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BELITE PRODUCED BY MEANS OF LOW-TEMPERATURE SYNTHESIS

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ABSTRACT

The mixture of the C-S-H phase of molar ratio about 1.6 and CH were prepared by shaking the amorphous silica and calcium hydroxide in molar ratio equal to 2, in water during one month. By burning this mixture at 800 and 900°C belite was obtained with a very small admixture of other calcium silicate phases. Some hardening activators were also added before burning, namely sodium and potassium sulphates and barium silicate. Belite phase had very high specific surface and quickly reacted with water giving one exothermic peak on the microcalorimetric curve. One sharp peak was also noted on the curve presenting calcium concentration in the paste immediately after mixing with water. The highest heat of hydration was found for the sample with 10% addition of barium silicate. *Copyright © 1997 Elsevier Science Ltd*

Introduction

Alite is the most important component of portland cement, though its formation needs high temperature and consumes comparatively large amounts of energy. On the other hand, the belite formation is much more easier and is connected with a lower energy consumption. This is evident when we compare the enthalpy of formation of both silicates from calcium carbonate and silica. The values, calculated on the basis of thermodynamic data [1], are as follows:

$$\sim 1810 \text{ kJ/kg of } C_3S \text{ and } \sim 1350 \text{ kJ/kg of } C_2S$$

so the difference is about 460 kJ/ kg of C_2S. This is the reason of great efforts towards the development of belite cements. Nevertheless a slow hydration process and low strength after 28 days are disadvantages of the belite phase.

Many works have been done to overcome this fault. They can be divided into two groups:
- stabilisation of high temperatures polymorphs of C_2S [2-4],
- synthesis of β phase in low temperatures [5-8].

In a relatively recent work Nanru and co-workers [6] prepared β C_2S by heating the autoclaved, hydrated calcium silicate at 950°C with the molar ratio C/S = 2. The obtained belite had a high specific surface and reacted with water as quickly as tricalcium silicate, but starting from the 14th day of hydration. In turn, Ishida and co-workers [7] obtained β C_2S by heating hillebrandite at 600°C. This belite reacted quickly with water giving C-S-H phase with the molar ratio C/S = 2, without the formation of calcium hydroxide.

Our experiments refer to this group of investigations and are devoted to the synthesis of belite from the C-S-H phase and to its reactivity.

Materials

Pure AR materials, i.e. Merck calcium hydroxide and amorphous silica (Aerosil, Degussa), were used. These substances, in the molar ratio C/S = 2, were being shaken in the water suspension (water/solid ratio equal to 10) for one month, at temperature 20°C ± 1°C. The X-ray analysis showed the lines of C-S-H and CH, two weak peaks of $CaCO_3$ and one weak line, which can be ascribed to afwillite [d = 0.635 nm].

Four peaks appear on the curves of DTA and TG of this substance (Fig. 1), washed with acetone and ether and dried at 40°C, with the maximum laying at 125°C, 472°C, 726°C, 898°C and at 1419°C and a diffuse peak at 1118°C. They correspond, respectively, to the dewatering of C-S-H phase, decomposition of $Ca(OH)_2$, decarbonation of $CaCO_3$, synthesis of dicalcium silicate and two polymorphic transformations: $\alpha'_L \rightarrow \alpha'_H$ C_2S at 1118°C and $\alpha'_H \rightarrow \alpha$ C_2S at 1419°C [9]. It is to be noted that the small peak at 898°C corresponds to the exothermic reaction of the formation of dicalcium silicate. Three losses of mass are to be noted on TG curve: first, in low temperature, starts at about 50°C and is linked to the decomposition of C-S-H phase, second at 450°C corresponds to the decomposition of portlandite and third in the range 600-750°C is due to calcination of $CaCO_3$.

The phase composition of the sample can be calculated from the loss of weight at different temperatures as well as the water content of the C-S-H phase and molar ratio C/S in this phase. All these data are given in Table 1.

Contrary to some opinions [10], the adopted system of drying seems to lower the water content in comparison with the original state.

