

Behavior of lead and chromium ions as toxic heavy metals between AFt and AFm phases based on C₃A and C₄A₃ \bar{S}

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Three calcium aluminate (C₃A) and calcium sulphoaluminate (C₄A₃ \bar{S}) as clinker minerals were synthesized to investigate the solidification/stabilization (S/S) mechanism of lead and chromium ions on cement matrix. Effects of AFt phases on S/S mechanism were analyzed using FT-IR, SEM(EDS) and heat evolution. Lead and chromium leachability from solidified AFt phases was also investigated using the toxicity characteristic leaching procedure (TCLP) recommended by the U.S. Environmental Protection Agency(EPA). The results showed that clinker mineral types considerably affected the S/S mechanism of AFt and AFm phases incorporating chromium and lead ions. In the case of adding chromium, both AFt and AFm phase based C₃A and C₄A₃ \bar{S} allowed ionic substitution Cr³⁺ for the trivalent ion as Al³⁺ and CrO₄²⁻ for SO₄²⁻. Moreover, chromate hydrocalumite[3CaO·Al₂O₃·CaCrO₄·nH₂O] was also observed. However, in the case of adding lead, it was found that when C₃A and C₄A₃ \bar{S} were hydrated, the formation of AFt and AFm phase based C₄A₃ \bar{S} was faster than C₃A. Especially, AFt phases and the calcium lead hydroxides (Ca[Pb(OH)₃·H₂O]₂) incorporating lead ions were formed during hydration of C₄A₃ \bar{S} in the early stage compared to the C₃A case. This showed that AFt and AFm phase based C₄A₃ \bar{S} for S/S of lead were more effective than that of C₃A.

Keywords : C₃A, C₄A₃ \bar{S} , AFt phases, Lead, Chromium(III)

1. INTRODUCTION

Cementitious material based S/S is one of the most widely used techniques for treating hazardous waste containing heavy metals such as lead, chromium, mercury, vanadium, zinc and cadmium. S/S mechanisms of the cement matrix for containing various heavy metals are well known as adsorption, ion exchange, formation of insoluble species, absorption, encapsulation and reprecipitation. These mechanism, especially ion exchange as the chemistry process of S/S, plays a key role in controlling leaching. The compounds among the group of layered Calcium aluminate hydrates are also important for the process of S/S. In recent years, cementitious materials causing numerous AFt or AFm phases in cement hydration for S/S materials have attracted growing attention[1]. When added heavy metal ions are added to the cement matrix, these hydration

products are referred to as solidifiers/stabilizers for heavy metal ions. In addition, in early stages these hydration products exhibit compressive strengths much higher than those observed with normal cement containing heavy metal ions. In other words, they can be used or added for the immobilization of inorganic and organic substances in contaminated water, gas and soil.

Many studies have been devoted to the S/S properties of cementitious materials for heavy metal ions. Fig. 1 shows the proposed S/S mechanisms of heavy metals using AFt, AFm and Hydrogarnet phases schematically. These phases are well known to allow ionic substitution, including Fe^{3+} and Cr^{3+} for the Al^{3+} and OH^- , CO_3^{2-} , SeO_4^{2-} , and CrO_4^{2-} for SO_4^{2-} [2]. However, although much data exists on the subject of AFt phases or AFm phases incorporating heavy metals, little is known about the precise speciation of these products on the compounds that are formed from both AFt and AFm phase based C_3A and $\text{C}_4\text{A}_3\bar{\text{S}}$. Especially, until now it was hypothesized that lead could be precipitated on the surface of hydrates [3] and no detailed report related the formation of AFt or AFm phases. Therefore, the aim of the present paper is to bring more information on the lead and chromium uptake in AFt or AFm related phases.

