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Effect of calcium chloride on the hydration and leaching of lead-retarded cement

C.R. Cheeseman *, S. Asavapisit

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

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Abstract

The effect of adding $CaCl_2$ to ordinary portland cement containing 10% (by weight) of a synthetic lead hydroxide waste has been investigated using differential thermal analysis, conduction calorimetry, and by analysing solutions extracted from mixes during the early stages of hydration. Lead wastes are known to retard initial cement hydration reactions, and for the waste loading used in these experiments the peak in the heat of hydration curve was delayed from 8.7 to 172 h. The addition of $CaCl_2$ reduced this retarding effect but was associated with a decrease in the overall extent of cement hydration, particularly at high $CaCl_2$ concentrations. The acceleration induced is associated with lower concentrations of hydroxyl ions in solution. This reduces dissolution and subsequent adsorption of $Pb(OH)_3^-$ ions onto C-S-H surfaces forming around hydrating cement particles. Samples containing $CaCl_2$ show significantly higher weight loss during leaching in 0.05 N acetic acid solutions. This observation, combined with the overall reduced level of hydration, suggests that addition of $CaCl_2$ does not produce improved materials for disposal.

Keywords: Chloride; Hydration; Lead; Retardation; Waste management

Interactions between metal-containing wastes and ordinary portland cement (OPC) mean that normal cement hydration reactions may not occur in cement solidified wastes, and that both the rate and extent of hydration reactions may change. Previous work has clearly demonstrated that Pb compounds affect cement and that Pb hydroxide wastes significantly retard OPC hydration [1–4]. Metal-induced retardation can limit formation of major cement hydration products and this will affect microstructural and physical properties including metal leaching. Therefore attempts to overcome the retardation effects induced by metals in order to produce materials with improved microstructures may produce solidified wastes with improved waste retention properties.

There are reports in the literature of accelerators being used in some commercial waste solidification processes in the United States to overcome waste-induced retardation of portland cement systems, although the effects of this have not been reported in detail [5]. This work has therefore investigated the effect of adding $CaCl_2$ to cement paste and cement/Pb hydroxide waste mixes. Calcium chloride ($CaCl_2$) is well known to accelerate hydration of C_3S and OPC and these effects have been well documented [6–8].

Conduction calorimetry and differential thermal analysis (DTA) have been used to investigate the changes induced by additions of a synthetic Pb hydroxide waste and $CaCl_2$ on OPC hydration. Conduction calorimetry provides data on the heat produced during the early stages of hydration and DTA determines the amount of $Ca(OH)_2$ formed, which is used to indicate the extent of normal cement hydration. Analysis of solutions extracted from hydrating cements at various times during the hydration process provides data on changing ionic concentrations as a function of time and gives additional information on hydration mechanisms.

1. Experimental

1.1. Materials

OPC used throughout these experiments was supplied by Blue Circle Northfleet, England [British Standard (BS) 12 class 42.5N, equivalent to U.S. Type 1 cement]. Synthetic Pb waste was prepared by adding 10 M NaOH (SLR grade) to 1 M $Pb(NO_3)_2$ solution until the pH reached 9.5 ± 0.1. The hydroxide slurry formed was vacuum filtered (Whatman No. 1, filter paper, Whatman, Maidstone, England) and the filter cake dried overnight at 105°C before being ground to a particle size of <500 μm. The dried synthetic Pb waste was stored prior to use in a sealed bottle. Analysis of this waste

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* Corresponding author. Tel.: 44-71-594-5971; Fax: 44-71-823-9401; E-mail: c.cheeseman@ic.ac.uk.

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has previously been reported [2]. The major crystalline phases believed to be present are lead nitrate hydroxide [$Pb_3(NO_3)(OH)_5$] and lead oxide nitrate hydroxide [$Pb_6O_3(NO_3)_2(OH)_4$] [9]. Other workers have also identified lead oxide nitrate hydroxide and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ as the major crystalline phase formed in similarly prepared sludges [10]. $Pb(OH)_2$ was not detected by X-ray diffraction, implying that if it is formed it must be in a poorly crystalline or amorphous form [8]. The average amount of Pb present in the wastes was 685.1 mg/g of dry sludge.

