

## Early Hydration of Modified Belite Cement Prepared by Adding Borax

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By adding borax into the raw mix, Modified Belite Cement clinker and cements were prepared. Clinkerization and hydration reactions were investigated in order to better understand. Borax-bearing MBC clinker sintered at 1300°C for 1 hour showed excellent burnability. Borax stabilized  $\alpha'$  and  $\beta$ -C<sub>2</sub>S at room temperature. In the hydration of the cement prepared with the borax-bearing clinker, ettringite, monosulphate, C-S-H hydrates and CH were formed. The hydration of calcium sulphoaluminate was less reactive than the cement prepared with the controlled clinker at early hydration time. But, as hydration time elapsed, this cement showed more active hydraulicity and higher compressive strength development.

**Key words :** Modified belite cement. Borax

### I. Introduction

Modified Belite Cement (hereafter MBC) which is composed of  $\beta$ -C<sub>2</sub>S, C<sub>4</sub>A<sub>3</sub> $\bar{S}$  and C<sub>4</sub>AF as major clinker minerals is generally synthesized around at 1300°C. At this relatively low firing temperature as compared with that of Ordinary Portland Cement (OPC), small amount of impurity can significantly influence on the clinkerization reaction and physical properties of MBC.

Additives as mentioned above impurity stabilizing the high-temperature polymorphism of clinker phase at room temperature are well known in the cement industry.<sup>1-6</sup> Especially, there has been many studies showing the effects of additives on the stabilization of high temperature polymorphs of C<sub>2</sub>S. Gies *et al.*<sup>6</sup> observed the stabilized  $\alpha'$  and  $\alpha$  type C<sub>2</sub>S by the effect of alkali solid solution showing excellent hydration properties of their belite rich cement. Using B<sub>2</sub>O<sub>3</sub> as a stabilizer, Jenic *et al.*<sup>7</sup> observed the different hydration behaviour between  $\alpha'$  and  $\beta$ -C<sub>2</sub>S having different structural imperfectness. Timashev<sup>8,9</sup> studied the effect of alkali components, such as K<sub>2</sub>O and Na<sub>2</sub>O on clinkerization. The alkali components affect increasing viscosity of melt during the clinkerization. Bucchi<sup>10</sup> reported that the viscosity of melt are related with electronegativity concerning with the outer-orbital electron arrangement of additives: K<sup>+</sup> or Na<sup>+</sup> (generally used as additives) increase the viscosity of melt due to large ionic radius and little electric charge. Fierens<sup>11</sup> showed that the early hydration of C<sub>2</sub>S is largely dependent on the ionic concentration of additives such as boron, vanadium, phosphorus, arsenic and chromium. Many researches concerning the effects of additives on

the activities of C<sub>4</sub>A<sub>3</sub> $\bar{S}$  and C<sub>4</sub>AF had been also conducted.<sup>12,13</sup> Therefore in order to thermodynamically stabilize clinker phases at room temperature, viscosity and surface tension of melt phase should be controlled adding special additives as stabilizers.

In this study, borax comprising of Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> was used for stabilizing C<sub>2</sub>S at room temperature in MBC. The clinkerization and hydration mechanism of cement were studied.

### II. Experimental Procedure

#### 1. Materials

To get clinker composed of 60 wt% C<sub>2</sub>S, 20 wt% C<sub>4</sub>A<sub>3</sub> $\bar{S}$  and 20 wt% C<sub>4</sub>AF, reagent grade chemicals were used, such as CaCO<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub>. Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) was added to this mixture (hereafter raw mix) 3 wt% as stabilizer for C<sub>2</sub>S at room temperature. Controlled sample was also prepared for comparing with borax-bearing sample. Table 1 shows the chemical compositions of the raw mixes.

#### 2. Clinker

The raw mixes were mixed for 24 hours in methanol, dried at 100°C and calcined at 1000°C. The calcined mixtures were pressed into pellets (2 cm diameter) at 1000 kg/cm<sup>2</sup>. The pellets were fired at 1300°C for 1 hour and quenched in air. Free CaO analysis was carried out according to the method in KS L 5120 as well as XRD analysis to identify their clinkerization.

#### 3. Hydration

**Table 1.** The Chemical Composition of the Raw Mixes of Controlled and Borax Bearing 3 wt%

Sample	Chemical composition (wt%)						
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>
Controlled	55.66	20.30	14.23	2.63	6.57	—	—
Borax-bearing	54.17	20.58	13.51	2.49	6.24	0.23	1.14

Modified belite cements were prepared adding 10 wt% gypsum and ground around Blaine specific surface area 3200 cm<sup>2</sup>/g. Samples for characterization of cement pastes were prepared with w/c=0.5 and cured for 28 days at 23°C, 100% RH. Hydration mechanisms were studied using conduction calorimeter, XRD and SEM. And the compressive strength were measured according to KS L 5105.

