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# Influence of $H_3BO_3$ on the hydration of calcium sulfoaluminate and calcium aluminate

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The influence of $H_3BO_3$ for the hydration of calcium sulfoaluminate and calcium aluminate was investigated. The addition of $H_3BO_3$ affects the solubility of the ions and the rate of solution of the ions from calcium sulfoaluminate and calcium aluminte. Especially the Al ion concentration showed a very low solubility in the $H_3BO_3$ solution. The gelatinous products were observed when the solution of calcium aluminate and $H_3BO_3$ solution reacted in this study. These gelatinous products are constituted by the basic Al ion with incorporated B ion and great quantity water. After all, these gelatinous products form the impermeable layer on the surface of the particles of calcium sulfoaluminate and calcium aluminate, and interrupt the diffusion process of the other ions, e.g. $Ca^{2+}$ and $SO_4^{2-}$.

**Key words :** calcium aluminate, calcium sulfoaluminate, $H_3BO_3$, retard, gelatinous products

## 1. INTRODUCTION

The characteristic of hydration of calcium aluminates (calcium sulfoaluminate and calcium aluminate) is known that when reacts with water a flash set happen accompanied by the significant evolution of heat. Because of this characteristic, calcium aluminates have been used as an admixture for rapid-hardening cements and expansive cements.[1)-3)] But because of the hydration of rapid-hardening, it is difficult to obtain the handling time. To solve this problem the retarders have been used, and $H_3BO_3$ is one of them.[4)-7)] But it hasn't been explained fully that the mechanism of the retarded hydration of calcium aluminates by $H_3BO_3$ until now. This study has been carried to explain the mechanism of the retarding hydration.

## 2. EXPERIMENTAL PROCEDURE

To investigate the effect of $H_3BO_3$ on the hydration of calcium aluminates, $C_4A_3\bar{S}$ and $C_3A$ were used as cements. According to the addition of $H_3BO_3$, the hydration reaction was observed by conduction calorimeter and SEM (Scanning Electron Microscopy). The variation of ion concentration in liquid was analyzed by using AAS (Atomic Absorption Spectrophotomety), when $H_3BO_3$ added to the solution of calcium aluminates.

The gelatinous products[8)] were observed when the solution of calcium aluminate and $H_3BO_3$ solution reacted. These gelatinous products analyzed by XRD (X-ray diffractometry), SEM, FT-IR (Fourier Transform-Infrared Spectrometry), TG-DTA (Thermogravimetric Analysis) and ICP-MS (Inductively Coupled

Plasma-Mass Spectrometry). To distinguish between complex ion and simply adsorption ion in gelatinous products, after these gelatinous products were washed by 500ml water at several times, the variation of ion concentration of the washed gelatinous products and the water washing were analyzed separately.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the rate of heat liberation during $C_4A_3\bar{S}$ and $C_3A$ in water and in 2% $H_3BO_3$ solution. The hydration of $C_4A_3\bar{S}$ and $C_3A$ in water, when they reacted with water, showed the significant evolution of heat. But when $C_4A_3\bar{S}$ and $C_3A$ hydrated in 2% $H_3BO_3$ solution, the evolution of heat of hydration didn't appeared. Figure 2 shows the SEM picture of the $C_4A_3\bar{S}$ hydrated in water and in 2% $H_3BO_3$ solution for 4days. In the case of the hydration of $C_4A_3\bar{S}$ in water, the crystalline products, card house and the sphere-like products, were as hydration products. But in the case of $C_4A_3\bar{S}$ hydrated in 2% $H_3BO_3$ solution, the hydrates produced in water weren't observed.

