

Influence of lead, chromium and zinc ions as toxic heavy metals between C-S-H phases based on C₃S

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Tricalcium silicate (C₃S) as clinker minerals was synthesized to investigate the solidification/stabilization (S/S) mechanism of lead, chromium and zinc ions on cement matrix. Effects of various hydration phases on the S/S mechanism were analyzed using XRD, SEM-EDS and heat evolution. Lead, chromium and zinc leachability from solidified hydration phases were also investigated using the toxicity characteristic leaching procedure (TCLP) recommended by the U.S. Environmental Protection Agency (EPA). The results showed that heavy metal ions considerably affected the S/S mechanism of C-S-H phases. The presence of lead appears to induce considerable retardation in the curing process during hydration of C₃S until 28 days. Moreover, in case of adding chromium, retardation of C₃S hydration due to the formation of CaCrO₄ · H₂O phases also appeared in the early stages. Especially, in case of adding zinc, it was founded that the leaching of zinc ions from specimens at 10,000 ppm was lower than that of specimens with lead at the same dosage.

Key words: C₃S, C-S-H phases, Lead, Chromium (III), Zinc.

Introduction

Stabilization and solidification (S/S) are well known as one of the most popular technologies for treating of various hazardous wastes containing heavy metals such as lead, chromium, mercury, vanadium, zinc and cadmium, prior to land disposal [1-4]. Especially, cementitious materials play an important role in the immobilization of heavy metals. C-S-H has a high specific surface area; measured values for N₂ sorption lie in the range of 10 to 50 m²g⁻¹. The large specific surface thus created, with its high density of irregular hydrogen bonding, creates a strong potential for sorption [5]. Fig. 1 shows the proposed S/S mechanism of heavy metal ions on C-S-H phases schematically. The surface charge of C-S-H has a positive surface charge and, as a consequence, tends to sorb anions. However, as the Ca:Si ratio of C-S-H changes, the surface charge gradually also changes. This means that sorption processes of cementitious materials can be occurred by competition of for anion and cation sorption sites in cement. Many researchers have established the theoretical and practical basis for the S/S mechanism. J.D. Ortego *et al.* [6] studied that lead retards the setting of cement, due to the formation of compounds, which cover the silicate phases. C. Tashiro

et al. [7] also report that common hydration products are formed during the hydration of C₃A in the presence of PbO. However, it decreased the compressive strength of C₃A by a considerable extent. Q. Yu *et al.* [8] report that amount of heavy metals leached from cement mortars is increased with fly ash addition and w/b. Increased leaching of Cr will take place in carbonated mortars. Compared with tank leaching method, shaking test method can extract more toxic heavy metals from hardened mortars

G. Qian *et al.* [9] reported that the effects of Zn²⁺ on the alkali-activated slag (AAS) matrix depend on Zn²⁺ ion concentration. Especially, at low Zn²⁺ ion concentrations, little negative influences on the compress strength, setting time and distribution of pore structure were observed.

Calcium Silicate Hydrate : C₃S₂H₃ (C-S-H gel)

• Adsorption reaction : CSH + M → MCSH

• Substitution reaction : CSH + M → MCSH + Ca⁺⁺

calcium silicate metallic metallic calcium calcium ion
hydrate ion silicate hydrate

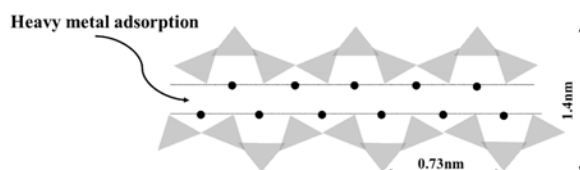


Fig. 1. Representative substitution mechanism of metallic ions on C-S-H phases.

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Therefore, low concentrations of Zn²⁺ ion could be effectively immobilized in the AAS matrix. However, solubility of ions was affected by pH and their amounts. In the previous research [10], behavior of three calcium aluminates (C₃A) and calcium sulfoaluminate (C₄A₃S̄) as clinker minerals were examined for the research of S/S mechanism under solution of toxic heavy metals such as lead and chromium. The aim of this study is to investigate S/S behavior on the cement with heavy metals ions in order to fabricate cement stabilizers using industrial waste sludge including heavy metals ions such as Pb, Cr and Zn. Therefore, the presented properties of C₃S pastes and the results of previous works compare their conditions for immobilization of heavy metals.

