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Effect of calcite on lead-rich cementitious solid waste forms

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Abstract

The effect of calcite on lead-rich solidified waste forms generated using Portland cement has been investigated. Samples of cementitious wastes in the absence and presence of Pb and in the absence and presence of calcite were examined separately at 2, 7, 14 and 28 days of hydration by X-ray diffraction and SEM/EDS and for compressive strength. The presence of lead was observed to produce lead carbonate sulfate hydroxide ($Pb_4SO_4(CO_3)_2(OH)_2$), lead carbonate hydroxide hydrate ($3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$) and two other unidentified lead salts in cavity areas, and was observed to significantly retard the hydration of cement. Calcite addition to the Pb wastes was found to induce the rapid crystallization of calcium hydroxide coincident with the onset of C–S–H gel germination. The rapid dissolution of lead precipitates was observed with the subsequent development of very insoluble gel products of the form C–Pb–S–H. These products are formed by chemical incorporation of re-dissolved Pb species into silicate structures.

Keywords: Cement; $CaCO_3$; Lead; X-ray diffraction; SEM

1. Introduction

Cement has been used worldwide for the solidification and stabilization (S/S) of hazardous and radioactive wastes. Cement-based solidification creates solidified waste forms (SWF), which have the physical and chemical properties of the cementing materials [1]. Since the alkalinity of cementitious materials greatly reduces the solubility of many hazardous inorganics, their use prevents pollutants from migrating into the environment by rendering the toxic contaminants physically immobile and chemically bound to the encapsulating solid [2–4]. Portland cement is one of most common S/S agents, in part because of its ability to set and harden under water (a hydraulic cement) [5,6].

The chemistry of cement, especially when combined with hazardous wastes, has been considered a “black box” due to the complexity of the system and inadequacy of analytical tools [7]. Indeed, the mechanism of hydration is still a very active and controversial area with the lack of understanding of such basic processes limiting development of S/S technology.

The presence of lead in wastes has been found to lower the rate of strength development in solid waste forms when cement is used for S/S purposes. Preliminary studies have revealed that addition of calcite to cement enhances strength development in the S/S of Pb wastes. The major objective of the present study is to illuminate the mechanism of the effect of calcite on the S/S of Pb wastes in the presence of Portland cement. The ‘fate’ of Pb wastes and calcite in the early stages of “setting” are investigated by SEM and by analysis of the cement–water solution. In addition, X-ray diffraction is used for the identification of mineral transformations occurring during the setting process.

2. Materials and methods

2.1. Materials

Cement used was purchased as normal Portland cement from Sangyong Cement in Korea. The cement has the following mineralogical composition: (i) 41.7% of trical-

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cium silicate (Ca_3SiO_5/C_3S), (ii) 27.9% of dicalcium silicate (Ca_2SiO_4/C_2S), (iii) 12.7% of tricalcium aluminate ($Ca_3Al_2O_6/C_3A$), (iv) 9.4% of calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}/C_4AF$) and (v) 2.9% of calcium sulfate ($CaSO_4 \cdot 2H_2O$).

Calcite used was of high grade crystalline form ($\geq$95.0% $CaCO_3$) with $\leq$4.0% $MgCO_3$ and $\leq$1.5% acid insolubles content. Its specific gravity was 2.7 and its BET specific surface area was 5.2 m^2/g. It was ground such that it exhibited an average diameter (D_{50}) of 1.8 μm, maximum particle size of 8 μm and residue on a 20 μm screen of <0.005%.

The wastes were prepared from lead nitrate, which precipitated to form hydroxide sludge on adjusting the pH to 8.5 with 6.0 N sodium hydroxide and then dried at 104 °C for 24 h. The major crystalline phases present were identified by X-ray diffraction and found to principally be lead nitrate hydroxide [$Pb_2(NO_3)(OH)_3$] and lead oxide nitrate hydroxide [$Pb_6O_3(NO_3)_2(OH)_4$]. The formation of these minerals is consistent with the results of Asavapisit et al. [8] and Gress and El-Korchi [9].

Varying ratios of dry Pb waste and cement were mixed with water at a water/solid (cement, calcite and Pb wastes) ratio (W/S) of 0.3. After thorough mixing, the samples were introduced into polyethylene cylindrical moulds measuring 20 mm diameter×40 mm height and removed after 24 h. The curing was carried out in humid air at 20 °C for 2, 7, 14 and 28 days for each sample, respectively. Samples were prepared in triplicate and are denoted KC*i*Pb*j*, where *i* is the calcite content and *j* is the Pb-doped waste content.

2.2. Methods

Unconfined compressive strength (UCS) testing was undertaken on the samples using an Instron testing machine. The top and bottom of the samples were capped with masonite to limit the effect of cracking. Load was increased until cracks began to appear. The compressive strength was calculated as the applied load divided by the cross-sectional area.

X-ray diffraction (XRD) was used to identify and quantify the crystalline mineral phases present in the SWF. The mineralogical composition of the samples was analyzed using Cu K_α radiation at 35 V and 25 mA on a Philips 1830 XRD diffractometer. XRD scans were obtained using 0.04° steps with 2 s counting time. Difftect 5.0 software and JCPDS diffraction files by JCPDS International Center for Diffraction Data were used for identifying mineral forms of SWF.

Scanning electron microscope (SEM) images were obtained using a Hitachi 4500 SEM fitted with electron dispersive spectroscopy (EDS). Samples for SEM analysis were cured for 28 days and then dried at 104 °C for 24 h. The dried solid samples were carefully fractured and coated with carbon to prevent electronic charging effects during the SEM analysis.

For solution analysis of cement slurries, cement slurries with a W/S ratio of 2 were prepared and the concentrations of ions in aqueous solutions of these cement slurries were measured as a function of time up to 30 min after slurry preparation. The slurry solutions were filtered with fine grade Whatman No. 50 filter papers prior to analysis of the filtrate by a variety of methods. All experiments were carried out at an ambient temperature of 22±2 °C. The analytical methods used are as follows:

(i) Ca, Al, Fe, Pb, K, Mg and Si were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). All samples were acidified using nitric acid and diluted for the analyses according to the detection limits suggested in Standard Methods (1995). Silicon was separately analyzed because silica easily precipitates in acidic solutions.

(ii) SO_4^{2-} was determined using a standard turbidimetric method (APHA, 1995) in which barium chloride ($BaCl_2$) was added with resultant barium sulfate precipitation. Any suspended matter present was removed by filtration prior to turbidimetric analysis since the presence of suspended matter in large amounts will interfere.