This C-S-H sample was used as starting material for the low temperature synthesis of belite. The hardening activators were also added to some samples. The following compounds and weight % of their addition were adopted:

$CaSO_4 \times 0.5\ H_2O$	5%	Na_2SO_4	3 and 6%
K_2SO_4	3%	Ba_2SiO_4	5 and 10%

All the activators were pure AR materials. They were mixed in dry conditions with C-S-H. Barium silicate was the only exception. This phase was prepared by heating barium carbonate with amorphous silica (Aerosil, Degussa) at 1500°C. The heating was repeated once with intermediate grinding. The sample was X-ray pure Ba_2SiO_4. The water suspension was made from this barium silicate and then mixed with the C-S-H sample in wet condition for 24 hours.

TABLE 1

Phase Composition of the Sample and the Characteristic of the C-S-H Phase

Sample		C-S-H phase
C-S-H	80.7 %	C/S ratio = 1.63
$CaCO_3$	8.6 %	water content ~ 18%
CH	10.7 %	approximative formula $1.63CaO \times SiO_2 \times 1.8H_2O$

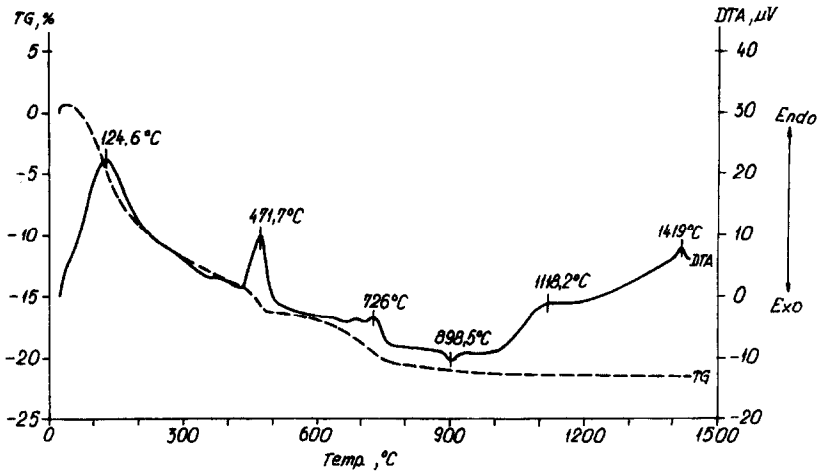

FIG. 1.
DTA curve of starting C-S-H phase.

All samples were heated in the laboratory furnace at 800°C and 900°C over the course of one hour. The sample with barium silicate addition was also burned at 1000°C. The burned samples were quickly cooled in the air.

Methods

The X-ray analysis was used to control the samples composition after heating and after hydration. SEM was the second method. For some samples DTA and TG curves were recorded and the measurements of specific surface were done by applying the BET method and nitrogen as an adsorbate with the ASAP 2000 apparatus.

The hydraulic activity of belite preparations were followed by microcalorimetry. The BMR differential microcalorimeter, constructed in the Institute of Physical Chemistry in Warsaw, was used. For the samples which presented the highest heat of hydration the micro-

TABLE 2
Phase composition of burned samples

Sample	phases present	Sample	phases present
No additions	β C_2S, small quantities of α' C_2S and γ	+ 6% Na_2SO_4	β C_2S, anhydrite, small quantity of γ
+ 5% gypsum	β C_2S, small quantities of γ C_2S	+ 5% Ba_2SiO_4	β C_2S, small quantity of α'*, trace of B_2Sss
+ 3% K_2SO_4 **	β C_2S, small quantities of' γ C_2S	+10% Ba_2SiO_4	β C_2S, small quantity of α' *, trace of B_2Sss

* The lines of α' are very close to bredigite according to Taylor [11]
** The sample with 3% of Na_2SO_4 has the same composition

