

# Investigation into the stabilization/solidification performance of Portland cement through cement clinker phases

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## Abstract

This research studied the influence of individual heavy metal on the hydration reactions of major cement clinker phases in order to investigate the performance of cement based stabilization/solidification (S/S) system. Tricalcium silicate (C<sub>3</sub>S) and tricalcium aluminate (C<sub>3</sub>A) had been mixed with individual heavy metal hydroxide including Zn(OH)<sub>2</sub>, Pb(OH)<sub>2</sub> and Cu(OH)<sub>2</sub>, respectively. The influences of these heavy metal hydroxides on the hydration of C<sub>3</sub>S and C<sub>3</sub>A have been characterized by X-ray diffraction (XRD) and differential scanning calorimetry–thermogravimetry (DSC–TG). A mixture of Zn(OH)<sub>2</sub>, Pb(OH)<sub>2</sub> and Cu(OH)<sub>2</sub> was blended with Portland cement (PC) and evaluated through compressive strength and dynamic leach test. XRD and DSC–TG data show that all the heavy metal hydroxides (Zn(OH)<sub>2</sub>, Pb(OH)<sub>2</sub> and Cu(OH)<sub>2</sub>) have detrimental effects on the hydration of C<sub>3</sub>A, but only Zn(OH)<sub>2</sub> does to the C<sub>3</sub>S at early curing ages which can completely inhibit the hydration of C<sub>3</sub>S due to the formation of CaO(Zn(OH)<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O. Cu<sub>6</sub>Al<sub>2</sub>O<sub>8</sub>CO<sub>3</sub>·12H<sub>2</sub>O, Pb<sub>2</sub>Al<sub>4</sub>O<sub>4</sub>(CO<sub>3</sub>)<sub>4</sub>·7H<sub>2</sub>O and Zn<sub>6</sub>Al<sub>2</sub>O<sub>8</sub>CO<sub>3</sub>·12H<sub>2</sub>O are formed in all the samples containing C<sub>3</sub>A in the presence of metal hydroxides. After adding CaSO<sub>4</sub> into C<sub>3</sub>A, the detrimental effect of heavy metals increases due to the coating effect of both calcium aluminate sulphates and heavy metal aluminate carbonates. The influence of heavy metal hydroxide on the hydration of C<sub>3</sub>S and C<sub>3</sub>A can be used to predict the S/S performance of Portland cement.

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**Keywords:** Leaching; Stabilization/solidification; Heavy metal; Cement clinker

## 1. Introduction

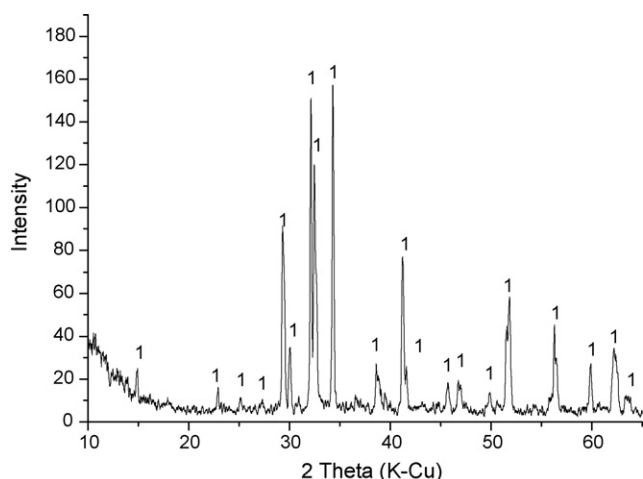
Stabilization/solidification (S/S) technologies are expected to increase in treating hazardous wastes prior to land disposal [1–3]. Cement based S/S processes are particularly appropriate for heavy metal-contaminated wastes, sludge and soils [4,5]. A major factor in applying these processes to wastes is that cement is easy to form a durable, monolithic material that will not leach hazardous components under the disposal conditions [6,7]. However, many research revealed that heavy metals had detrimental effects on the hydration reactions of cement and accordingly lowered the S/S performance. Hills and Pollard [8] reported that a 3% (w/w) addition of zinc containing waste in cement resulted in 99% reduction in 28 day strength. Bobrowski