Experimental

Materials

Pure C₃S was prepared by blending the stoichiometric quantities of analytical reagent grades of CaCO₃ and SiO₂. Mixtures were initially fired at a temperature of 1000 °C several times with intermediate blending for 1-2 hours. Next, C₃S was fired at 1500 °C for 24 hours. Then these materials, ground to the specific surface of 3500 ~ 3700 cm²/g, were used for the formation of M-C-S-H phases. Lead, chromium (III) and zinc which were listed as the priority pollutant by the EPA and other environmental agencies, were used in order to clarify the S/S mechanism according to cementitious material in this work. Three metal oxides, Pb(NO₃)₂, Cr(NO₃)₃ · 9H₂O and Zn(NO₃)₂ · 6H₂O have been selected to study the setting and hardening behavior of C-S-H phases/metal oxides.

Experimental Method

A water-to-solid ratio of 0.4 was used for all mixes and the specimens were cured in air at 23 ± 1 °C with RH 95%. Lead, chromium (III) and zinc were added 5 wt% respectively. All compounds were treated with acetone after 1, 3, 7 and 28 days curing to prevent further hydration in the early stage and ground in order to analyze their XRD. Also, all specimens for SEM/EDS were examined at different ages in order to clarify behavior of heavy metal ions between C-S-H phases based on C₃S. The leaching tests of heavy metals were conducted on S/S waste forms based on the TCLP method. To pure C₃S phases, various heavy metal oxides in concentrations of 1000, 5000 and 10,000 ppm were added. The specimens were crushed to reduce the particle size to less than 9.5 mm. The leaching solution used was distilled water pH-adjusted to 6.0. The crushed specimens in the pH-adjusted water (Solid/liquid = 1 : 10 by weight) were stirred for 6 h on a magnetic stirrer, and filtered using filter paper No. 5. Heavy metals in the filtered solution were measured

using ICP spectroscopy.

Results and discussion

The effects of various lead, chromium (III) and zinc concentrations on the degree of immobilization, and hydration properties of C₃S were investigated. The test results are reported and discussed in the following sections.

Effect of lead and chromium on the formation of M-C-S-H phases

The results of X-ray diffraction analysis for hydration phases based on C₃S with Pb(NO₃)₂ and Cr(NO₃)₃ · 9H₂O until 28 days curing are shown in Fig. 2 and Fig. 3, respectively. As shown in Fig. 2, the presence of lead appears to induce considerable retardation in the curing process during hydration of C₃S until 28 days. The XRD patterns of the precipitated lead salts, as calcium lead hydroxides (Ca[Pb(OH)₃ · H₂O]₂), also were observed [10]. In particular, they coexisted with Ca(OH)₂ and pb(OH)₂ after 1 day curing and then, through precipitated products on the surface of C₃S, they disturbed

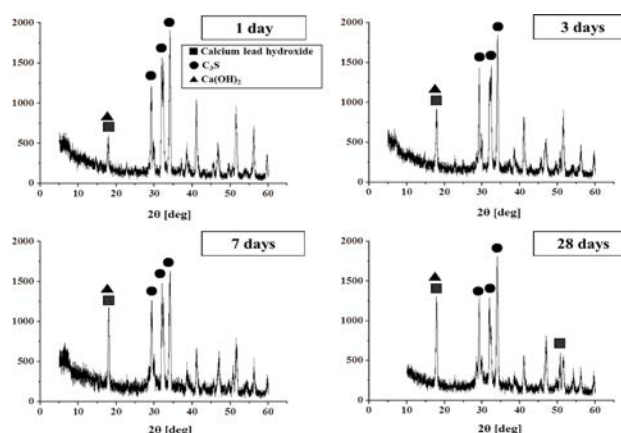


Fig. 2. XRD patterns of C₃S pastes incorporating 5 wt % lead as curing days.

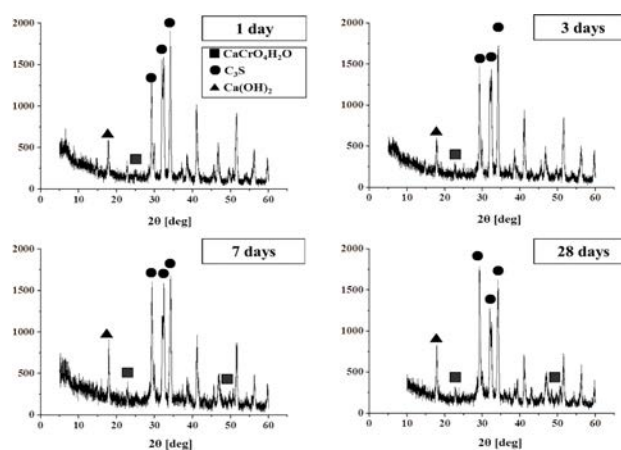


Fig. 3. XRD patterns of C₃S pastes incorporating 5wt% chromium as curing days.