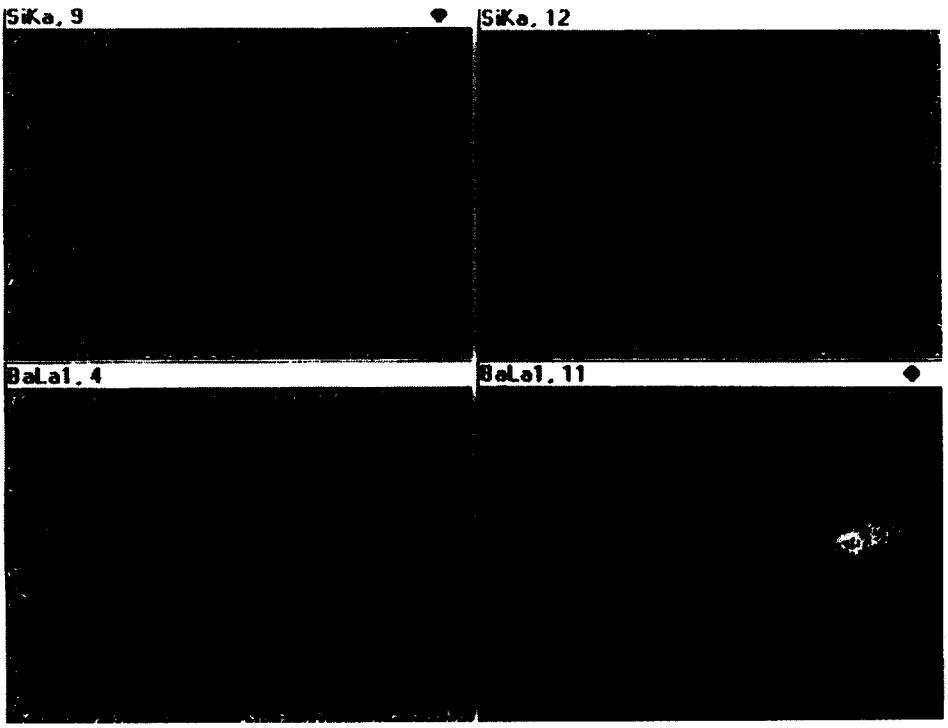

FIG. 2.
Barium and silicium ions distributions in burned samples.

hardness was measured after different times of water curing. The Vickers apparatus was used for these measurements and the samples were a pure paste with water/C_2S ratio equal to 1. Small prism elements with dimensions 10 × 10 × 60 mm were prepared from this paste. The samples were cured 3 days in moist atmosphere (100% relative moisture) and then, after demoulding, in water, all the time at the temperature 20°C ± 1°C.

Experimental Results

The phase composition of the samples burned at 800°C and 900°C, according to the X-ray measurements, is presented in Table 2. Because there was no difference in the phase composition of the samples burned in these two temperatures, only one composition is given in the table.

β C_2S is the major phase in all samples and in majority of samples small quantities of α'_L and γ phases were also found. The samples with the barium silicate addition were exceptions, which contained, apart from β phase, only a small quantity of α' C_2S, with X-ray lines close to bredigite, according to Taylor [11]. No one line of CaO can be detected on X-rays patterns. So according to X-ray analysis synthesis is completed even in the lowest temperature i.e. 800°C.

