

## Early Hydration Properties of Calcium Aluminosulfate ( $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ ) Prepared by Chemical Synthesis

Hoon Sang Kim, Hyung Chul Kim and Jong Taek Song<sup>†</sup>

Department of Materials Science and Engineering, Dankook University, Cheonan 330-714, Korea  
(Received February 28, 2002; Accepted June 8, 2002)

### ABSTRACT

Calcium aluminosulfate ( $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  or  $\text{C}_4\text{A}_3\bar{\text{S}}$ ) was prepared by chemical synthesis from the nitrate salts and aluminum sulfate.  $\text{C}_4\text{A}_3\bar{\text{S}}$  was the main phase after calcination at  $1100^\circ\text{C}$ . The specific surface areas after calcination at  $1100^\circ\text{C}$  and  $1300^\circ\text{C}$  were about 2.5 and  $1.0 \text{ m}^2/\text{g}$ , respectively. Hydration was investigated by XRD, DSC, SEM, EDS, conduction calorimetry and analysis of the liquid phase. Calorimetry showed that the induction period was longer than that of a sample prepared by conventional solid state sintering and this was attributed to the formation of amorphous coatings in abundance of  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$ . Crystalline hydration products, principally calcium monosulfoaluminate hydrate and  $\text{Al}(\text{OH})_3$ , appeared subsequently.

**Key words :**  $\text{C}_4\text{A}_3\bar{\text{S}}$ , Induction period, Amorphous coating, Calcium monosulfoaluminate,  $\text{Al}(\text{OH})_3$

### 1. Introduction

Calcium aluminosulfate,  $\text{C}_4\text{A}_3\bar{\text{S}}$ , is an important mineral phase for rapid hardening calcium aluminate sulphate-based cement.<sup>1,2)</sup> Formation of  $\text{C}_4\text{A}_3\bar{\text{S}}$  takes place at a relatively low temperatures,<sup>3-5)</sup> it can be used for the preparation of special low energy calcium aluminosulfate cement by using gypsum along with low grade limestone, clay, fly ash, red mud and blast furnace slag, etc.<sup>6,7)</sup> The formation of pure mono-mineralic  $\text{C}_4\text{A}_3\bar{\text{S}}$  is reported to be difficult since the gypsum decomposes to varying degrees and  $\text{SO}_3$  volatilizes during sintering,<sup>8)</sup> but it can be prepared by repeated firing of a stoichiometric mixture of oxides and gypsum at  $1350^\circ\text{C}$ .

$\text{C}_4\text{A}_3\bar{\text{S}}$  hydration proceeds with formation of  $\text{C}_4\text{A}_3\bar{\text{S}}\text{H}_x$  and  $\text{AH}_3$ .<sup>9-12)</sup> Simultaneous crystallization of  $\text{C}_4\text{A}_3\bar{\text{S}}\text{H}_x$  and  $\text{AH}_3$  occurs after initial induction period up to total conversion. Three mono-sulphoaluminate hydrates,  $\text{C}_4\text{A}_3\bar{\text{S}}\text{H}_x$  have been identified in the hydrated products, with  $x = 10, 12$  and  $15$ .<sup>11)</sup>

In this paper,  $\text{C}_4\text{A}_3\bar{\text{S}}$  has been chemically synthesized by the PVA process, which has been used to prepare other cement compounds.<sup>13)</sup> Because the PVA synthesis involves primarily steric entrapment of cations into a polymer network, it results in a pure, highly reactive and homogeneous powder at the molecular level.<sup>13,14)</sup> The early hydration of the powders were studied by XRD, DSC, SEM, EDS, conduction calorimetry and analysis of the liquid phase. Comparison is made with the conventional solid-state reaction method.

