Journal of Thermal Analysis, Vol. 46 (1996) 597-605

APPLICATION OF CONDUCTION CALORIMETRY FOR STUDY OF THE REACTIVITY OF C_2S IN THE SYSTEM $C_2S-C_4A_3\bar{S}-C\bar{S}-H$*

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Abstract

A conduction calorimeter was used to determine the effect of the ignition temperature on the hydration reactivity of C_2S in the system $C_2S-C_4A_3\bar{S}-C\bar{S}$ relevant to sulphoaluminate belite cement. The results thus obtained showed that the kinetics and mechanism of hydration of the system $C_2S-C_4A_3\bar{S}-C\bar{S}$ are influenced by the temperature of C_2S synthesis. The hydration reactivity of C_2S increases with increasing temperature of ignition.

Keywords: conduction calorimeter, hydration reactivity of C_2S

Introduction

During the past ten years, sulphoaluminate belite (SAB) cement, involving five component oxides, $CaO-Si_2O-Al_2O_3-Fe_2O_3-SO_3$, in a system containing the main phases C_2S, $C_4A_3\bar{S}$, C_4AF and $C\bar{S}$, has occupied the attention of many investigators [1–3]. The low hydrating reactivity of the macrophase C_2S leads to the formation of C–S–H (tobermorite-like) and to the precipitation of $Ca(OH)_2$ (Eq. 1). Nevertheless, this low reactivity contributes substantially to the later strength development. In the initial period, the formation of C–S–H gel plays an important role in the diffusion phenomena by reducing the rate of diffusion of reacting ions.

The phase $C_4A_3\bar{S}$ reacts in the presence of calcium sulphate to form ettringite (Eq. 2), which is responsible for the setting and hardening properties in the initial period. The hydration of C_4AF also leads to ettringite formation [1]. The precipitation of $Ca(OH)_2$ from the hydrolysis of C_2S and from hydration of the free lime greatly favours ettringite formation (Eq. 3).

In the modelled SAB system with the main phases C_2S (50%), $C_4A_3\bar{S}$ (30%) and $C\bar{S}$ (20 wt%), the reactions during hydration can be summarized schematically as follows:

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* Cement chemistry notation is used, where C =CaO, S =SiO_2, A =Al_2O_3, $\bar{S}$ =SO_3 and H =H_2O.

0368–4466/96/ $ 5.00

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$$C_2S + H \rightarrow C\text{-}S\text{-}H + CH \tag{1}$$

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \tag{2}$$

$$C_4A_3\bar{S} + 6C\bar{S} + 8CH + 88H \rightarrow 3C_6A\bar{S}_3H_{32} \tag{3}$$

The kinetics and the mechanism of the hydration reaction depend on many factors besides the mineralogical composition, such as the water/cement ratio, the temperature of hydration, the *pH*, the particle size, etc.

The hydration reactivity of C_2S towards water depends not only on these factors, but also on the reactivity of the starting materials, the crystal imperfections, the polymorphic form and the conditions of synthesis. Nevertheless, owing to the low hydrating reactivity of C_2S, which hampers calorimetric investigations of the hydration of this phase, we have proposed and experimentally verified a method permitting investigation of the reactivity of C_2S in the system $C_2S\text{-}C_4A_3\bar{S}\text{-}C\bar{S}\text{-}H$ relevant to the model of SAB cement. The weight ratio was chosen so as to favour ettringite formation in the presence of $Ca(OH)_2$ resulting from the hydrolysis of C_2S.

The mineralogical composition and the parameters such as the specific surface, and the conditions of the hydration were maintained identical, and the differences in the courses of the calorimetric curves obtained from the hydration of the model SAB system were used to interpret the hydrating reactivity of C_2S prepared by the sol-gel process in the temperature range 900–1100°C.

Calorimetric studies of the heat evolution from this model SAB system demonstrated two heat evolution peaks. Numerous studies have concluded that the first peak (up to 30 min) corresponds to the exothermic wetting effect (which depends on the specific surface) of the sample, the hydration of the free lime [4] and the formation of ettringite-gel, which creates a protective layer around the hydrating particles, and thus causes the induction period. The second major peak, which arises after the early hydration period, characterizes the main exothermic reaction corresponding to the formation of ettringite crystals.

The aim of this work was to determine the influence of the ignition temperature on the hydration reactivity of dicalcium silicate in the system $C_2S\text{-}C_4A_3\bar{S}\text{-}C\bar{S}\text{-}H$. The investigations were performed by means of conduction calorimetry and X-ray diffraction analysis.