Figure 3 shows the variation of ion concentration in liquid as the addition of $H_3BO_3$ to $C_4A_3\bar{S}$ solution. The ion concentration for Ca, Al and $SO_4$ was lower than that in water. Especially the ion concentration for Al and $SO_4$ was nearly zero in 2% and 4% $H_3BO_3$ solution. These data indicated that the hydration of calcium aluminate in 2% $H_3BO_3$ solution didn't almost occurs. Figure 4 is the SEM picture and XRD pattern of gelatinous products, which precipitated out when the liquid filtered from the solution of calcium aluminate was dropped on $H_3BO_3$ solution. It could be known that these products are a fluffy mass type of a non-crystalline material. Table I shows the adsorption water content in gelatinous products. The evaporable water content was determined about 43 – 49wt% at 80°C, and 67wt% at 25°C under 8kPa. Figure 5 is the FT-IR pattern of gelatinous products. The curve pattern of FT-IR revealed that these products formed from $C_4A_3\bar{S}$ and $C_3A$ were the same things, and the ions of Al and B were contained in these products. Especially in the case of product formed from $C_4A_3\bar{S}$, the ion of $SO_4$ was also contained. Figure 6 shows the variation of ion concentration in liquid by which gelatinous products were washed. The ion concentration of Ca and B decreased greatly as washing times. In particular, the ion concentration of Ca became a zero. But the ion concentration of Al was a constant in the range of 0.1 to 0.4 $mmol{\cdot}dm^{-3}$. We considered that when ion is adsorbed simply in gelatinous products, the concentration of the ion decreases abruptly according as washing process and finally becomes approximately a zero. From these results, it was considered that the gelatinous products were constituted by the basic Al ion with incorporated B ion, and that Ca ion is simply adsorbed on gelatinous products. Table II shows the ion concentration of gelatinous products according as washing process. The ion mole ratio between Al and B increased and the ion concentration of Ca becomes a zero at one time washing. This result is similar to that of the variation of ion concentration in liquid by which gelatinous products were washed. The ion concentration of B was a constant as 0.8 $mmol{\cdot}dm^{-3}$ in liquid by which gelatinous products were washed even at five times washing. The ion mole ratio between Al and B became 1 : 0.31. Table III shows the ion concentration of the both of solution with or without the separation of gelatinous products in the liquid of the filtered $C_4A_3\bar{S}$ solution. As the gelatinous products was formed in liquid, the ion concentration of Al decreased greatly. Ca ion decreased about 1.2 $mmol{\cdot}dm^{-3}$ and the decrease of $SO_4$ ion wasn't observed. This result means that the gelatinous products are constituted approximately by Al ion. As gelatinous products formed, the ion concentration of Al and Ca decreased about 8.26 and 1.16 $mmol{\cdot}dm^{-3}$ respectively, and the ion mole ration between Al and Ca became 1 : 0.14. This result was similar to the result of analysis for non-washing gelatinous products, 1 : 0.17. Table IV shows an ion concentration of Al and Ca in gelatinous products. It was concluded that the gelatinous products, which was produced between the solution of calcium aluminates and $H_3BO_3$ solution, are constituted by the basic Al ion with incorporated B ion, and that Ca ion is simply adsorbed in gelatinous products.

## 4. CONCLUSION

1. The hydration of calcium sulfoaluminate and calcium aluminate in 2% $H_3BO_3$ solution doesn't occur.
2. It was observed that the gelatinous products were precipitates by the reaction between calcium aluminates solution and $H_3BO_3$ solution.
3. The gelatinous products are constituted by the basic Al ion with incorporated B ion and the large amount of water.
4. The ion mole ratio between Al and B is about 1 : 0.3, and water content is about 42 – 67wt%.

## REFERENCE

1. Aroni, S., Polivka, M., and Bresler, B., Structures and Materials Research Repor, 2, 66-679(1966).
2. A. Bentur and M. Ish-Shalom, Cement and Concrete Research, 3[5], 709-21(1974).
3. K. Ogawa and D.M. Roy, Cement and Concrete Research, 12[1], 101-9(1982).
4. W. Leiber and W. Richartz, Z-K-G, 9, 403-9(1972)
5. W. Leiber, Z-K-G, 2, 75-79(1973)
6. H. Uchikawa and S. Uchida, Onoda Lab. Reporter, 29[2], 43-51(1977)
7. K.S.You and K.H.Lee, Journal of the Korean Ceramic Society, 35[6], 583-93(1998)
8. Ramachandran, V.S., and Feldman, F.R., Materaux et Constructions, 5, 67-76(1972)