### 2. Experimental Procedure

#### 2.1. Chemical Synthesis

$\text{Ca}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 29\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$  (Junsei Chemical Co., Ltd.) were used as starting materials. A spray-dried preparation of 78% hydrolyzed PVA with a particle size of about  $150 \mu\text{m}$  (Goshenol KH-17s, Nippon Gosei) also was used. A stoichiometric mixture of the three salts was added to a 5 wt% aqueous solution of PVA. Water was evaporated by continuous stirring during heating on a hot plate. The gel-type precursor was completely dried at  $105^\circ\text{C}$  after approximately 12 h. The resulting gel was finely ground and then calcined at a rate  $5^\circ\text{C}/\text{min}$ , both  $1100^\circ\text{C}$  and  $1300^\circ\text{C}$  for 1 h. Because  $\text{C}_4\text{A}_3\bar{\text{S}}$  was the main phase after calcination at  $1100^\circ\text{C}$ . The specific surface areas after calcination at  $1100^\circ\text{C}$  and  $1300^\circ\text{C}$  were 2.5 and  $1.0 \text{ m}^2/\text{g}$ , respectively.

#### 2.2. Solid State Sintering

$\text{C}_4\text{A}_3\bar{\text{S}}$  was prepared by the conventional solid-state reaction and hydrated, for comparison. A stoichiometric mixture of reagent grade  $\text{CaCO}_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  was sintered  $1350^\circ\text{C}$  for 1 h. The specific surface area measured by BET was  $0.54 \text{ m}^2/\text{g}$ .

#### 2.3. Hydration Experiments

The calcined powder was mixed with deionized water at water/solid ratios of 1.0. The pastes were sealed in plastic bottles and held at  $23^\circ\text{C}$  for times from 30 min to 72 h. Hydration of the solid was stopped by immersing the crushed samples in acetone. Acetone-exchanged samples were filtered and dried at  $45^\circ\text{C}$  for 72 h and kept in a desiccator until analysis. The water to solid ratio used for analysis of the liquid phase is 10. The liquid phase in the

<sup>†</sup>Corresponding author : Jong Taek Song

E-mail : song8253@dku.edu

Tel : +82-41-550-3533 Fax : +82-41-550-3530

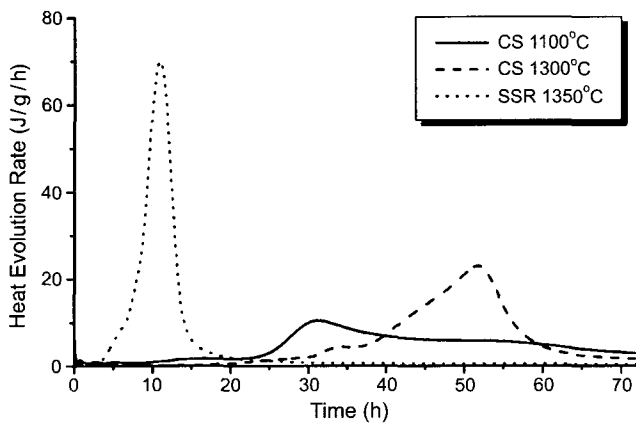
hydrated paste was separated by absorption with a filter paper and concentrations of CaO, Al<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub> therein contained were measured by Inductively Coupled Plasma-mass Spectrometry(ICP) (Shimadzu ICPS-1000) and Ion Chromatography(IC) (Bionex DX-100).

**2.4. Materials Characterization**

The specific surface area of calcined powders was determined by nitrogen absorption (BET) (Quantachrome Autosorb-1) and the phases of the calcined powder and hydrated samples were identified by X-Ray Diffraction (XRD) (Shimadzu DX-D1) using Cu K<sub>α</sub> radiation (30 kV, 30 mA). The liberation of heat of hydration was measured by conduction calorimetry (Tokyo Riko TCC). Differential Scanning Calorimetry(DSC) (Shimadzu DSC-50) was used to determine the phases of the hydrated pastes using a heating rate of 5°C/min. The microstructure and the analysis of hydrated samples were observed by Scanning Electron Microscopy(SEM) (JEOL JSM-5200) and EDS (Kevex Superdry), respectively.

