HYDRATION OF THE MODEL SULPHOALUMINATE-BELITE CEMENTS COMPOSED OF BLENDS OF MINERALS WITH CLASSIFIED PARTICLE SIZES

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The hydration of clinker mineral mixtures at keeping their constant mineralogical composition (45 wt.% C_2S, 20 wt.% $C_4A_3\bar{S}$ and 35 wt.% $C\bar{S}$) but differing in particle size of individual clinker minerals (0-5 μm, 5-20 μm and 20-40 μm) has been studied by conduction calorimetry. The characteristic features of calorimetric curves, namely positions and intensities as well as shapes of peaks are differentiated in relationship to particle size of clinker minerals. Hydration kinetics is mainly governed by C_2S and $C\bar{S}$ (duration of induction period), while $C_4A_3\bar{S}$ seems to influence predominantly the mechanism of hydration. The "sensitivity " of induction period to the changes in particle size of individual clinker minerals is demonstrated by maps of curves of equal induction periods.

INTRODUCTION

Numerous theories have been advanced to explain the mechanism and kinetics of sulphoalumate belite (SAB) cement hydration [1-5]. Considerable progress which has been made towards our understanding of principal factors controlling the hydration process is that the modification of the hydraulic activity of SAB depends on the change of phase composition [2], or on the addition of admixtures [6]. Some studies in this area [7], however allow to state that the factors influencing the conditions of ettringite formation in SAB-system is the *pH* value of the liquid surrounding. The solubility of $C_4A_3\bar{S}$-phase and the process of $Al(OH)_4^-$ ions transfer into solution are dependent on the *pH*. This fact confirms the importance of *pH* in the mechanism of ettringite formation. There are two major theories of the hydration mechanism, the topochemical and the trough-solution theory. According to the first one, ettringite is formed on the surface of $C_4A_3\bar{S}$ particles. According to the second idea ettringite is precipitated from the supersaturated liquid with respect to Ca^{2+}, Al^{3+}, SO_4^{2-} ions [8].

The conditions under which ettringite forms are important with regard, not only to the setting of SAB-paste, but also to its long term behaviour [9].

It is documented in literature [4] that the particle size (PS) or fineness of cements has a dominant influence on the rate of hydration and the resulting structural parameters of concrete bodies. Cement powder is a polysize specimen. The PS of individual clinker minerals is in invariably proportioned by milling process, e.g. essentially by the grindability of clinker minerals (their hardness), but also by milling equipment, structure of clinkers, etc.

Relying upon the knowledge that the cement specific surface by Blaine method alone is not sufficient for characterization of relationship among fineness and mechanism of formation of hydrated products and strength development of concrete, an information on the particle size of individual minerals is greatly desirable for deeply understanding of hydration kinetics. That means, from the thermodynamic point of view, if for the same phase composition of clinker the stable hydrated products are the same, the initial products and the kinetics of hydration and its mechanism are expected to be strongly influenced by the PS of individual clinker phases taking part in the reaction.

There is still a wide divergence of views on the mechanism of ettringite formation as well as the conditions of its formation, which makes the present investigations all the more justified. In addition, the effect of PS of individual clinker mineral on hydration process has not been deeply investigated [4].

In order to proceed in understanding of the hydration mechanism and the kinetics of hydration of sulphoaluminate belite cement a model of the reported SAB has been considered taking into account only main mineral phases: C_2S, $C_4A_3\bar{S}$, $C\bar{S}$ in the constant weight proportion 45 %, 20 % and 35 % respectively. This proportion allows ettringite formation and assures conditions of its stability. The procedure considers individual clinker minerals with different grain size and characterizes the influence of PS-composition upon the kinetics and mechanism of SAB hydration. It is presumed

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In this paper usual chemistry notation is used in which:
$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$, $H = H_2O$.

that the microstructure development that is responsible for physical and mechanical properties depends on the PS of initial reacting particles.

EXPERIMENTAL PART

$C_4A_3\bar{S}$ has been synthesized from homogenized stoichiometric mixture of $CaCO_3$, $CaSO_4.2H_2O$ and $Al(OH)_3$ of analytical reagent at 1300 °C by twice heating with intermittent grinding, likewise, C_2S was synthesised from stoichiometric mixture of $CaCO_3$ and pure quartz (99.99 % of SiO_2). Anhydrite was obtained by heating gypsum at 1200 °C. The purity of phases was controlled by X-ray diffraction. All prepared minerals were ground and air separed into fraction 0-5 µm (F-fine fraction), 5-20µm (M- middle-size fraction) and 20-40 µm (C-coarse fraction).

From these fractions, 27 cement blends have been made divided into 3 main groups according to the PS of C_2S (table I).

A-group comprises fine particle of C_2S (SAB1-SAB9).
B-group comprises the medium of C_2S (SAB10-SAB18).
C-group comprise the coarse of C_2S (SAB19-SAB27).

Each group is divided into 3 sub-groups according to the PS of $C_4A_3\bar{S}$, and in each sub-group, we have investigated the influence of PS of $C\bar{S}$.

The heat evolution was monitored by conduction calorimeter described in [10] using a fixed water/cement ratio of 0.5.