### III. Results and Discussion

#### 1. Clinkerization

The values of free CaO of the clinkers fired at 1300°C for 1 hour showed 0.38% for the controlled sample and 0.15% for the borax-bearing sample, respectively. The clinker samples were considered to be clinkerized almost completely.

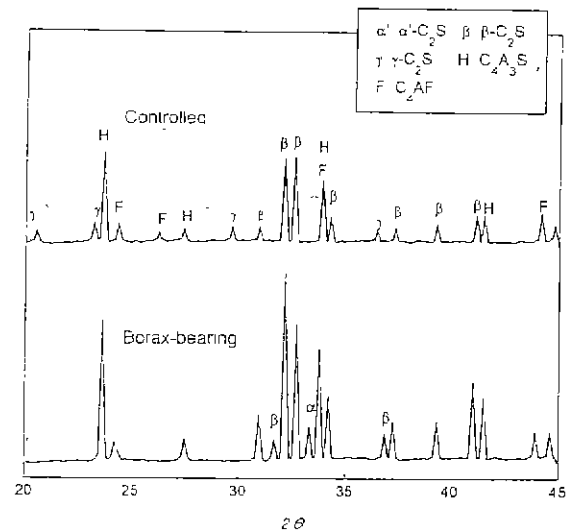
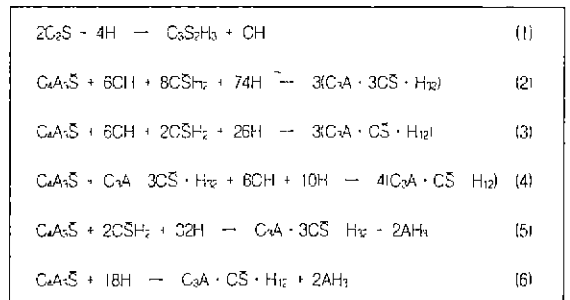
Figure 1 shows XRD patterns of these clinkers. Major clinker minerals in both samples were β-C<sub>2</sub>S, C<sub>4</sub>A<sub>3</sub>S̄ and C<sub>4</sub>AF. γ-C<sub>2</sub>S appeared in the controlled clinker and α'-C<sub>2</sub>S was detected in borax-bearing clinker. Borax influence on stabilizing high temperature polymorphs α' and β-C<sub>2</sub>S as it restrains phase transformation of β-C<sub>2</sub>S to γ-C<sub>2</sub>S.

The restrained phase transformation can be explained as follows. Firstly, Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> easily substitute SiO<sub>2</sub> framework of C<sub>2</sub>S at high temperature, resulting in maintaining its structure at room temperature.<sup>14</sup> Secondly, Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> act as flux, so the high viscous liquid phase forms at lower temperature. The liquid phase physically inhibits volume expansion occurring by the transformation from β-C<sub>2</sub>S to γ-C<sub>2</sub>S on cooling.<sup>15</sup>

The peak intensity of C<sub>4</sub>AF for the borax-bearing clinker present lower than that of the controlled clinker. This result is attributed to high viscosity of melt due to additives.<sup>8,10,16</sup>

#### 2. Hydration of cement

In general, hydration of C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S̄ which are the major clinker minerals of MBC can be expressed as equations shown in Fig. 2. When C<sub>2</sub>S hydrate, C-S-H hydrate and CH form as expressed in equation (1). At presence of gypsum, ettringite (C<sub>3</sub>A·3C<sub>2</sub>S̄·H<sub>32</sub>) forms as a result of hydration of C<sub>4</sub>A<sub>3</sub>S̄ with gypsum and CH in aqueous as expressed in equation (2). But if gypsum is not sufficient, monosulphate (C<sub>3</sub>A·C<sub>2</sub>S̄·H<sub>12</sub>) forms as expressed in equation (3) and (4). When CH is insufficient, AH<sub>3</sub> forms with ettringite or monosulphate as expressed

**Fig. 1.** XRD patterns of controlled and borax-bearing MBC clinkers fired at 1300°C for 1 hr.**Fig. 2.** Hydrations of C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S̄.<sup>17)</sup>

in equation (5) and (6).

Figures 3 and 4 show XRD patterns of the hydrates using the cement prepared with controlled clinker.

