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CALCIUM HYDROXIDE FORMATION IN CEMENT-SOLIDIFIED INDUSTRIAL WASTES

R.A. HANNA, C.R. CHEESEMAN*, C.D. HILLS¹, C.J. SOLLARS, P.M. BÜCHLER²
AND R. PERRY

Centre for Environmental Control and Waste Management, Imperial College of Science, Technology and Medicine, London SW7 2BU, UK

¹Present address: Civil Engineering Department, Imperial College of Science, Technology and Medicine, London SW7 2BU, UK.

²Chemical Engineering Dept., São Paulo University, PO Box 61548, Brazil

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ABSTRACT

Differential thermal analysis (DTA) and X-ray diffraction (XRD) were used to compare the formation of calcium hydroxide ($\text{Ca}(\text{OH})_2$) in cement solidified wastes hydrated for different times. Both techniques confirm a decrease in the relative amount of $\text{Ca}(\text{OH})_2$ and an increase in unreacted cement clinker phases in samples containing three different commercially produced industrial wastes. All three wastes induce significant changes to normal cement hydration reactions which increase with increasing waste addition. When metal leaching has been assessed using the TCLP test, the concentration of metals present in leachates are not significantly affected by the amount of waste present in the solidified product. This demonstrates that acceptable results from single extraction batch leach tests such as the TCLP test may not adequately indicate the quality of solidified wastes.

Keywords: solidification, heavy metals, cement hydration, leach testing.

INTRODUCTION

The treatment of heavy metal containing wastes from electroplating, metal finishing and many other industries using cement-based solidification has been widely practised in the US and to a lesser extent in Europe, despite the fact that understanding of the mechanisms involved in the formation of solidified wastes and their long-term performance are not particularly well advanced (1,2). Solidification of industrial wastes using portland cement and other pozzolanic materials represents a relatively cheap and attractive waste management option. Therefore it is important to characterise real cement-solidified waste materials and understand how wastes interact with cement during hydration.

Solidification normally involves mixing pre-treated or stabilised wastes with inorganic binding materials so that hazardous waste components are physically and/or chemically

retained within a monolith (3). A number of different fixation mechanisms operate, some of which depend on pre-treatment of the waste prior to solidification. These may include adsorption, precipitation and incorporation of species into hydrated components of the solidified "system" (4). The solidification additives, the resulting acid neutralisation capacity of the solidified waste and the materials permeability have a key role in determining the retention of waste components during leach testing.

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is formed during normal hydration of the calcium silicate phases (C_3S and C_2S) in cement. Its crystalline form, portlandite, constitutes about 20 to 25% of the weight of a typical well hydrated cement paste. C-S-H gel, the other major hydration product of the calcium silicates, has a Ca:Si ratio of approximately 1, while the ratio in unhydrated cement is typically about 2.5. The excess of Ca which cannot be accommodated in C-S-H precipitates as portlandite. In mature cement

pastes it is characteristically found as massive intergrowths, filling porosity and reducing permeability. The high internal pH of the aqueous phase present in cement pastes of approximately 12.4 results primarily from the solubility of $\text{Ca}(\text{OH})_2$, the C-S-H gel phase and other alkali metal salts (5). This is an important characteristic of cement systems, as the high pH means that many heavy metals present in solidified wastes have low solubility and the high acid neutralisation capacity of the matrix ensures they remain insoluble over extended periods of time. In cement solidified wastes the major acid consuming species is generally considered to be $\text{Ca}(\text{OH})_2$, and this suggests the amount of portlandite may be important in determining long-term leaching behaviour of solidified wastes.

Research concerning solidification has often used synthetic wastes or single compounds added at relatively low levels to form materials which are very different from commercially treated waste products (2). Studies monitoring the heat of hydration of cement solidified metal plating sludges using conduction calorimetry have shown retardation effects resulting from increased waste additions, and reduced amounts of the reaction products normally associated with hydraulic activity (6,7,8,9,10). The aim of this work was to study formation of portlandite in cement-solidified industrial wastes typically treated using this technology.

Very little work has been reported to date on the use of differential thermal analysis (DTA) on cement pastes containing real industrial wastes. DTA determines thermal changes associated with the decomposition of $\text{Ca}(\text{OH})_2$ which normally occurs between around 470 and 540°C. This may also include the small amount of amorphous $\text{Ca}(\text{OH})_2$ reported to be present in cement pastes (11). The limitations of the technique are (12):

- a) interference from free water;
- b) overlapping of dehydration temperatures for different phases;
- c) dehydration temperatures depend on experimental conditions (type of instrument and crucible, sample size, preparation method, heating rate).