RESULTS AND DISCUSSION

Specimens with fine fraction of C_2S (SAB1-SAB9)

From calorimetric curves (figures 1, 2 and 3) of the first group of cements (SAB1-SAB9), we can evidently see the influence of the PS of $C\bar{S}$ upon the rate of hydration as it is manifested by the position and intensi-

ties of the main peaks. The presence of a small peak before the second main one (SAB1 in figure 1) was observed. Due to the fineness of the phases and their ability to dissolve, we can expect that the fine particles oversaturate the solution with respect to the Ca^{2+}, Al^{3+}, SO_4^{2-} ions. These ions cause formation of the "primary ettringite-gel" by the through-solution mechanism. The Ca^{2+} ions released by the C_2S hydrolysis increase pH of liquid phase and have an important effect on the rate of $Al(OH)_4^-$ transfer into the solution.

In figure 2 (SAB4-SAB6), we can observe a general reduction trend of intensities of the second main peaks and also the length of induction periods. A considerable change is observed in the shape of calorimetric curves. They are more extended in time and their maxima are clearly distinguished. This change in shape of the calorimetric curves can be related to the change in the mechanism of the hydration. Indeed, the precipitation of ettringite via trough-solution process depends on the presence of $Al(OH)_4^-$ ions in the liquid phase. The gradient of these ions depends on the pH and on the rate of dissolution of $C_4A_3\bar{S}$ that is in a correlation with its PS. It means that the coarse $C_4A_3\bar{S}$-particles input less aluminium ions into the solution in the early period, and thus limit the possibility of ettringite formation in the neighbourhood of $C_4A_3\bar{S}$-particles.

When coarse $C\bar{S}$-particles are in presence of fine C_2S-particles, calorimetric curves show the appearance of the "pseudo-third peak" (SAB3, SAB6, SAB9). After 24 hours, X-ray diffraction has not shown the presence of monosulphate. This fact eliminates the hypothesis of the decomposition of ettringite in the case of sulphate lack. The explanation of these phenomena escapes still our full understanding but, we can make a postulation as follows: when coarse fraction of $C\bar{S}$-particles are present, the hydration rate of C_2S highly increases, and more C-S-H is formed. Accordingly, sulphate ions from slow dissolving of coarse $C\bar{S}$-particles are consumed by C-S-H gel forming new phase that the authors[11] has called

Table 1. Particle size characteristic of individual blends of clinker minerals.

A				B				C			
no.	C_2S	$C_4A_3\bar{S}$	$C\bar{S}$	no.	C_2S	$C_4A_3\bar{S}$	$C\bar{S}$	no.	C_2S	$C_4A_3\bar{S}$	$C\bar{S}$
1	F	F	F	10	M	F	F	19	C	F	F
2	F	F	M	11	M	F	M	20	C	F	M
3	F	F	C	12	M	F	C	21	C	F	C
4	F	M	F	13	M	M	F	22	C	M	F
5	F	M	M	14	M	M	M	23	C	M	M
6	F	M	C	15	M	M	C	24	C	M	C
7	F	C	F	16	M	C	F	25	C	C	F
8	F	C	M	17	M	C	M	26	C	C	M
9	F	C	C	18	M	C	C	27	C	C	C

F - fine, M- middle, C - coarse
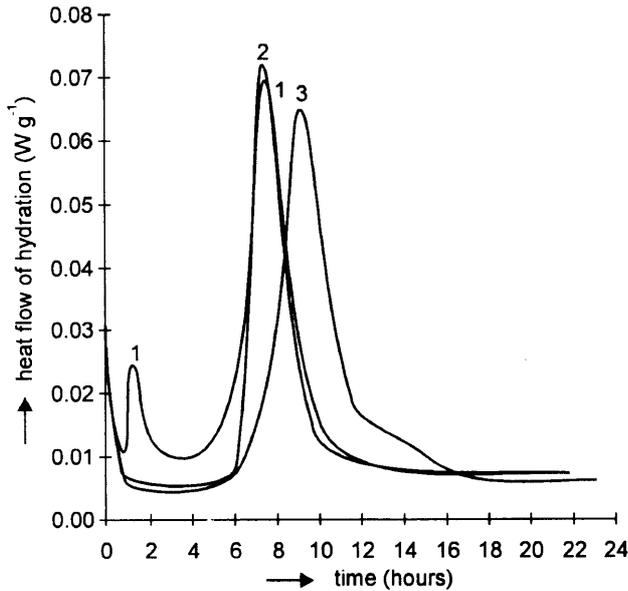
Figure 1. Hydration curves of cements SAB1-SAB3.
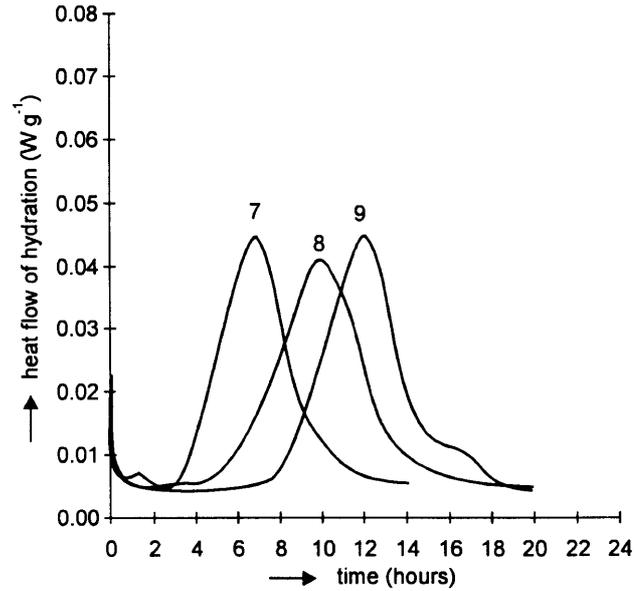
Figure 3. Hydration curves of cements SAB7-SAB9.
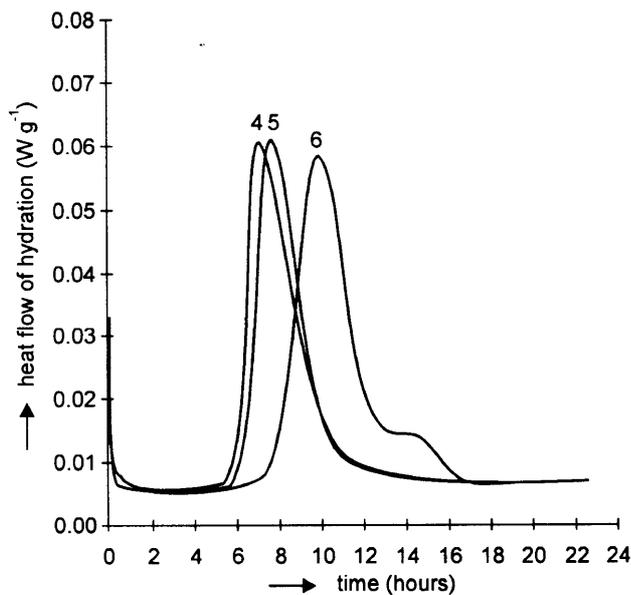