Peaks of ettringite and C<sub>4</sub>A<sub>3</sub>S̄ detected at one hour hydrates disappeared at three hours. A peak of monosulphate (C<sub>4</sub>A<sub>3</sub>S̄H<sub>10</sub>) appears after six hours. This monosulphate (C<sub>4</sub>A<sub>3</sub>S̄H<sub>10</sub>) is one of three types of monosulphates (C<sub>4</sub>A<sub>3</sub>S̄H<sub>x</sub>, x=10, 12, 15) which could be formed due to the lack of CH in the hydration system such as C<sub>4</sub>A<sub>3</sub>S̄-H or C<sub>4</sub>A<sub>3</sub>S̄-C<sub>2</sub>S̄-H.<sup>17)</sup> C<sub>4</sub>AF and gypsum were remained at 12 hours, but disappeared after 18 hours. Peaks of ettringite appeared after 12 hours. Peaks of C<sub>2</sub>S decrease as increasing a curing date up to 28 days. A peak of C-S-H hydrate, which is formed by the hydration of C<sub>2</sub>S, appeared at 28 days, but a peak of CH was not detected. As hydration proceeds, ettringite decreases with increasing monosulphate (C<sub>4</sub>A<sub>3</sub>S̄H<sub>12</sub>) which begins to appear at three days.

The above results explain that C<sub>2</sub>S hydrates slowly at an early hydration time. It seems that CH was not found in the XRD patterns because most of it was exhausted to react with C<sub>4</sub>A<sub>3</sub>S̄. Since the amount of gypsum added in this study was less than the stoichiometrical amount which is needed in the hydration of C<sub>4</sub>A<sub>3</sub>S̄ to form et-

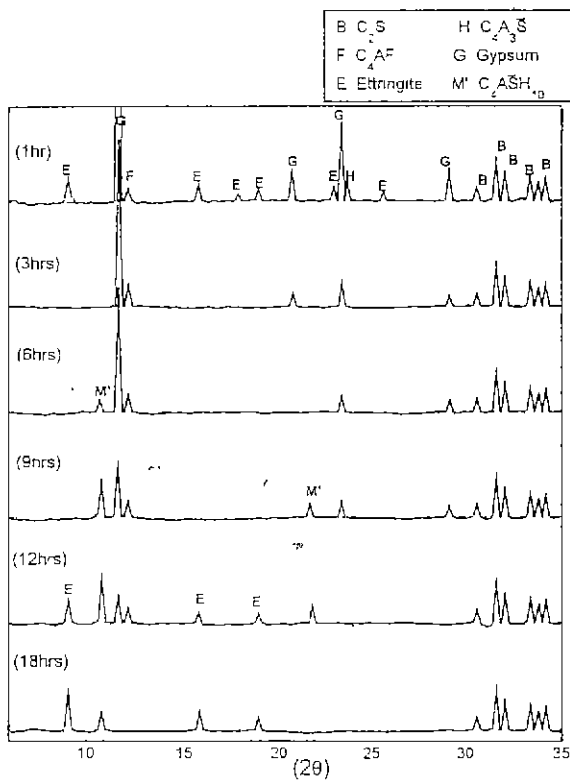


Fig. 3. XRD patterns of the hydrates in the cement prepared with the controlled clinker at the different curing times; 1, 3, 6, 9, 12 and 18 hrs

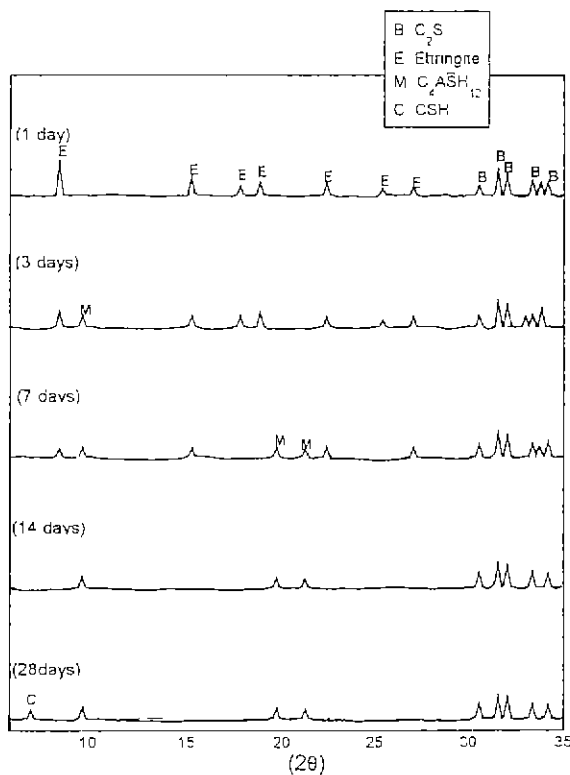


Fig. 4. XRD patterns of the hydrates in the cement prepared with the controlled clinker at the different curing times; 1, 3, 7, 14 and 28 days.

tringite (that is to say,  $CaSO_4 \cdot 2H_2O/C_4A_3\bar{S}=8$  mol/mol), monosulphate ( $C_4A\bar{S}H_{12}$ ) could be stable due to lack of gypsum after three days.