Control of test conditions and materials preparation can minimise these effects, and despite these limitations DTA can give reliable results for the total $\text{Ca}(\text{OH})_2$ content in portland cement pastes.

X-ray diffraction (XRD) allows identification of crystalline phases in unhydrated cement and the products of hydration which include portlandite. The intensity of reflections can be affected by the amount of hydration, sample preparation and the operating conditions of the diffractometer (12). In this

study XRD has been used to identify major crystalline phases forming in solidified wastes and to confirm conclusions on $\text{Ca}(\text{OH})_2$ formation derived from thermal analysis techniques.

EXPERIMENTAL

Materials

Three industrial wastes of different chemical compositions were used. These were supplied as filter cakes from:

- a) Borough Plating Ltd., Southend, UK (waste 1)
- b) a commercial solidification plant operating in southern England (waste 2)
- c) Metal Colours Ltd., Slough, UK (waste 3),

Two were metal plating wastes and one (waste 2) was a neutralised mix of wastes from different industries which is commercially treated by cement-based solidification. Ordinary portland cement (OPC) was supplied by Blue Circle Ltd., and deionized water was used in all mixes.

Methods

Wastes were oven dried at 105°C for 24 hours and ground to a particle size of less than 150µm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an ARL 3580B determined the metal content of samples prepared in duplicate by nitric acid digestion (13). pH was measured following a standard method for solids and sediments (14). Total carbon was analysed in a 240C Perkin Elmer Elemental Analyser, using dry combustion of 3-5mg of waste previously decarbonated with HCl. Concentrations of selected anions were determined using standard techniques (13).

Solidified wastes were prepared by pre-mixing dry powders. After addition of water they were vigorously mixed for 3 minutes and cured in sealed vials. Samples were produced containing waste additions of 2, 10 and 30 weight percent of the total mix using a constant water:solids ratio of 0.5. The water content was marginally increased for mixes containing 30% of waste in order to form homogenous pastes. Previous studies have indicated that a 2% waste addition would cause some retardation, 10% severe retardation and 30% complete retardation of the main heat of hydration peak determined using conduction calorimetry (6).

DTA used a Polymer Laboratories STA 1500 furnace, with quartz crucibles. 10mg of sample was heated at 10°Cmin⁻¹ to 800°C in a N₂ atmosphere. Dry burnt alumina was the reference standard. In order to quantitatively

determine the amount of Ca(OH)_2 in samples using DTA, Ca(OH)_2 peak area has been determined for a series of unhydrated cement/synthetic Ca(OH)_2 mixes. This gave a linear relationship, allowing Ca(OH)_2 development with hydration time to be determined. XRD analysis of samples ground to $<150\mu\text{m}$ used a Philips PW 1820 system with $\text{Cu K}\alpha$ radiation at a scanning speed of 1°min^{-1} over 2θ from $8 - 65^\circ$.

Leach testing of solidified wastes was completed using the TCLP test procedure (15) using an aqueous solution of acetic acid as leachant with pH of 2.88, a liquid:solid ratio of 20:1 and an extraction time of 18 hours. Leachates were acidified to 10% HNO_3 (Aristar, BDH) and analysed for 25 metals by ICP-AES.

RESULTS

Waste analysis

Results of waste analysis are shown in Table 1. All three are complex mixtures of

Table 1. Chemical characterisation of wastes

	WASTE 1	WASTE 2	WASTE 3
pH	9.84	7.91	8.58
% carbon	0.5	3.6	3.9
Na	14	161	132
K	1500	58	18
Mg	79	38	59
Ca	2723	2533	557
Sr	1870	3	7
Ba	0.7	2.4	4.6
Al	7	181	5
Ti	0.7	18.0	0.7
Cr	570	157	278
Mn	9.5	27.0	24.2
Fe	36	729	1,630
Ni	518	114	2
Cu	1128	196	4
Zn	16	487	5,770
Cd	0.2	11.0	0.1
Pb	2.6	55.0	2.1
P	15	153	244
Total PO_4	133,200	24,700	152,000
Total NO_3	620	2,080	118
Total SO_4	37	39	4,200
Free CN	<1	380	20,200
Total CN	<1	380	39,300
Cl	142	17,253	48,000
CO_3	81,300	69,100	81,900

Units= mgL^{-1} except pH and % carbon

insoluble metals at the alkali pH's used in the stabilisation process, and contain various anionic species, including high levels of phosphates, nitrates and carbonates. Wastes 2 and 3 had total carbon contents exceeding 3 weight percent and contained particularly high levels of Zn and Fe. Waste 3 contained high levels of CN. Waste 1 contained significant amounts of Cu, Cr and Ni.