1.2. Sample preparation

The composition of solidified waste samples prepared in this work are given in Table 1. Reverse osmosis (RO) purified water was used in all the mixes. Cement-solidified wastes containing accelerator were prepared by first dissolving $CaCl_2 \cdot 2H_2O$ in the RO water prior to mixing. Slurries were hand mixed in a plastic beaker to achieve a uniform distribution of metal waste before being transferred to cylindrical plastic moulds that were sealed to avoid the effects of carbonation. All mixes in Table 1 were used for conduction calorimetry and DTA studies, but only mixes with compositions equivalent to mixes five and six have been used for solution chemistry experiments and leaching studies.

1.3. Conduction calorimetry

The conduction calorimeter used in this work was supplied by Wexham Development Ltd., Reading, England [11]. Samples were initially mixed in polythene bags outside the calorimeter until a uniform paste was produced. The bag was then wrapped around the heater disc and placed in conductive oil that acts as a buffer to thermal discontinuities. The sample was positioned on the thermopile sensors fixed at the bottom of the calorimeter, which was then immersed in a water bath controlled to 20 ± 0.1°C. The test was run until the rate of heat evolution had reached a steady-state.

1.4. Differential thermal analysis

The development of $Ca(OH)_2$ in the mixes given in Table 1 were followed using DTA (Polymer Laboratories PL-STA TG/DTA, Epsom, England). In this technique the difference in temperature between the sample and an inert reference material (Al_2O_3) is monitored as a function of temperature. The temperature range used was 20–600°C and was sufficient to completely dehydrate $Ca(OH)_2$, which occurs between 370–430°C. Both the sample and Al_2O_3 were heated at 5°C/min. Dry nitrogen gas that had passed through a silica gel column was supplied into the furnace at a rate of 50 mL/min. DTA samples had a particle size of <150 μm and 15 ± 0.1 mg of sample and Al_2O_3 were weighed into the test crucibles. The area under the DTA peak was calibrated by analysing varying amounts of general purpose reagent (GPR) grade $Ca(OH)_2$ mixed with Al_2O_3 and this gave a linear relationship between the 370–430°C peak area and the amount of $Ca(OH)_2$ in the mix [12].

1.5. Solution chemistry

Solution chemistry studies were completed by mixing 30 g of OPC with 3 g of the synthetic Pb waste and sufficient water was then added to give a water/cement ratio of 3. For the sample containing accelerator, $CaCl_2.H_2O$ was initially dissolved in the RO water before being added to the OPC/Pb waste mix. The amount of $CaCl_2$ added was the same as that used in mix six (0.9 g $CaCl_2$), although the concentration will be different due to the increased water/cement ratio used in these experiments. The slurry was then continually agitated for 72 h for the accelerated mix and 120 h for the OPC/Pb waste mix. All mixing and filtering operations were completed under an N_2 atmosphere to exclude the effects of CO_2 from the experiments, and were completed at least in duplicate. The percentage differences in ionic concentrations between the two runs were less than 5% and the concentrations presented are the average values. After each mixing time solutions were separated by vacuum filtration through a Whatman No. 1 filter paper and analysed for OH^- concentration by titration against standardised HCl using phenolphthalein indicator, metals by ICP-AES (ARL 3580, Applied Research Laboratories, Ecublens, Switzerland), and SO_4^{2-} and Cl^- ions by ion chromatography (Waters IC-Pak A Column Borate/Gluconate eluent, method #GABG-101, Massachusetts, USA).

1.6. Leach testing

A static leach test was completed on mixes five and six by suspending cylindrical samples in a plastic net in 0.05 N acetic acid solution at a leachant volume to sample surface area ratio of 20:1. The initial pH of the acetic acid leachant was 3.15 and the initial weight and dimensions of each sam-

Table 1
OPC and OPC synthetic Pb waste mixes containing different $CaCl_2$ additions

	Mix no.	OPC (g)	Pb waste (g)	$CaC1_2$ (g)	Water (g)	OPC:waste:$CaCl_2$
OPC	1	30	0	0	15.00	100:0:0
	2	30	0	0.9	15.16	100:0:3
	3	30	0	1.5	15.26	100:0:5
	4	30	0	3.0	15.53	100:0:10
OPC/Pb	5	30	3	0	16.50	100:10:0
	6	30	3	0.9	16.66	100:10:3
	7	30	3	1.5	16.76	100:10:5
	8	30	3	3.0	17.03	100:10:10

ple were recorded. A similar static leaching test procedure has previously been used to investigate leaching from solidified wastes [13].