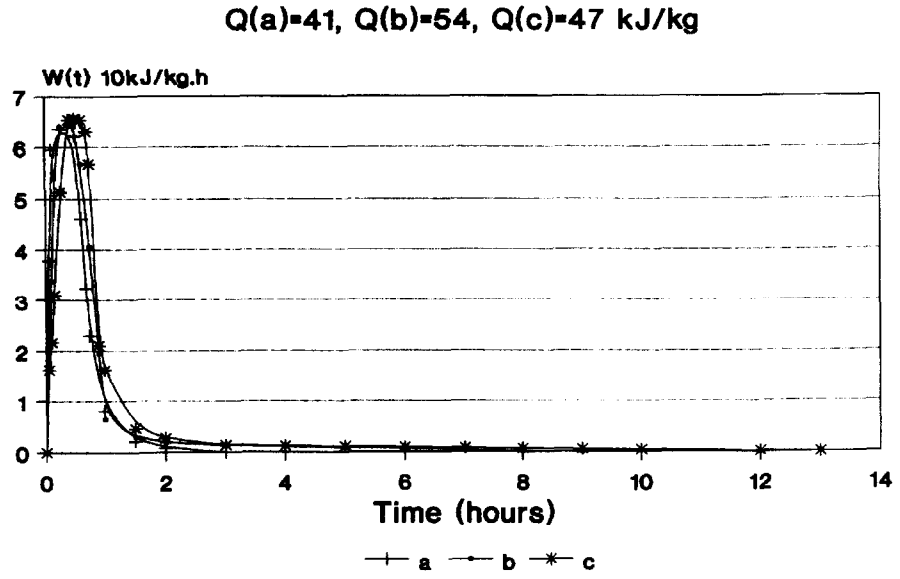

FIG. 3.
Microcalorimetric curves of samples without addition, burned at 800°C, (a) and with the addition of 3% of sodium (b) and potassium (c) sulphates, burned at 900°C.

The appearance of anhydrite in the sample with the addition of 6% of Na_2SO_4 seems to indicate that sodium, after the reaction with calcium hydroxide, forms a solid solution with dicalcium silicate*:

$$Ca(OH)_2 + Ca_2SiO_4 + Na_2SO_4 \text{ --> } (Ca,Na)_2SiO_4 + CaSO_4$$

Also the barium silicate forms a solid solution with dicalcium silicate with the disappearance of γ phase and a stabilisation of high temperature α' polymorph, whose X-ray characteristic is very close to bredigite [11]. The distribution of barium in the dicalcium silicate matrix is uniform but in some cases small crystals of barium silicate are also found (Fig. 2). It is in good agreement with the X-ray data in which the lines of $Ba_{1.55}Ca_{0.45}SiO_4$ were found.

The microcalorimetry measurements showed the unconventional behaviour of belite. One sharp peak appeared on the microcalorimetric curves, in the first hour after mixing with water (Fig. 3).

The heat of hydration is higher for the lower burning temperature, i.e. for 800°C. It increases strongly with the addition of barium silicate and only slightly with sodium and potassium sulphates. The heat of hydration is the highest for the sample with the addition of 10% of Ba_2SiO_4, burned in 800°C (Table 3). Nonetheless, the total heat of hydration, which can be measured in the used equipment until the 5th-7th hour of hydration (Fig. 3 and 4), is relatively low when compared to normal PC 35. In this case the heat of hydration is about 250 kJ/kg after 24 hours. In case of the sample with 10% of barium silicate, burned at 800°C

*Thilo and Funk [12] give a solubility limit in phase β 0.3 molar % of Na_2O

TABLE 3
Heat of hydration of the samples, kJ/kg

Sample	Burning temperature	Heat of hydration	Sample	Burning temperature	Heat of hydration
No addition	800°C	41	5% Ba_2SiO_4	800°C	92
No addition	900°C	33	5% Ba_2SiO_4	900°C	56
5% gypsum	800°C	33	5% Ba_2SiO_4	1000°C	41
5% gypsum	900°C	30	10% Ba_2SiO_4	800°C	133
3% K_2SO_4	900°C	47	10% Ba_2SiO_4	1000°C	59
3% Na_2SO_4	900°C	54			
6% Na_2SO_4	900°C	64			

a small second peak appears on the microcalorimetric curve which starts after about 1.5 hour, and ends after about 4 hours.

A large thermal effect immediately after contact with water, may have its source in a relatively very high specific surface of the samples. The BET surface area is very large (Table 4) and is incomparably higher than for the samples of cement or belite of the high-temperature synthesis. This specific surface is extremely large when the temperature of synthesis is 800° and is decreasing strongly for the higher temperature, i.e. 900°C. The specific surface is decreasing also with the addition of activators, i.e. sodium sulphate. Barium silicate seems to have only a very limited influence on the sintering process. Ishida obtained similar, but not so large, specific surface [7] in his experiments and also noted one exothermic peak on the microcalorimetric curve.