Figure 2. Hydration curves of cements SAB4-SAB6.
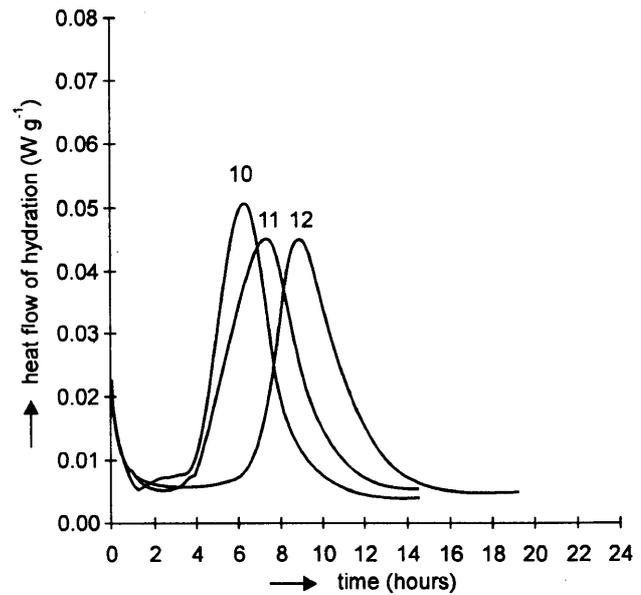
Figure 4. Hydration curves of cements SAB10-SAB12.

"phase X". This consumption reduces sulphate concentration in cement paste and influences the kinetics of hydration. Then calciumaluminate hydrate, furthermore, reacts with released sulphate by C-S-H gel to form "delayed ettringite".

Fine C_2S-particles influence the kinetics and mechanism of ettringite formation by:

− saturation of the surrounding liquid with respect to Ca^{2+}. Consequently, the aqueous $Ca(OH)2$ con-

centration enhances the *pH*-value and thus, delays ettringite formation [9].

− consumption of $SO_4^{2−}$ by C-S-H gel leading to the formation of "X-phase" and thus allows the formation of "delayed ettringite" [11].

The duration of induction period can be explained by physical process. Indeed, during dormant period, from the supersaturated solution begins the formation of nuclei that are more and less thermodynamically stable

according to the nuclei-size. The number of nuclei's sites depends on the presence of $Al(OH)_4^-$ ions. Nuclei having reached the critical size can grow and fill the pores of the structure at the early period of hydration. This ettringite precipitates in water-filled space and consequently reduces the porosity of the cement matrix. In accordance with the present observations derived from calorimetric curves relevant to hydration kinetics of SAB1-SAB9, it can be assumed that the process of nucleation and growth, followed by an eventual impingement of products prolongs the induction period.

Specimens with middle-size fraction of C_2S (SAB10-SAB18)

Figures 4, 5 and 6 (SAB10-SAB18) represent the second group of samples with middle-size fraction of C_2S. Owing to the size of C_2S, saturation of liquid interlayer with respect to Ca^{2+} in the earlier period of hydration is negligible. Dissolution kinetics of $C\bar{S}$ and $C_4A_3\bar{S}$ are the starting driving force in all hydration process in this group. The second main peaks appear earlier than it was observed with the first group, and their intensities are also reduced. This change can be attributed to the lower *pH* value of the liquid surrounding the hydrating particles. Indeed, fine particles of anhydrite oversaturate liquid-water with respect to SO_4^{2-} and thus decrease *pH* and retard the $Al(OH)_4^-$ transfer into the liquid [7].

From the calorimetric curve of figure 4, it is observed, when the combination M-F-F is taken, a small peak evolution similar to that observed in the case of F-F-F combination. X-ray diffraction report does not show the presence of gypsum as was reported by [4], but only ettringite. In the case of coarse $C\bar{S}$-particles, supersaturating the liquid with respect to SO_4^{2-} suitable for ettringite formation is relatively slow because of the dissolution rate of anhydrite. The formation of thermodynamically stable nuclei allowing the growth of ettringite crystals is retarded, and this fact may support the formation of monosulphate that further reacts with sulphate anions to form ettringite. With the middle-size fraction of $C_4A_3\bar{S}$ (figures 4-6), we can observe the reduction of the intensities of the main peaks, and induction periods here tend to disappear. Calorimetric curve of SAB15 presents convolutions (figure 5). The reduction of induction period characterizes the fact that hydration process occurs via another mechanism that it was in the case of SAB1-SAB9.

