(OH)_5$], and lead oxide nitrate hydroxide [$Pb_6O_3(NO_3)_2(OH)_4$]. Other workers have also identified lead oxide nitrate hydroxide and $Pb(NO_3)_2 5Pb(OH)_2$ as the major crystalline phases formed in similarly prepared sludges (22). The Zn hydroxide sludge contained crystalline zinc nitrate hydroxide hydrate [$Zn_5(NO_3)_2(OH)_8 2H_2O$], ZnO and $NaNO_3$. The Cd hydroxide sludge was predominantly crystalline $Cd(OH)_2$.

The major crystalline phase present in the cement/Pb waste system hydrated for 28 days was portlandite [$Ca(OH)_2$]. Lead nitrate hydroxide was detected, and the high background level indicated that significant quantities of amorphous material were present. Unreacted cement clinker phases were detected in the cement/Zn waste system, and no portlandite had

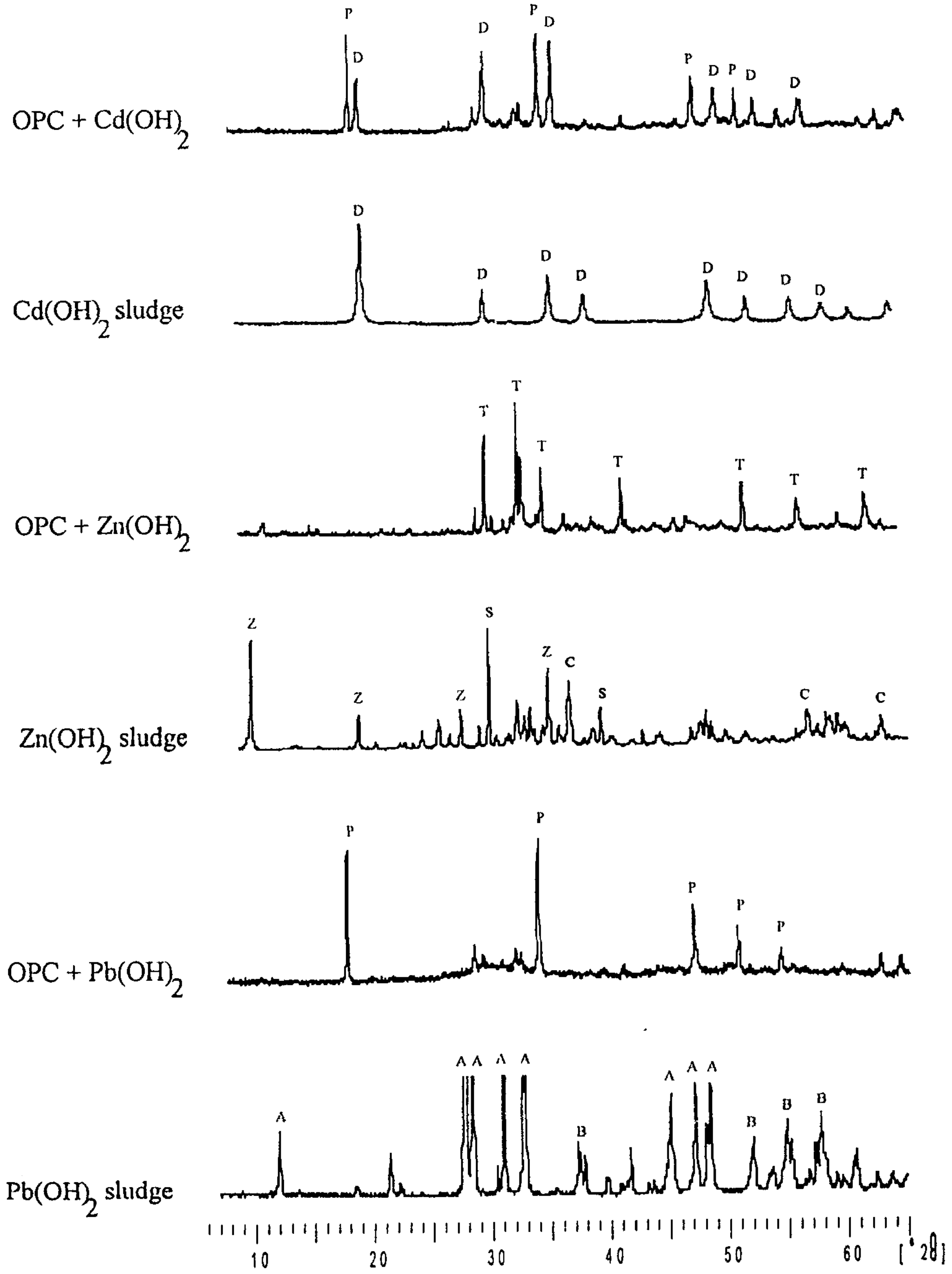

FIG. 1.