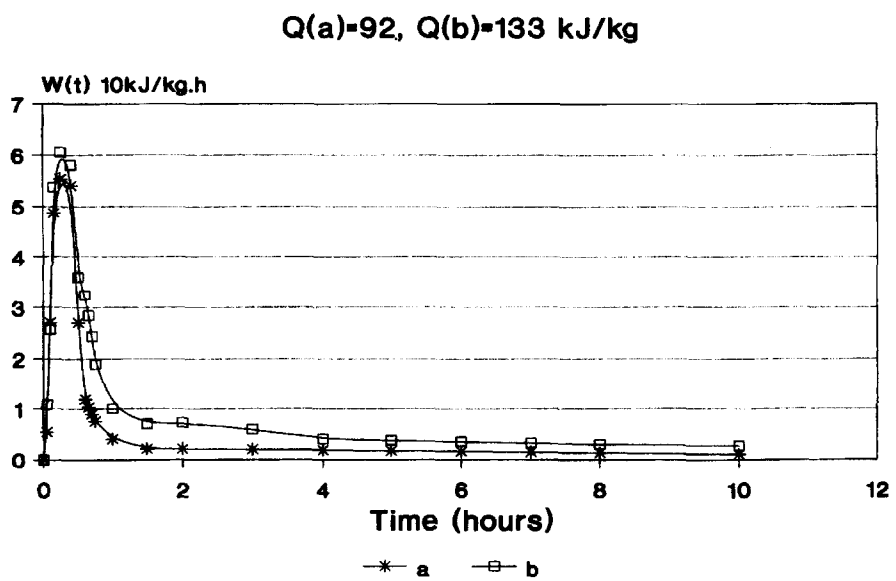

FIG. 4.
Microcalorimetric curves of the samples with the addition of 5 (a) and 10% (b) Ba_2SiO_4, burned at 800°C.

TABLE 4
Specific surface of some samples

Sample	Burning temperature	Specific surface, m^2/g	Sample	Burning temperature	Specific surface, m^2/g
No addition	800°C	19.34	5% Ba_2SiO_4	800°C	16.1
No addition	900°C	11.17	10% Ba_2SiO_4	800°C	16.77
3% Na_2SO_4	900°C	7.9	10% Ba2SiO4	900°C	9.5
6% Na_2SO_4	900°C	6.52			

All the samples after 10 hours of hydration in microcalorimetry apparatus were subjected to the X-ray examination. The X-ray patterns were very similar to those before hydration and principally presented the lines of β C_2S. It was the proof that the degree of hydration is small. Only for the samples with addition of 5% of gypsum and 6% of Na_2SO_4 in the X-ray patterns the lines of gypsum appeared. Additionally, in the X-ray of the samples with 6% of Na_2SO_4 and barium silicate, the line for C-S-H phase at d = 1.2 nm had to be noted and in case of preparation with 10% of barium silicate also the lines of portlandite. The X-ray study indicate that the highest degree of hydration after 10 hours of reaction with water is present in the samples with the addition of barium silicate and with 6% of Na_2SO_4.

The peak with the maximum at about 150°C on DTA and TG curves seems to indicate a relatively large amount of the C-S-H phase except the samples without the addition and with the addition of gypsum. The examples of DTA curves are presented in Figure 5. In the curve of the sample with the addition of 5% of barium silicate, a peak of portlandite decomposition is also present, but its quantity was under the threshold of detection for the X-ray method.

Also the SEM observation gives the picture of a relatively important reactivity of the obtained belite. The samples after 10 hours of hydration were, in the majority of cases, com-