(iii) CO_3^{2-} content was determined by measuring the phenolphthalein alkalinity (P) and total alkalinity (T) in the range of $P>1/2T$ (pH above 12.5) ($[CO_3^{2-}]=2(T-P)$).

3. Results

3.1. Effect of calcite on the UCS of Pb-rich solidified waste forms

The results of UCS measurements on cementitious wastes in the absence and presence of Pb and in the absence and presence of calcite over 28 days of curing time are shown in Fig. 1. While regular OPC attains a compressive strength of over 6000 N/cm^2 within 7 days of curing and approximately 9000 N/cm^2 after 28 days of curing, lead contaminated material has almost no compressive strength at 7 days and only 2000 N/cm^2 after 28 days. Addition of 5% calcite is observed to partially rectify this poor strength development behavior with a UCS of almost 2000 N/cm^2 at 7 days and over 6000 N/cm^2 at 28 days. Strength development in OPC to which 5% calcite has been added is observed to be slightly superior to that of regular OPC.

3.2. X-ray diffraction analysis of solid waste form

3.2.1. Absence of calcite

In the absence of any significant proportions of added lead or calcite, it is clear from Fig. 2 that OPC rapidly hydrates with clear evidence of the diminution of OPC constituents (C_3S, C_2S, C_3A and C_4AF) and of the high formation of portlandite ($Ca(OH)_2$) and probably C–S–H gel after only 2 days of curing. Strong crystalline versions of hydrated products, which are unidentified, are observed at 2θ values of 44.6°, 65.0° and 78.1° after 7 to 14 days of curing.

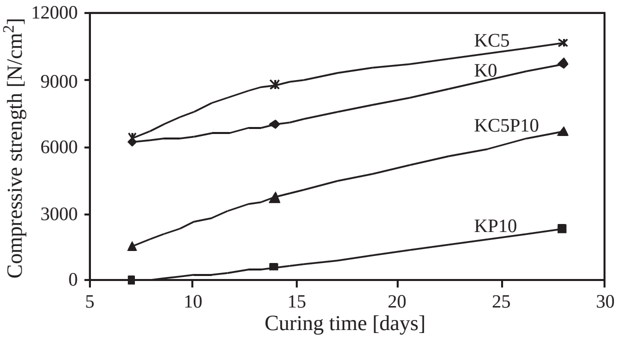
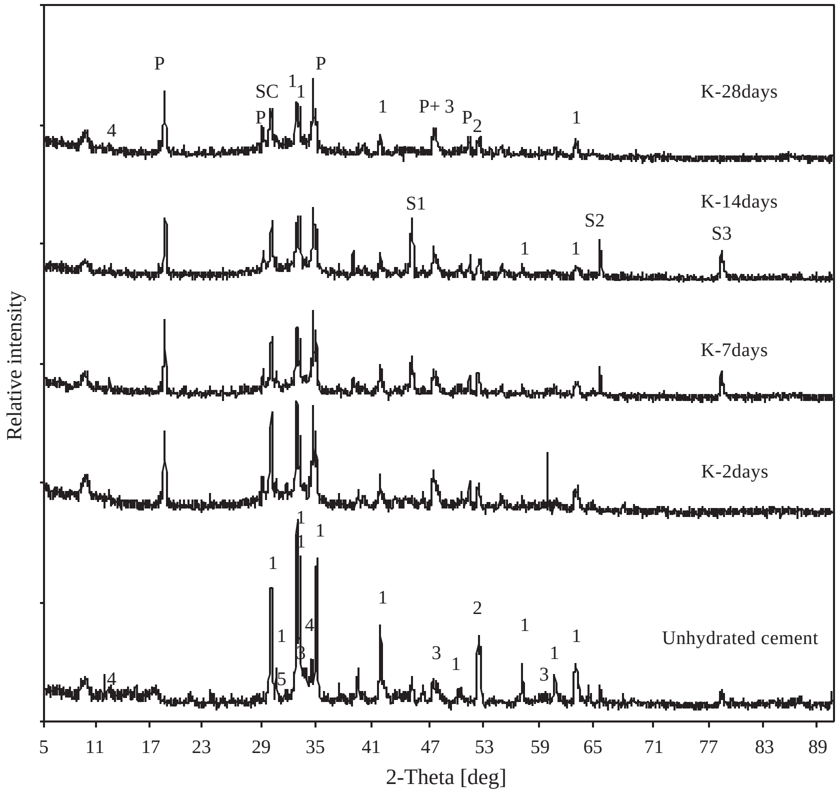


Fig. 1. Effect of lead and calcite additives on unconfined compressive strength development in ordinary Portland cement. (K0—OPC, KC5—OPC+5% calcite, KP10—OPC+10% Pb solids, KC5P10—OPC+5% calcite+10% Pb solids).

As can be seen from Fig. 3, the presence of lead appears to induce considerable retardation in the curing process with C_3S, C_2S, C_3A and C_4AF little changed from that present in the unhydrated cement even after 14 days. There is very little evidence of the presence of hydration products other than a little portlandite at 14 days curing time.