Calorimetric curves for SAB16, SAB17 and SAB18 are referred in figure 6. The induction periods are reduced and calorimetric curves present some convolutions. The observed convolutions can be caused by the consecutive reaction process allowing the formation of intermediate products.
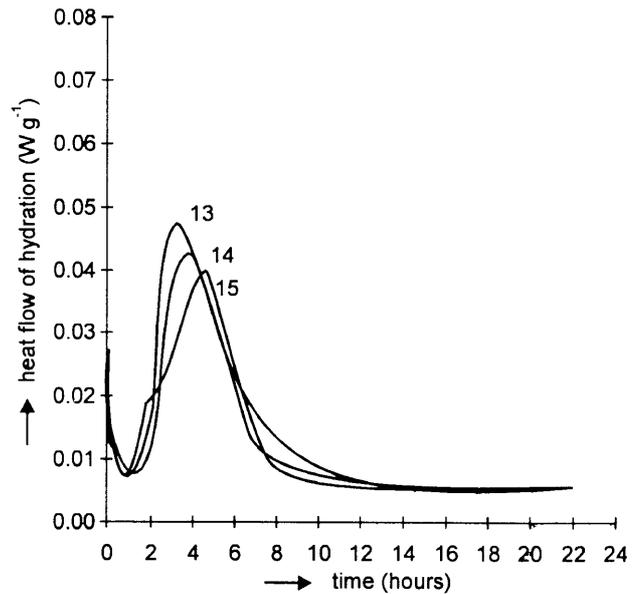

Figure 5. Hydration curves of cements SAB13-SAB15.
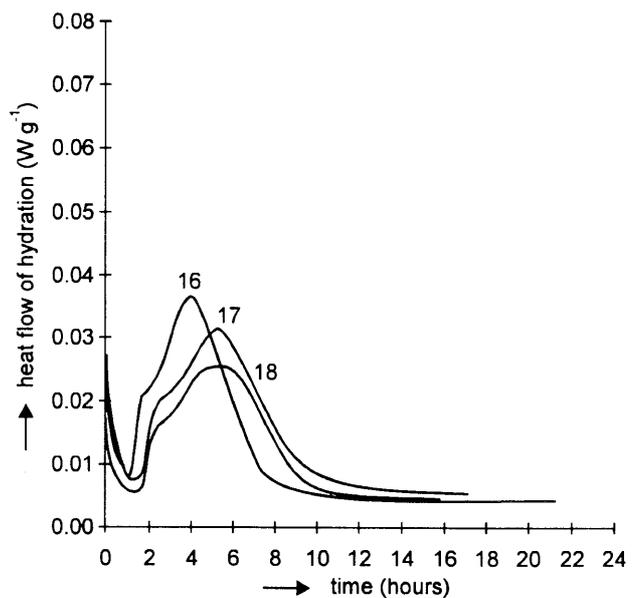
Figure 6. Hydration curves of cements SAB16-SAB18.

Specimens with coarse fraction of C_2S (SAB19-SAB27)