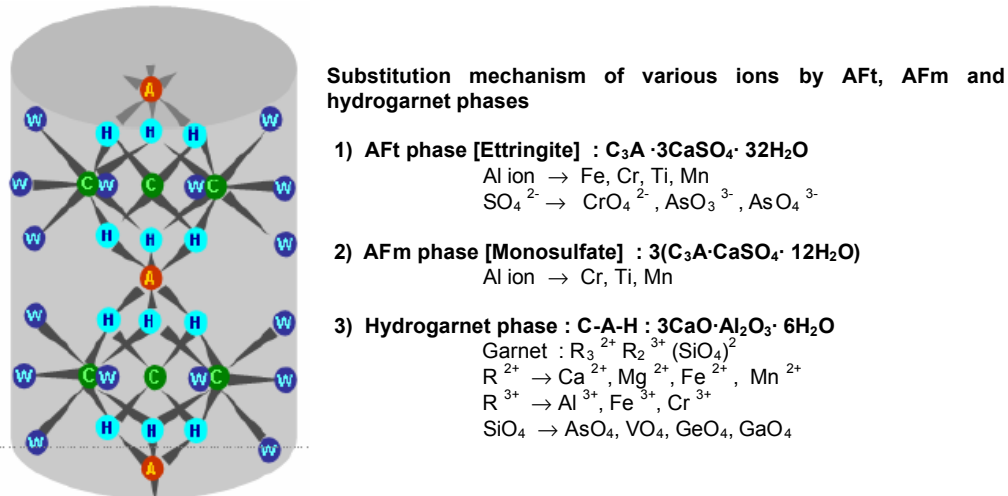


Fig. 1 Representative substitution mechanism of various ions on AFt, AFm and Hydrogarnet phases. (Crystal structure of ettringite: A=Al C=Ca, H=O of an OH group, W=O of an H_2O molecule) [2]

2. EXPERIMENTAL

2.1 Materials

Pure C_3A and $\text{C}_4\text{A}_3\bar{\text{S}}$ were prepared by blending the stoichiometric quantities of analytical reagent grades of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and Al_2O_3 . Mixtures were fired several times with intermediate blending for 1-2 hours at temperatures initially at 1000°C . C_3A was fired at 1400°C for 7 hours

and $C_4A_3\bar{S}$ was fired at 1300°C for 7 hours. Then these materials, ground to the specific surface of 3500 cm²/g, were used for the formation of AFt phases and AFm phases with CaSO₄·2H₂O. Lead and chromium(III), 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. Two metal oxides, Pb(NO₃)₂ and Cr(NO₃)₃·9H₂O, have been selected to study the setting and hardening behavior of AFt phases/metal oxides.

2.2 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 and chromium (III) were added 5wt% respectively. All compounds were treated with acetone after 1, 3 and 7 days to prevent further hydration in the early stage and ground in order to analyze their XRD and FT-IR patterns. Also, all specimens for SEM/EDS were examined at different ages in order to clarify behavior of heavy metal ions between AFt phases based C₃A and AFt phases based C₄A₃ \bar{S} . The leaching tests of heavy metals were conducted on S/S waste forms based on the TCLP method. To pure phases C₃A and C₄A₃ \bar{S} with CaSO₄·2H₂O, 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 9.5mm. 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 6h on a magnetic stirrer, and filtered using filter paper No. 5. Heavy metals in the filtered solution were measured using ICP spectroscopy. The hydration curves were also estimated using an isothermal conduction calorimeter.

3. RESULTS AND DISCUSSIONS

The effects of various lead and chromium(III) concentrations on the degree of immobilization, and hydration properties of C₃A and C₄A₃ \bar{S} were investigated. Fig. 2 shows the fabrication of AFt and AFm phases based C₄A₃ \bar{S} with CaSO₄·2H₂O in order to carry out this work. SEM images of these phases based C₄A₃ \bar{S} showed AFm phases to be comprised of hexagonal shape platelets. The hexagonal form of the plates is consistent with the morphology reported for sulfate hydrocalumite [4,5]. The test results are reported and discussed in the following sections