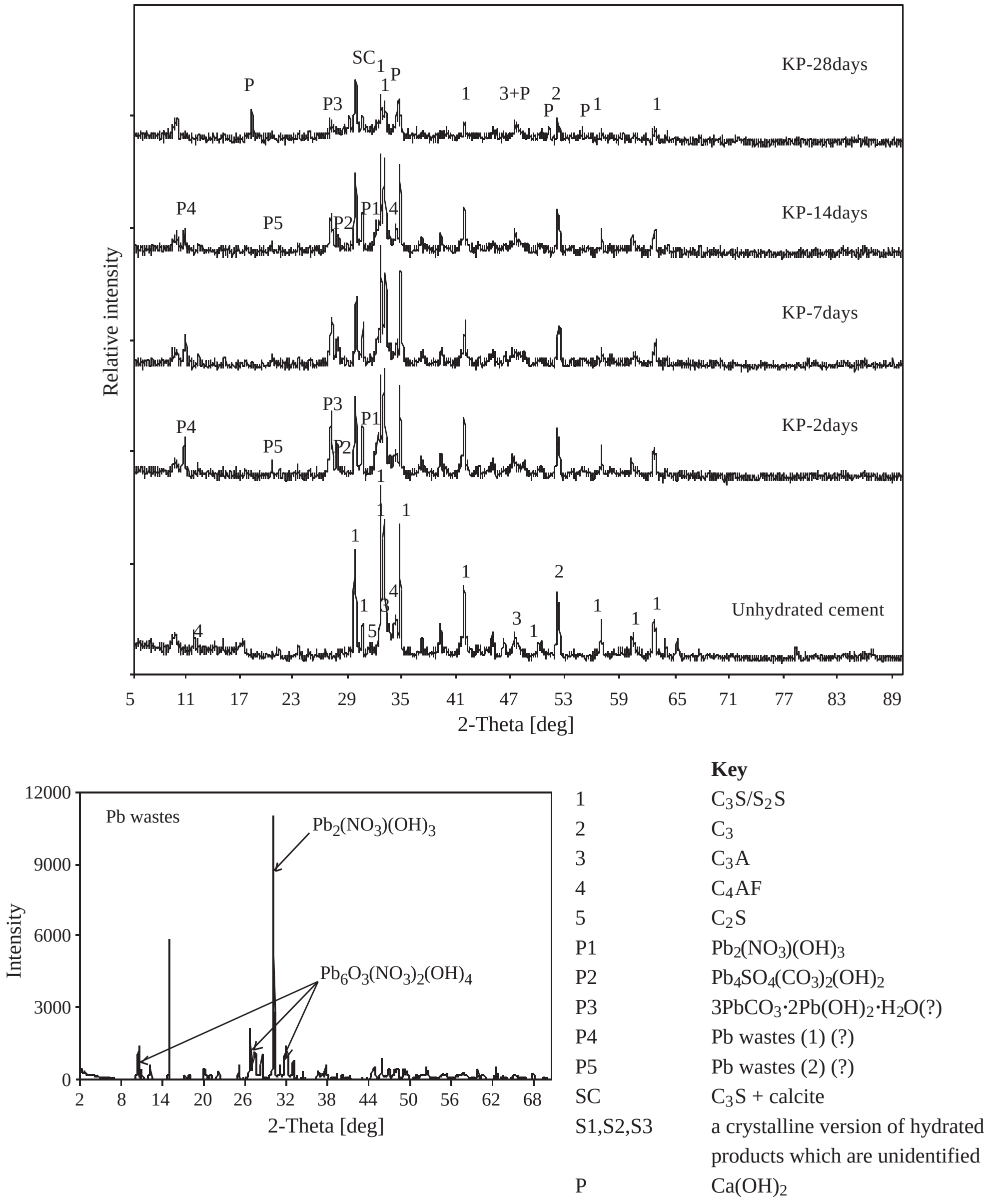
The XRD signature of the precipitated lead salt present in the initial synthetic waste ($Pb_2(NO_3)(OH)_3$) is evident in the cemented solid as are a number of secondary precipitates presumably as a result of interaction of solubilised lead with sulfate derived from the OPC and carbonate anions from the atmosphere. In particular, there is evidence for the presence of lead carbonate sulfate hydroxide [$Pb_4SO_4(CO_3)_2(OH)_2$, JCPDS file no. 38-354], lead carbonate hydroxide hydrate [$3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$, JCPDS file no. 9-356] and two other unidentified lead salts (P4 and P5) (Fig. 3). From the diffraction studies, there is no evidence of $Pb(OH)_2$, cerussite ($PbCO_3$), hydrocerussite ($Pb(CO_3)_2(OH)_2$) or anglesite ($PbSO_4$) in substantially crystalline form.

The peaks of the five precipitated lead salts (P1–P5) in KP10 maintain a reasonably high albeit diminishing intensity over the first 14 days of curing. By 28 days, however, the XRD peaks of P2, P4 and P5 lead compounds



	Key
1	C_3S/C_2S
2	C_3S
3	C_3A
4	C_4AF
5	C_2S
SC	C_3S + calcite
S1, S2, S3	a crystalline version of hydrated products which are unidentified.
P	$Ca(OH)_2$

Fig. 2. X-ray diffraction patterns of K0 samples up to 28 days of curing.



Key

1	C_3S/S_2S
2	C_3
3	C_3A
4	C_4AF
5	C_2S
P1	$Pb_2(NO_3)(OH)_3$
P2	$Pb_4SO_4(CO_3)_2(OH)_2$
P3	$3PbCO_3{\cdot}2Pb(OH)_2{\cdot}H_2O$(?)
P4	Pb wastes (1) (?)
P5	Pb wastes (2) (?)
SC	C_3S + calcite
S1,S2,S3	a crystalline version of hydrated products which are unidentified
P	$Ca(OH)_2$

Fig. 3. X-ray diffraction patterns of KP10 samples up to 28 days of curing.

have essentially disappeared with only residual traces of P1 and P3 evident. After 28 days of curing, hydration appears well advanced with C_3S, C_2S and C_3A peaks markedly decreased and a strong portlandite peak present though C–S–H gel peaks are not particularly evident.

3.2.2. Presence of calcite

It is clear from Fig. 4 that calcite addition accelerates the onset of hydration compared to that in wastes containing lead. Crystalline peaks of S1, S2 and S3, which did not appear even after 14 days of curing in the presence of lead alone, are now evident after only 7 days of curing. As in the case of K0, these peaks are no longer evident at 28 days. The individual clinker components C_3S, C_2S, C_3A and C_4AF have essentially vanished after 14 days of curing. Portlandite (P) appears a little more slowly than in K0, but, by 28 days, is identified as a very sharp, strong XRD signal.

The peaks indicative of the precipitation of lead secondary products (P2–P4) have almost disappeared by 14 days. As can be seen from Fig. 5, there is some evidence for the formation of calcium lead silicate sulfate hydroxide [Roeblingite, JCPDS file no. 18-292] at 2θ values of 30.3°, 31.1°, 29.8° and 29.1° after 28 days of curing.

3.3. SEM and EDS analysis

SEM images and electron dispersive X-ray spectra of the solid matrix of KP10 and KC5P10 at 7 days of curing are shown in Figs. 6 and 7. An obvious difference in the images of the two samples is the appearance of white deposits in KC5P10. The results of higher resolution analysis shown in