XRD data indicated that hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) was the main crystalline component in both metal plating wastes. Calcium carbonate and sodium sulphate were present in all three wastes and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was detected in wastes 1 and 3. Waste 1 also contains some Ca(OH)_2 which is frequently used as a flocculating agent. The commercially stabilised mixed waste contains a significant amount of amorphous material as indicated by a relatively high XRD background level. There was evidence of gypsum and calcite, although corresponding peaks tended to be significantly shifted.

DTA of the three wastes resulted in a broad minimum centred at approximately 110°C

due to evaporation of residual moisture and water of crystallisation. The presence of relatively small amounts of Ca(OH)_2 detected in waste 1 by XRD was confirmed.

Differential Thermal Analysis of solidified wastes

DTA has been completed on cement pastes with a water cement ratio of 0.5, hydrated for 1, 10, 30, 59 and 281 days. All show an endothermic peak centred at just below 400°C attributed to Ca(OH)_2 dehydration. At lower temperatures, a broad endotherm results from the decomposition of other products of hydration such as ettringite, monosulphate, C-S-H gel and residual gypsum. Ettringite and C-S-H decomposition has been identified by other workers at around 135 and 120°C (12), although it was not possible to distinguish these crystalline phases as separate peaks in this DTA data.

Figure 1 shows Ca(OH)_2 formation as a function of hydration time for both the OPC samples and solidified wastes containing 2% of each waste. Ca(OH)_2 content increases during the

first 30 days of hydration, but then appears to decrease to a constant level of approximately 12 weight %. The amount is affected by the type of waste, and is significantly reduced after extended periods of hydration by the presence of wastes 1 and 2, even at this relatively low level of waste addition.

Figure 2 shows the effect on Ca(OH)_2 formation of increasing waste addition to solidified wastes cured for approximately 2 years. As the waste content increases Ca(OH)_2 formation is significantly reduced, with waste 3 clearly demonstrating the greatest inhibiting effect.

XRD of cement solidified wastes

The complex nature of these materials made complete characterisation by XRD difficult. A number of low intensity peaks could not be identified. The effect of adding increasing amounts of each waste on XRD data in samples cured for 30 days is shown in Figure 3. Qualitative analysis indicates:

a) there is a significant increase in the intensity of calcite peaks in all samples containing