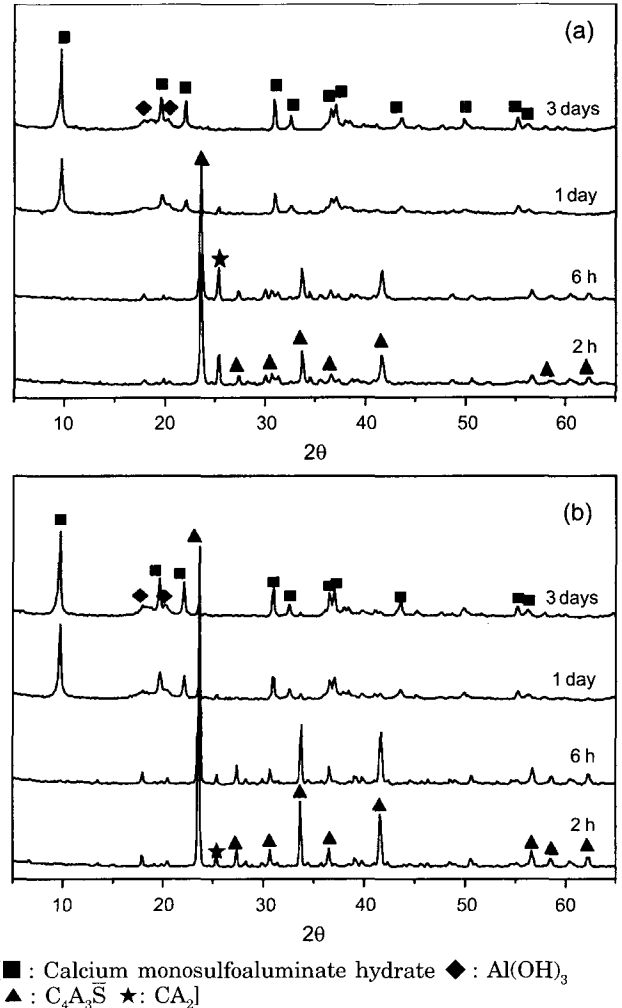
**3. Results and Discussion**

Conduction calorimetry reveals a long induction period

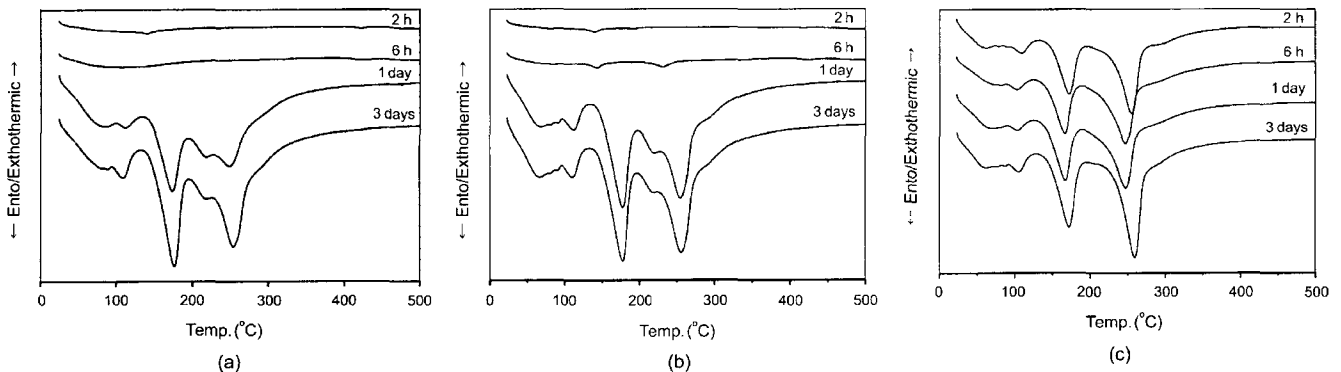


**Fig. 1.** Heat evolution rate in C<sub>4</sub>A<sub>3</sub>S̄ + H<sub>2</sub>O system.

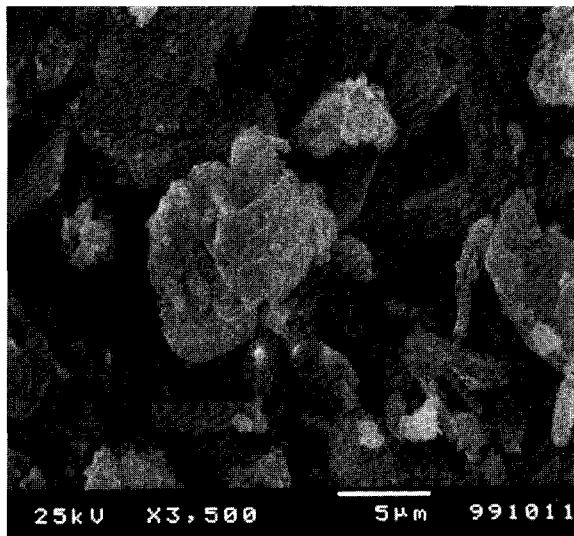
when little reaction occurs, followed by a period of relatively rapid reaction (Fig. 1). Surprisingly, the induction periods for the directly synthesized samples are much longer than that for the sintered sample and the subsequent rate of heat evolution is much slower.