et al. [9] found that lead ions prolonged the initial and final setting time and reduced the strength of cement mortar by up to 30%. It was also reported that the addition of copper containing sludge decreased the strength development of paste with cement and pulverised fuel ash (PFA), while increased the early strength of paste with only cement [10]. Reliable methods for assessing the performance of cement based S/S materials are increasingly demanded to reduce uncertainties during the application of S/S technologies.

The cement clinker consists of four main crystalline phases which are called alite, belite, aluminate phase and ferrite phase. Of these four phases, alite is tricalcium silicate (C<sub>3</sub>S) and constitutes 50–70% of the total weight of Portland cement clinkers. Tricalcium aluminate (C<sub>3</sub>A) constitutes 5–10% [11]. Some research on the influences of heavy metals on the hydration of tricalcium silicate and aluminate phase and ferrite phase has been reported [12–14]. However, few studies have introduced these influences to assess the S/S performance of cement based system.

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Fig. 1. X-ray diffraction pattern of C<sub>3</sub>S (1: C<sub>3</sub>S).

The object of this study was to study the influences of individual heavy metal hydroxide on the hydration of C<sub>3</sub>S and C<sub>3</sub>A at earlier curing ages than 28 days in order to introduce a reasonably easy method to assess the S/S performance of cement binder.

## 2. Experimental

### 2.1. Materials

Individual heavy metal hydroxide (Pb(OH)<sub>2</sub>, Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub>) was prepared using required amount of metal nitrate and NaOH solution, filtered through a Whatman No. 41 filter paper and washed with deionized distilled water until NaOH was not detected in the filtrate by pH measure. The residues of Pb(OH)<sub>2</sub>, Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub>, were then transferred into plastic tubes and freeze dried using a Flexi-Dry freeze-drier (FTS Systems, New York, USA).

Tricalcium silicate (C<sub>3</sub>S) was synthesized by calcining a compacted mix of reagent grade Ca(OH)<sub>2</sub> and SiO<sub>2</sub> (molar ratio of 3:1) once for 2 h and then ground and repeated 5 times for 10 h at 1500 °C. Tricalcium aluminate (C<sub>3</sub>A) was synthesized by calcining a compacted mix of reagent grade Ca(OH)<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (molar ratio of 6:1) for 3 h at 1400 °C. The purities of C<sub>3</sub>S and C<sub>3</sub>A produced were characterized by X-ray diffraction (XRD) (Bruker D8 Advanced Scanner with Cu target, run at 2θ steps of 0.02°) and the data are shown in Figs. 1 and 2.

A commercially available Type I Portland cement (PC) (Green Island Cement Ltd., Hong Kong) was used as the S/S binder. Chemical and physical properties of the PC are given in Table 1. Reagent grade CaSO<sub>4</sub> was used as additive of C<sub>3</sub>A.

### 2.2. Preparation of specimens

Fourteen mixes shown in Table 2 were prepared by mixing raw materials with deionised distilled water. Of the twelve mixes containing C<sub>3</sub>S or C<sub>3</sub>A, three were blanks with only C<sub>3</sub>S, C<sub>3</sub>A or C<sub>3</sub>A + CaSO<sub>4</sub>. The other nine were designed by adding 0.033 mole of each metal hydroxide (Pb(OH)<sub>2</sub>, Cu(OH)<sub>2</sub> and