The last group of these combinations consists of the coarse fraction of dicalcium silicate. Induction period is not exemplified or it may be involved in the early part of hydration process. Calorimetric curves present some unordinary behaviour: wide shape and 3 or 4 peaks. These convolutions can be explained by the different steps of hydration. SAB21 (figure 7) presents normal
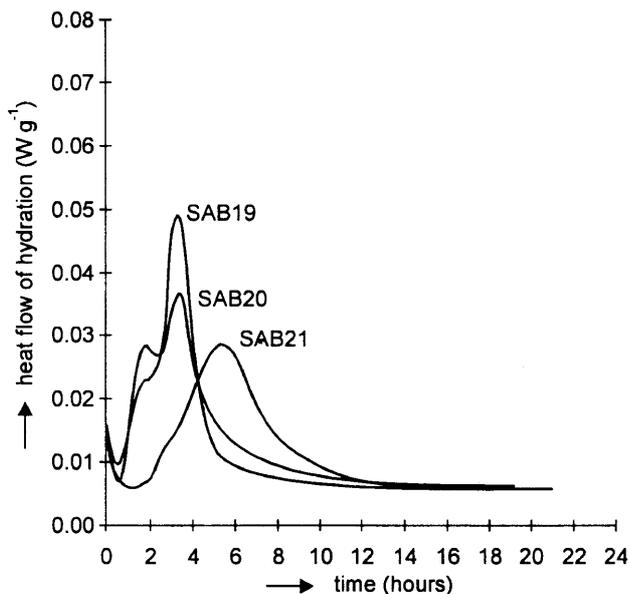
Figure 7. Hydration curves of cements SAB19-SAB21.
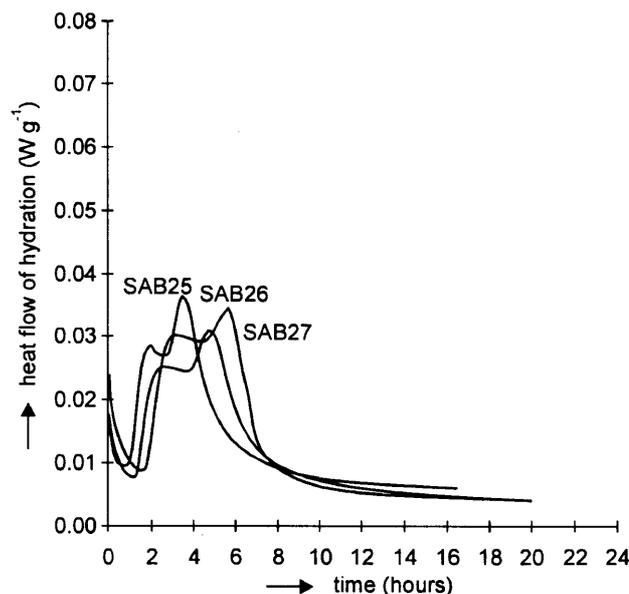
Figure 9. Hydration curves of cements SAB25-SAB27.
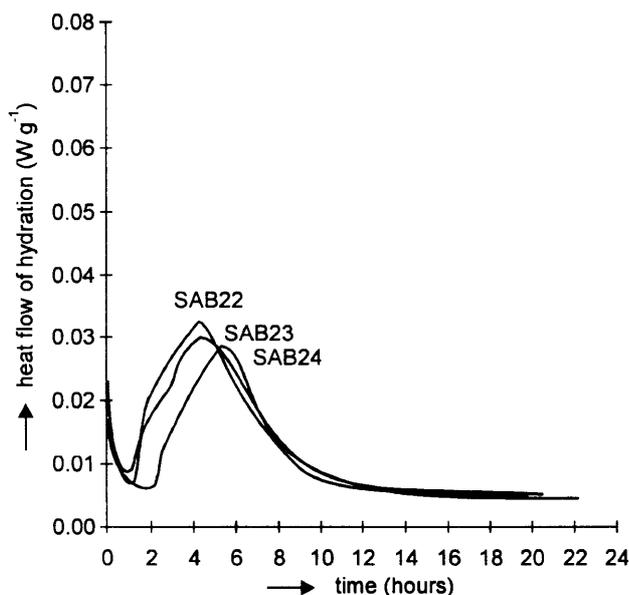
Figure 8. Hydration curves of cements SAB22-SAB24.

characteristics of calorimetric curve with longer induction period.

SAB22-SAB24 (figure 8) present a rather wide shape of peaks and hydration ends prior to 12 hours.

SAB25-SAB27 (figure 9) present calorimetric curves with two maxima. Calorimetric profiles clearly show the shortening of the induction period and the production of large peaks instead of normal single peaks as it was observed in the other cases. It is probable that the doublet is produced because the diffusion controlled hydration of

the surface layer becomes more active due to a high concentration of ions near the particles of C_4A_3S.

It, is particularly difficult to examine the microstructure development at each stage of a "calorimetric time". Even apart damage caused by drying, the time taken for specimen preparation makes it difficult to follow the progress of microstructure development accurately during the initial period up to 24 hours. X-ray diffraction pattern has shown the presence of ettringite as the only aluminate sulphate hydrate after the first day.

The durations of induction period were evaluated from calorimetric curves. For each clinker mineral, it was considered influence of individual fraction of one mineral in presence of various fractions of other two phases. The figures 10, 11 and 12 represent maps of the curves connecting points with equal time of induction period. The density of curves corresponds to the "rate" at which the induction periods are influenced by changes in particle size of clinker minerals. Three regions are distinguished: The regions with high density of curves are the areas that are very sensitive to the change of grain-size combination of two minerals in the presence of third one with constant size, the regions of the low density of curves and the transitional regions. In our analysis of curve densities we considered only the regions of high density.

Following specific remarks can be dawn from this analysis. Figure 10a, b, c represent the influence of grain-size of C_2S upon induction period.