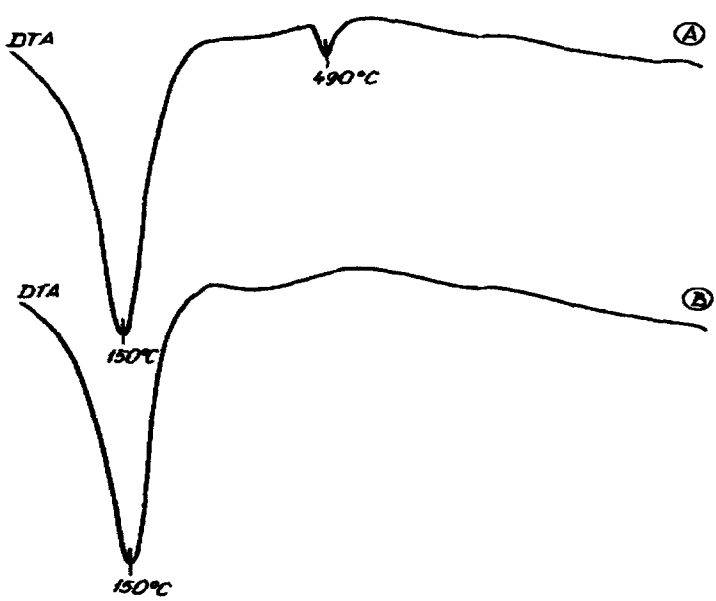

FIG. 5.
DTA curves of sample with the addition of 5% Ba_2SiO_4 (A) and 3% K_2SO_4 (B), both burned at 900°C after 10 hours of hydration.

FIG. 6.
SEM picture of the sample + 5% Ba_2SiO_4, burned at 1000°C after 10 hours of hydration.

posed of the well-developed C-S-H phase with the fibres microstructure. It refers particularly to the samples with the barium silicate addition (Fig. 6). In the samples without addition and with 3% of potassium sulphate the amorphous microstructure prevails (Fig. 7). In these samples also a small quantity of gypsum crystals can be found, which was not detected by X-ray method.

The X-ray examination of the samples after a longer period of hydration, i.e. after 14 and 42 days of hardening in water, revealed a much larger quantity of the C-S-H phase which gave the lines for d = 1.27 nm, 0.973 nm, 0.695 nm, 0.304 nm and 0.182 nm. In the X-ray pattern of the sample with the addition of barium silicate also the line for 1.47 nm appeared

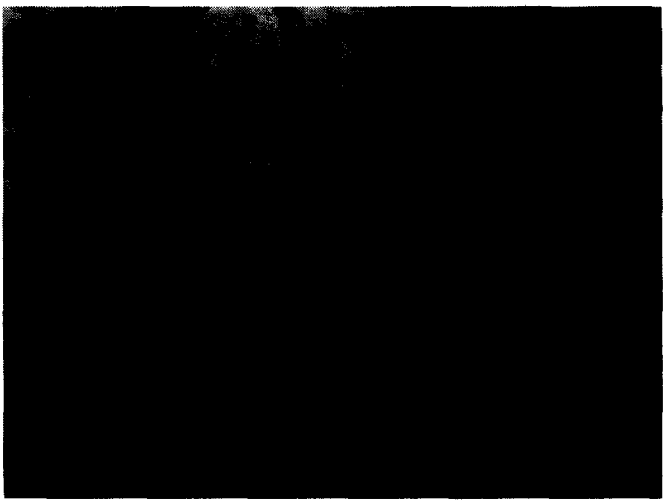

FIG. 7.
SEM picture of the sample + 3% K_2SO_4, burned at 1000°C after 10 hours of hydration.