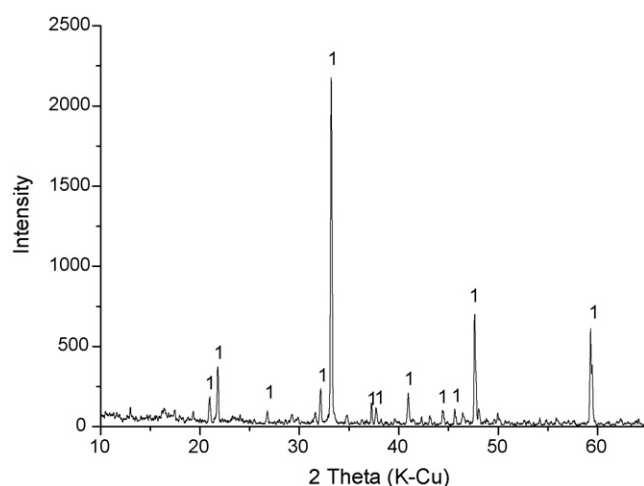
Fig. 2. X-ray diffraction pattern of C<sub>3</sub>A (1: C<sub>3</sub>A).

Table 1

Chemical compositions (wt.%) and physical properties of material (PC) used in experiment

SiO <sub>2</sub>	19.61
Fe <sub>2</sub> O <sub>3</sub>	3.32
Al <sub>2</sub> O <sub>3</sub>	7.33
TiO <sub>2</sub>	–
CaO	63.15
MgO	2.54
SO <sub>3</sub>	2.13
K <sub>2</sub> O	–
Na <sub>2</sub> O	–
LOI	2.97
Total	101.05
Fineness (m <sup>2</sup> /kg)	352.0
Density (kg/m <sup>3</sup> )	3.16

Total iron expressed as Fe<sub>2</sub>O<sub>3</sub>, fineness: Blaine method, density: pycnometer method.

Zn(OH)<sub>2</sub>) into 100 g of binder (C<sub>3</sub>S, C<sub>3</sub>A or C<sub>3</sub>A + CaSO<sub>4</sub>). The Al<sub>2</sub>O<sub>3</sub>/SO<sub>3</sub> ratio in binder C<sub>3</sub>A + CaSO<sub>4</sub> is similar to that of PC used in this study. The amount of heavy metal added is designed according to previous results which showed that higher than 5%

Table 2

Mix proportions (wt.%)

Mix No.	PFA	C <sub>3</sub> S	C <sub>3</sub> A	CaSO <sub>4</sub>	Metal hydroxide	PC
CS	–	100	–	–	–	–
CSPb	–	100	–	–	8.04	–
CSZn	–	100	–	–	3.31	–
CSCu	–	100	–	–	3.25	–
CA	–	–	100	–	–	–
CAPb	–	–	100	–	8.04	–
CAZn	–	–	100	–	3.31	–
CACu	–	–	100	–	3.25	–
CAS	–	–	85	15	–	–
CASPb	–	–	85	15	8.04	–
CASZn	–	–	85	15	3.31	–
CASCu	–	–	85	15	3.25	–
Cblank	–	–	–	–	–	100
Cwaste	–	–	–	–	3.07 <sup>a</sup>	100

<sup>a</sup> Mixture of 0.007 mol of each Pb(OH)<sub>2</sub>, Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub>.