As demonstrated by calorimetric curves, evidently fine fraction (figure 10a) gives greater values of induction period. The zone of high curve density is constituted by coarse fraction of C_4A_3S in the combination of fine and
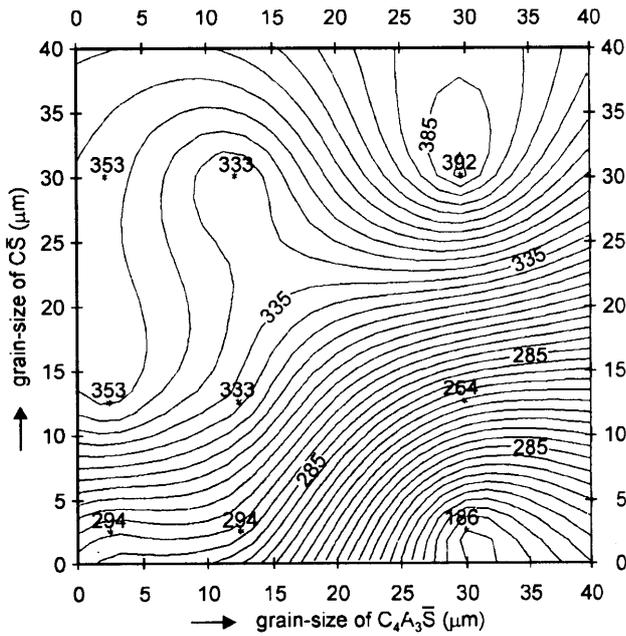
a)
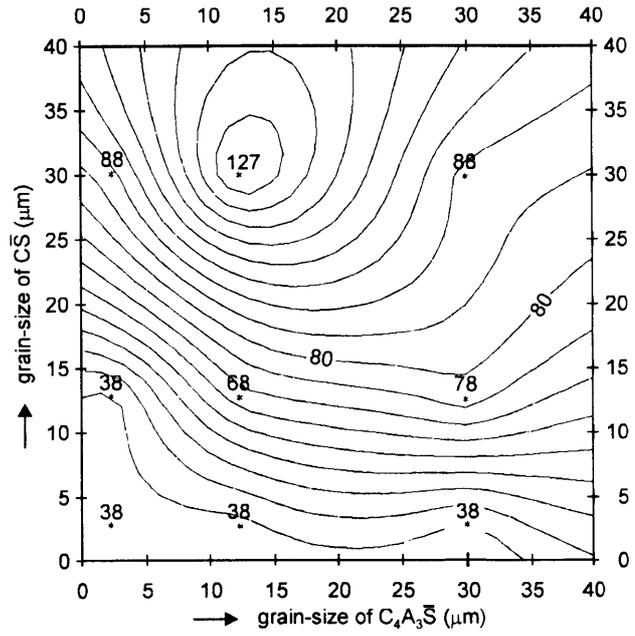
b)
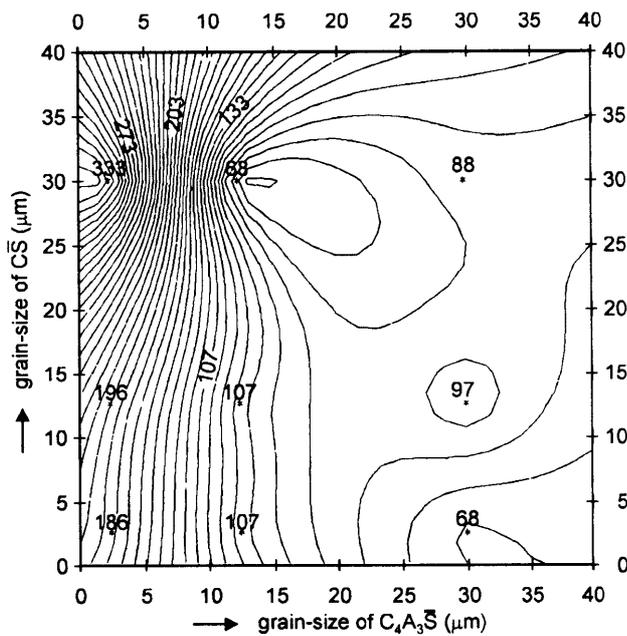
c)

Figure 10. Density map of induction periods (min).
a) fine fraction of C_2S, b) middle size fraction of C_2S, c) coarse fraction of C_2S.

middle-size fraction of C$\overline{S}$. With middle-size fraction, sensitive area is consisted with fine fraction of C_4A_3S and coarse fraction of C$\overline{S}$ whereas coarse fraction of C_2S reduces induction period, but with scattered density of curves in the whole map. In all figures, reduction of induction period is governed by fraction of C$\overline{S}$.

In the presence of fine fraction of C_4A_3S (figure 11a), curve density is homogeneously distributed in the area constituted by middle-size and fine fraction of C_2S in the one hand and fine and middle-fraction of C$\overline{S}$ in

the other hand. With middle-size fraction of $C_4A_3\overline{S}$, a zone of high density of curves and transitional one are observed along C$\overline{S}$-axe (figure 11b). Likewise in the case of coarse fraction of $C_4A_3\overline{S}$, one can see high density namely in the region of coarse fraction of $C_4A_3\overline{S}$ and middle-size fraction of C_2S (figure 11c).

In the presence of fine fraction of C$\overline{S}$ (figures 12a, b, c), high density is observed along the axe of $C_4A_3\overline{S}$. Induction periods are reduced in the zone with coarse fraction of dicalcium silicate.

CONCLUSION

A model of sulphoaluminate belite cement (SAB) comprising the main clinker phases C_2S, $C_4A_3\overline{S}$, and C$\overline{S}$, in the weight proportion of 45 %, 20 %, and 35 %, respectively, has been set up in order to understand the

a)

b)