Individual samples were leached for 1, 7, 14, 28, or 56 days without renewing the leachant during the leaching period. Leachates were then filtered through a 0.45 μm cellulose nitrate filter paper and the pH determined prior to acidification to 10% HNO_3 (Aristar, BDH, Poole, England) for metal analysis by ICP-AES. Tests were completed in duplicate to confirm the reproducibility of data. Leached samples were then dried in air and reweighed.

2. Results

2.1. Heat of hydration

The rate of heat evolution data is shown in Fig. 1, and the conduction calorimetry data for all mixes is summarised in Table 2, where Q_{max} is defined as the maximum rate of heat evolution. The effect of $CaCl_2$ additions on OPC hydration was to significantly reduce the time required to achieve maximum heat liberation (mixes one to four). For OPC hydration this was 8.7 h but this reduced to 4, 3.2, and 2.3 h, respectively, in the presence of increasing concentrations of $CaCl_2$. The accelerator also caused the maximum rate of heat liberated to increase from 2.17 to 5.45 and 9.97 W/kg, although in mix four it was reduced to 9.0 W/kg. The approximate amount of total heat evolved during the test to the time when a steady state was achieved initially increased from 290.6 to 334.2 kJ/kg when $CaCl_2$ was added. However, further additions decreased the total heat evolved to 305.5 and 275.8 kJ/kg, respectively.

The effect of Pb addition to OPC is seen in mix five that was severely retarded compared to mix one. The retardation effect was reduced by the addition of $CaCl_2$ as the time required to achieve Q_{max} decreased from 172 h in mix five to

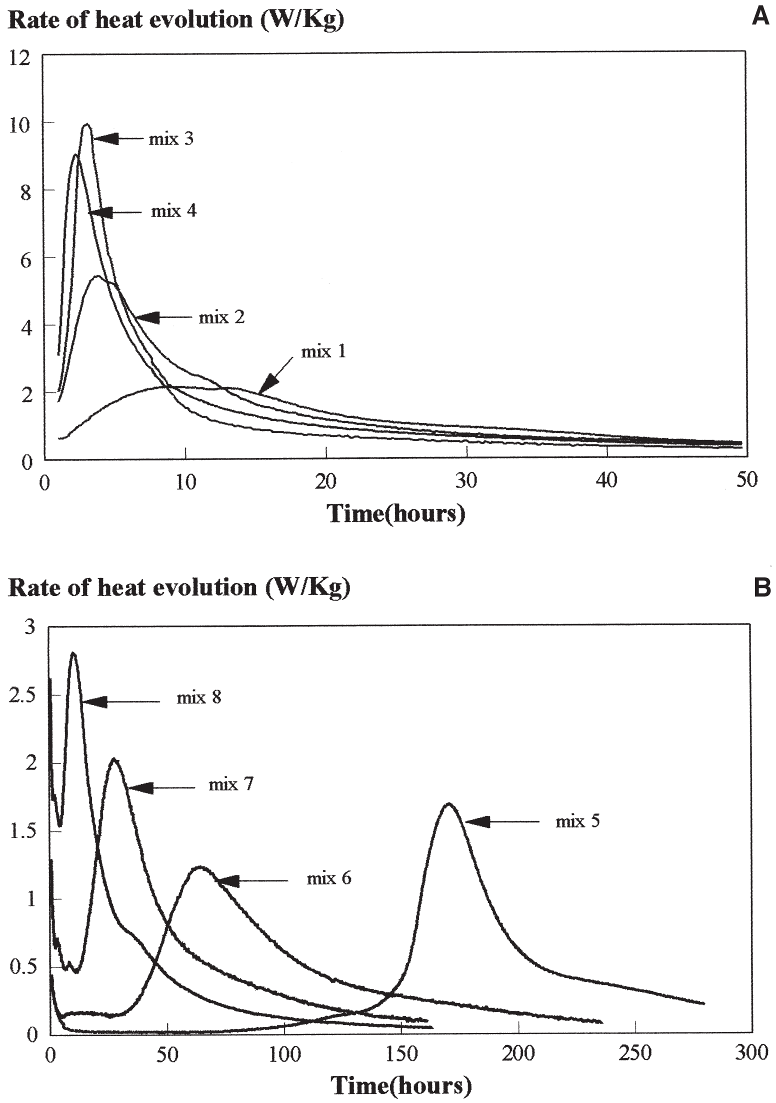

Fig. 1. Rate of heat evolution data for *(A)* OPC and *(B)* OPC/Pb waste mixes containing different amounts of $CaCl_2$.