3.1 Effect of Lead on the Formation of AFt and AFm Phases

XRD was used to study changes in the crystalline phases based between C₃A and C₄A₃ \bar{S} with 5wt% Pb(NO₃)₂ in the early stage. Fig. 3 showed that the most prominent peaks in these specimens were those of unhydrated CaSO₄·2H₂O in both C₃A and C₄A₃ \bar{S} cases at day 1. However, in the case of C₄A₃ \bar{S} , it was found that the formation of AFt and AFm phases

was faster than that of C_3A . Moreover, calcium lead hydroxides ($Ca[Pb(OH)_3 \cdot H_2O]_2$) incorporating lead ions were formed during hydration of $C_4A_3\bar{S}$ in the early stage compared to the C_3A case.

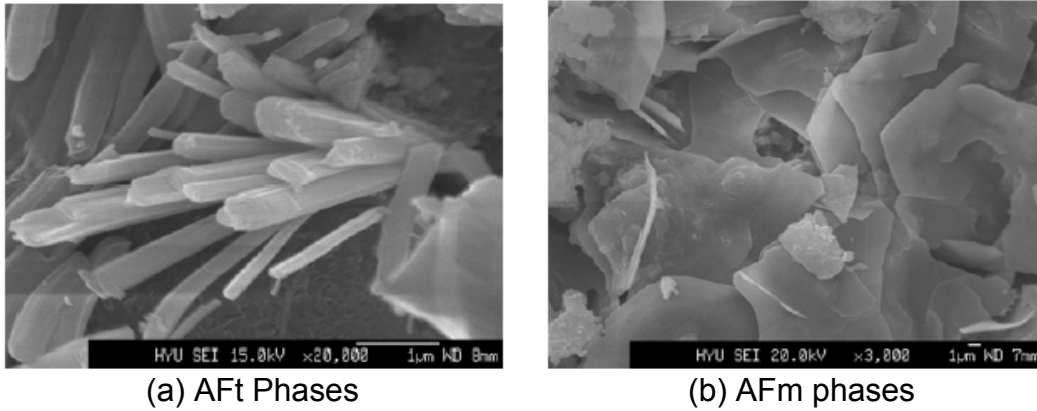


Fig. 2 Hydration products of AFt and AFm phases based $C_4A_3\bar{S}$ at 1 day

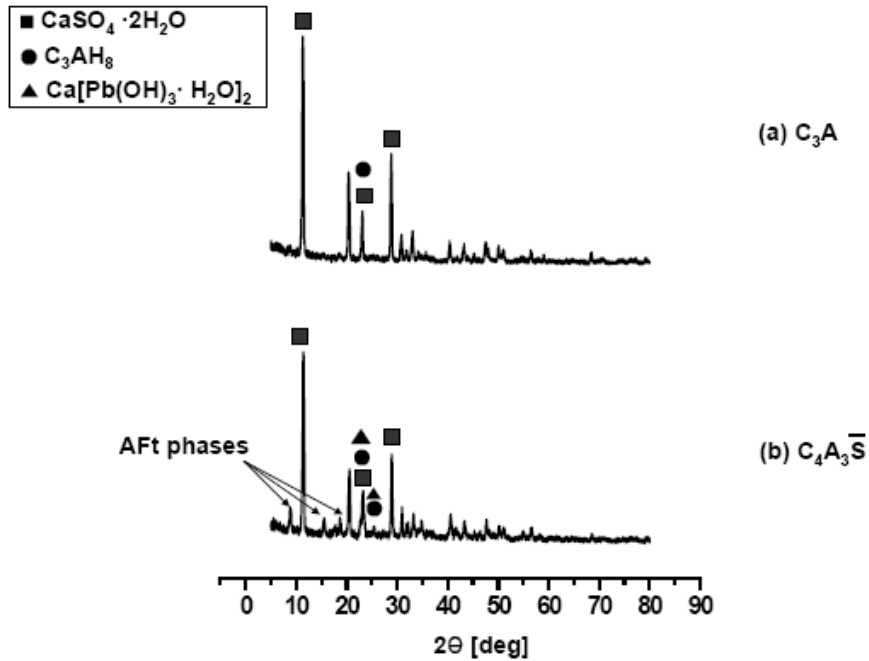


Fig. 3 XRD patterns of C_3A and $C_4A_3\bar{S}$ pastes incorporating lead cured at 1 day.