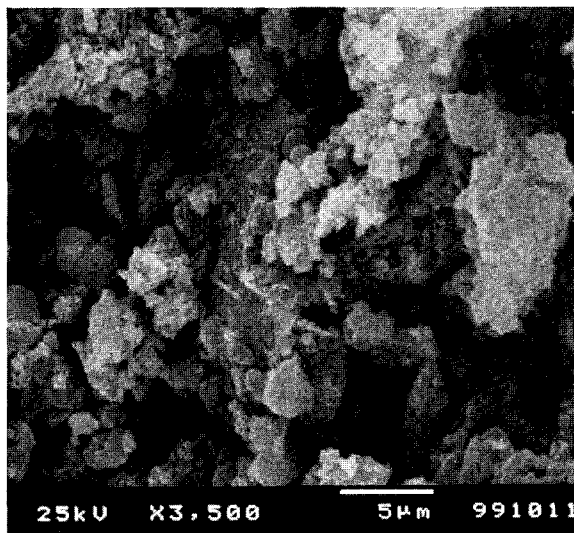
**Fig. 3.** XRD patterns of hydrated C<sub>4</sub>A<sub>3</sub>S̄ powders at (a) 1100°C and (b) 1300°C.



**Fig. 2.** DSC thermograms of hydrated C<sub>4</sub>A<sub>3</sub>S̄ powders synthesized by : (a) calcination at 1100°C, (b) calcination at 1300°C and (c) solid state sintering.



(a)



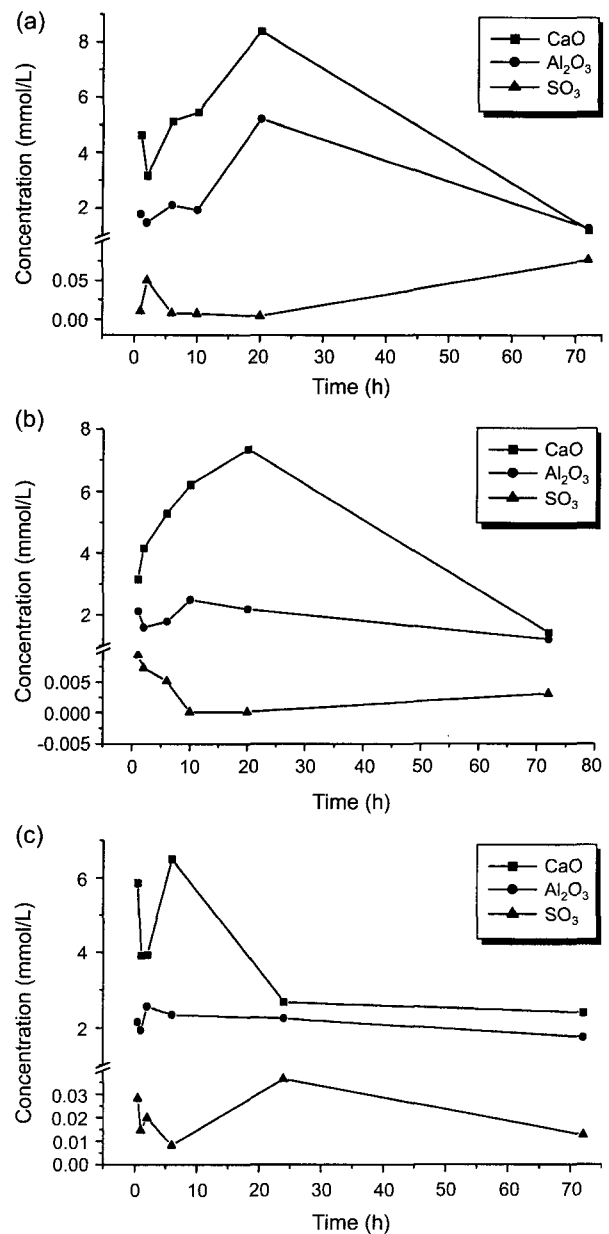
(b)

**Fig. 4.** SEM micrographs of  $\text{C}_4\text{A}_3\bar{\text{S}}$  hydrated for 1 day; powders calcined at (a)  $1100^\circ\text{C}$  and (b)  $1300^\circ\text{C}$ .