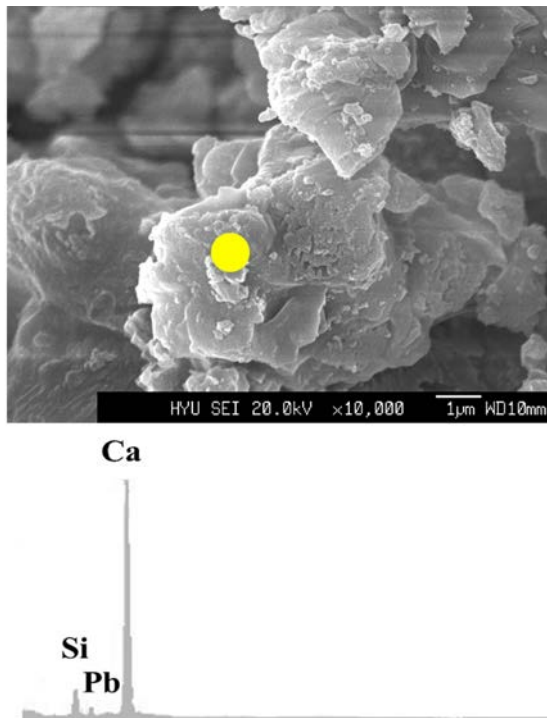


Fig. 4. X-ray spectrum from C-S-H phase based on C_3S containing 5 wt% lead at 3 days curing.

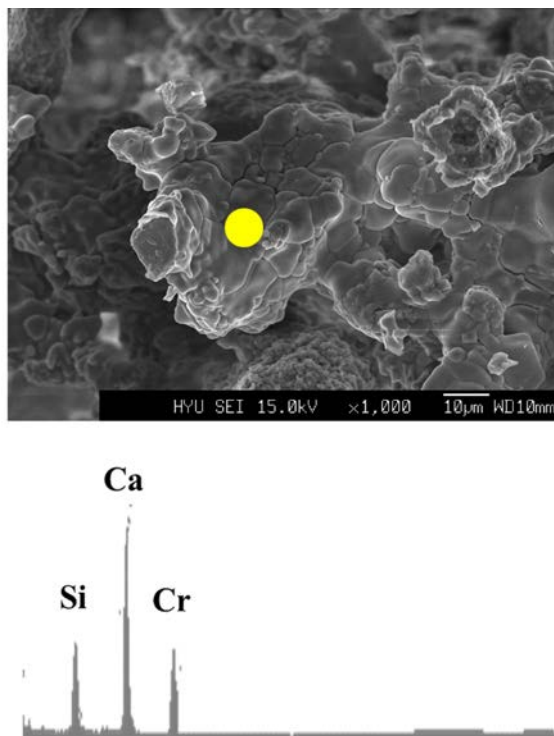
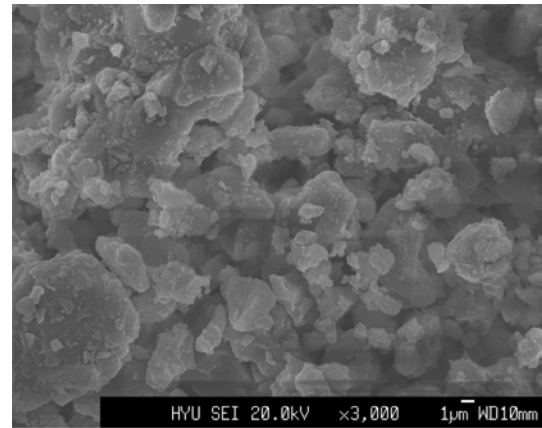
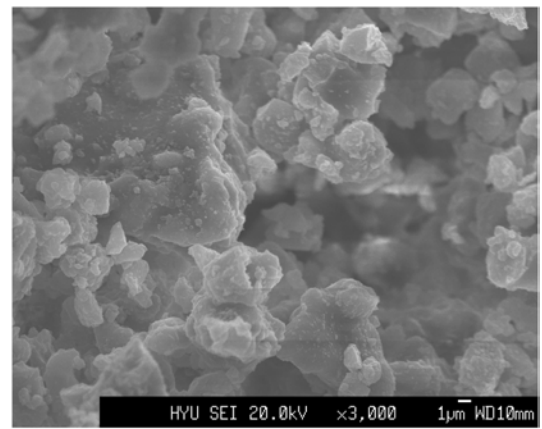