Figures 5 and 6 show XRD patterns of the hydrates using the cement prepared with the borax-bearing clinker.

This cement also produce calcium sulphoaluminate hydrates such as ettringite and monosulphate. But hydration reaction of calcium sulphoaluminate seems slower than the controlled considering the detected time of monosulphate (at 9 hours) and ettringite (at 18 hours). The peaks of  $C_2S$  decrease after seven days. C-S-H hydrate appears at three days and CH appears at seven days. As hydration proceeds, ettringite transformed to monosulphate at seven days.

From these results, it seems that a lot of CH forms because of more active hydration of  $C_2S$ . At seven days the ettringite-forming reaction converted to the monosulphate-forming reaction. Therefore unreacted CH remained to be found by XRD analysis. The results of formation of C-S-H hydrate and CH were caused by  $\alpha'$ - $C_2S$  having more active hydration property.

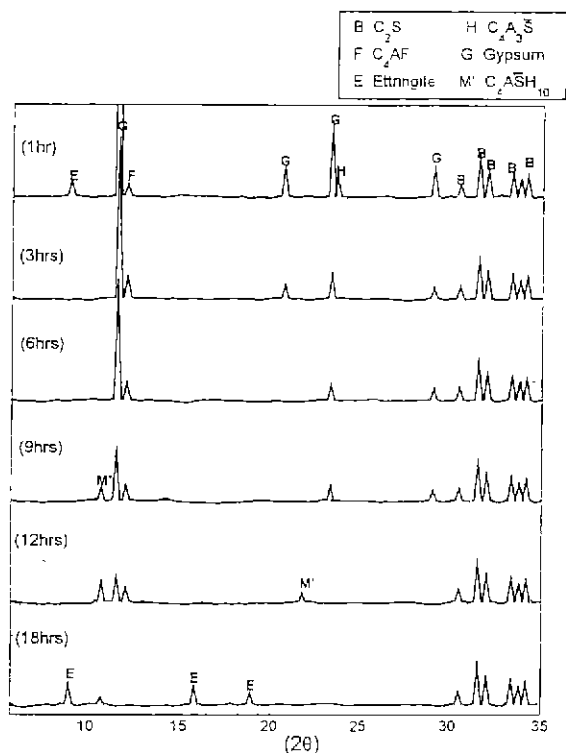
In both cement, there were no dominant hydrates but metastable hydrates were formed due to the difference of saturated concentration in water between clinker minerals and gypsum at an early hydration time. As hydration time elapsed, these hydrates were stabilized into monosulphate form.

Figure 7 shows the heat evolution curves of the MBC cements measured by a conduction calorimetry.

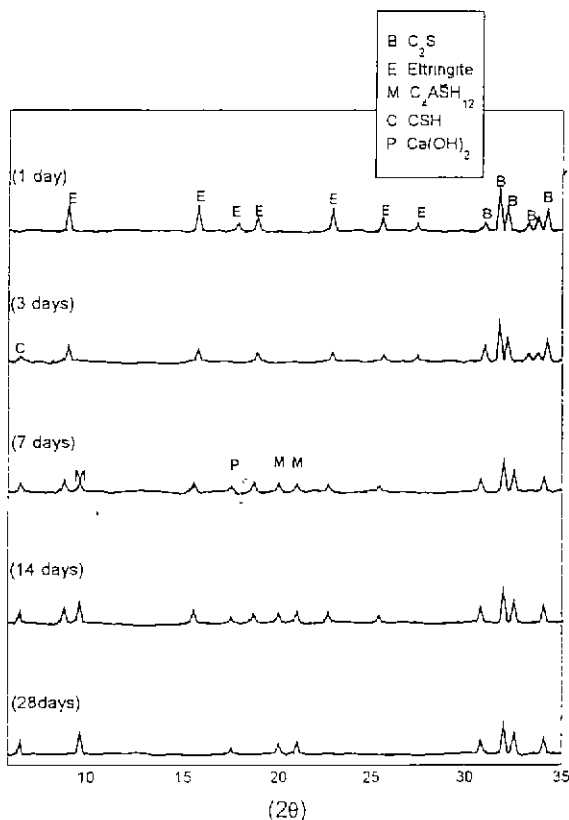
In the cement prepared with the controlled clinker, the heat evolution curves showed a sharp peak as soon as hydration began. This result is attributed to the dissolution of clinker minerals and the formation of ettringite. And, the following second peak seems to be corresponded to the formation of monosulphate ( $C_4A\bar{S}H_{10}$ ). The smooth third peak around 13 hours seemed to be caused by the accelerated formation of monosulphate or of ettringite.