XRD data of metal wastes and 10:1 cement/waste mixes hydrated for 28 days. Z = zinc nitrate hydroxide hydrate; D = $Cd(OH)_2$; S = sodium nitrate; P = $Ca(OH)_2$; C = zinc oxide; T = C_3S; A = lead nitrate hydroxide; B = lead oxide nitrate hydroxide.

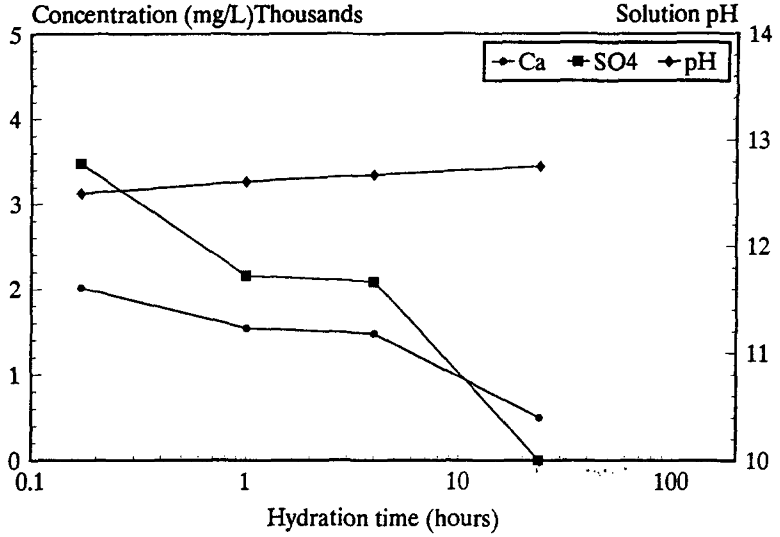

FIG. 2.
Control OPC slurry Ca^{2+}, SO_4^{2-} and pH data.

formed. In comparison, portlandite and $Cd(OH)_2$ were present in the hydrated cement/Cd waste.

Solution Chemistry. Variations in ionic concentrations of Ca^{2+} and SO_4^{2-} in filtrates separated from control OPC slurries hydrated for different times are shown in Figure 2. The SO_4^{2-} concentration during the first minutes of hydration was approximately 4,400 mg.l^{-1} but decreased with increasing hydration time. After 1 hour its concentration had reduced to approximately half its initial value, and then appeared to remain at this level during at least the next 3 hours of hydration. SO_4^{2-} originates from the dissolution of gypsum which is added to the cement clinker to control hydration of the tricalcium aluminate (C_3A) phase. The reduction in concentration is due to SO_4^{2-} combining with the aluminate phases, to form insoluble ettringite or sulphoaluminate gel. After 24 hours SO_4^{2-} ions had disappeared from solution.

The Ca^{2+} concentration shows a similar variation to SO_4^{2-} except that at the end of 24 hours it remained in the filtrate at a concentration of about 500 mg.l^{-1}. It also originates from dissolution of gypsum and from the hydration of cement clinker phases.

The pH of the solution increased gradually from 12.3 to 12.8 during the first 24 hours. The concentration of K^+ was initially about 1450 mg.L^{-1} and increased with hydration time up to 1875 mg.L^{-1}. Na^+ similarly increased in concentration from 135 to 267 mg.L^{-1}. Average concentrations of Zn, Cd and Pb throughout the hydration period were 0.03, 0.01 and 0.28 mg.L^{-1} respectively. Al, Fe, and Mg were only present at very low concentrations.

Ca^{2+} and SO_4^{2-} concentrations and the pH of solutions extracted from OPC/metal waste mixes are shown in Figure 3 a-c. Corresponding Pb^{2+}, Zn^{2+}, and Cd^{2+} concentrations are shown in Figure 4.