Fig. 5. X-ray spectrum from C-S-H phase based on C_3S containing 5wt% chromium at 3 days curing.

hydration of C_3S significantly. Strong crystallization of these hydrates was observed at 18° and 52° after 1day curing. These results mean that solidification of lead



(a) Pb



(b) Zn

Fig. 6. Surface morphology of M-C-S-H phase based on C_3S containing 5 wt% heavy metal ions at 3 days curing.

ions is considered based on two reasons as follows: 1) the precipitation of metallic hydroxide and then, 2) the encapsulation of this compound in the C-S-H phase by the hydration of C_3S .

In the case of chromium, retardation of C_3S hydration was occurred, because of the formation of $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ phases in the early stages as shown in Fig. 3. However, C_3S pastes were hydrated until 28 days curing continuously, different from lead case. This means that lead had a greater affected on the retardation of C_3S hydration than chromium in early stages of hydration. X-ray spectra obtained from these phases revealed differential trends in their chemical composition as the formation of Metallic Calcium Silicate Hydroxide [M-C-S-H] phases proceeded. Especially, Fig. 4 and Fig. 5 showed the difference in the formation of M-C-S-H phases after leaching tests between lead and chromium clearly. It was observed that there was a greater increase in the ratio of chromium peak height compared to lead from the formation of M-C-S-H. In other words, it indicates that the efficiency of ordinary Portland cement (OPC) on the S/S of waste including lead, which was composed

Table 1. Leaching concentration of lead, chromium (III) and zinc ions from C₃S pastes. (5,000 ppm)

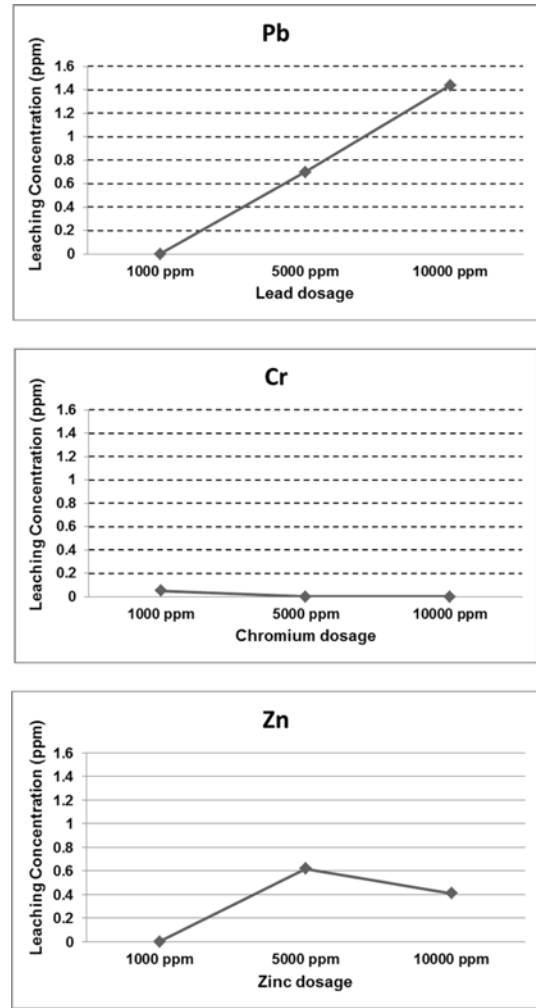
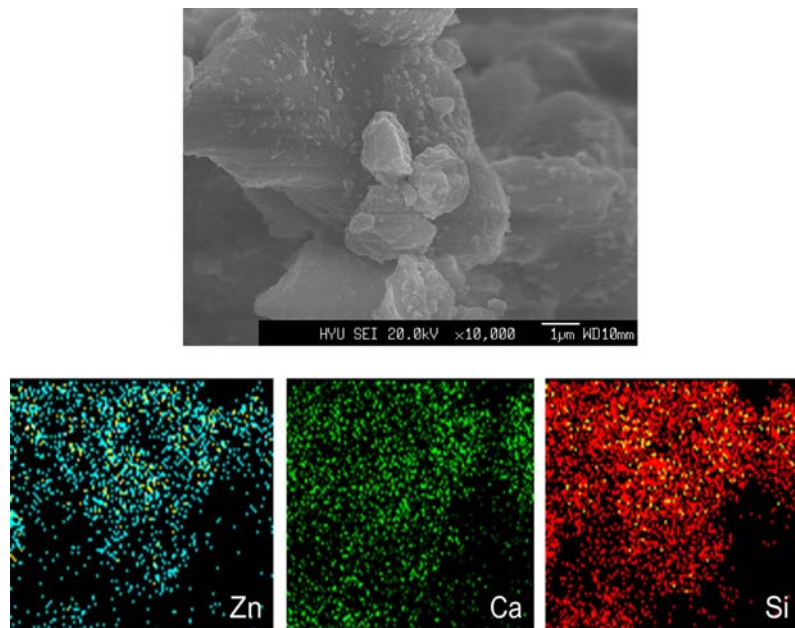
Heavy Metals Curing days	(ppm)		
	Pb	Cr	Zn
1 day	0.83	Tr	0.64
3 days	0.70	Tr	0.62
7 days	0.51	0.05	0.40