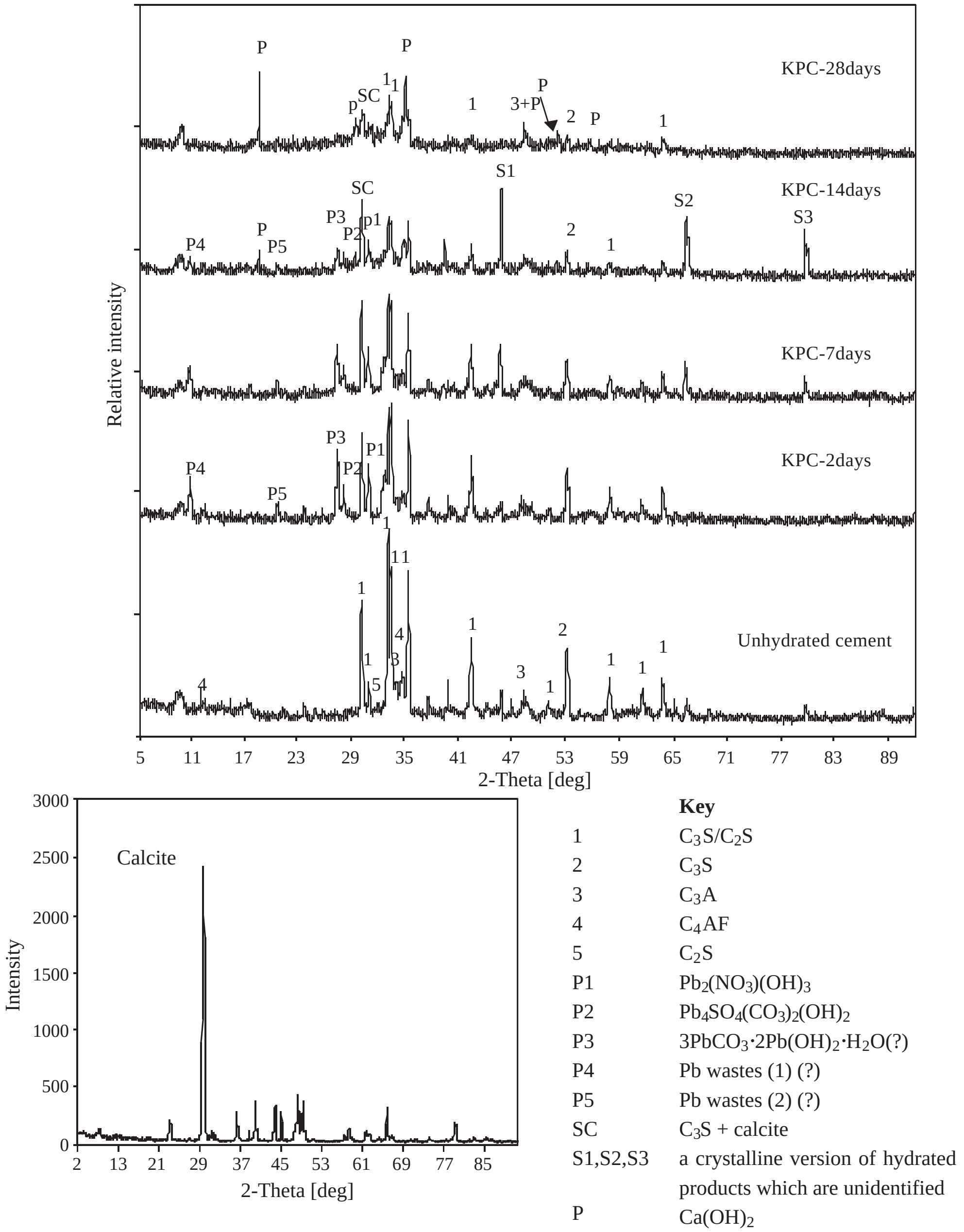


Fig. 4. X-ray diffraction patterns of KC5P10 samples up to 28 days of curing.

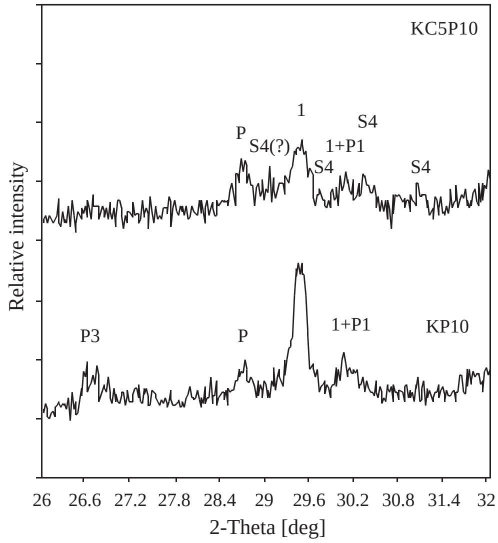
Fig. 8 indicate that white deposits contain C–S–H components and possess a large quantity of lead and sulfate with a little aluminate. At 28 days of curing time, micrographs of KP10 show germination of developed C–S–H gel including high Pb and sulfate. The behaviour of lead-rich waste solidified with OPC is further clarified in the microscopic images and EDS results for solids containing 20% lead in the absence and presence of 10% calcite shown in Figs. 9 and 10, respectively. In the absence of calcite, large accumulations of precipitated lead solid rich in sulfate are evident. These lead precipitates are consistent with the P3 X-ray diffraction peak remaining in KP10 at 28 days of curing time. In comparison, calcium-rich "coral-like" deposits are evident in the calcite-doped case with strong evidence of C–S–H formation.

3.4. Solution chemistry of cement–water systems

The variations in ionic concentration of solutions extracted from each sample over the 30 min after mixing at W/S=2 are shown in Fig. 11 and Table 1.

3.4.1. OH^-

The OH^- concentration rises very sharply in the K0 and KC5 cases (Fig. 11a and b, respectively). For K0, the pH of the solution exceeds 12.9 within the first few seconds and a similar result is evident for KC5. The average OH^- concentration in the Pb-rich waste (KP10) is somewhat reduced compared to samples without Pb and may reflect the lowered rate of hydration of clinker components in this



Key

1	C_3S/C_2S
P1	$Pb_2(NO_3)(OH)_3$
P3	$3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$(?)
S4	Calcium lead silicate sulfate hydroxide
P	$Ca(OH)_2$

Fig. 5. Comparison of XRD patterns of KP10 and KC5P10 at 28 days of curing time in the 2θ range of 26–32°.

sample. Interestingly, despite the apparent ability of calcite to minimize the Pb-induced inhibition of hydration, the solution pH observed for KC5P10 is similar to the Pb-rich sample to which calcite was not added (KP10) [10].

3.4.2. Pb

The solution concentration of lead for both KP10 and KC5P10 is initially around 10^{-2} M suggesting that solid lead precipitates present in the waste (mainly $Pb_2(NO_3)(OH)_3$) partially dissolve on mixing with the clinker slurry. There then follows a rapid decrease in solution concentration in lead, presumably reflecting the formation of secondary precipitates. The concentration of lead in solutions resulting from KP10 and KC5P10 (after 30 min of equilibration) is relatively similar at 2.4 and 3.0 mM, respectively, though with a slightly higher concentration resulting from the sample to which calcite was added.