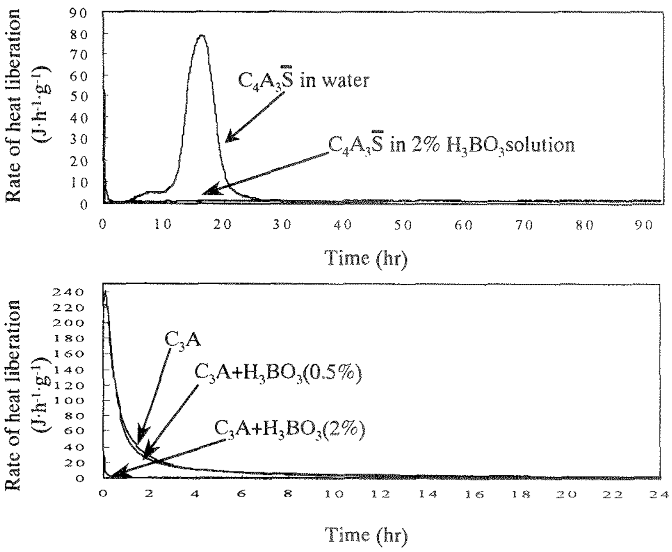


**Fig. 1.** Heat liberation curve of $C_4A_3S$ and $C_3A$ in water and $H_3BO_3$ solution.

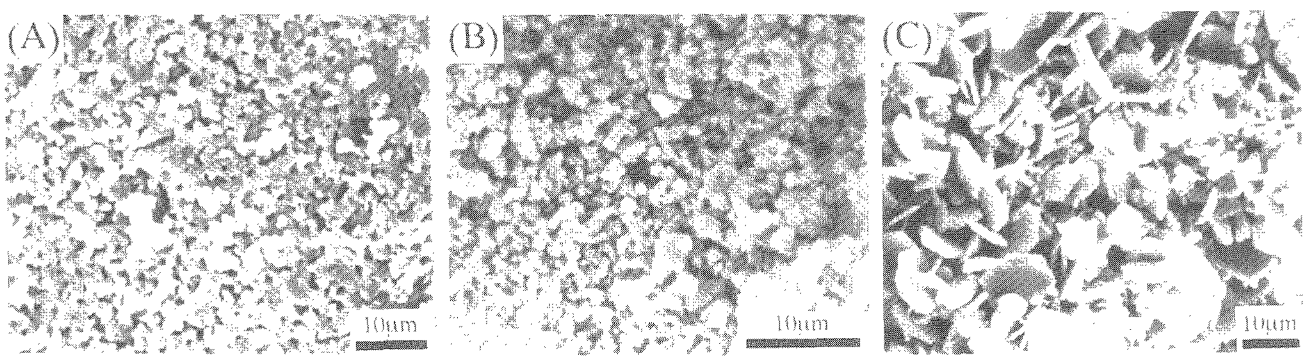


**Fig. 2.** SEM picture of $C_4A_3\bar{S}$ hydrates.
(A) non-hydrates
(B) 4days in water
(C) 4days in $H_3BO_3$ solution

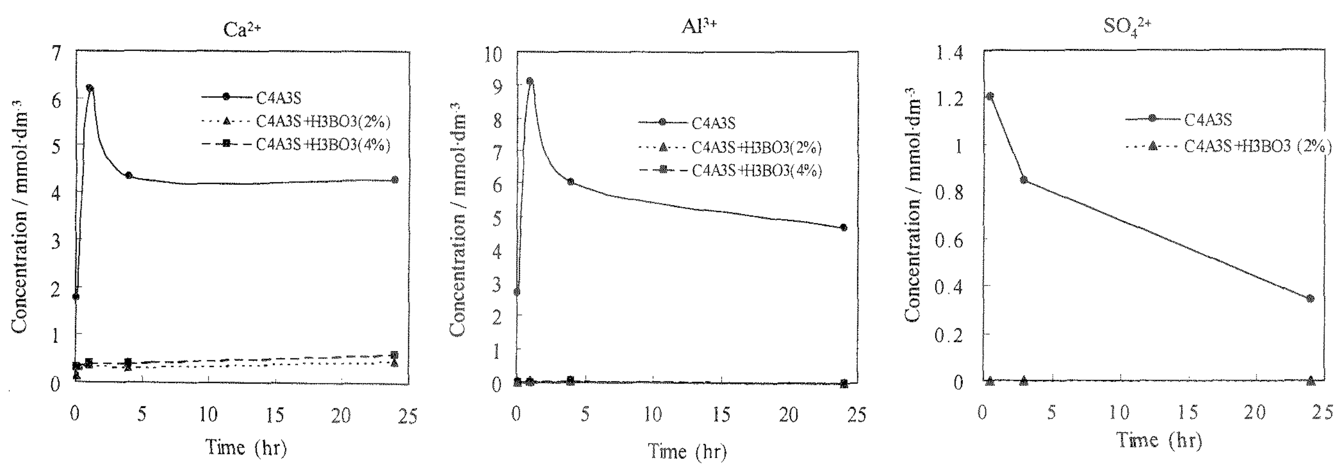


**Fig. 3.** Ion concentration of liquid phase of $C_4A_3\bar{S}$ in paste with time elapsed.

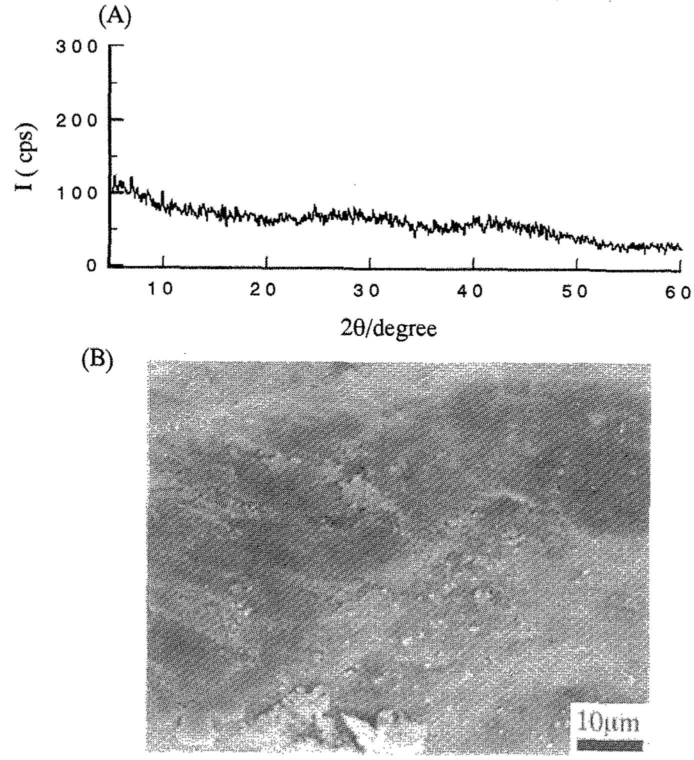


**Fig. 4.** XRD pattern(A) and SEM picture(B) of precipitates.

**Table I.** Water Content in Gelatinous products

| Dried condition | At 80 C° | At 25C° under 8kPa |
|---|---|---|
| Water content (wt%) | 43 ~ 49 | About 67 |

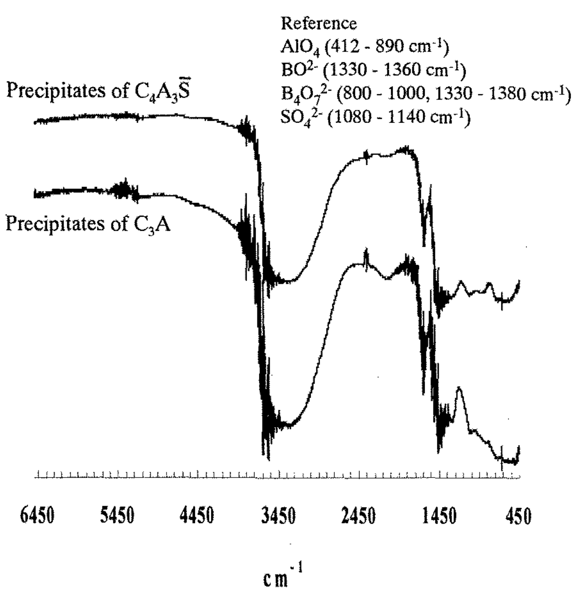


**Fig. 5.** FT-IR pattern of gelatinous products from $C_4A_3\overline{S}$ and $C_3A$.

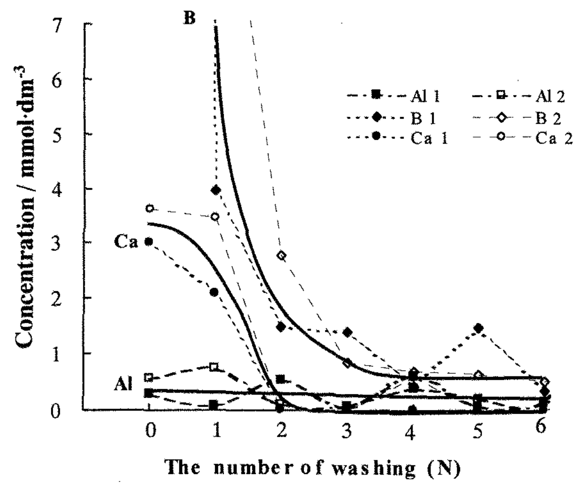


**Fig. 6.** Variation of ions concentration in liquid, which wash gelatinous products.

**Table II.** Ion Concentration of Gelatinous products according as washing process

| | Al | B | Ca | $SO_4$ |
|---|---|---|---|---|
| Non-washing | 1.00 | 1.02 | 0.17 | 0.00 |
| One time Washing | 1.00 | 0.51 | 0.00 | 0.00 |
| Five times washing | 1.00 | 0.31 | 0.00 | 0.00 |

**Table III.** Ion Concentration, When Gelatinous Products Absence and Presence in liquid of the filtered $C_4A_3\overline{S}$ solution

| | Al | Ca | $SO_4$ |
|---|---|---|---|
| Gelatinous product absence in liquid | 8.56 | 5.94 | 2.10 |
| Gelatinous product presence in liquid | 0.30 | 4.78 | 2.30 |

**Table IV.** Ion Concentration of Al and Bin Gelatinous Products (=When gelatinous products absence, the ion concentration of liquid -When gelatinous products presence, the ion concentration of liquid)

| | Al | Ca |
|---|---|---|
| Ion concentration (mmol ¡ dm$^{-3}$) | 8.26 | 1.16 |
| Mole ratio | 1 | 0.14 |

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