Experimental

Dicalcium silicate samples were prepared from a homogenized mixture of silica gel (Tosil) with a calculated amount of calcium nitrate solution [5]. The amounts of the starting reactants were calculated so as to furnish CaO and SiO_2 in a molar ratio of 2 to 1 on ignition. The solutions were evaporated at 100°C

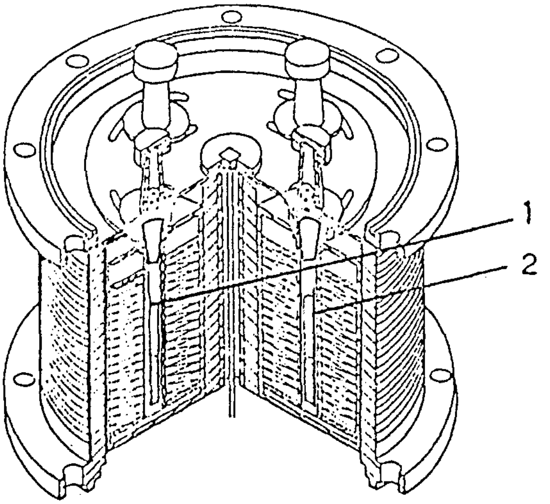

Fig. 1 Scheme of conduction calorimeter apparatus; 1 – Cell with standard sample, 2 – Cell containing hydrating sample

and calcined in a platinum dish at 700°C. The individual samples were obtained by heating the samples thus prepared at 900, 950, 1000 or 1100°C during 2 h (Table 1).

Table 1 Sample preparation

Ignition temperature / °C	Duration of ignition / h	Content of free lime / wt.%
900	2	1.31
950	2	1.31
1000	2	1.09
1100	2	0.25

The rate of heat evolution was measured with a conduction calorimeter (ZIAC, developed by the ex-East German Academy of Science) (Fig. 1). The equipment easily lends itself to a computer link of type PP06 for continuous monitoring of the rate of heat generation. The sensitive part of the ZIAC calorimeter consists of a system of two cells inserted in an isolating metallic block. The first, containing the standard sample, acts as a reference, and the second one contains the sample of hydrating cement. The diameter of the cells is 10 mm. This system is covered by a solid foam of polyuret, which isolates the metallic block from the lid. The two cells are linked by a heatflux transducer. When the exothermic hydration reaction starts, the temperature difference between the two cells generates electromotive tension such that the flux, propor-