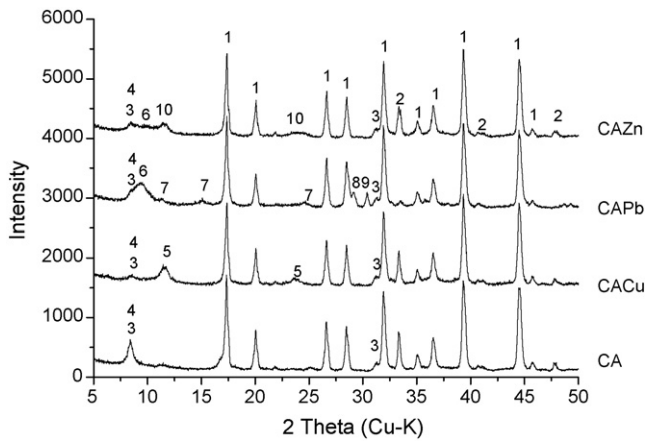


Fig. 4. Influence of the heavy metals on the hydration product of  $C_3A$  (1:  $Ca_3Al_2O_6 \cdot 6H_2O$ ; 2:  $C_3A$ ; 3:  $Ca_4Al_2O_7 \cdot 19H_2O$ ; 4:  $Ca_2Al_2O_5 \cdot 8H_2O$ ; 5:  $Cu_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ; 6:  $Ca_6Al_2O_6(CO_3)_3 \cdot 32H_2O$ ; 7:  $Pb_2Al_4(OH)_8(CO_3)_4 \cdot 3H_2O$ ; 8:  $CaCO_3$ ; 9:  $Ca_3(CO_3)_2(OH)_2$ ; 10:  $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ).

The influences of metal hydroxides on the hydration of  $C_3A$  and  $C_3A + CaSO_4$  are shown in Figs. 4 and 5. The XRD data in Fig. 4 show that  $Ca_3Al_2O_6 \cdot 6H_2O$ ,  $Ca_2Al_2O_5 \cdot 8H_2O$  and  $Ca_4Al_2O_7 \cdot 19H_2O$  are the major hydration products in the sample CA which contains only  $C_3A$ . After adding heavy metal hydroxides formations of  $Ca_2Al_2O_5 \cdot 8H_2O$  and  $Ca_4Al_2O_7 \cdot 19H_2O$  decrease. However, a new hydration product  $Cu_6Al_2O_8CO_3 \cdot 12H_2O$  appears in the sample containing  $Cu(OH)_2$ . A series of products including  $Ca_6Al_2O_6(CO_3)_3 \cdot 32H_2O$ ,  $Pb_2Al_4O_4(CO_3)_4 \cdot 7H_2O$ ,  $CaCO_3$ , and  $Ca_3(CO_3)_2(OH)_2$  are formed in the sample containing  $Pb(OH)_2$ .  $Ca_6Al_2O_6(CO_3)_3 \cdot 32H_2O$  and  $Zn_6Al_2O_8CO_3 \cdot 12H_2O$  are produced in the sample containing  $Zn(OH)_2$ .

The XRD data in Fig. 5 show that hydration products  $Ca_4Al_2O_7SO_3 \cdot 12H_2O$  as well as  $Ca_3Al_2O_6 \cdot 6H_2O$ ,  $Ca_2Al_2O_5 \cdot 8H_2O$  and  $Ca_4Al_2O_7 \cdot 19H_2O$  are formed when adding  $CaSO_4$  into  $C_3A$  and decrease in amount after addi-

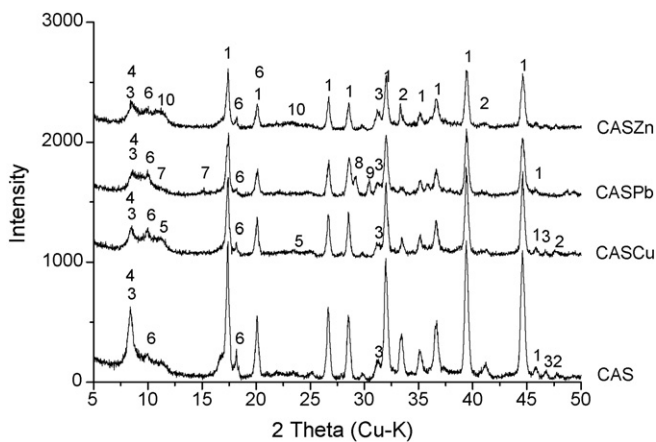


Fig. 5. Influence of the heavy metals on the hydration product of  $C_3A$  containing  $CaSO_4$  (1:  $Ca_3Al_2O_6 \cdot 6H_2O$ ; 2:  $C_3A$ ; 3:  $Ca_4Al_2O_7 \cdot 19H_2O$ ; 4:  $Ca_2Al_2O_5 \cdot 8H_2O$ ; 5:  $Cu_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ; 6:  $Ca_4Al_2O_7SO_3 \cdot 12H_2O$ ; 7:  $Pb_2Al_4(OH)_8(CO_3)_4 \cdot 3H_2O$ ; 8:  $CaCO_3$ ; 9:  $Ca_3(CO_3)_2(OH)_2$ ; 10:  $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ).