The FT-IR analysis corroborated the XRD results. As can be seen in Fig. 4, in the case of $C_4A_3\bar{S}$, the band appeared at 1350 cm^{-1} from 1 day compared to the C_3A case. It seemed that the vibrations of lattice $[SO_4]^{2-}$ and $[AlO_2]^-$ groups were related with the formation of AFt or AFm phases.

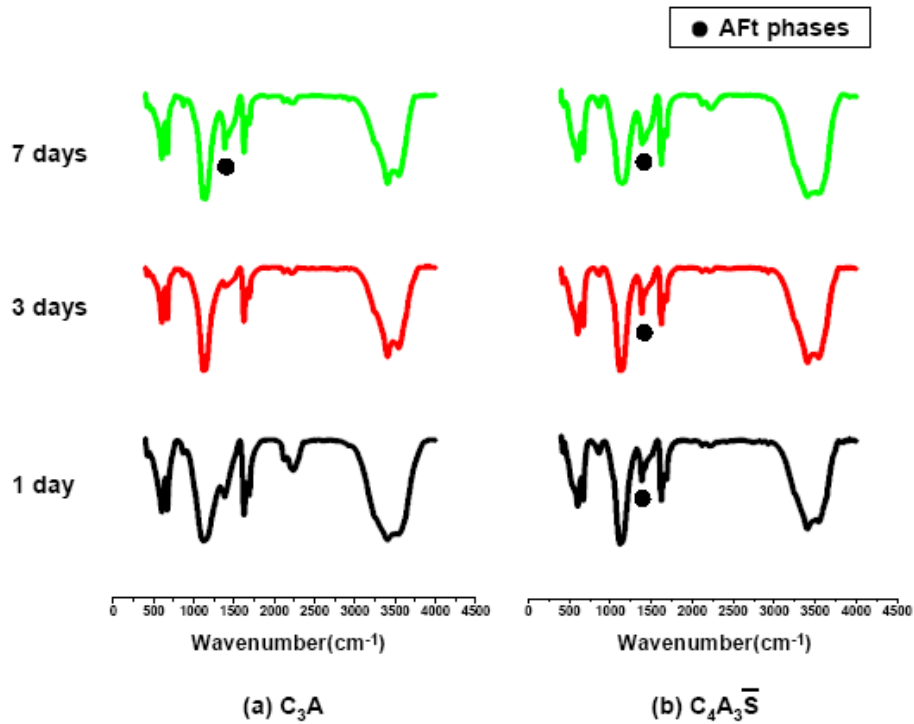


Fig. 4 FT-IR analysis of C_3A and $C_4A_3\bar{S}$ pastes with 5wt% lead

On the other hand, in the case of C_3A the formation of AFt or AFm phases was delayed by lead until day 7. This seemed that metal anions as $Pb(OH)_4^{2-}$ precipitated on the surface of C_3A pastes when AFt or AFm phases were formed. Namely it revealed that the $C_4A_3\bar{S}$ case had a high potential to undergo ionic substitution of $Pb(OH)_4^{2-}$ for $[SO_4]^{2-}$, compared to the C_3A case, when lead ions are added to the cementitious system. SEM/EDS and hydration heat evaluation also corroborated this.