mainly C₃S and C₂S phases, should be decreased compared to other cases.

Effect of zinc on the formation of M-C-S-H phases

In the case of Lead and zinc, it has been reported that they reacted to calcium ions easily for the formation of insoluble salts on the portland cement [11]. Therefore, morphologies of M-C-S-H with insoluble precipitated salts by lead and zinc were investigated as shown in Fig. 6, in order to understand behaviors of insoluble salts with lead and zinc. It shows the surface morphology M-C-S-H phase based on C₃S containing 5 wt% Pb(NO₃)₂, and Zn(NO₃)₂ · 6H₂O respectively at 3 days curing. In the case of zinc, morphology of M-C-S-H phase was similar to that of M-C-S-H phase with lead. Furthermore, leaching concentration of lead and zinc ions from M-C-S-H phase were also similar to those of 5,000 ppm according to curing days as shown in Table 1. However, on the other hands, it was also found that M-C-S-H phase containing 5 wt% zinc after leaching test had high concentrations of zinc from X-ray mapping results compared to lead case as shown in Fig. 7.

This indicates that S/S behaviors of M-C-S-H phase can be significant differences at the initial curing stage

**Fig. 8.** Leaching concentration of each ions from M-C-S-H with various heavy metals 1000 ppm, 5000 ppm and 10,000 ppm (3 days curing) .**Fig. 7.** X-ray mapping results of M-C-S-H phases based on C₃S containing 5wt% zinc at 3 days curing after leaching test.

according to kinds of heavy metal ions and amounts of dosage. Actually, leaching concentrations of various heavy metal ions from M-C-S-H phase are significantly different. Fig. 8 shows leaching concentrations with various heavy metals such as lead, chromium and zinc in case of 1000 ppm, 5000 ppm and 10,000 ppm at curing 3 days respectively. In the case of lead, leaching concentration was increased according to the dosage of lead. However, in the case of chromium, it was decreased continuously by S/S mechanisms until 10,000 ppm. Furthermore, in the case of zinc, the formation of insoluble salts as lead, it showed difference behaviors. It means that substitution ability of zinc to C_3S paste is higher than that of lead at the 10,000 ppm. From these results, it was considered that the utilization of appropriate other cementitious materials was desirable in order to increase chemical stability of S/S mechanism according to types of heavy metals. And influence of pH values on the S/S mechanism will be also studied according to curing days in future works.

Conclusions

The heavy metal ions considerably affected the S/S mechanism of C-S-H phases. The presence of lead appears to induce considerable retardation in the curing process during hydration of C_3S until 28 days. In the case of adding chromium, retardation of C_3S hydration due to the formation of $CaCrO_4 \cdot H_2O$ phases also appeared in the early stages. In the case of adding zinc, it was founded that the leaching of zinc ions from M-C-S-H phase at 10,000 ppm was lower than that of M-

C-S-H with lead at the same curing days after leaching test.

Acknowledgments

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