c)
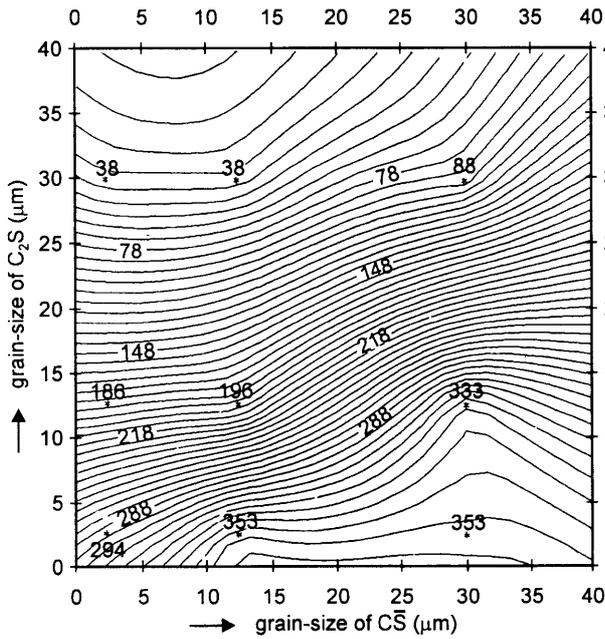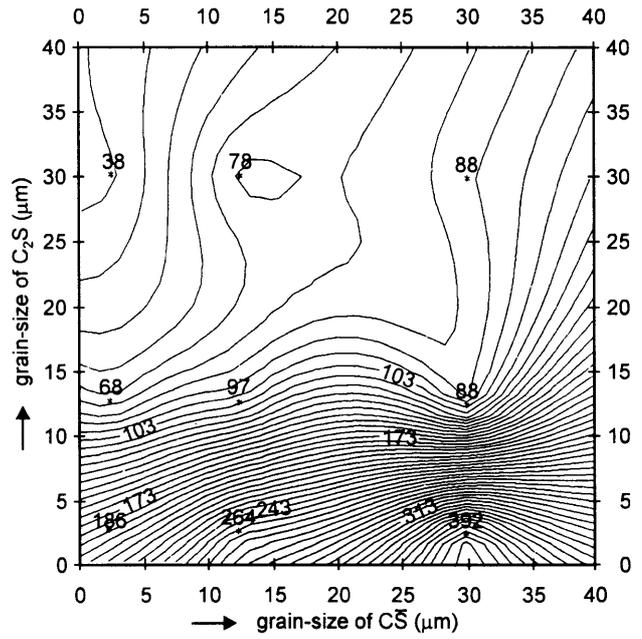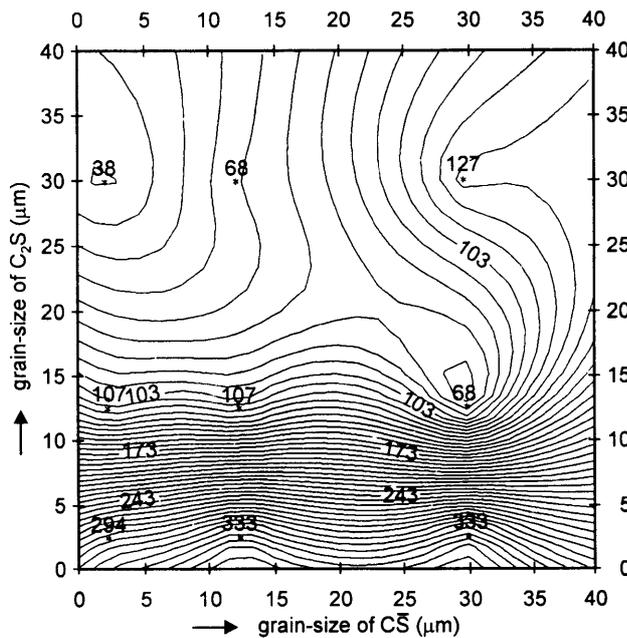
Figure 11. Density map of induction periods (min).
a) fine fraction of $C_4A_3\bar{S}$, *b)* midlle size fine fraction of $C_4A_3\bar{S}$, *c)* coarse fraction of $C_4A_3\bar{S}$.

mechanism and rate of hydration reactions in the systems which differ only by particle-size composition. According to these results, some concrete conclusions can be drawn:

— Samples with fine C_2S-particles have long induction period (figures 1, 2, 3). Ettringite formation is retarded in these systems due to the presence of Ca^{2+} and OH^- released by hydrolysis of dicalcium silicate.

— Particle size of $C\bar{S}$ significantly influences the kinetics of ettringite formation. This fact is illustrated by peak positions (SAB1-SAB27). Dissolution of anhydrite (process relying on particle size) inputs more SO_4^{2-} ions into solution, decreases *pH* in the earlier period and causes formation of ettringite in neighbourhood of $C_4A_3\bar{S}$ with middle and coarse fraction.

— $C_4A_3\bar{S}$-particle influences changes in mechanism of hydration and amount of the formed ettringite. The dissolution rate of this mineral phase determines whether hydration will occur via through-solution or by topochemical mechanism.

Map of curves connecting points with equal induction periods showed that there are three major zones: zone of high density, zone of slow density and transi-

a)

b)