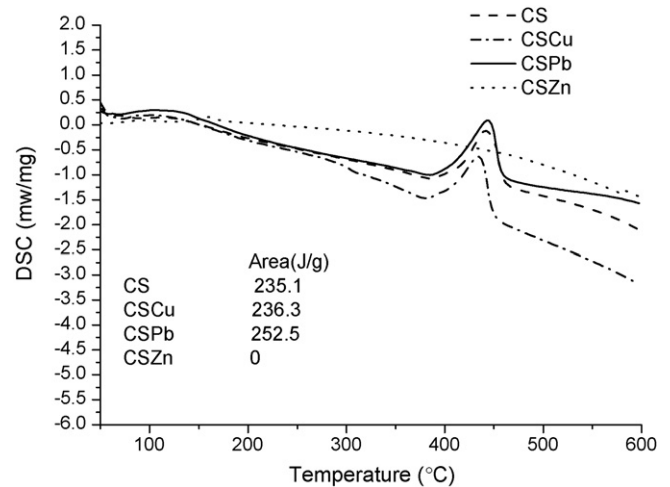


Fig. 6. Influence of heavy metals on the hydration of  $C_3S$ .

tion of heavy metal hydroxides. New products resulted from the addition of heavy metal hydroxides are the same as those in the samples CACu, CAPb and CAZn, except for  $Ca_6Al_2O_6(CO_3)_3 \cdot 32H_2O$  which is not produced in the sample CASPb.

### 3.1.2. DSC-TG

The effects of heavy metals on the hydration degree of  $C_3S$ ,  $C_3A$  or  $C_3A + CaSO_4$  are shown in Figs. 6–8, respectively. The DSC-TG data in Fig. 6 show that the addition of  $Pb(OH)_2$  and  $Cu(OH)_2$  into  $C_3S$  have few influences on the formation of  $Ca(OH)_2$ . However, this was completely stopped after the addition of  $Zn(OH)_2$ . The decompose heat in Fig. 7 shows that the hydration degree of  $C_3A$  decreases after addition of the metal hydroxides. Fig. 8 shows that the decompose heat of all the specimens containing  $C_3A + CaSO_4$  decrease after addition of heavy metal hydroxides and the decompose heat of specimen contained  $Zn(OH)_2$  is the lowest, followed by  $Pb(OH)_2$  and  $Cu(OH)_2$ .

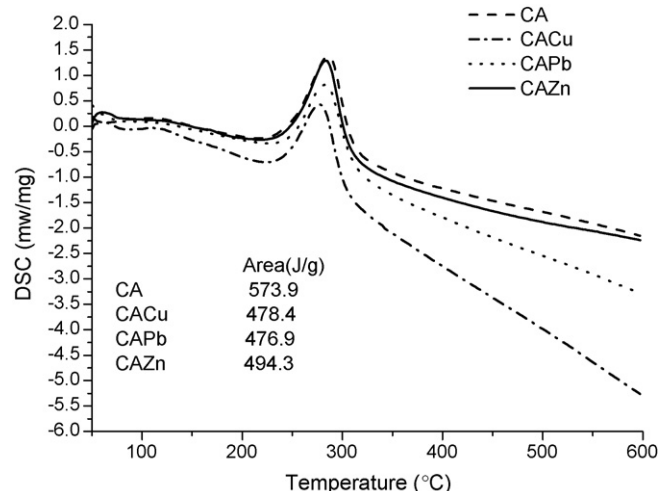


Fig. 7. Influence of heavy metals on the hydration of  $C_3A$ .