3.4.3. Ca^{2+}

The calcium concentration in solutions in contact with solids to which calcite was added is higher than non-calcite samples.

3.4.4. SO_4^{2-}

Higher concentrations of sulfate are observed in solutions contacting Pb-doped samples compared to un-doped samples.

3.4.5. CO_3^{2-}

Higher concentrations of carbonate are observed in solutions contacting Pb-doped samples compared to the un-doped samples regardless of the presence of calcite.

3.4.6. K^+

The K^+ concentration in solutions resulting from samples to which Pb was added are lower than that in un-doped samples. The result of K concentrations higher in non Pb-doped samples is consistent with the result in ionic concentrations of cement slurry by Thomas et al. [11].

4. Discussion

4.1. Fixation mechanisms of lead in cement-based solidified forms

Solidification/stabilization processes are able to produce solids that are non-hazardous or less hazardous than the original waste, and to prevent pollutants from migrating into the environment [2]. The non- or less hazardous effect of S/S for hazardous substances is achieved by making the toxic contaminants physically immobile and/or chemically bound to the binding agents present [12]. However, heavy metals

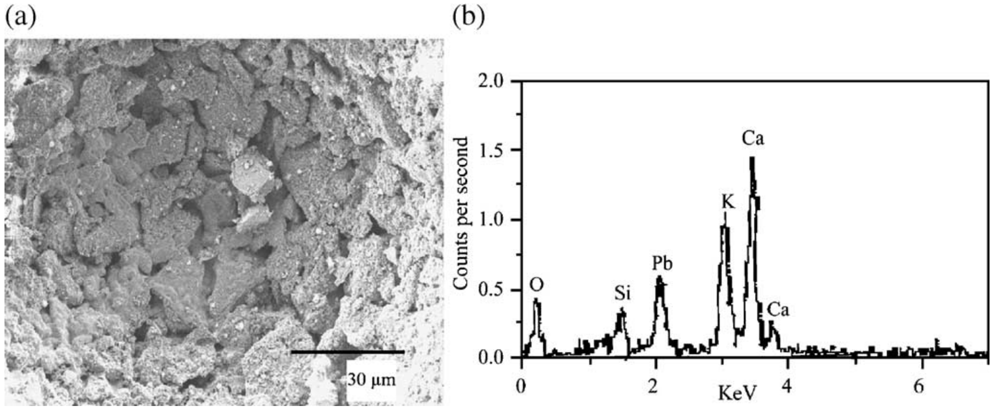


Fig. 6. (a) Microscopic image and (b) elemental analysis of KP10 at 7 days.

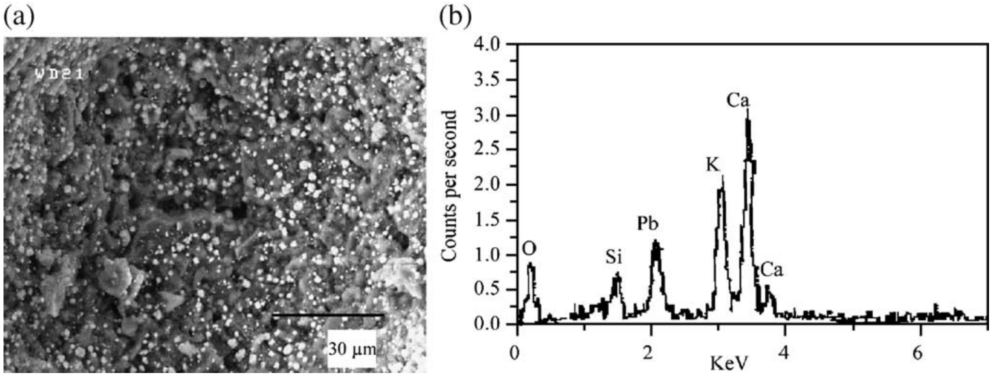


Fig. 7. (a) Microscopic image and (b) elemental analysis of KC5P10 at 7 days.

in the cement-based S/S process (which has generally been considered to be a suitable process for managing such wastes) may, at times, exhibit (or induce) specific interactions between the waste and the binding agent which limit the fixation process. In addition, the effect of additional binding agents, which may be added in order to rectify specific limitations in the fixation of heavy metals, is an area of research in which many challenges remain not least because of the extreme complexity of the heterogeneous systems of interest.

4.1.1. *'Fate' of lead wastes on the cement-based S/S*

Lead, one of the priority metallic pollutants, has been found to hinder the S/S process due to the retarding effect it induces [2,7,11,13]. Lead ions (Pb^{2+}) released from lead precipitates such as $Pb_2(NO_3)(OH)_3$ and $Pb_6O_3(NO_3)_2(OH)_4$ may form polynuclear species such as $Pb_6O(OH)_6^{4+}$ at the high pH (of 12–13) approached in cement–water solution [7]. The pH is especially important for the behaviour of lead as it exhibits amphoteric properties and is highly soluble both at low and high pH with maximum insolubility shown in the pH range of 7.5–10 [2]. In view of this, the solubility of lead in the early cement hydration period may actually be higher than that in the original Pb wastes and the possibility exists that a portion of the Pb wastes may rapidly dissolve in the initial stages of cement hydration.

The lead hydroxy-cations derived from the original Pb solids can adsorb to silicate surfaces and/or precipitate as sulfate or carbonate compounds. Results of the present study indicate that the Pb concentration in the cement solution sharply decreases to approximately 600 mg/l within 2 min. A likely explanation for this effect may be that the original Pb wastes rapidly convert to secondary precipitates through dissolution and re-precipitation processes in the early hydration of cement.

4.1.2. *Lead precipitates in the cavity areas*

Based upon the XRD investigation of lead enriched solidified samples, precipitates of lead carbonate sulfate hydroxide ($Pb_4SO_4(CO_3)_2(OH)_2$), lead carbonate hydroxide hydrate ($3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$) and two other unidentified lead salts (P4 and P5) are found in cavity areas (Fig. 3).