The increased induction period is confirmed by the DSC data (Fig. 2) and XRD (Fig. 3) although subsequent hydration appears to be similar. However, by 1d large amounts of calcium monosulphoaluminate hydrate ( $\text{C}_4\bar{\text{A}}\bar{\text{S}}\text{H}_{12}$ ) and crystalline  $\text{Al}(\text{OH})_3$  form (Fig. 4). SEM observations of the 1d samples show abundant plate-like crystals attributed to  $\text{C}_4\bar{\text{A}}\bar{\text{S}}\text{H}_{12}$  (Fig. 4).

The DSC curves of hydrated  $\text{C}_4\text{A}_3\bar{\text{S}}$  pastes are shown in Fig. 2. As temperatures approach and exceed  $100^\circ\text{C}$ , uncombined water is expelled including some loosely bound water which may be associated with amorphous alumina gel.<sup>15)</sup> The endothermic peaks of  $\text{C}_4\bar{\text{A}}\bar{\text{S}}\text{H}_{12}$  (around  $180^\circ\text{C}$ ) and crystalline aluminum hydroxide (about  $250^\circ\text{C}$ ) increase with hydration time.

Sera and Tsuchiya<sup>9)</sup> proposed that the long induction period might be due to the rapid formation of an amorphous



**Fig. 5.** Concentrations of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  in the liquid phase; powders synthesized by : (a) calcination at  $1100^\circ\text{C}$ , (b) calcination at  $1300^\circ\text{C}$  and (c) solid state sintering.

$\text{Al}(\text{OH})_3$  coatings on the surface of  $\text{C}_4\text{A}_3\bar{\text{S}}$  particles. Similar coatings have been claimed in the early hydration of calcium aluminate cements.<sup>15-18)</sup> In this case unequivocal evidence of such a coating was not obtained by SEM observations, but only a very thin coating would be sufficient to influence reaction kinetics but not necessarily observable by SEM. The length of this induction period depends on the calcination temperature and specific surface area of  $\text{C}_4\text{A}_3\bar{\text{S}}$ . At the end of the induction period there is relatively rapid reaction to form  $\text{C}_4\bar{\text{A}}\bar{\text{S}}\text{H}_{12}$  and aluminum hydroxide.

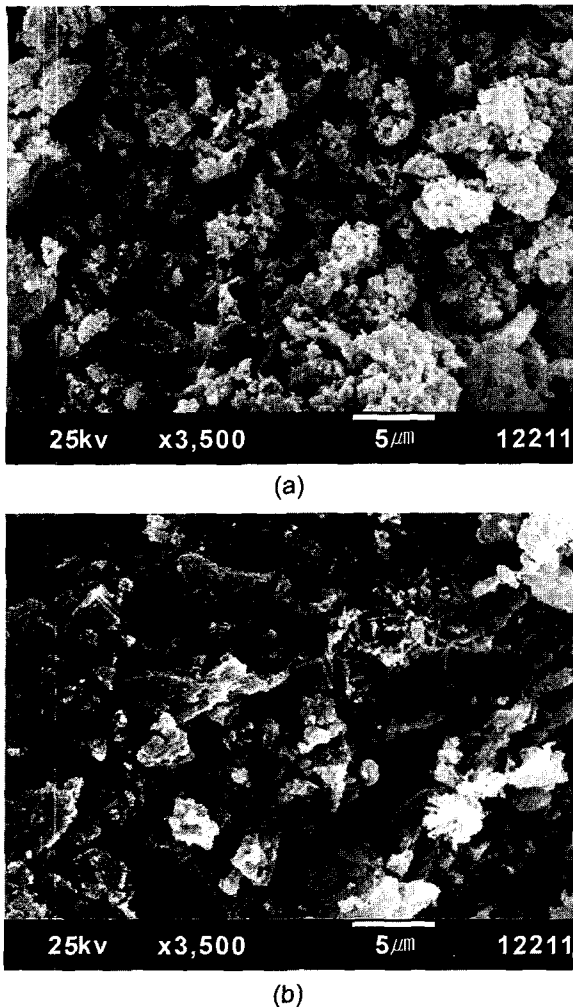


Fig. 6. SEM micrographs of  $C_4A_3\bar{S}$  hydrated for 6 h; powders calcined at (a) 1100°C and (b) 1300°C.