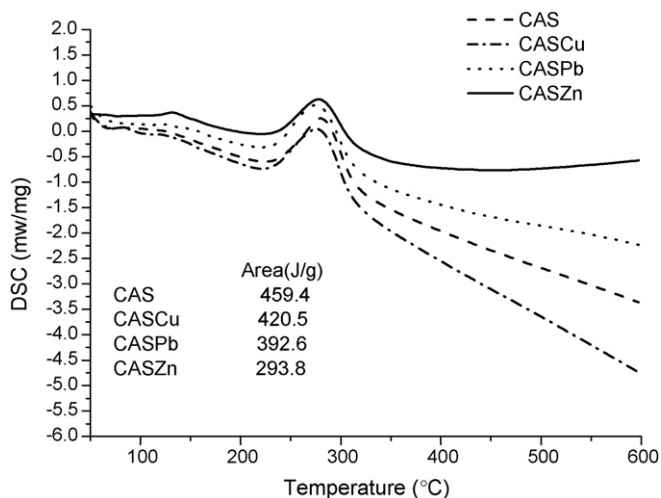


Fig. 8. Influence of heavy metals on the hydration of  $C_3A$  with  $CaSO_4$ .

### 3.2. Performance of stabilization/solidification

#### 3.2.1. Compressive strength development

The compressive strengths of cement blank samples (Cblank) are 65.58 and 90.52 MPa at 28 and 56 days, respectively. A 15.5% reduction in strength occurred in the 28 day cured samples after addition of heavy metal mixture ( $Pb(OH)_2$ ,  $Cu(OH)_2$  and  $Zn(OH)_2$ ) and 14.0% did in the 56 day cured samples.

#### 3.2.2. DLT

The cumulative fractions of heavy metals leached in the DLT are shown in Table 4. After curing for 28 days zinc content leached from sample Cwaste is the highest, followed by copper and lead contents. Only zinc content can be measured in 56 day cured samples under the condition of this study.

Table 4  
Cumulative fraction of heavy metals leached in DLT (wt.%)

Heavy metal	Cumulative time (h)	Cwaste	
		28 days	56 days
Pb	4	0.34	n.d.
	24	0.46	n.d.
	31	0.57	n.d.
	72	0.64	n.d.
	104	0.71	n.d.
	168	0.71	n.d.
Zn	4	0.64	0.34
	24	1.48	0.34
	31	2.09	0.34
	72	2.98	0.34
	104	3.76	0.34
	168	3.76	0.34
Cu	4	1.05	n.d.
	24	1.36	n.d.
	31	1.46	n.d.
	72	1.54	n.d.
	104	1.68	n.d.
	168	1.68	n.d.

n.d.: not detected, detection limit = 0.001 mg/L.

## 4. Discussion

XRD and DSC–TG results show that the addition of  $Zn(OH)_2$  totally prevented formation of  $Ca(OH)_2$  during hydration of  $C_3S$ . This may be due to the coating effect of insoluble  $CaO(Zn(OH)_2) \cdot 2H_2O$  on the surface of  $C_3S$  [17], which retarded further hydration of  $C_3S$ . However, the addition of  $Pb(OH)_2$  and  $Cu(OH)_2$  have little detrimental effect on the hydration of  $C_3S$  which is similar to the results reported by Minocha et al. [18].

During hydration of  $C_3A$  a number of metastable hydrated phases including  $CaAl_2O_4 \cdot 10H_2O$ ,  $Ca_2Al_2O_5 \cdot 8H_2O$  and  $Ca_4Al_2O_7 \cdot xH_2O$  ( $x=7, 11, 13$  and  $19$ ) can be formed [16,17]. These metastable hydrated aluminates will convert to stable cubic hydrate  $Ca_3Al_2O_6 \cdot 6H_2O$  with time [19–21]. After the addition of heavy metal hydroxides the formations of  $Ca_2Al_2O_5 \cdot 8H_2O$  and  $Ca_4Al_2O_7 \cdot 19H_2O$  decrease (Fig. 4). However, new hydrated phases including heavy metal aluminate carbonate hydrates and calcium aluminate carbonate hydrates are formed at the same time. This suggests that heavy metal cations can substitute for calcium cations to give new hydration products during hydration of  $C_3A$ .  $Ca(OH)_2$  is hence formed which could be carbonated to give  $CaCO_3$ . Intermediate heavy metal aluminate hydrates produced after the addition of heavy metal hydroxides should be more metastable due to larger ion radii of these heavy metals and thus are easy to be carbonated.