Large accumulations of lead precipitates rich in sulfate are found in the large cavity area (120 μm×120 μm) by electron microscopy and energy dispersive X-ray analysis (Fig. 9a and b). These precipitates are encapsulated in the cavity by the cement-solidified materials. However, as pH in the cement pore waters undergoes fluctuations during the progress of hydration, the Pb salts undergo solubilization and reprecipitation periodically [11,13]. Pb salts (P1–P5) undergo a very slow dissolution over 14 days of curing but have essentially disappeared after 28 days. These Pb solids located in the cavity areas are readily accessible to leach water and would

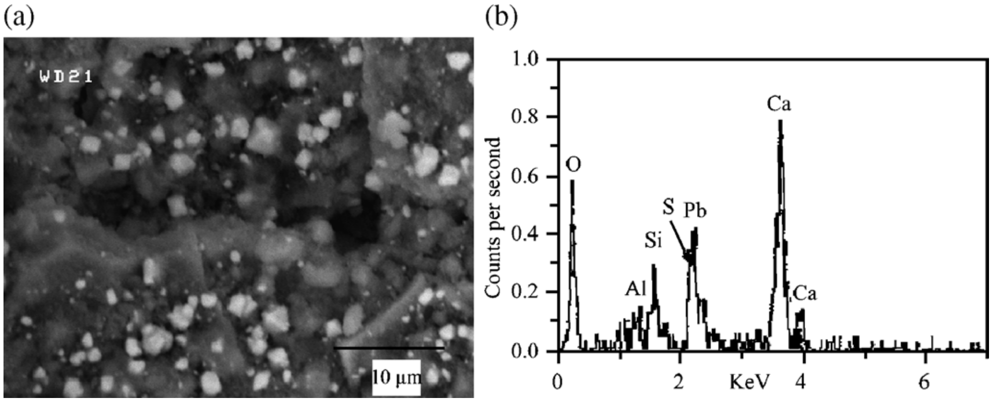


Fig. 8. (a) Higher resolution image of KC5P10 at 7 days and (b) elemental analysis of only white disposals shown in (a).

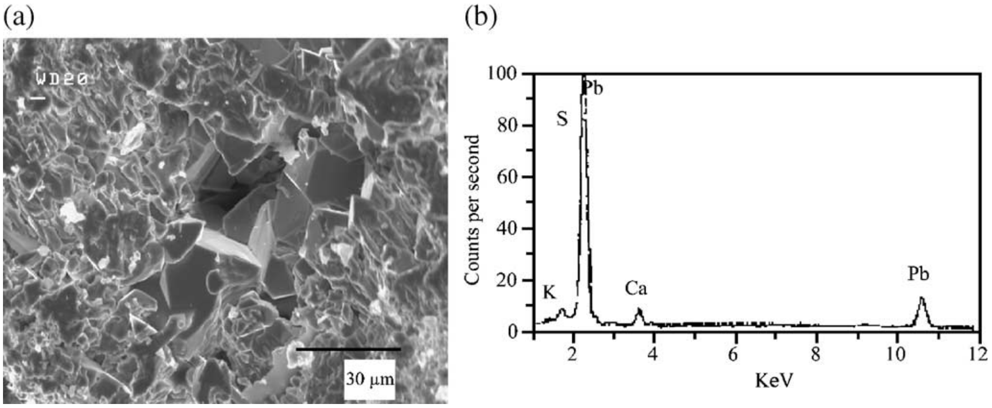


Fig. 9. (a) Microscopic image and (b) elemental analysis of lead precipitates in the cavities of KP20.

be expected to dissolve under both strongly acidic conditions as well as under strongly basic conditions [13].

4.1.3. Membrane formation and retarding effect of lead species

A significant finding of this study is the preferential deposition of lead both as lead precipitates in the cavity areas and as a membrane of impervious coating of lead species around cement clinker grains in the early stages of curing. These are consistent with the arguments of Cote [1] and Parapar et al. [14], respectively. In the latter stage of lead deposition, the membrane of lead species around the cement clinker grains prevents the hydration by encapsulating some of the calcium silicate phases in the clinker. Thomas et al. [11] found that as little as 0.15 wt.% of the Pb admixture can induce a retardation effect in solidification by slowing the hydration process. The presence of the membrane formed by lead species significantly weakens the cement-solidified forms physically as shown by the UCS (Fig. 1). There is clear evidence for the retarding effect of lead in that the intensities of the XRD peaks of the main clinker components C_3S, C_2S, C_3A and C_4AF are not reduced, portlandite is not produced and there is little reduction in the intermediate lead precipitates (P1–P5) till 14 days of curing.

Cement–water solution concentrations of calcium and sulfate in samples without Pb (K0) suddenly decrease in the first few minutes as a result of formation of calcium sulfoaluminate (ettringite) (Thomas et al., 1981). The rapid decrease in concentration of these ions is not apparent however in samples containing Pb (KP10) due presumably to the retardation in clinker dissolution by the Pb-rich membranes that form around clinker components.

At 28 days, most XRD peaks of lead secondary precipitates (P1–P5) almost disappear with only minor peaks of P1 and P3 evident. There is evidence for the development of hydration at 28 days with C_3S, C_2S and C_3A peaks markedly decreased though any specific peaks of C–S–H are not apparent (possibly because of its XRD amorphous nature). It is argued that the coating around clinker components by lead compounds retards the dissolution of all cement components. C_4AF is generally considered most resistant to hydration and peaks still remain at 14 days though its dissolution is essentially complete by 28 days.

4.1.4. Fixation model on the cement-based S/S of lead wastes

From the findings of this study, the following model for the fixation mechanism of lead in the cement-based S/S

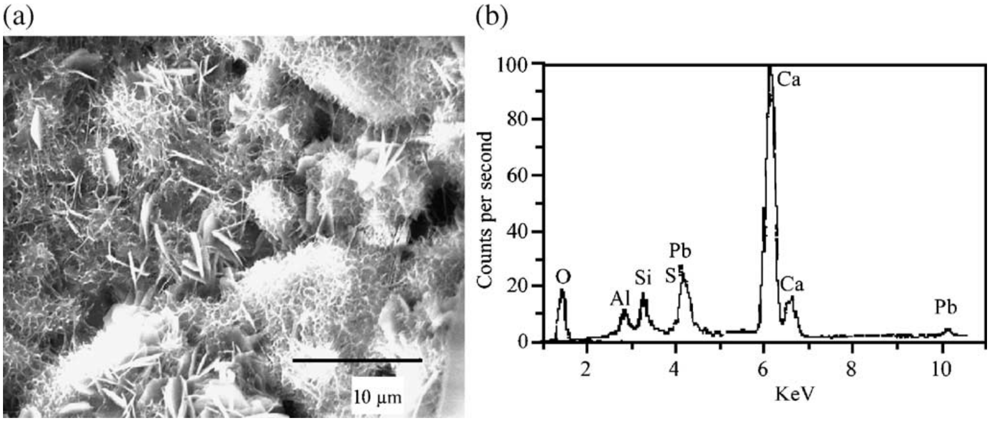


Fig. 10. (a) Microscopic image and (b) elemental analysis of crystalline C–Pb–S–H in the cavities of KC10P20.