The pH of the cement/Pb waste system was approximately 12.5 within the first minutes of hydration and remained fairly constant for 24 hours, before increasing to 13.3 between 1 and 4 days. In this high pH environment the Pb sludge is resolubilized, probably forming $Pb(OH)_3^-$ species, giving an initial Pb concentration of approximately 500 mg.l^{-1} (Fig. 4). It

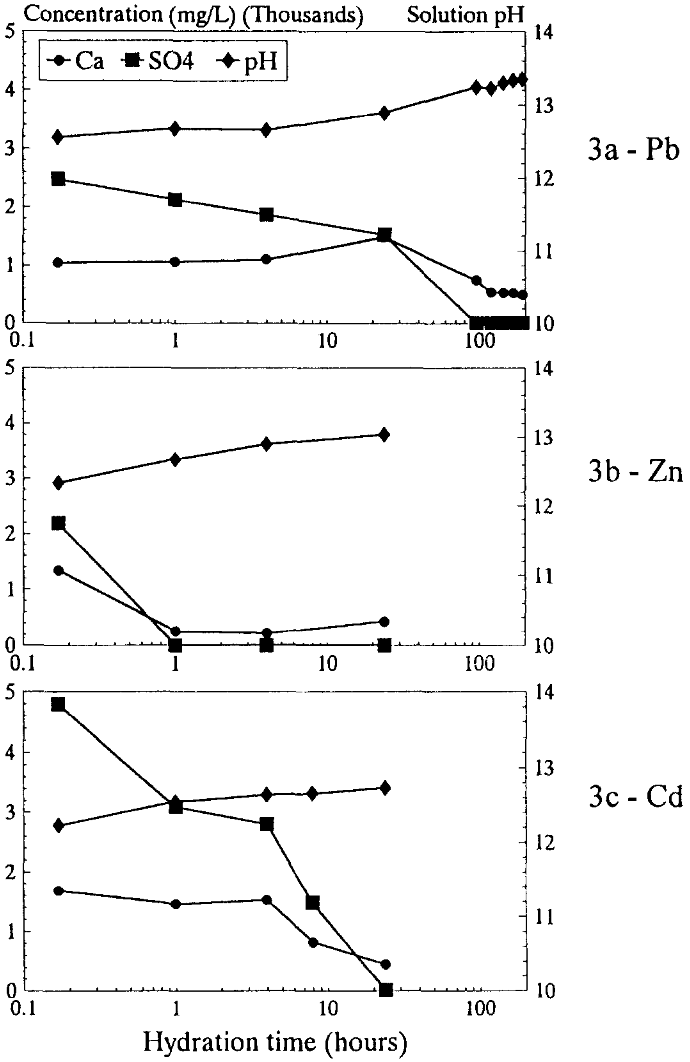

FIG. 3.
(a, b and c) Solution composition data (Ca^{2+}, SO_4^{2-}) and pH for cement + Pb, Zn and Cd wastes.

continues to increase in concentration up to a maximum of 2,000 $mg.l^{-1}$ after 24 hours. The concentration then falls to below 100 $mg.l^{-1}$ between 24 and 100 hours and remains at 20-30 $mg.l^{-1}$ throughout the remainder of the hydration period examined. This removal of Pb^{2+} from solution occurs while the pH > 13.

The Ca^{2+} concentrations are much lower than observed in the OPC control and remain constant during the first 24 hours. The SO_4^{2-} concentration does fall, although at a reduced rate compared to the control.

The extent of Zn solubilization was relatively low, with concentrations reaching a maximum of 8$mg.l^{-1}$. The filtrate pH slowly increased from 11.9 to 13.0 during the first 24 hours of hydration, and at these pH values soluble $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are expected to form.