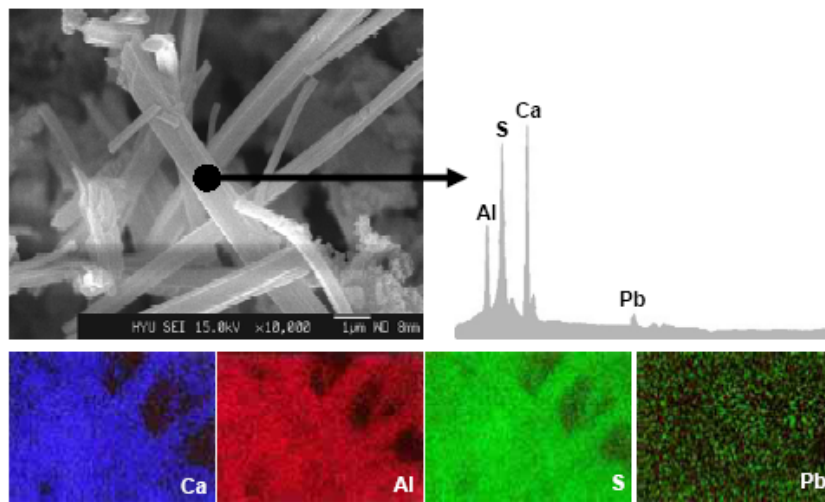


Fig. 5 X-ray spectrum from AFt phase based C_3A containing 5wt% Pb

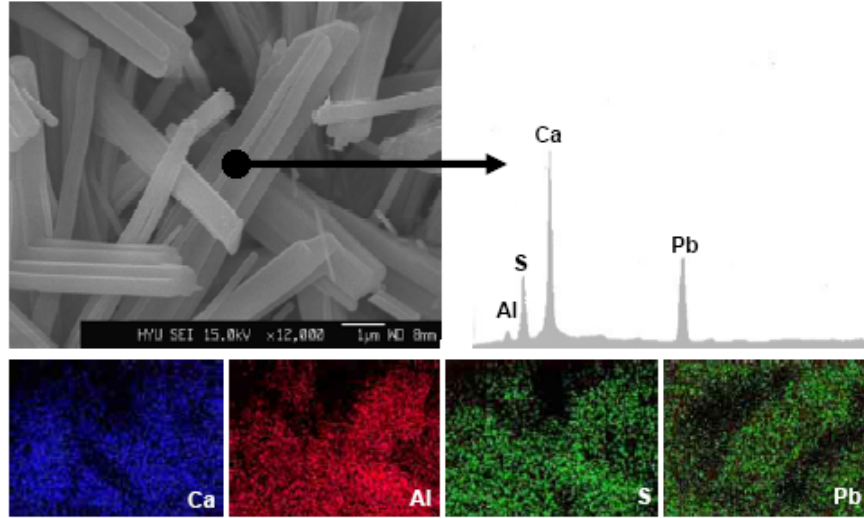


Fig. 6 X-ray spectrum from AFt phase based $C_4A_3\bar{S}$ containing 5wt% Pb

Fig. 5 and Fig. 6 showed that the difference in formation of AFt phases between based C_3A and based $C_4A_3\bar{S}$ were detected. X-ray spectra obtained from these phases revealed differential trends in their chemical composition as the formation of AFt and AFm phases proceeded. It was observed that the ratio of lead peak height increased. On the other hand, the ratio of Al^{3+} and SO_4^{2-} peak heights decreased considerably compared to the C_3A case. Because these observed changes in the ratios of Al and Pb, it was supposed that lead ions exchanged with aluminate and sulfate ions during the formation of AFt phases in the case of $C_4A_3\bar{S}$.