Table 2
Conduction calorimetry data for OPC and OPC/Pb waste samples containing increasing additions of $CaCl_2$

	Mix no.	Maximum rate of heat evolution $- Q_{max}$ (W/kg)	Time of maximum rate of heat evolution (h)	Total heat evolved to steady state (kJ/kg)
OPC	1	2.17	8.7	290.6
	2	5.45	4.0	334.2
	3	9.97	3.2	305.5
	4	9.05	2.3	275.8
OPC/Pb	5	1.69	172.0	349.4
	6	1.24	64.3	345.8
	7	2.04	28.5	335.7
	8	2.82	11.2	302.8

64.3, 28.5, and 11.2 h in mixes six, seven, and eight, respectively. The maximum rates of heat evolution were not as high as those liberated from OPC/$CaCl_2$ mixes. The approximate total heat evolved during the test decreased with increasing amounts of $CaCl_2$ in the OPC/Pb mixes, although the maximum rate of heat evolution was greater for higher concentrations of $CaCl_2$, as observed for the OPC/$CaCl_2$ samples.

2.2. $Ca(OH)_2$ formation

Development of $Ca(OH)_2$ in OPC/heavy metal waste/ $CaCl_2$ mixes is shown in Fig. 2. In the OPC samples containing $CaCl_2$, the level of $Ca(OH)_2$ formed in mixes two and three was similar to that in mix one. The addition of higher levels of $CaCl_2$ limited development of $Ca(OH)_2$ as demonstrated by mix four, where the extent of $Ca(OH)_2$ formation was significantly lower than for other mixes.

Addition of $CaCl_2$ significantly reduced the retardation effects on $Ca(OH)_2$ formation caused by the Pb waste (Fig. 2). In mix five, which contained no $CaCl_2$, significant development of $Ca(OH)_2$ was delayed by up to 7 days. $Ca(OH)_2$ formation occurred during the first day in mix eight, whereas it took 3 days to produce approximately 5% of $Ca(OH)_2$ in mixes six and seven. Although $Ca(OH)_2$ was rapidly formed in mix eight, the amount existing at later stages was lower than for other mixes.

2.3. Ionic concentrations during hydration

Typical ionic concentrations of Pb^{2+}, OH^-, Ca^{2+}, Cl^-, and SO_4^{2-} ions in solutions extracted from OPC/Pb mixes with and without additions of $CaCl_2$ after various mixing times from tests completed at least in duplicate are shown in Fig. 3. The Pb^{2+} is initially present in solution at around 2.5 mM but rapidly increases in concentration to reach a peak between 24 and 96 h for OPC/Pb and at around 48 h for the OPC/Pb/$CaCl_2$ mix. The Pb^{2+} concentration then rapidly falls. For the OPC/Pb mix the Pb^{2+} concentration reached approximately 10 mM after 24 h hydration but had fallen to 5 mM after 96 h of hydration. For the OPC/Pb/$CaCl_2$ mixes the maximum Pb^{2+} concentration measured was approximately 15 mM.

Hydroxyl ions show a similar increase in concentration with hydration time, although the levels are somewhat lower in solutions extracted from the mix containing $CaCl_2$. A peak concentration occurs after about 48 h for both mixes. The pH varied from 11.7 to 12.3 for the mixes containing $CaCl_2$ and from 12.6 to 13.3 for the mix without accelerator during the hydration period monitored.

The concentration of Ca^{2+} ions initially present in the OPC/Pb waste slurry at approximately 25 mM remained constant during the first few hours, gradually increased to 37 mM at 24 h, but then reduced to approximately 12 mM after 120 h. The Ca^{2+} concentrations were much higher in the samples containing accelerator due to the rapid dissolution of the $CaCl_2$, and reached a maximum of 157 mM after 48 h before falling sharply to 113 mM after 72 h.

SO_4^{2-} variations were similar in both mixes and steadily declined from around 30 mM to zero during the hydration period examined. The concentration of Cl^- ions in solution extracted from the sample containing accelerator remained fairly constant throughout the hydration period examined at approximately 155 mM. Therefore it seems likely that most of the chloride remains in the pore water of $CaCl_2$ containing OPC/Pb waste mixes.

