

# THE DICALCIUM ORTHOSILICATE AND ITS HYDRAULIC ACTIVITY EXAMINATION BY DTA-TG AND CALORIMETRIC METHODS

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## Abstract

The belite material produced from limestone and waste silica was the subject of numerous investigations. In order to improve the hydraulic activity, some amount of barite was added to the raw mixture. The properties of belite phase were studied by use of differential thermal analysis, calorimetry and other methods. The influence of barium on the hydraulic activity of belite has been thus confirmed. The hydraulic activity increase in the presence of barium depends on the stabilizing action of additive accompanied by the proper thermal treatment in the  $\alpha'$ -Ca<sub>2</sub>SiO<sub>4</sub> stability range.

**Keywords:** belite hydraulic activity, belite stabilization, calcium orthosilicate hydration, calorimetry of hydrated belite

## Introduction

The modification of portland cement composition consisting in the belite phase content increase is one way of the energy consumption lowering in the clinker production. However, the reactivity of belite is much lower than the reactivity of alite which content is reduced in such a belite clinker. Therefore the properties of belite phase should be modified to obtain the material of hydraulic activity as high as possible and to produce the good quality cement. It should be mentioned that in several concrete technologies the cements having a lowered heat of hydration are needed and the belite cements meet well this requirement.

Among many auxiliary materials which can be used in cement manufacturing, the barium containing ones bring about the acceleration of belite phase synthesis and the significant improvement of belite activity. The extensive studies on the role of barium in clinker production were carried out by Kurdowski [1]. A positive influence of Ba on the sintering and properties of clinker phases have

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been demonstrated in other works [2, 3]. In Germany the class 45 cement and rapid hardening cement were produced on the basis of BaO doped batch [4]. Sytchev studied the clinker production at BaO and CaSO<sub>4</sub> admixture. The stabilizing effect of  $\alpha'$ -C<sub>2</sub>S has been thus achieved [5].

The influence of barium is strongly related to the chemical and mineral composition of Ba-bearing material. This work is a part of the studies on the low-energy cement modified by barium to improve the hydraulic activity of belite [6]. The authors focused on the synthesis of dicalcium silicate from the industrial raw materials: limestone, waste silica, Ba-bearing material and stabilizing agent. The properties of initial components and synthesized cementitious materials were investigated.

## Experimental

### Materials

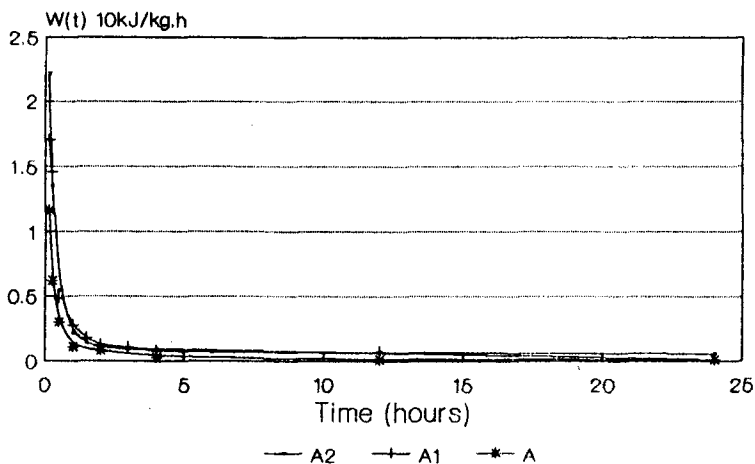
The basic initial materials of the composition given in Table 1 have been used. Calculated phase composition of this belite was as follows: C<sub>2</sub>S – 95%, C<sub>3</sub>A – 2.3%, C<sub>4</sub>AF – 2.1%.

**Table 1** Chemical composition of raw materials, raw meal and belite

Material	Percentage of component / %					
	L.O.I.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
limestone	42.9	1.6	0.8	0.3	53.9	0.2
silica	0.0	96.0	1.5	1.9	0.5	0.0
raw meal	33.7	21.7	0.9	0.4	42.5	0.2
belite	–	32.8	1.4	0.7	64.2	0.2