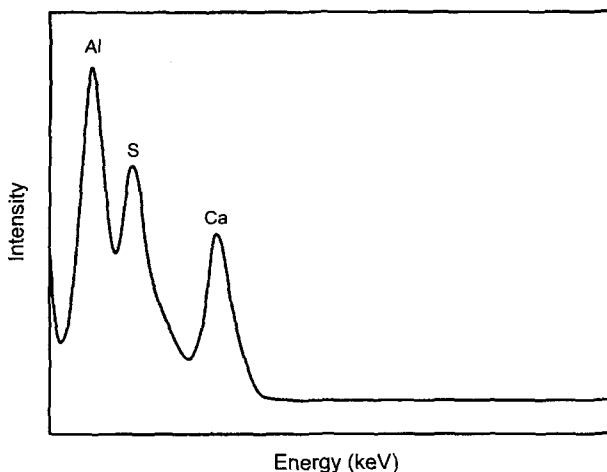


Fig. 7. EDS analysis in chemical synthesized samples at 10 h.

The results obtained by measuring the concentrations of  $CaO$ ,  $Al_2O_3$  and  $SO_3$  in the liquid phase are shown in Fig. 5.

In the case of chemically synthesized samples, concentrations of  $CaO$  and  $Al_2O_3$  were increased with hydration time in the induction period for ab. 20 h. After it, those were decreased due to the formation of crystalline hydration products, calcium monosulfoaluminate hydrate and  $Al(OH)_3$ . However, during the induction period the concentration of  $SO_3$  might be consumed by the formation of an amorphous hydrates. When the induction period was ended,  $SO_3$  concentration was increased with hydration time. It was considered that calcium monosulfoaluminate hydrate was formed and  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $OH^-$  and  $Al(OH)_3$  were dissociated from the above amorphous hydrates.<sup>19)</sup>

From the relatively low concentrations of  $Al_2O_3$  and  $SO_3$  in the induction period, the amorphous hydrate in abundance of  $Al_2O_3$  and  $SO_3$  formed over the entire surface  $C_4A_3\bar{S}$  particles. The EDS analysis of hydrated  $C_4A_3\bar{S}$  pastes are shown in Fig. 7. In the hydrated Al and Si were abundant comparing to Ca.

SEM observation of  $C_4A_3\bar{S}$  particle surfaces after 6 h hydration revealed that an amorphous or nearly amorphous hydrates with a partially needle-shaped one were formed on the surfaces of particle (Fig. 6). Accordingly, the long induction period would be due to the rapid formation of an amorphous hydrated on the surface of  $C_4A_3\bar{S}$  particles.

#### 4. Conclusion

Although  $C_4A_3\bar{S}$  is more reactive when synthesized chemically, it has the longer induction period before crystalline hydration products form compared to a sample prepared by solid state sintering. This may be due to the rapid formation of a protective and amorphous coating, which prevents further hydration until the crystalline products, calcium monosulfoaluminate hydrate and  $Al(OH)_3$ , can nucleate and grow. In chemically synthesized sample, amorphous or nearly amorphous hydration products containing abundant  $Al_2O_3$  and  $SO_3$  are formed in  $C_4A_3\bar{S}$  particle surroundings and needle-shaped phase is observed before crystalline products are detected at the induction period. The formation of amorphous hydration products may be due to a rapid reactivity of  $C_4A_3\bar{S}$  powders.

#### Acknowledgement

This present research was conducted by the research fund of Dankook University in 2001.