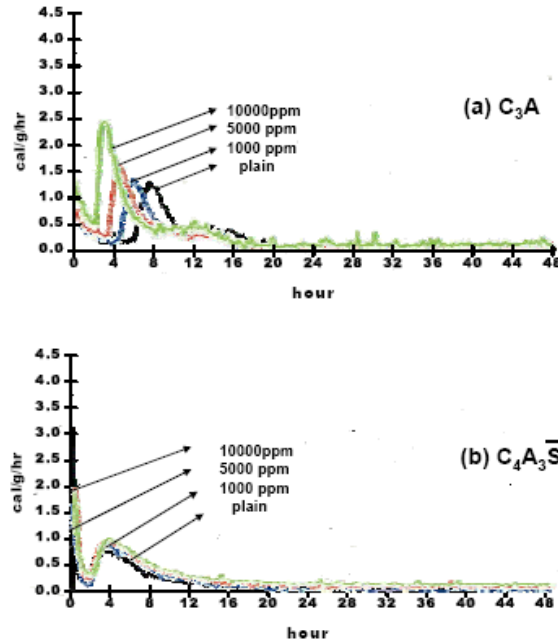


Fig. 7 Hydration of C_3A and $C_4A_3\bar{S}$ pastes with lead 1000 ppm, 5000 ppm and 10,000 ppm

Especially, X-ray maps showed the differential behavior of lead clearly. In the case of AFt phase based $C_4A_3\bar{S}$, the distribution of lead focused on AFt phases. This means that the lead affected the formation of AFt phase based $C_4A_3\bar{S}$ slightly, compared to the C_3A case.

Fig. 7 shows the hydration heat curves with lead 1000 ppm, 5000 ppm and 10,000 ppm respectively. Results of the hydration heat of the $C_4A_3\bar{S}$ case showed that there was no notable change in hydration heat with the variation of lead concentrations. It means that the formation of AFt or AFm phases are effected slightly by lead ions, especially compared to the C_3A case in the early stage. For the case of C_3A , it was observed that hydration heat was increased in order to form the metal hydroxide gradually when lead ions were added. These impermeable membranes of metal hydroxides also showed the hydration retardation of C_3A [6]. These results showed good correlation of the FT-IR with SEM/EDS results. From these results, lead significantly affected the formation of AFt phases according to the cementitious minerals used. Finally, the effects of S/S of lead ions by AFt or AFm phases are dependent on the amounts of sulfate ions within cementitious clinker minerals. Furthermore, calcium sulfoaluminate cement with $C_4A_3\bar{S}$ also has the potential to be useful for S/S materials.

3.2 Effect of Chromium(III) on the Formation of AFt and AFm Phases

Similar XRD patterns were observed when chromium(III) was added to the C_3A and $C_4A_3\bar{S}$ system. (Fig. 8)

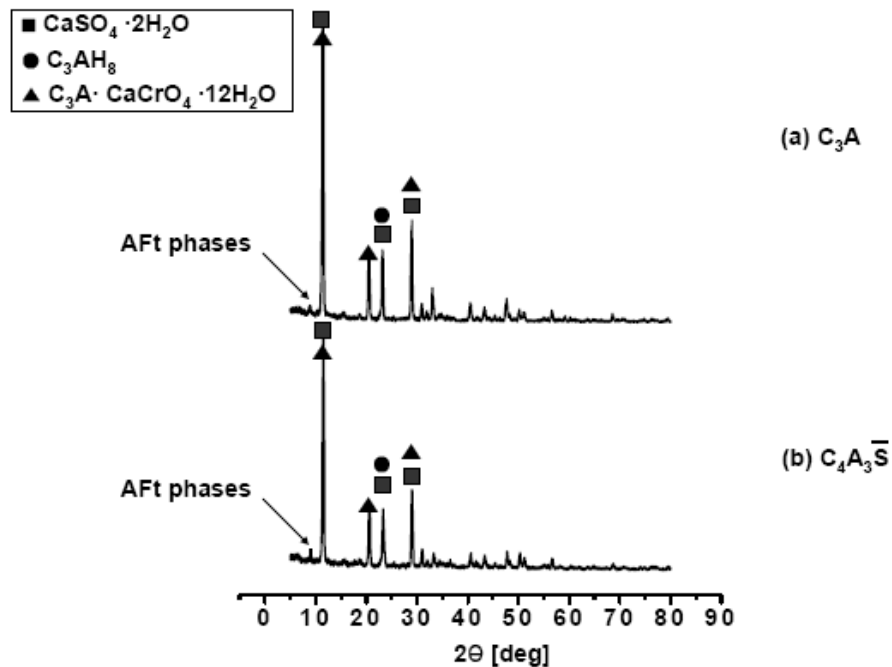


Fig. 8 XRD patterns of C_3A and $C_4A_3\bar{S}$ pastes incorporating chromium(III) cured at 1 day.