In the cement prepared with the borax-bearing clinker, the first and the second peaks are lower than that of the controlled. The third peak around 10 hours (started around 7 hours) is seemed to be caused by the accelerated formation of monosulphate and the hydration of  $\alpha'$ - $C_2S$  after dormant period. The following fourth peak is seemed to be caused by the formation of ettringite and continuing hydration of  $\alpha'$ - $C_2S$

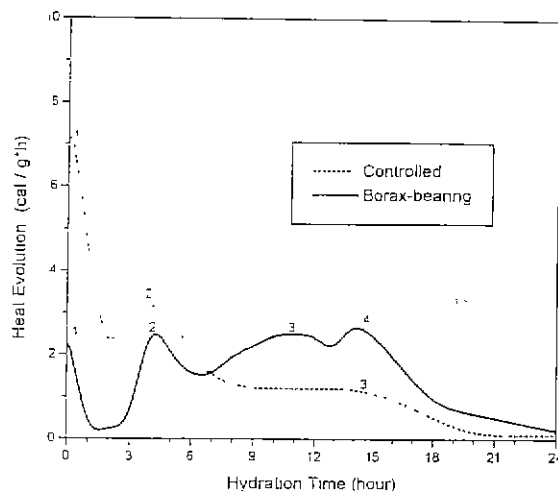
Figure 8 shows the results of compressive strength developments of two types of cements. At one day, appreciable difference in strength was not found between two samples. After three days, the borax-bearing sample showed higher strength than the controlled sample. The results show that the higher compressive strengths of the former are dependent on formation of C-S-H hydrate at later time as well as on that of ettringite at early hydration time while those of the latter dependent only on formation of ettringite.



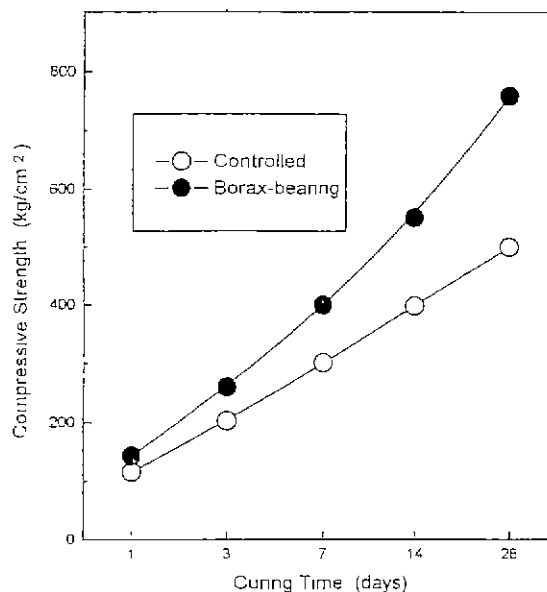
**Fig. 5.** XRD patterns of the hydrates in the cement prepared with the borax-bearing clinker at the different curing times; 1, 3, 6, 9, 12 and 18 hrs.



**Fig. 6.** XRD patterns of the hydrates in the cement prepared with the borax-bearing clinker at the different curing times; 1, 3, 7, 14 and 28 days.



**Fig. 7.** Heat evolution curves of the cements prepared with the controlled clinker and with the borax-bearing clinker.



**Fig. 8.** Compressive strength developments of the cement mortars prepared with the additive-free clinker and with the borax-bearing clinker.

### IV. Conclusions

Modified belite cement (MBC) clinker containing borax as a stabilizer for  $C_2S$  was synthesized and the cement using this clinker were hydrated. From the characterization of clinker and the study of hydration of cement, results were obtained as follows:

1. Borax-bearing MBC clinker synthesized at  $1300^\circ C$  for 1 hour showed excellent burnability. Borax acts as a flux for clinkerization and stabilizes  $\alpha'$  and  $\beta$ - $C_2S$  at room temperature.

2. In the hydration of the cement prepared with the borax-bearing clinker, ettringite, monosulphate, C-S-H hydrates and CH were produced. The hydration of calcium sulphoaluminate was less reactive than the cement

prepared with the controlled clinker at early hydration time. But, as hydration time elapsed, this cement showed more active hydraulicity and higher compressive strength development.

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