#### REFERENCES

1. I. Kapralik, *et al.*, "Sub-solidus Phase Relations in the System  $CaO-Al_2O_3-SiO_2-Fe_2O_3-MgO-CaSO_4-K_2SO_4$  at 950°C in Air referred to Sulphoaluminate Cement Clinker," *Trans. J. Brit. Ceram. Soc.*, **85** 107-10 (1986).
2. I. D. Hwang, *et al.*, "Expansion Factors of Cement Motors Containing Expanding Admixture," *J. of the Kor. Ceram. Soc.*, **37** [6] 576-82 (2000).

3. I. Kapralik, *et al.*, "Phase Changes in System,  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3\text{-MgO-CaSO}_4$  in Air up to 1300 referred to Sulphoaluminate Cement Clinker," *J. Brit. Ceram. Soc.*, **85** 131-36 (1986).
4. F. Hanic, *et al.*, "Crystal Chemistry and Thermodynamics of the Sulphate Compounds  $\text{C}_4\text{A}_3\bar{\text{S}}$  and  $\text{C}_5\text{A}_2\bar{\text{S}}$ ," *Trans. J. Brit. Ceram. Soc.*, **85** 52-7 (1986).
5. M. M. Ali, *et al.*, "Studies on the Formation Kinetics of Calcium Sulphoaluminate," *Cem. Conc. Res.*, **24** [4] 715-20 (1994).
6. S. Muzhen, *et al.*, "Development in Non-portland Cements," *Proc. 9th Intern. Congr. Chem. Cement*, New Delhi, **1** 317-54 (1992).
7. C. D. Lawrence, "The Production of Low-energy Cements," pp. 421-470 in *Lea's Chemistry of Cement and Concrete 4th Ed.*, Ed. by P. C. Hewlett, Arnold, London (1997).
8. Z. Peixing, *et al.*, "The Crystal Structure of  $\text{C}_4\text{A}_3\bar{\text{S}}$ ," *Proc. 9th Intern. Congr. Chem. Cement, New Delhi*, **III** 201-08 (1992).
9. N. Sera and M. Tsuchiya, "Hydration of Calcium Sulphoaluminate," *Semento Gijutsu Nenpo(in Jpn.)*, **12** 95-8 (1968).
10. N. Fukada, "Fundamental Studies on the Expansive Cement," *Proc. 5th. Intern. Symp. Chem. Cement, Tokyo*, **IV** 341-50 (1969).
11. I. Kapralik and F. Hanic, "Phase Relations in the Subsystem  $\text{C}_4\text{A}_3\bar{\text{S}}\text{-C}\bar{\text{S}}\text{H}_2\text{-CH-H}_2\text{O}$  of the System  $\text{CaO-Al}_2\text{O}_3\text{-C}\bar{\text{S}}$ - $\text{H}_2\text{O}$  referred to Hydration of Sulphoaluminate Cement," *Cem. Conc. Res.*, **19** 89-102 (1989).
12. W. Kurdowski and F. Sorrentino, "Special Cements," pp. 471-554 in *Structure and Performance of Cements.*, ed. P. Barnes, Applied Science Publishers, London and New York (1983).
13. J. Y. Jeun, *et al.*, "Synthesis and Hydration Property of  $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  Clinker by Solid State Reaction," *J. of the Kor. Ceram. Soc.*, **37** [5] 459-65 (2000).
14. J. Y. Jeun and J. T. Song, "Synthesis and Properties of Calcium Sulfoaluminate Type Expansive," *J. of the Kor. Ceram. Soc.*, **37** [4] 388-94 (2000).
15. S. J. Lee, *et al.*, "Preparation of Portland Cement Components by PVA Solution Polymerization," *J. Am. Ceram. Soc.*, **82** [8] 2049-55 (1999).
16. M. A. Gulgun, *et al.*, "Polymerized Organic-inorganic Synthesis of Mixed Oxides," *J. Am. Ceram. Soc.*, **82** [3] 556-616 (1999).
17. K. L. Scrivener and A. Capmas, "Calcium Aluminate Cements," pp. 709-778 in *Lea's Chemistry of Cement and Concrete 4th Ed.*, Ed. by P. C. Hewlett, Arnold, London (1997).
18. K. Fujii, *et al.*, "Kinetics of Hydration of Monocalcium Aluminate," *J. Am. Ceram. Soc.*, **69** 361-64 (1986).
19. H. F. W. Taylor, *et al.*, "Delayed Ettringite Formation," *Cem. Conc. Res.*, **31** 683-93 (2001).