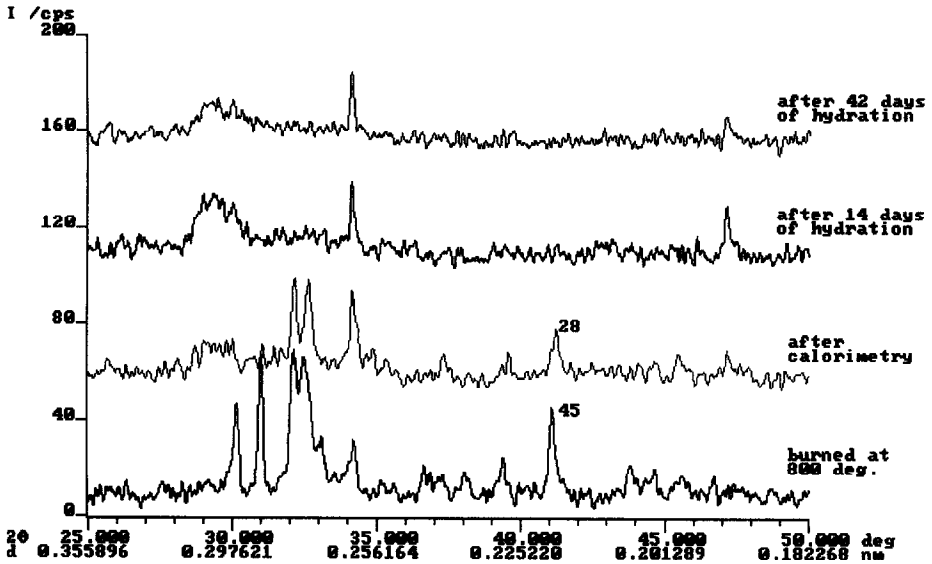

FIG. 8.
X-Ray pattern of samples containing the addition of 10% Ba_2SiO_4 after different times of hydration.

which seems to indicate that the ordering of the structure of C-S-H took place. On the X-ray pattern of the sample with the addition of 6% of sodium sulphate no lines of portlandite could be found. Also the lines of gypsum, present after 10 hours of hydration, practically disappeared.

For the sample with 10% of barium silicate, burned at 900°C, the content of belite was evaluated by measuring the intensity of the peak at 0.219 nm. This intensity decreased from

FIG. 9.
SEM of sample with 10% Ba_2SiO_4 addition after 42 days of hydration.

TABLE 5
Microhardness of the samples

Sample	Microhardness after hardening in water, in MPa			
	3* + 7 days	3* + 14 days	3* + 28 days	3* + 42 days
No addition	17	23	29	30
6% Na_2SO_4	34	59	100	127
10% Ba_2SiO_4	27	33	29	41
PC 35**	160	210	280	285

* Three days in moist atmosphere
** For the sake of comparison

45 to 28 after 10 hours of reaction with water and practically to 0 after 14 days of hydration (Fig. 8). This means that belite had hydrated fully after two weeks. The samples with 5% of Ba_2SiO_4 gave very similar results.

The observation under SEM showed that the fundamental matrix of the samples is composed of the fibrous C-S-H phase (Fig. 6). Only in the samples with the addition of barium silicate the single crystals of portlandite appear (Fig. 9) and in the samples with 6% of Na_2SO_4 the inclusion of gypsum can be found.

For the samples which gave the highest heat of hydration, the microhardness was measured. The time of measurements was 7, 14, 28 and 42 days of water curing. Because before immersion in water the samples were, as mentioned earlier, cured for 3 days in moist atmosphere, the total time of hardening was 10, 17, 31 and 45 days respectively. The results are presented in Table 5. As it can be seen in the Table 5, the microhardness of the samples with the addition of 6% of Na_2SO_4 is much higher than of the others. The hardening of these samples is much more rapid than of the remaining ones, without the addition and with the addition of barium silicate. Yet when we compare them to Ordinary Portland Cement, it can be well seen that the strength of synthetic belite is much lower and the best result after 42 days is lower than for PC35 after 7 days of hardening.

For two samples, i.e. without the addition burned at 800°C and with 10% of barium silicate burned also at 800°C, the changes of concentrations of calcium ions in water solution for water/solid ratio equal to 15 were followed. Both samples demonstrated the same behaviour, i.e. a very quick increase of calcium concentration almost immediately after mixing with water and also a quick decrease of this concentration to the level corresponding to the saturation of calcium hydroxide. These phenomena shown in Figure 10 prove that the reaction is very quick and the instantaneous dissolution of C_2S took place. Then, according to the SEM observations the C-S-H phase is formed very quickly and the calcium concentration falls down.