c)
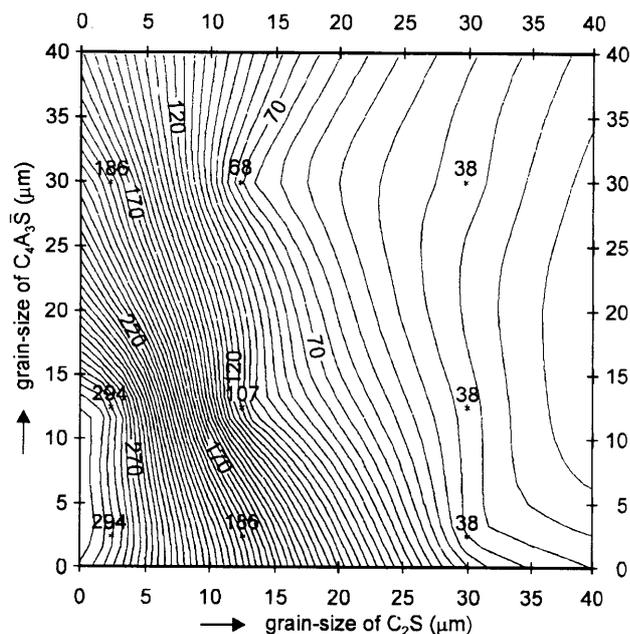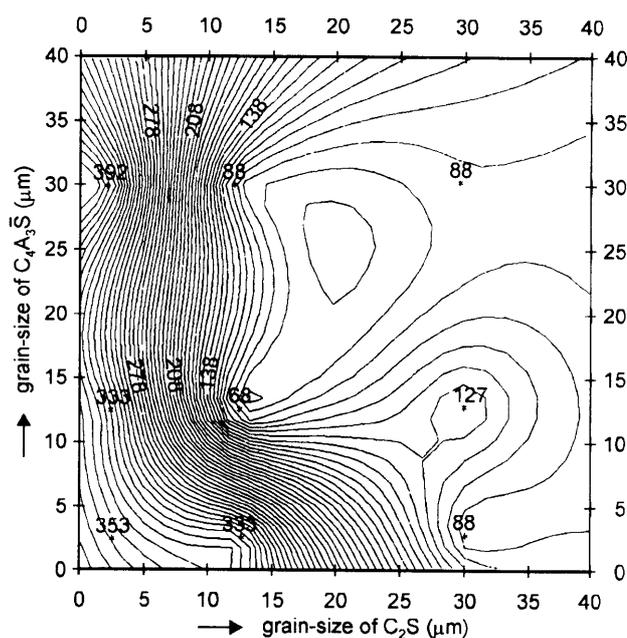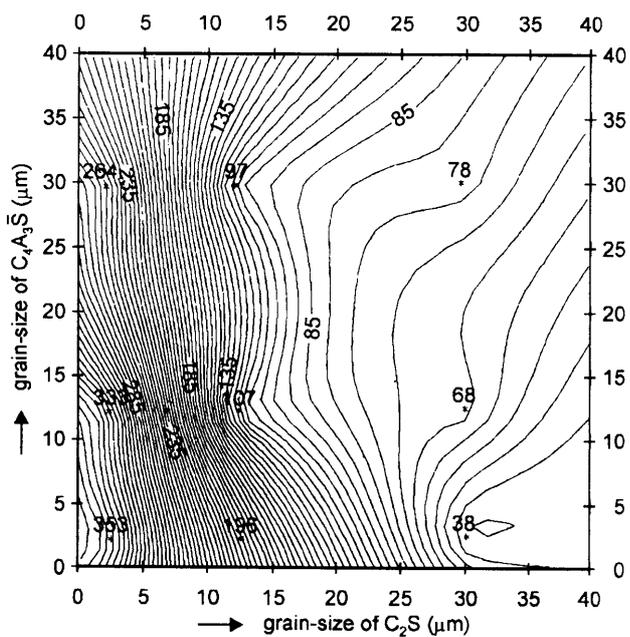
Figure 12. Density map of induction periods (min).
a) fine fraction of CS, *b)* middle size fraction of CS, *c)* coarse fraction of CS.

tional zone expressing the sensibility of induction period upon change of grain-size of individual clinker minerals.

Acknowledgement

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HYDRATÁCIA
MODELOVÝCH SULFOALUMINÁT-BELITOVÝCH CEMENTOV POZOSTÁVAJÚCICH ZO ZMESÍ MINERÁLOV S URČENOU VEĽKOSŤOU ČASTÍC

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Hydratácia cementu a tým aj nadobúdanie štrukturálnych a pevnostných charakteristík cementového kameňa sú do značnej miery podmienené jemnosťou mletia. V závislosti od meliteľnosti slinkových minerálov a povahy mlecieho zariadenia sa potom zrnitosti jednotlivch slinkových minerálov nachádzajú vo vzájomnej väzbe. V tejto práci sme dopredu syntetizovali tri základné slinkové minerály sulfoaluminát-belitového cementu (C_2S, $C_4A_3\bar{S}$ a $C\bar{S}$), pričom každý z nich sa po mletí separoval na tri frakcie, jemnú, strednú a hrubú (0-5, 5-20, 20-40 μm).

Prostredníctvom vodivostnej kalorimetrie sa sledovala hydratácia modelových cementov pozostávajúcich zo zmesí uvedených minerálov pri ich stále rovnakých hmotnostných pomeroch (45 % C_2S, 20 % $C_4A_3\bar{S}$ a 35 % $C\bar{S}$). Jednotlivé zmesi sa však líšili pomerom zrnitostí slinkových minerálov. Celkove bolo vyšetrených 27 zmesí (tabuľka I), ktoré sa rozdelili na tri skupiny podľa veľkosti frakcie C_2S.

Výsledková časť práce zahrňuje hydratačné krivky jednotlivých zmesí (obr. 1-9) ale tiež takzvané hustotné mapy idukčnej periódy, ktoré predstavujú znázornenie čiar rovnakej idukčnej periódy pre zvolenú frakciu jedného minerálu v závislosi od veľkosti frakcí zostávajúcich dvoch minerálov (obr. 10-12).

Z výsledkov meraní vyplýva, že vzorky cementov s jemnou frakciou C_2S vykazujú dlhu indukčnú dobu. Tvorba etringitu je zabrzdená prítomnosťou Ca^{2+} a OH^- iónov uvoľnených hydrolýzou C_2S.

Veľkosť častíc $C\bar{S}$ významne ovplyvňuje rýchlosť tvorby etringitu. Rozpúšťanie anhydritu znižuje *pH* kvapalnej fázy v počiatočnom štádiu hydratácie a vyvoláva tvorbu etringitu v blízkosti častíc $C_4A_3\bar{S}$ (pri ich strednej a hrubej frakcii).

Rýchlosť rozpúšťania $C_4A_3\bar{S}$ určuje, či sa etringit tvorí topochemicky, alebo cez roztok.