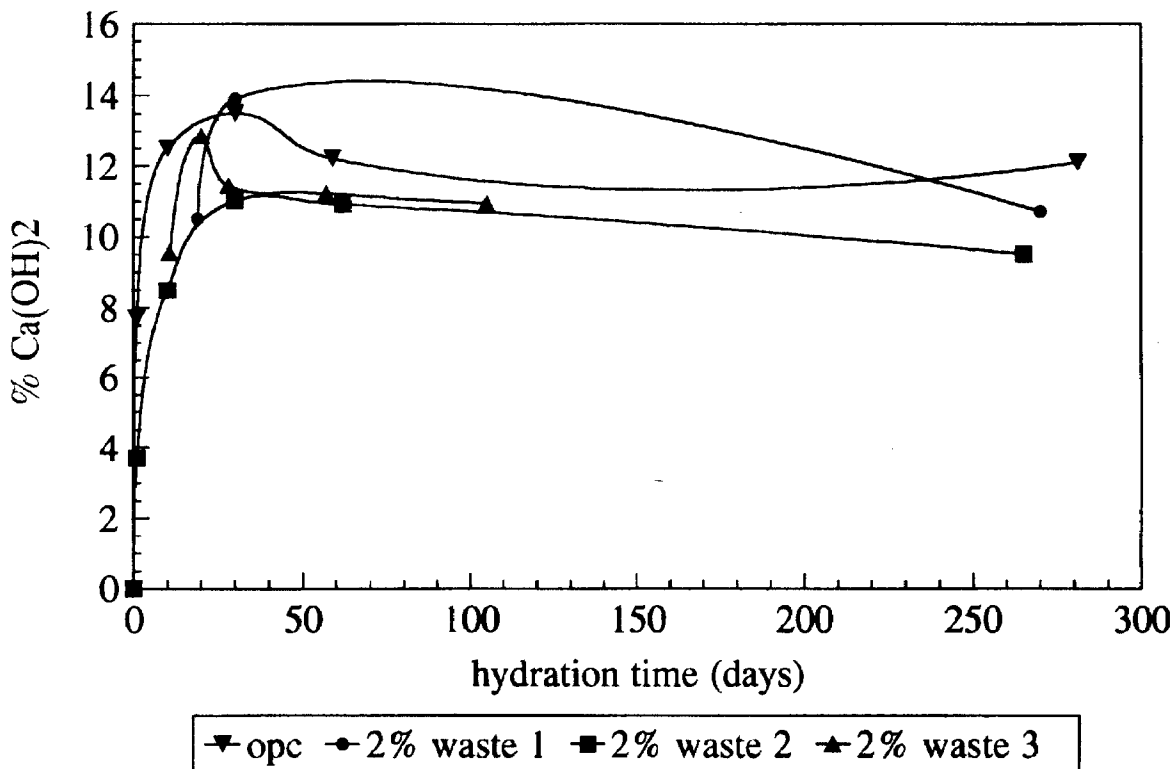


Figure 1. Ca(OH)_2 formation with hydration time for opc and opc +2% waste mixes.

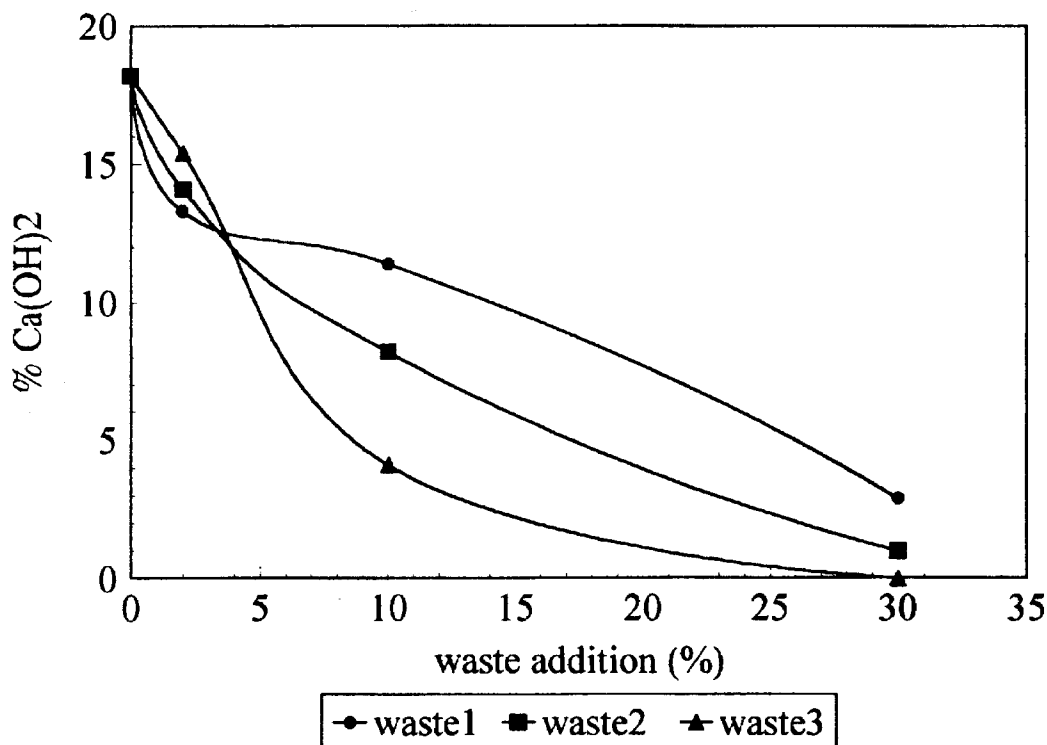


Figure 2. Effect on Ca(OH)_2 formation of increasing waste addition in 2 year old solidified wastes.

wastes;

b) 10% additions of wastes 1 and 2, increase the relative intensity of ettringite, belite and alite peaks. Ca(OH)_2 peaks are present in all samples except those containing waste 3;

c) solidified products containing 30% of wastes 2 and 3 are significantly more amorphous. Ca(OH)_2 peaks have disappeared, whereas the relative intensities of ettringite, belite, alite, gypsum and calcite peaks have all increased.

XRD of solidified waste samples containing 30% of each waste hydrated for 220 days show that the crystalline phases continue to develop between 30 and 220 days. Ca(OH)_2 was present in mixes containing 30% of waste 1 and 2 and 10% of waste 3. Ettringite and calcite were the major crystalline phases, and gypsum peaks present in solidified samples containing wastes 1 and 2 after 30 days were no longer apparent. XRD confirmed the DTA data that Ca(OH)_2 was not present in solidified wastes containing 30% of waste 3, even after hydrating for 220 days.