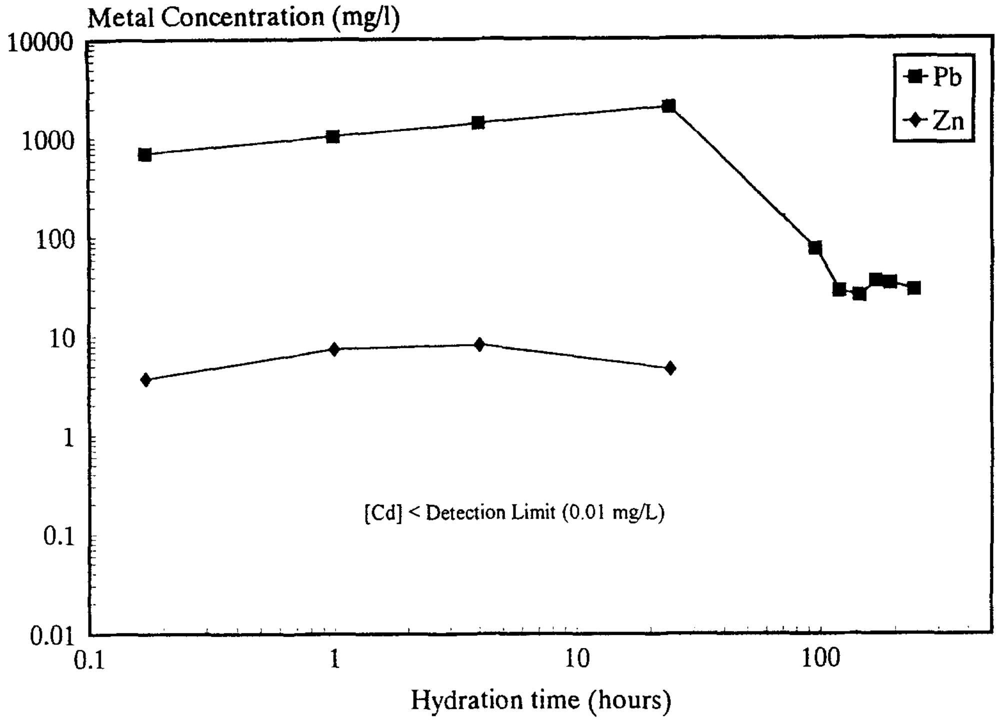

FIG. 4

Pb^{2+}, Zn^{2+} and Cd^{2+} concentrations in solutions extracted from cement/waste mixes.

After 10 minutes of hydration lower concentrations of Ca^{2+} and SO_4^{2-} are in solutions extracted from the Zn waste/cement system compared to the other metals. The concentration of SO_4^{2-} is initially somewhat lower than in the control, at approximately 2000mg.l^{-1}, and falls very rapidly. No SO_4^{2-} was present in solution after the first hour of hydration.

Filtrates extracted from the OPC/Cd waste system contained concentrations of Cd^{2+} which were below the analytical detection limit of 0.01 mg.L^{-1} throughout the hydration period examined. Ca^{2+} concentrations were similar to those found in OPC control filtrates, but SO_4^{2-} concentrations were particularly high during the very early stages of hydration compared to OPC control data.

Conduction Calorimetry. Conduction calorimetry data for OPC in the presence of the metal wastes is shown in Figure 5 and the data summarized in Table 1, where Q_{max} is the maximum rate of heat evolution. The Pb containing waste caused severe retardation of cement hydration, although a high rate of heat evolution occurred between 150 and 200 hours and the total heat evolved during the test period monitored was highest for the cement/Pb waste system. No Q_{max} was observed for OPC doped with the Zn containing waste, implying inhibition of normal cement hydration reactions. The Cd waste caused a significant increase in Q_{max}, which occurred at approximately the same time as for OPC.

DTA Result. Figure 6 shows the development of $Ca(OH)_2$ in OPC and OPC doped with different synthetic metal wastes. The most striking results were obtained for the cement/Zn

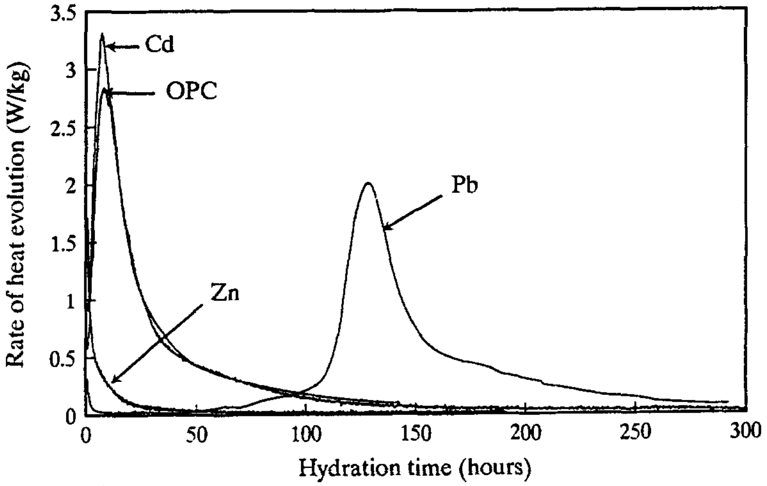

FIG. 5.
Conduction calorimetry data for OPC in the presence of Pb^{2+}, Zn^{2+} and Cd^{2+} wastes.

waste system. No $Ca(OH)_2$ was detected during the first 28 days, and only approximately 5 weight percent was present after 90 days hydration.