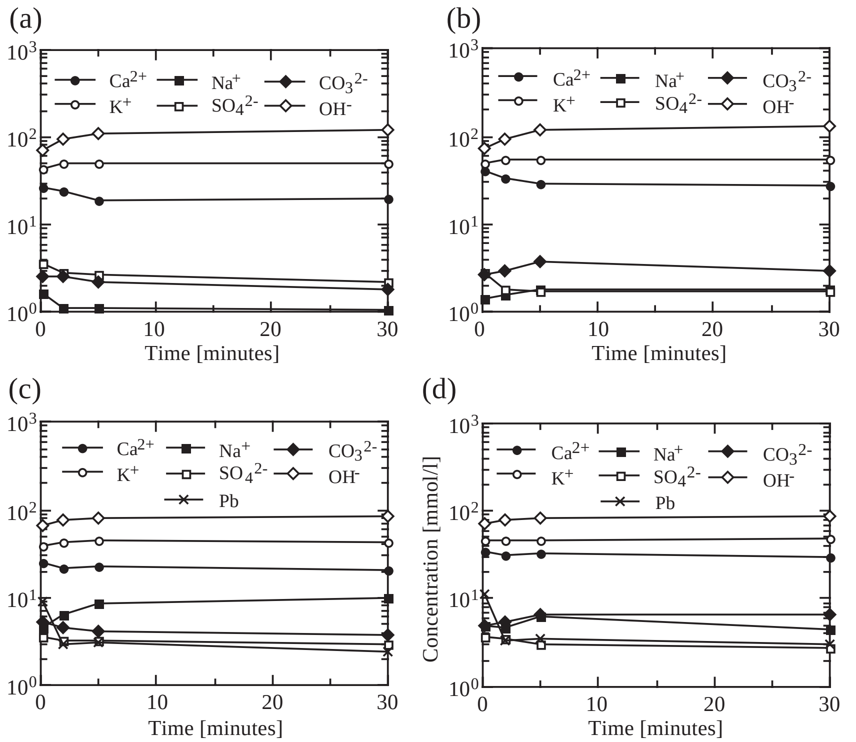


Fig. 11. Equivalent curve of ionic concentration for cement–water solution filtered from (a) K0, (b) KC5, (c) KP10 and (d) KC5P10.

appears reasonable. The original Pb wastes dissolve very rapidly in the highly alkaline environment of cement and produce extremely insoluble precipitates such as lead carbonate hydroxide and lead sulfate carbonate hydroxide (P1–P5). Lead species also coat the clinker components, preventing their hydration for long periods. At the same time, as hydration is not completely prevented by the coating of Pb species, diffusion processes through the coating are still active at a reduced rate [7,12]. As a result, an excess of portlandite will accumulate on the fluid side of the membrane particularly after 14 days as shown in the XRD investigation on Pb enriched solidified material. Precipitation of portlandite will induce a marked differential ionic strength on either side of the membrane with a resultant buildup in osmotic pressure. This pressure will induce rupture of the membrane with a subsequent normalization in ionic composition [12,15]. The membrane will then reform and the process of osmotic pressure buildup will begin again.

The time of periodical rupture of the membrane depends on the properties of the cement components. Precipitation processes to fix lead compounds occur within a narrow zone between the solutions at high degrees of supersaturation [16]. It is also likely that the silicate-rich pore water within the membrane will induce the formation of fresh Pb

Table 1
Ionic concentration (mM) of cement–water solution

	Time	Ca	K	SO_4^{2-}	CO_3^{2-}	OH^-	Pb	pH
KO	10 s	27.3	43.5	3.6	2.6	70.8	0.0	12.85
	2 min	24.0	49.4	2.9	2.6	93.3	0.0	12.97
	5 min	19.3	49.9	2.7	2.2	112.2	0.0	13.05
	30 min	19.6	50.6	2.2	1.8	120.2	0.0	13.08
KC5	10 s	41.4	50.4	2.8	2.7	72.4	0.0	12.86
	2 min	32.9	55.0	1.8	2.9	95.5	0.0	12.98
	5 min	29.7	55.2	1.7	3.7	117.5	0.0	13.07
	30 min	27.4	53.5	1.7	2.9	128.8	0.0	13.11
KP10	10 s	24.9	39.6	3.5	5.2	67.6	9.2	12.83
	2 min	22.0	42.7	3.3	4.5	77.6	3.0	12.89
	5 min	22.6	45.0	3.2	4.0	79.4	3.1	12.9
	30 min	20.2	43.2	2.9	3.7	83.2	2.4	12.92
KC5P10	10 s	34.4	45.5	3.6	5.0	70.8	11.5	12.85
	2 min	31.9	47.3	3.5	5.3	79.4	3.3	12.9
	5 min	32.4	46.5	3.0	6.5	83.2	3.5	12.92
	30 min	29.9	48.3	2.8	6.7	87.1	3.0	12.94

precipitates from Pb acquired from the transient P1–P5 species. It is expected that solids of the general form calcium lead silicate hydrate (C–Pb–S–H) will accumulate.

Both micrographs and chemical composition of the C–Pb–S–H gel were identified by SEM/EDS as shown in Fig. 12. Bhatty [17] has argued that the lead is fixed into the cement matrix, forming a metallic calcium silicate hydrate during cement-based solidification. Some investigators found the metal hydroxide simply encapsulated in a silica matrix that prevents its removal except by destroying the matrix [2,18]. Lead solidified in this way is leached at rates that are much below those that would be predicted based on the solubility of lead hydroxides. Conner [2] has argued that lead is strongly bound in the hydrated product matrix, at least in cement-based systems. Cocke [7] gave evidence that binding energies of lead ions are consistent with silicate, carbonate or hydroxide compounds by XPS.