The mineral composition of waste barite used as a 1% and 5% admixture was as follows: BaSO<sub>4</sub> – 91%, SiO<sub>2</sub> – 7.1%, Fe<sub>2</sub>O<sub>3</sub> – 0.3%, CaF<sub>2</sub> – 0.5%. The DTA measurements of barite material show the endothermic peak at 1160°C corresponding to the polymorphic transition of rhombohedral barium sulphate to the monoclinic polymorph. The decomposition of barium sulphate takes place in the range 1250–1350°C. Unfortunately, the admixtures present in the batch did not prevent the transition  $\beta \rightarrow \gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> on cooling from 1350°C. Therefore the boric acid added as 0.5% B<sub>2</sub>O<sub>3</sub> was applied in order to stabilize the  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> phase. At 1% BaO the belite clinker of the following composition has been thus produced: SiO<sub>2</sub> – 32.8%, Fe<sub>2</sub>O<sub>3</sub> – 0.7%, Al<sub>2</sub>O<sub>3</sub> – 1.2%, CaO – 61.7%, MgO – 0.7%, BaO – 1.0%, B<sub>2</sub>O<sub>3</sub> – 0.6%. The reference sample without BaO admixture was also produced.

A-9.2kJ/kg A1-22.1kJ/kg A2-24.3kJ/kg



**Fig. 1** Calorimetric curves of belite materials with *B* stabilizer and *B* + BaO additions. The heat of hydration is given as a header; *A* - 0.5% B<sub>2</sub>O<sub>3</sub>; *A1* - 0.5% B<sub>2</sub>O<sub>3</sub> + BaO, *A2* - B<sub>2</sub>O<sub>3</sub> + 5% BaO

### *Properties of belite clinkers*

The following notation for the samples will be further used:

*A* - belite clinker with *B* stabilizer

*A1*, *A2* - belite clinker with Ba admixture (*A1* - 1% BaO, *A2* - 5% BaO) and *B* stabilizer.

The belite clinkers were subjected to XRD measurements and microscopic observations. As it results from the XRD pattern,  $\beta$ -C<sub>2</sub>SiO<sub>4</sub> is a main constituent of the B<sub>2</sub>O<sub>3</sub> stabilized belite clinker. Some amount of aluminate phase is also detectable. The barium admixture does not change the XRD pattern of the clinker.

As it results from the microscopic observations, the clinkers are porous with the belite phase occurring as a main component. Some amount of the liquid phase forms small areas between the grains of lamellar character. In the presence of barium the belite crystals are better developed and the gaps between the lamellae are filled with the liquid phase.

### *Studies of the hydration process*

The belite materials thus obtained were subjected to calorimetric measurements and the results indicate that the hydration proceeds very slowly (Fig. 1).

The same conclusion have been drawn basing on DTA–TG studies (Fig. 2). The calcium silicate hydrate phase decomposition peak in the range 100–200°C as well as the calcium hydroxide dehydration peak under 500°C for the samples 28 days hydrated are rather small; the latter one does not occur in the case of belite without Ba.

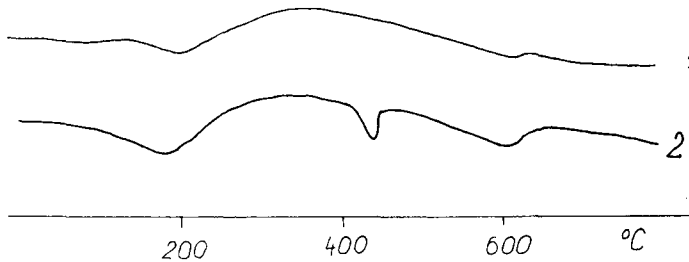


Fig. 2 DTA curves of 28 days hydrated belite materials; 1 – with 0.5%  $B_2O_3$  stabilizer, 2 – with 0.5%  $B_2O_3$  + 2% BaO

### Modification of belite material by thermal treatment

As it is mentioned above, in the samples with no admixture and with barium, the  $\beta$ - $Ca_2SiO_4$  stabilization was not achieved. Therefore the samples were subjected to the repeated heating at 1350°C. The self-disintegration was thus stopped. The following notation for these samples will be used:

*B* – belite clinker without stabilizer

*B1*, *B2* – belite clinker with Ba admixture (*B1* – 1% BaO, *B2* – 5% BaO).

The increased amount of  $\beta$ - $C_2S$  was found in the samples doped with Ba, together with some  $\alpha'$ - $C_2S$  phase content. The microstructure of the products differs significantly from the microstructure of the stabilized previously  $\beta$  phase and consists of the  $\gamma$  "collapsed" forms transformed to  $\alpha'$  and  $\beta$  on subsequent heating and cooling. In the microcalorimetric studies these samples show a slightly higher heat of hydration (Fig. 3). In DTA–TG studies they exhibit more advanced hydration process (Fig. 4), even after 2 days reaction with water. The dominating role of thermal treatment in modification of belite hydraulic activity has been thus confirmed.