2.4. Static leach test results

The changes in pH of the 0.05 N acetic acid solution during the leaching period were very similar for samples either with or without accelerator, and gradually increased from an initial value of 3.2 until it had reached approximately 11 after 14 days. Under these high pH conditions the solubility of Pb is relatively low and therefore the concentration of Pb in solution is low and leaching is minimal. However during the leaching period high weight loss occurred for both samples, as shown in Fig. 4, although much greater weight loss occurred for mix six samples containing $CaCl_2$ accelerator.

3. Discussion

Conduction calorimetry and DTA have been used to investigate the accelerating effect of $CaCl_2$ on the hydration of OPC and OPC/Pb waste mixes. The addition of $CaCl_2$ to OPC results in an earlier and higher peak in the rate of heat

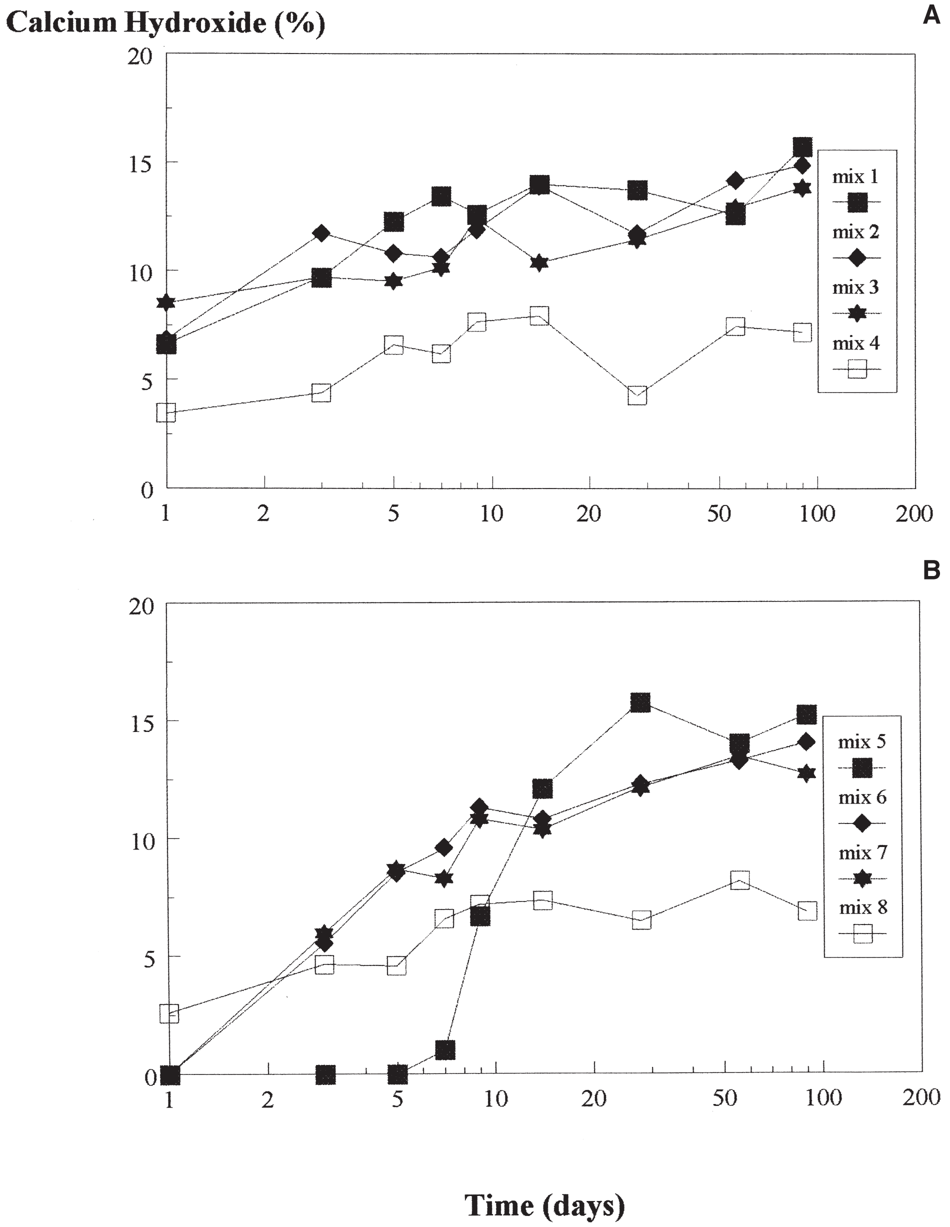

Fig. 2. DTA data showing development of $Ca(OH)_2$ in the presence of $CaCl_2$. *(A)* OPC and *(B)* OPC/Pb mixes.

evolution. The amount of $Ca(OH)_2$ formation was not significantly changed by the addition of $CaCl_2$ until the level reached that in mix four, when its formation was significantly reduced.