Leach testing

Compositions of TCLP leachates extracted from 28 day old solidified waste samples containing 2, 10 and 30 weight % of each waste are given in Table 2. Final leachate pH's are consistently around 12, and the

concentrations of metals in solution are generally low, apart from the Cr leached from the solidified waste containing 30% of waste 1. The DTA and XRD data has clearly shown that the degree of cement hydration of the higher waste loaded mixes was severely limited. This therefore demonstrates that normal cement hydration is not a necessary requirement for achieving low metal leaching rates in single extraction batch leach tests such as the TCLP.

DISCUSSION

The complex chemistry and inherent variability in the composition of real waste slurries and filter cakes treated by cement-based solidification means the exact speciation of the heavy metals is not normally known. Solidification should ideally produce a 'concrete-like' material in which insoluble particles containing hazardous components of the original waste are effectively encapsulated within a normally hydrated cementitious matrix. This work using DTA and XRD, and other recent studies using a range of other techniques have demonstrated that the addition of insoluble treatment residues to cement, particularly at the levels used commercially, can seriously inhibit normal cement hydration. Poorly characterised,

- CP = cement paste
 1 : CP + 2% waste 1
 2 : + 10% waste 1
 3 : + 30% waste 1
 4 : + 2% waste 2
 5 : + 10% waste 2
 6 : + 30% waste 2
 7 : + 2% waste 3
 8 : + 10% waste 3
 9 : + 30% waste 3

- A = alite
 B = belite
 C = calcite
 E = ettringite
 G = gypsum
 P = portlandite
 S = sodium sulphate