4.2. S/S mechanism of calcite in Pb-doped solidified forms

4.2.1. Increase of calcium ions in the cement–water system

The accelerating effect induced by the addition of calcite also induces a marked increase in calcium and carbonate concentrations in the cement–water solution. The calcium ions are normally derived from the dissolution of C_3S and C_3A through Eqs. (1) and (2) below and from the dissolution of gypsum.

$$3CaO \cdot SiO_2 + H_2O \leftrightarrow 3Ca^{2+} + SiO_4^{4-} + 2OH^-, \mathrm{Log}K_{sp} = 0.47 \tag{1}$$

$$3CaO \cdot Al_2O_3 + 6H_2O \leftrightarrow 3Ca^{2+} + 2Al(OH)_4^- + 4OH^-, \mathrm{Log}K_{sp} = 10.6 \tag{2}$$

Calcium ions would begin to be removed earlier from the cement–water solution in the presence of calcite and would enhance further dissolution of calcium ions [19]. There would therefore be a higher concentration gradient for migration of calcium ions through the hydration membrane that engulfs the cement particles. The same observation in the presence of calcite could be indicated on the S/S of Pb wastes as well as on the hydration of cement without Pb wastes. This is evidence of the accelerating effect induced by the addition of calcite. Carbonate ions in the cement–water solution are derived from CO_2 in air. Samples with calcite (KC5P10) make a stronger concentration of carbonate ions because calcite not only accelerates the hydration of C_3S, but a certain percentage of calcite is consumed in the first day in this process [20]. Cocke [7] also suggested the enhanced presence of carbonate in the doped samples of Pb and Cr wastes. Higher concentration of carbonate in the doped samples was investigated compared to the un-doped samples regardless of the presence of calcite as shown in Fig. 11c and d.

4.2.2. The action of calcite in the fixation of lead

As shown in the solution chemistry of cement, the presence of calcite enhances further dissolution of C_3S resulting in higher concentrations of Ca^{2+}, silicate, carbonate and hydroxide in the cement solution. It also induces a stronger outward migration of these ions on the fluid side of the membrane formed by Pb species. The membrane/osmosis model has suggested that the removal of Ca^{2+} and OH^- from solution by portlandite precipitation increase the osmotic driving force and hence promotes membrane rupture [16]. At the early stage of hydration, calcite addition induces the rapid crystallization of calcium hydroxide coincident with the onset of C–S–H gel germination.

As a result, calcite addition induces more rapid dissolution of lead precipitates (P1–P5) with the development of early hydration compared to those in SWF without calcite (KP10). The presence of calcite also increases the rate of formation of portlandite in accord with the increasing rate of C_3S hydration at 14 days, and clinker components are markedly decreased according to curing time due to the marked development of hydration. C_3A peaks in particular almost disappear at 14 days and most of the C_4AF peaks decrease significantly. It is likely that the presence of calcite increases the rate of hydration of C_3A/C_4AF as well as C_3S/C_2S on the S/S of Pb wastes. At 28 days, SWF to which calcite had been added produce peaks of portlandite of similar intensity to those in normal cement hydrated sample (K0). Calcite addition induces the development of very

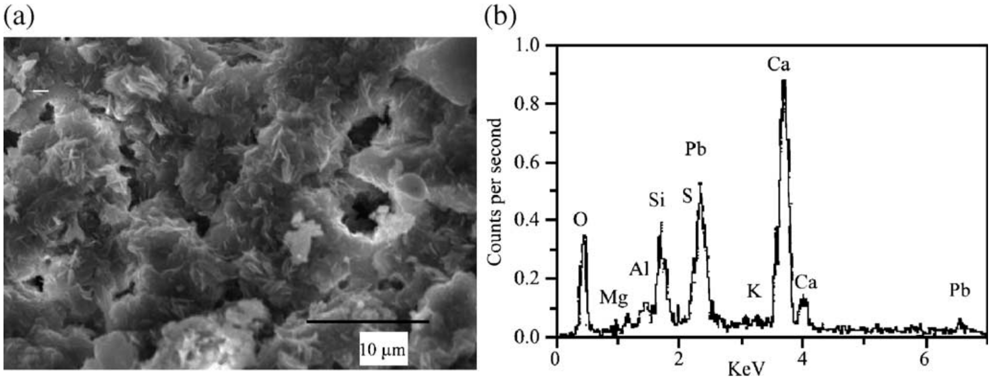


Fig. 12. (a) Microscopic image and (b) elemental analysis of KP10 at 28 days curing.

insoluble products by chemical incorporation of re-dissolved Pb species forms such as calcium lead silicate and calcium lead silicate sulfate hydroxide over extended times.

4.2.3. Crystallinity of C–Pb–S–H on calcite addition

In the early stages of hydration (7 days), lead ions dissolved from lead salts produce white deposits with high calcium and silicate including sulfate and aluminates (Fig. 8). The presence of calcite in the S/S of Pb wastes promotes re-crystallization of the hydrated products involving Pb ions as well as the accelerated dissolution of C_3S.

The addition of calcite induces an acceleration in hydration, even in the 20% lead-doped materials. The presence of calcite enhances the further development of C–S–H and portlandite with the rapid rupture of the coating of Pb species and, at the same time, promotes incorporation of Pb salts into silicate minerals. As indicated in Fig. 10, re-dissolved Pb species from salts of lead carbonate (sulfate) hydroxide creates new morphologies with C–S–H as calcium lead silicate sulfate hydroxide (C–Pb–S–H). This “coral reef” morphology is found in the cavity of lead enriched SWF (Fig. 10). The coral-like crystal is identified as calcium lead silicate sulfate (probably hydroxide) with slightly elevated aluminum and iron. The result by SEM/EDS is consistent with our XRD investigation on Pb incorporated C–S–H (S4).

5. Conclusions

In this study, we have examined the effect of lead and calcite on the cement-based solidification/stabilization process. Preliminary investigation of the effects of calcite and lead on compressive strength indicated that, while the UCS of lead contaminated material is markedly lower than the UCS of regular OPC at 28 days, calcite addition essentially reverses the effect.

The reduced rate of strength development arises because lead species coat the surface of cement components in the clinker and, in so doing, hinders the hydration of these entities. In cavity areas, a large quantity of lead precipitates, which, based upon the results of SEM/EDS and XRD investigations, have been shown to be principally lead carbonate sulfate hydroxide ($Pb_4SO_4(CO_3)_2(OH)_2$), lead carbonate hydroxide hydrate ($3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$) and two other unidentified lead salts.

The presence of calcite in the S/S of Pb wastes enhances the dissolution of C_3S leading to elevated concentrations of calcium, silicate, hydroxide and carbonate in the cement solution. The highly supersaturated solution present within the membrane-coated clinker components leads to rupture of the coating as a result of osmotic pressure buildup, which, in turn, leads to a periodic acceleration in cement hydration. As a result, at the early stage of hydration, calcite addition results in the rapid crystallization of calcium hydroxide coincident with the onset of C–S–H gel germination and a simultaneous enhancement in dissolution of lead precipitates. Calcite addition is observed to develop very insoluble products denoted as C–Pb–S–H and formed by chemical incorporation of re-dissolved Pb species into the silicate structure of the cement.

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