Conclusions

The results of our experiments indicate that the mixture of C-S-H phase with C/S molar ratio about 1.6 and CH is very reactive and gives, after burning at 800°C, practically pure β C_2S. This β phase has a very high specific surface, close to 20 m^2/g, and reacts quickly with water, giving one sharp exothermic peak on the microcalorimetric curve. The specific surface

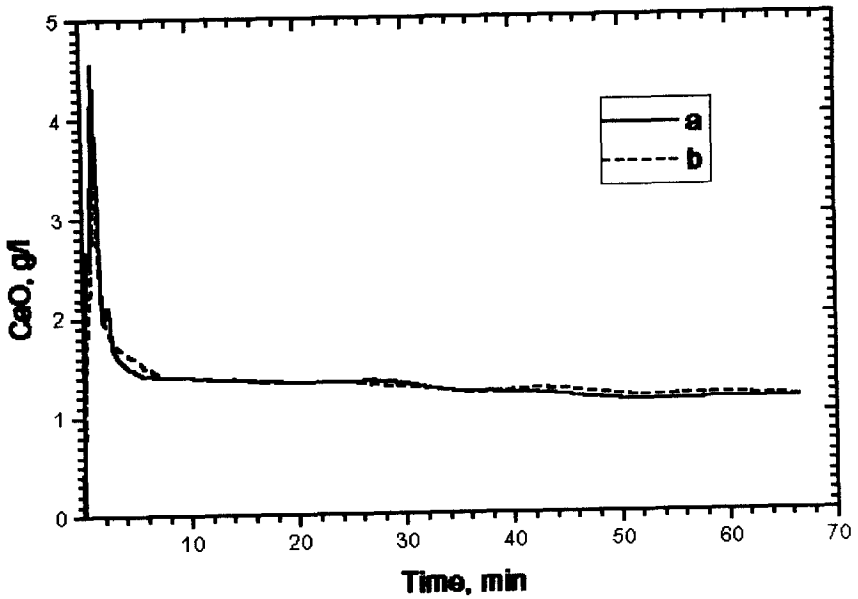

FIG. 10.
Concentration curves of calcium ions in the solution during the reaction with water: a) sample without addition, burned at 800°C, b) sample with addition of 10% Ba_2SiO_4, burned at 800°C.

decreases with the burning temperature and for 900°C is about 11 m^2/g with a further slow diminution for 1000°C.

The highest heat of hydration is for the sample with the 10% barium silicate addition and for the temperature of burning at 800°C. For this sample a second peak on the microcalorimetric curve appears.

The thermal peak takes place in the first half an hour which seems to indicate that the reaction with water took place mainly on the surface of dicalcium silicate and being of a topochemical character. The heat connected with this reaction is proportional to the specific surface of the solid phase. This topochemical character of the reaction is supported subsequently by the X-ray patterns of the majority of samples in which even after 10 hours of hydration no lines of calcium hydroxide were observed.

The calcium hydroxide crystals were found only in the samples with the barium silicate addition and in this case the process of hydration of dicalcium silicate runs probably classically, i.e. the hydrolysis of C_2S took place. These samples, especially with 10% of addition give rather classical microcalorimetric curves, i. e. with the second exothermic peak.

Also the measurements of lime concentration in solution during hydration gives further evidence of a very quick reaction of synthetic belite with water. A high oversaturation of solution took place in a few minutes after mixing with water and the concentration of lime returns quickly, after about 10 minutes, to the level corresponding to the saturation of solution towards calcium hydroxide. The understanding of the mechanism of hydration of these active belites needs further investigations.

The examined activators have different influences on the hydraulic activity of C_2S. Gypsum remains anhydrite after burning and its influence is rather negative which can be seen in the lower heat of hydration.

Potassium and sodium sulphate react with calcium hydroxide forming anhydrite, while sodium and potassium ions form solid solutions with dicalcium silicate. These solid solutions present higher hydraulic activity and, especially in case of sodium, give much higher heat of hydration.

Barium silicate has a very positive influence, because barium forms the solid solution with dicalcium silicate and gives the increase of reactivity of this phase [13]. Belite samples with the addition of barium silicate hydrated fully after 14 days of curing in water.

The measured microhardness of some samples which demonstrated high heat of hydration gave relatively small values. In the light of the X-ray measurements these results, which seem to indicate the slow hydration of obtained dicalcium silicate with the practical increase of strength only after 28 days of hardening, are not clear and need further complementary studies.

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