Two major crystalline phases detected in these samples were the unreacted $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and AFt phases at 1day. The monochromate ($\text{C}_3\text{A} \cdot \text{CaCrO}_4 \cdot 12\text{H}_2\text{O}$) was also expected to appear due to the hydration of CrO_4 , and it was found that the peak overlapped with those of unhydrated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 11° , 21° and 28° [7,8]. Especially in the case of chromium, AFt or AFm phases appeared in both samples from day 1. This shows the differential behavior of chromium ions compared to the lead ions in the both C_3A and $\text{C}_4\text{A}_3\bar{\text{S}}$ case. Moreover, X-ray spectra taken from these pastes adding chromium(III) revealed similar trends in their chemical composition as the formation of AFt or AFm phases proceeded. (Fig. 9) This showed that C_3A pastes allowed ionic substitution Cr^{3+} for the trivalent ion as Al^{3+} and CrO_4^{2-} for SO_4^{2-} . It was also observed that the ratio of Al peak height decreased due to the substitution of Cr^{3+} ions.

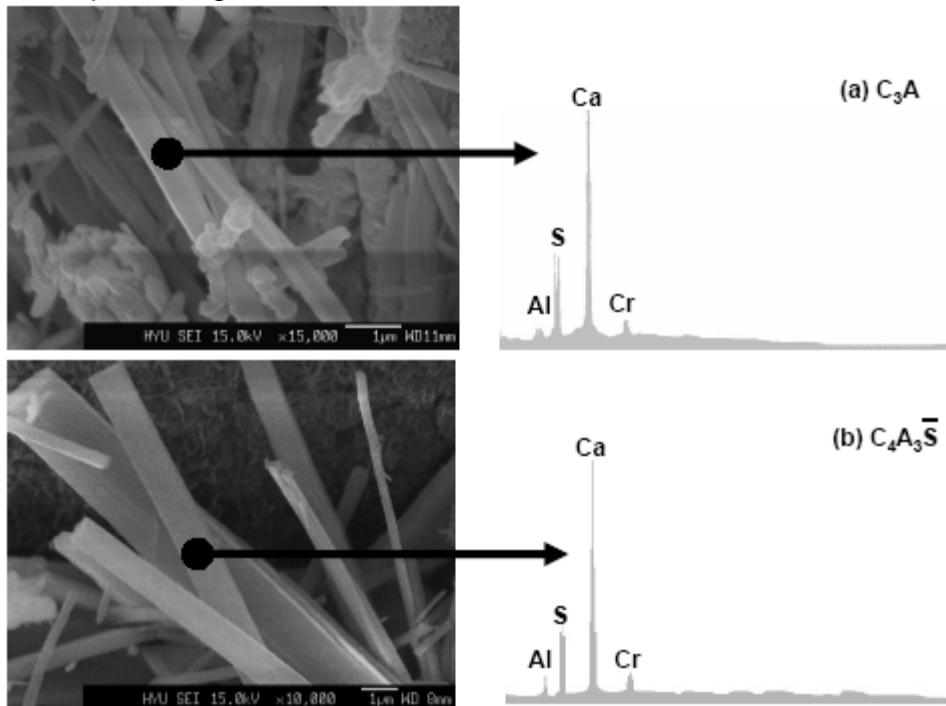


Fig. 9 X-ray spectrum from AFt phase containing 5wt% chromium(III)

The heat evolution curves for these adding chromium(III) are shown in Fig. 10. The hydration curve of $\text{C}_4\text{A}_3\bar{\text{S}}$ clearly shows differential trend in the early stage, compared to the result from the lead addition. The addition of chromium(III) affected the $\text{C}_4\text{A}_3\bar{\text{S}}$ paste hydration processes compared to the lead case. In the case of 10,000 ppm Cr, many chromium hydroxides caused by a surface passivation of the hydration products retarded hydration in all specimens. 5,000 ppm and 1,000 ppm Cr accelerated the hydration for both cases. This acceleration causes a good fixation of the chromium ions through the AFt or AFm phases [9].