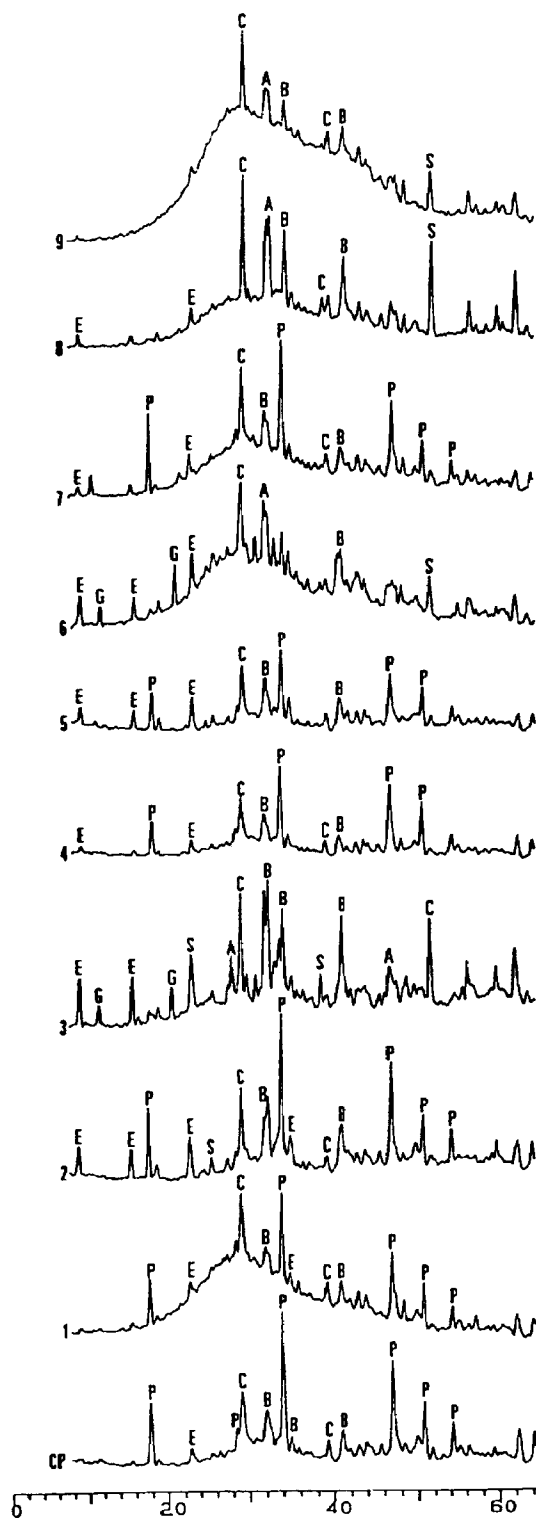


Figure 3. X-ray diffraction data of solidified wastes cured for 30 days

Table 2. TCLP results for solidified wastes

(mgL ⁻¹) waste addition	TCLP limit	cement solidified waste 1			cement solidified waste 2			cement solidified waste 3		
		2%	10%	30%	2%	10%	30%	2%	10%	30%
leachate	-	12.0	11.9	12.1	12.2	11.8	12.1	12.4	12.2	11.7
pH										
Na	-	16.2	15.4	17.4	23.6	63.9	173	23.6	52.2	110
K	-	112	90.2	66.1	100	114	97	114	90	61
Ca	-	1770	1730	2280	1690	1610	2360	1890	1890	1800
Al	-	0.25	0.07	0.07	0.25	0.10	0.05	0.32	0.05	0.05
Cr	5	0.17	0.61	2.35	0.11	0.20	0.99	0.14	1.12	0.99
Mn	-	<0.01	<0.01	<0.01	<DL	<DL	<DL	<DL	<DL	<DL
Fe	-	0.19	<0.01	<0.04	<DL	0.01	0.44	<DL	0.40	0.44
Ni	-	0.02	<0.01	<0.01	<DL	<DL	<DL	<DL	<0.01	0.03
Cu	-	0.34	0.02	0.09	0.34	0.02	0.17	0.02	0.02	0.17
Zn	-	0.03	0.02	<0.01	0.02	0.02	0.12	0.07	0.43	0.12
Cd	1	0.002	0.001	<0.005	<DL	<DL	<DL	<DL	<0.01	<DL
Pb	5	<0.05	<0.05	<0.05	<DL	<DL	<DL	<DL	<DL	<DL

<DL=below detection limit

- concentration limit in TCLP leachate not specified

variable materials with unproven long-term durability are produced (5). The observation that $\text{Ca}(\text{OH})_2$ is sometimes absent from cement-solidified wastes indicates how different these materials are from normal cements and concretes.

The main quality criteria used to assess commercial cement solidified wastes are single extraction batch leach tests such as the TCLP test used in the US. Because of the alkali nature of solidification additives like cement, these tests invariably produce conditions under which most heavy metals remain insoluble. The results indicate that treated waste products are expected to provide adequate retention of hazardous components during subsequent landfill disposal. However it is clear that sole reliance on the results of tests such as the TCLP can result in cement-solidified wastes being disposed to landfill which have variable and often very low degrees of normal cement hydration.

In commercial solidification processes, wastes in the form of sludges, filter cakes, other residues from waste water treatment systems and contaminated soils may be treated, all of which generally contain hazardous components in an insoluble form. On mixing with cement, the insoluble waste particles are exposed to a different chemical environment, and previously insoluble components of the waste may solubilise and reprecipitate on the surfaces of cement grains, thereby interfering with normal hydration reactions. The result is severe

retardation and formation of a rigid but weak, often highly porous material with reduced levels of Ca^{2+} in solution during hydration. As a result $\text{Ca}(\text{OH})_2$ precipitation is reduced, although the material still has an inherently high alkali buffering capacity capable of neutralising acid leachants. The main crystalline phases formed during the hydration of cement in the presence of real industrial wastes in this work were ettringite, gypsum and calcite. XRD and DTA results are in good agreement, and the presence or absence of portlandite was consistently confirmed using both techniques.

CONCLUSIONS

DTA has been used to determine $\text{Ca}(\text{OH})_2$ formation in cement-solidified hazardous wastes after various hydration times. The three wastes studied were 'real wastes,' two from the metal plating industry and the third a stabilised residue produced for commercial solidification by blending wastes produced from a range of different industries. All three interfered with normal cement hydration reactions and significantly reduced the amounts of $\text{Ca}(\text{OH})_2$ forming, even at the relatively low levels of addition used in this work. Waste 3 had the greatest retarding effect and inhibited $\text{Ca}(\text{OH})_2$ formation over extended hydration times. Increasing additions of wastes resulted in larger amounts of unhydrated cement clinker phases and increased formation of ettringite, calcite and gypsum.

TCLP leach testing solidified wastes demonstrated that leachate pH is not dependent on $\text{Ca}(\text{OH})_2$ formation, and that levels of metals leaching may be low even for cement solidified wastes exhibiting significantly retarded hydration. This emphasises the potential difficulties in using the TCLP test as a major indicator of the quality and performance of solidified wastes.

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