### Conclusions

1) In the presence of barite the belite materials stabilized by proper thermal treatment reveal a higher hydraulic activity as measured by calorimetry and DTA–TG.

B-8.0kJ/kg B1-25.5kJ/kg B2-23.8kJ/kg

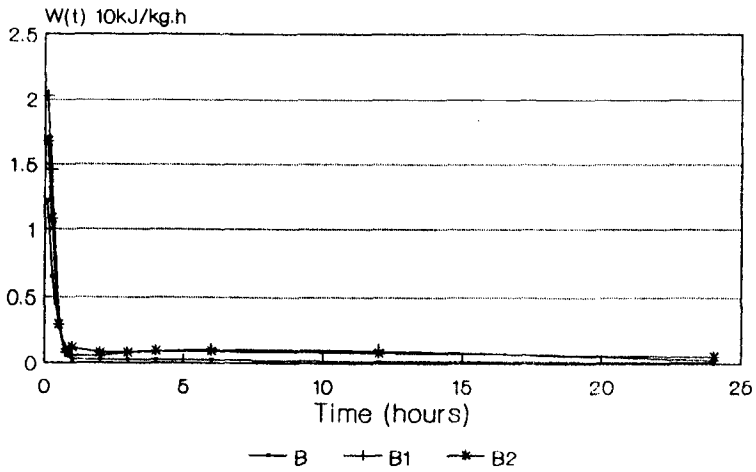


Fig. 3 Calorimetric curves of belite materials thermally stabilized with BaO additions. The heat of hydration is given as a header

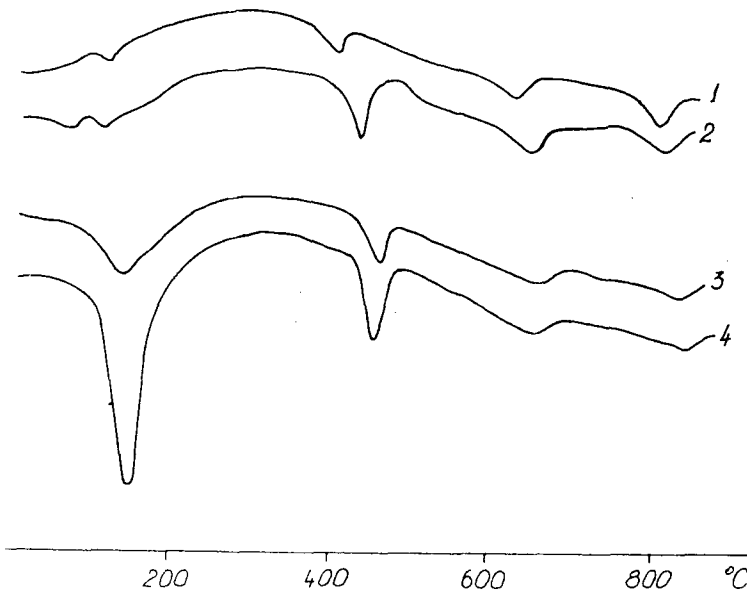


Fig. 4 DTA curves of 2 (curves 1, 2) and 28 (curves 3, 4) days hydrated belite materials. 1,3 – without BaO; 2,4 – with 2% BaO addition

2) In the presence of barite the belite materials stabilized by  $B_2O_3$  also reveal a higher hydraulic activity as measured by calorimetry and DTA-TG.

## References

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**Zusammenfassung** — Das aus Kalkstein und Abfall-Silikagel produzierte Belit-Material war bereits Gegenstand zahlreicher Untersuchungen. Zur Verbesserung der hydraulischen Aktivität wurde den Rohmischungen etwas Baryt zugesetzt. Die Eigenschaften der Belitphase wurden mittels Differential-Thermoanalyse, Kalorimetrie und anderen Methoden untersucht. Der Einfluß von Barium auf die hydraulische Aktivität von Belit wurde damit bestätigt. Das Ansteigen der hydraulischen Aktivität in Gegenwart von Barium hängt von der stabilisierenden Wirkung des Additives ab, begleitet von einer richtigen thermischen Behandlung im Stabilitätsbereich von  $\alpha'$ - $Ca_2SiO_4$ .