The Pb hydroxide sludge also severely retarded $Ca(OH)_2$ formation throughout the first week of hydration, although there was then a rapid acceleration in formation, so that after 2 weeks the level was similar to that found in control samples. In comparison, addition of Cd hydroxide caused rapid formation of $Ca(OH)_2$. After 1 day, approximately 9 weight % of $Ca(OH)_2$ had formed in the cement/Cd waste paste, although after 28 days $Ca(OH)_2$ levels were similar to those found in the other cement/metal waste systems.

Comparison of the DTA and the conduction calorimetry data shows that, as would be expected, the period of rapid $Ca(OH)_2$ production occurs towards the end of the main conduction calorimetry peak.

TABLE 1

Conduction Calorimetry Data for OPC/Metal Waste Mixes

sample (w/s=0.5)	Max. rate of heat evolution (Q_{max}) (W/Kg)	Time of max. rate of heat evolution (Hours)	Total heat evolved during test (KJ.Kg^{-1})
OPC	2.17	8.7	290.6
OPC/Pb waste	1.69	172	349.4
OPC/Zn waste	-	-	41.3
OPC/Cd waste	2.88	7.0	317.9

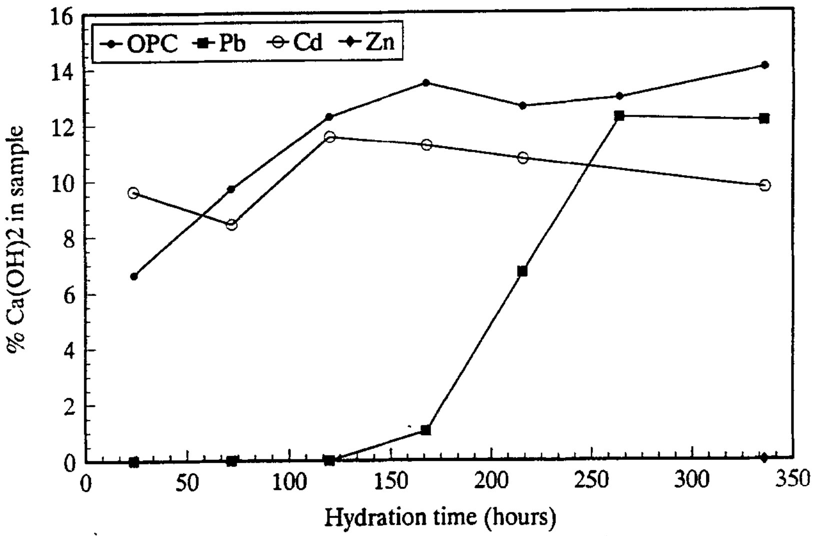

FIG. 6.
DTA data showing development of $Ca(OH)_2$ in 10:1 OPC:metal waste samples.

Discussion

The experimental techniques used in this work have provided complementary data which has clearly demonstrated differences in the way Pb^{2+}, Zn^{2+}, and Cd^{2+} containing wastes interact with hydrating OPC. Although the metals are insoluble when precipitated to form the synthetic waste sludges, addition of cement causes the pH to increase, typically to between 12 and 12.5. The pH of filtrates extracted from OPC/metal waste mixes continued to increase throughout the hydration period studied, and in this environment the speciation of metals present in the wastes changes.

Under the specific conditions used in the solution chemistry experiments, Pb^{2+} rapidly entered solution, reaching concentrations of around 500 $mg.L^{-1}$ within minutes of cement addition. This high Pb concentration indicates extensive dissolution of the Pb waste. The retardation of cement hydration implies Pb complexes are also initially precipitated onto the surfaces of cement clinker particles.