Compared with the results in Figs. 4 and 7 the hydration degree of  $C_3A$  decreased (Figs. 5 and 8) after adding the  $CaSO_4$ . This may be due to the formation of  $Ca_4Al_2O_7SO_3 \cdot 12H_2O$  which could coat on the surface of  $C_3A$  and delay the hydration of  $C_3A$  [11]. The disappear of ettringite ( $Ca_6Al_2O_6(SO_3)_3 \cdot 32H_2O$ ) in the sample containing  $C_3A + CaSO_4$  might be due to the transformation of ettringite to  $Ca_4Al_2O_7SO_3 \cdot 12H_2O$  [11] or the formation of calcium aluminate carbonate substituted for ettringite [20].

The addition of heavy metal hydroxides into sample containing  $C_3A$  or  $C_3A + CaSO_4$  produced the same heavy metal aluminate carbonate hydrates. However, the hydration degree of  $C_3A$  was much lower after the addition of  $CaSO_4$ . It is hence possible that the formation of heavy metal aluminate carbonate hydrates could also result in coating effect which retards continuous hydration of  $C_3A$ .

It is reported that hydrations of alite ( $C_3S$ ), aluminate phase ( $C_3A$ ) and ferrite phase ( $C_4AF$ ) contribute to the strength of sample before 28 days [11]. The influences of heavy metals on the hydration of  $C_3S$  and  $C_3A + CaSO_4$  show that  $Zn(OH)_2$  is the most detrimental. Therefore, the zinc content leached from 28 day cured cement solidified/stabilized sample is the highest. Although  $Pb(OH)_2$  had less detrimental effect on the hydration of  $C_3A + CaSO_4$  than  $Cu(OH)_2$  did (Fig. 8), it produced more  $Ca(OH)_2$  content during the hydration of  $C_3S$  (Figs. 3 and 6). Higher  $Ca(OH)_2$  content benefits the S/S of contaminants [5]. Copper content leached from sample is hence higher than lead. After coating layer  $CaO(Zn(OH)_2) \cdot 2H_2O$ ,  $Ca_4Al_2O_7SO_3 \cdot 12H_2O$  and heavy metal aluminate carbonates was broken  $C_3S$  and  $C_3A$  in cement could solidify/stabilize heavy metals well with time. This would result in lower leaching of heavy metals at later curing ages (Table 4).

## 5. Conclusions

1. The addition of  $\text{Zn}(\text{OH})_2$  completely prevents the formation of  $\text{Ca}(\text{OH})_2$  during the hydration of  $\text{C}_3\text{S}$  at early curing ages due to the coating effect of  $\text{CaO}(\text{Zn}(\text{OH})_2) \cdot 2\text{H}_2\text{O}$ , while the addition of  $\text{Pb}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$  has no retarding effects.
2.  $\text{Zn}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$  have little effect on the hydration of pure  $\text{C}_3\text{A}$  but show detrimental effect in the presence of  $\text{CaSO}_4$  due to coating effect.
3. Zinc, lead and copper can substitute for calcium during the hydration of  $\text{C}_3\text{A}$  to give heavy metal aluminate carbonates.
4. The coating effect retards the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  which increases the leaching of heavy metals at early curing ages. However, the heavy metals can be solidified/stabilized well with time after this coating layer break is broken.
5. The S/S performance of Portland cement can be assessed by investigating the influence of heavy metal on the hydration of cement clinker phases.

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