The addition of the Pb waste significantly retarded the OPC hydration but both experimental techniques have indicated that $CaCl_2$ accelerates hydration of the OPC/Pb waste mix. The maximum rate of heat evolution occurs at much earlier times for all the mixes containing $CaCl_2$ and $Ca(OH)_2$ formation is increased. However, the total amount of hydration determined either from the total heat evolved or the total amount of $Ca(OH)_2$ formed during the entire hydration period examined decreases at the higher additions of $CaCl_2$ examined.

The $CaCl_2$ addition results in very high concentrations of Ca^{2+}, and reduced OH^- concentrations during hydration [7]. The amphoteric nature of Pb^{2+} means this probably causes reduced dissolution from the hydroxide waste due to the lower pH environment, and therefore lower concentrations of $Pb(OH)_3^-$ are available to adsorb onto C-S-H coatings formed around hydrating cement clinker particles. The surfaces of cement particles will be negatively charged during cement hydration and they are therefore able to adsorb metal cations [14]. The Ca^{2+} ions therefore coat the silicate surfaces forming a high density Ca^{2+} layer [15]. Anionic species compete for adsorption sites on this positively charged layer, forming a bilayer. The reduction in $Pb(OH)_3^-$

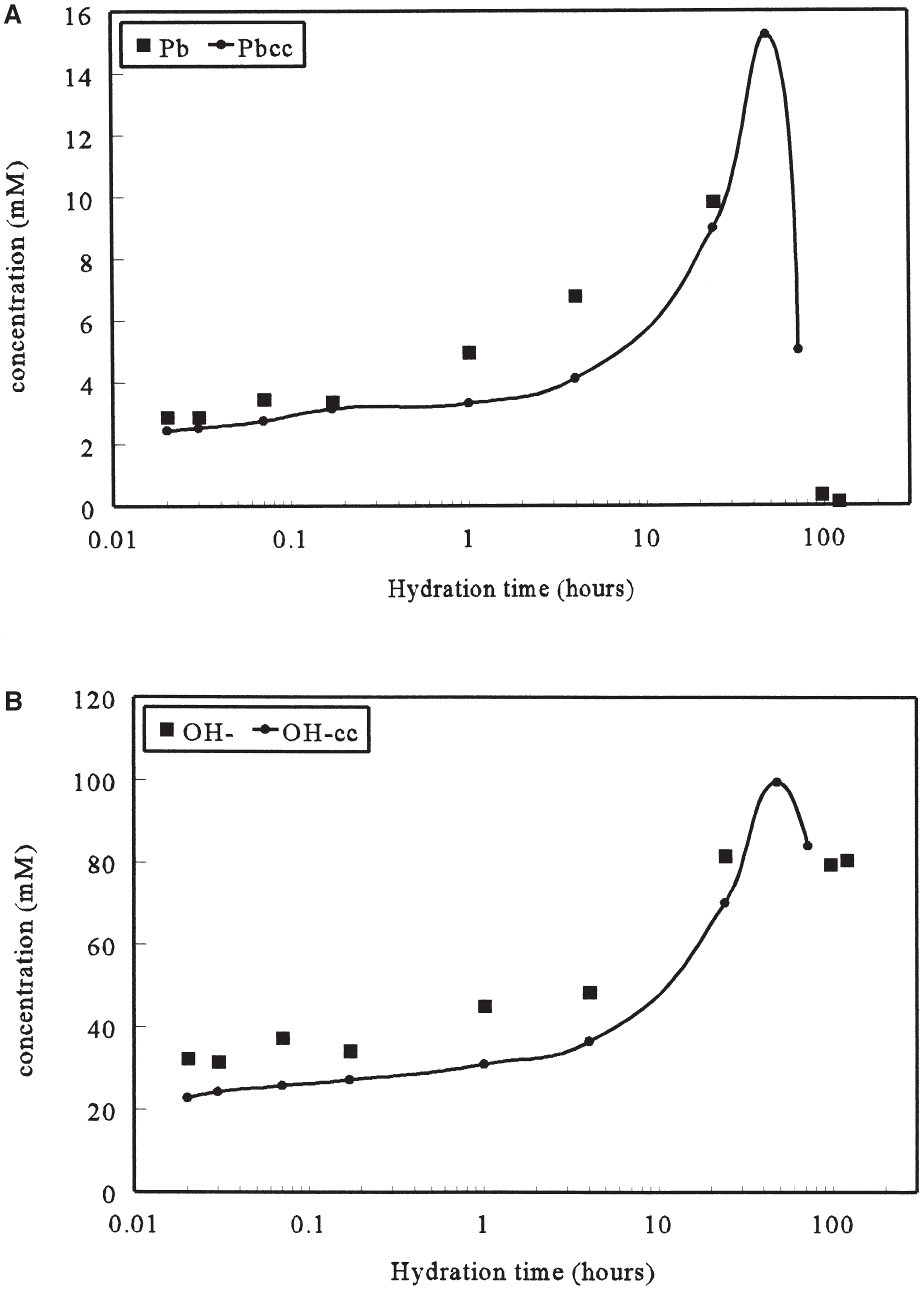

Fig. 3. Ionic concentrations in solutions separated from OPC/Pb waste (30:3) and OPC/Pb containing $CaCl_2$ (cc) at an OPC:Pb:$CaCl_2$ ratio = 30:3:0:9. *(A)* Pb, *(B)* OH^-, *(C)* Ca, and *(D)* SO_4^{2-} and Cl^-.

concentration in solutions extracted from samples containing $CaCl_2$ may result in increased permeability of the surface coating so that the retardation effect caused by the Pb waste is reduced. Concentrations of Pb, present in the form of $Pb(OH)_3^-$, and hydroxyl ions peak after about 48 h hydration. The reduction in concentration is probably associated with the onset of the formation of new silicate surfaces.

The static leach test data shows that samples containing $CaCl_2$ had reduced ability to resist acetic acid attack compared to samples with no added accelerator, as demonstrated by the increased weight loss during leaching. This observation combined with the reduction in the overall extent of hydration resulting from the addition of $CaCl_2$ to cement retarded by metal containing wastes means that this process modification is unlikely to produce improved solidified waste materials for disposal.

4. Conclusions

The addition of $CaCl_2$ was found to reduce retardation of OPC hydration caused by a 10% weight addition of a Pb-hydroxide waste. Although the effect of $CaCl_2$ is to acceler-