In the basic environment present during cement hydration, the surfaces of cement particles will be negatively charged and are therefore able to adsorb metal cations (16). The most readily available cations in solution are Ca^{2+}, and these are believed to coat the silicate surfaces forming a high charge density Ca^{2+} layer (17). Anionic species in solution such as $Pb(OH)_3^-$, SO_4^{2-}, NO_3^- and OH^- will then compete for adsorption sites, forming a further layer. The low permeability of layers containing high concentrations of $Pb(OH)_3^-$ ions are believed to be responsible for the retardation of cement hydration (12).

The limited specific surface area of cement grains initially available will limit the total amount of $Pb(OH)_3^-$ which can be adsorbed and as a result an increasing concentration of $Pb(OH)_3^-$ is found in solution. The onset of increasing heat evolution corresponds to the production of new silicate hydration products. At about the same time the soluble Pb concentration falls from 1000 to 20 $mg.L^{-1}$. This probably occurs because the $Pb(OH)_3^-$ species are being rapidly adsorbed onto the newly created silicate surfaces.

During early hydration of cement, SO_4^{2-} concentrations are determined by the rate of dissolution of gypsum and the rate at which they react to produce calcium sulphoaluminates. The addition of the Pb waste reduced Ca^{2+} and SO_4^{2-} concentrations compared to control OPC data, indicating that either gypsum dissolution is inhibited or calcium sulphoaluminates are rapidly forming. However, the observation that SO_4^{2-} ions remain in solution after 24 hours hydration suggests production of calcium sulphoaluminates is reduced, probably because hydrated C_3A surfaces, like the calcium silicate cement phases, are also rapidly coated with $Pb(OH)_3^-$ species.

The behaviour of Zn is similar to Pb except it is rapidly resolubilized, hydrolyzed and adsorbed onto solid surfaces. At the pH in the solution chemistry experiments, $Zn(OH)_3^-$ anions are the dominant species. Concentrations of Zn ranged between 1 and 8 $mg.L^{-1}$ in the solution chemistry experiments, and this low concentration suggests they compete very effectively with other anions for available adsorption sites. The severe retardation caused by the Zn waste indicates formation of a very low permeability membrane coating cement particles. No peak in the rate of heat evolution was observed during hydration, and $Ca(OH)_2$ formation was very limited during at least the first 28 days. SO_4^{2-} was removed from solution much more rapidly than during normal cement hydration, and this suggests that the $CaZn_2(OH)_6 . H_2O$ precipitates which are reported to form in Zn doped cement systems not only cover cement grains but also inhibit gypsum dissolution.

Cd was present in both the waste sludge and the cement solidified product as $Cd(OH)_2$. It was not resolubilized and hydrolyzed as observed for Pb and Zn. The major effects of the Cd waste on cement hydration was to increase Q_{max} and increase the initial rate of $Ca(OH)_2$ formation. Cd^{2+} and Ca^{2+} are similar in size, and therefore the $Cd(OH)_2$ probably acts as a nuclei for $Ca(OH)_2$. $Cd(OH)_2$ therefore appears to accelerate hydration during approximately the first 24 hours, although $Ca(OH)_2$ levels in samples hydrated for longer periods are similar to those found in control samples. The interactions of Cd with hydrating cement are very different from those of Zn, despite the reported formation of similar $CaCd_2(OH)_4$ and $CaZn_2(OH)_6 . H_2O$ species on the surface of hydration products (16).

Conclusions

Analysis of solutions extracted from hydrating cement/metal waste systems when combined with data obtained using other techniques has provided useful information on the hydration processes of cement solidified wastes.

Pb was resolubilized from the waste into solution at high concentrations during early hydration. The delayed production of new silicate hydration products caused by the Pb waste was associated with $Pb(OH)_3^-$ adsorption. The Ca^{2+} and SO_4^{2-} concentrations were reduced relative to OPC control data. The Zn waste was rapidly resolubilized and Zn adsorbed onto solid surfaces causing severe inhibition of hydration. SO_4^{2-} was rapidly removed from solution, indicating calcium zincate precipitates affect gypsum dissolution. Cd was present in both the waste and the cement solidified product as $Cd(OH)_2$. It was not detected in solutions extracted during hydration, appears to promote rapid formation of crystalline $Ca(OH)_2$ and therefore behaves very differently from the Pb and Zn containing wastes.

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