Table 1 shows the results of leaching tests of Pb and Cr for the specimens as a function of curing time. It was founded that Pb and Cr were leached

from $C_4A_3\bar{S}$ pastes at lower concentrations compared with C_3A pastes at 3 days. From these results, it could be predicted that the S/S ability of AFt or AFm phases based $C_4A_3\bar{S}$ is higher than that of C_3A in the case of Pb and Cr ions in early stages.

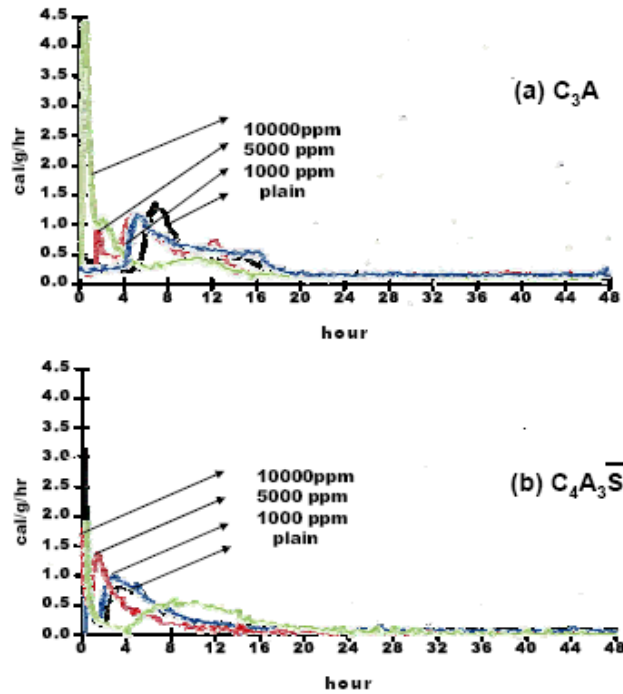


Fig. 10 Hydration of C_3A and $C_4A_3\bar{S}$ pastes with chromium(III) 1000 ppm, 5000 ppm and 10,000 ppm

Table 1. Leaching Concentration of Lead and Chromium(III) from C_3A and $C_4A_3\bar{S}$ pastes (3 days).

Heavy Metals	Pb (1000 ppm)	Cr (1000 ppm)
C_3A	0.27	0.06
$C_4A_3\bar{S}$	Tr	0.06

CONCLUSIONS

1. The clinker mineral type considerably affected the S/S mechanism of AFt and AFm phases incorporating lead and chromium (III) ions.
2. In the case of adding lead, it was found that when C_3A and $C_4A_3\bar{S}$ were hydrated, the formation of AFt and AFm phase based $C_4A_3\bar{S}$ was faster than in C_3A . Especially, AFt phases and the calcium lead hydroxides ($Ca[Pb(OH)_3 \cdot H_2O]_2$) incorporating lead ions were formed during hydration of $C_4A_3\bar{S}$ in the early stage.

3. In the case of adding chromium(III), both AFt and AFm phase based C_3A and $C_4A_3\bar{S}$ allowed for ionic substitution of Cr^{3+} for the trivalent ion as Al^{3+} and CrO_4^{2-} for SO_4^{2-} . Moreover, chromate hydrocalumite [$3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$] was also observed. This showed that AFt and AFm phase based $C_4A_3\bar{S}$ for S/S of lead and chromium(III) were more effective than those of C_3A .

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