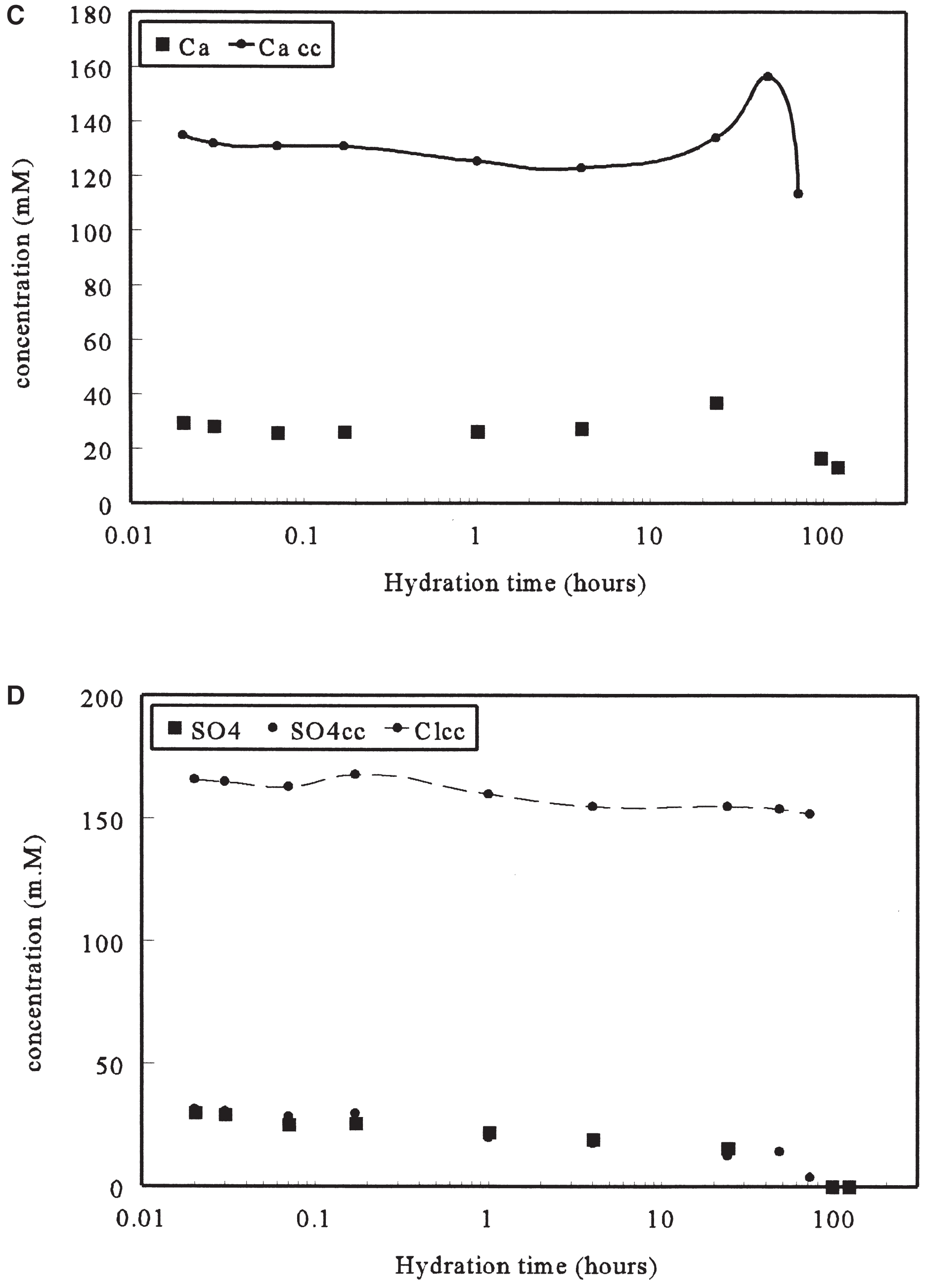

Fig. 3. (*continued*).

ate the early stages of hydration, both conduction calorimetry and DTA data show that $CaCl_2$ decreases the total extent of hydration. The effect of the accelerator is to increase $Ca(OH)_2$ formation and this reduces the hydroxyl ion concentration and solution pH during early hydration. As a result it is probable that reduced dissolution of the Pb-hydroxide waste occurs and less $Pb(OH)_2$ is available to adsorb onto C-S-H surfaces forming around hydrating cement clinker phases. The addition of $CaCl_2$ is associated with increased sample weight loss during leaching in a 0.05 N acetic acid solution.

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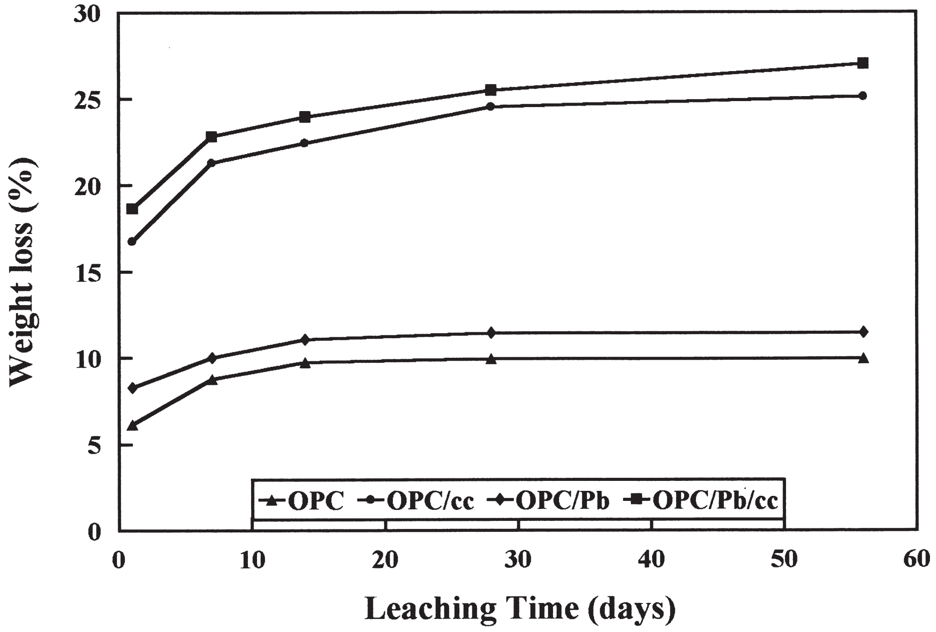

Fig. 4. Sample weight loss during static leach testing in 0.05 N acetic acid.

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