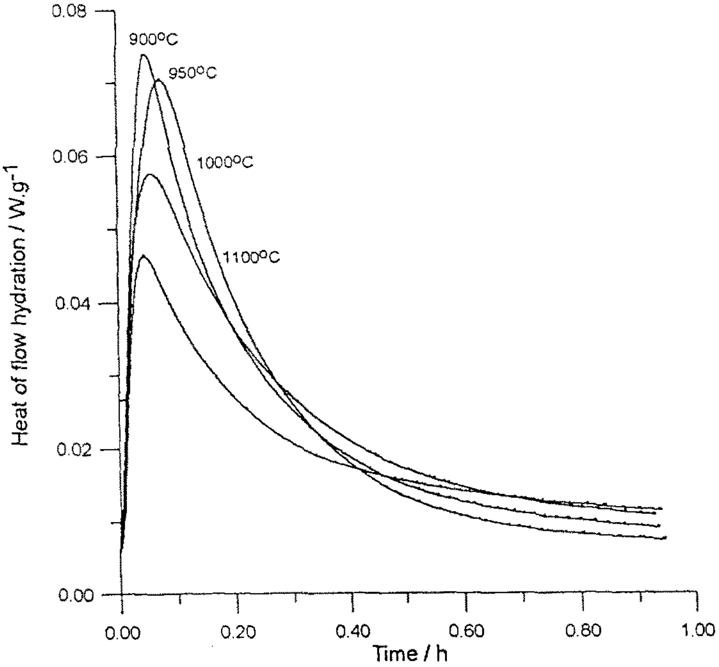

Fig. 2 Early period of hydration in the C_2S–$C_4A_3\bar{S}$–$C\bar{S}$–H system

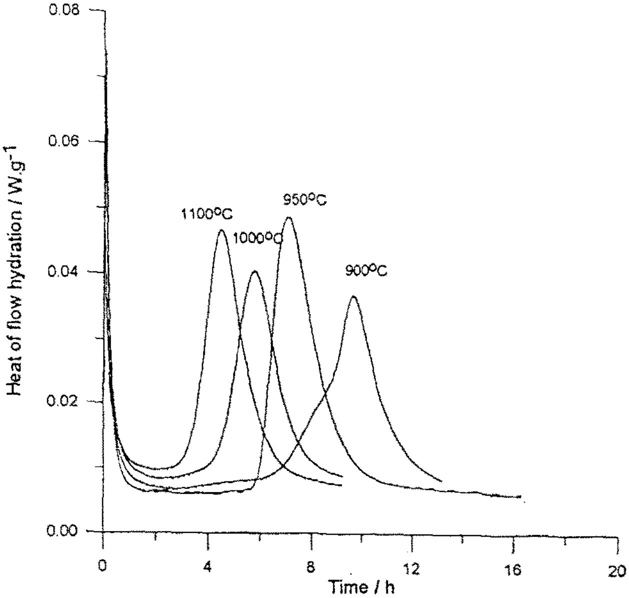

Fig. 3 Calorimetric curves of C_2S–$C_4A_3\bar{S}$–$C\bar{S}$–H system

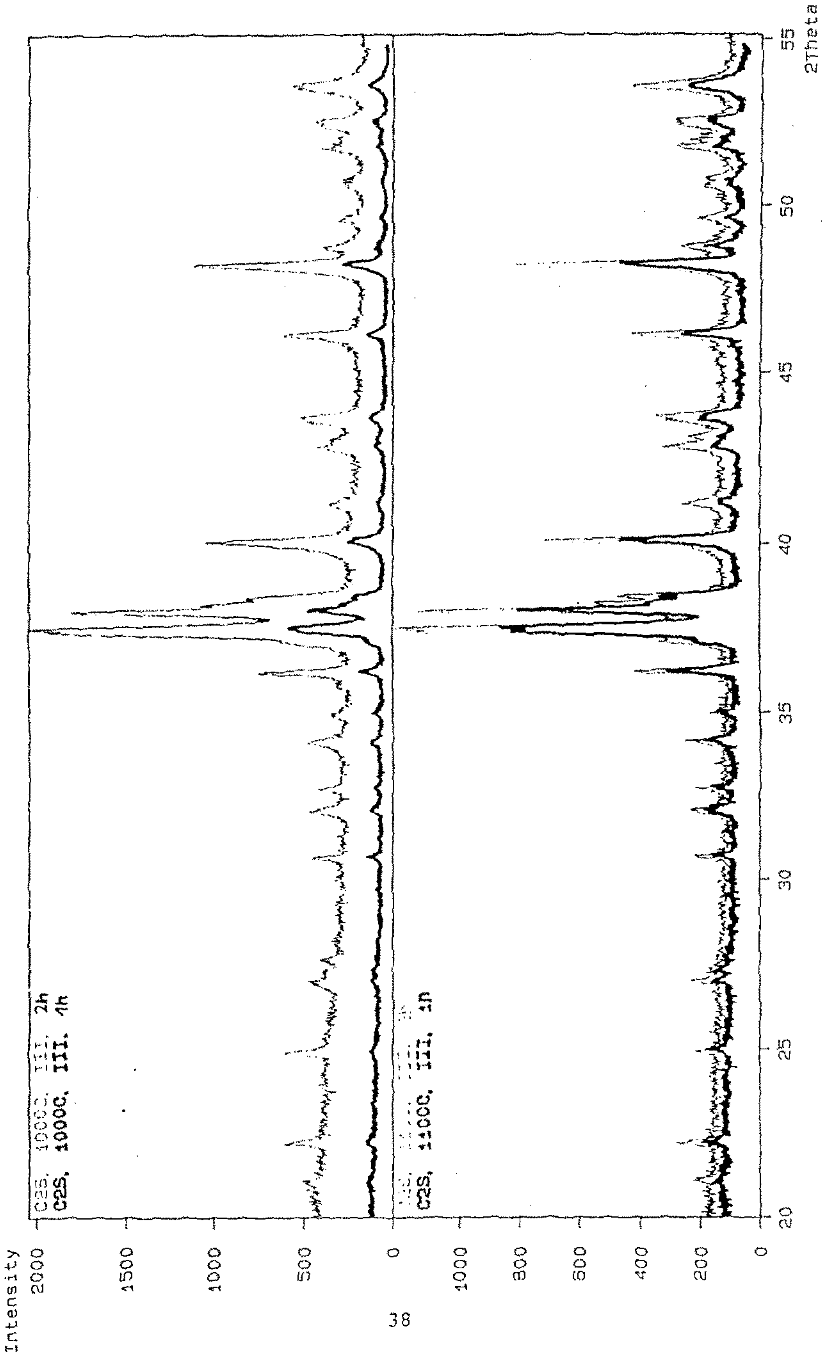

Fig. 4 X-ray patterns (using radiation Co K_{α_1}) of C_2S synthesized at 1000 and 1100°C during 1 and 2 h

tional to the heat transfer, is continuously monitored through an A/D-converter module as a temperature rise in the hydrating cement. The temperature data are then used to determine the flow of heat generated and the heat of hydration.

For measurements, a plastic bag containing 2 g of fresh sample was plunged into the cell of hydrating cement containing dibutylphthalic acid, which is poorly volatile and has an appreciable thermal conductivity. A syringe containing water corresponding to a fixed water/cement ratio of 0.5 was placed in the calorimeter 1 h before the starting of hydration.

The free lime content was determined by extraction in ethylene glycol and measurement with benzoic acid.

X-ray powder diffraction analysis (Fig. 4) was used in the identification of C_2S in the prepared samples and in the hydrated products (Figs 5–6). Hydration

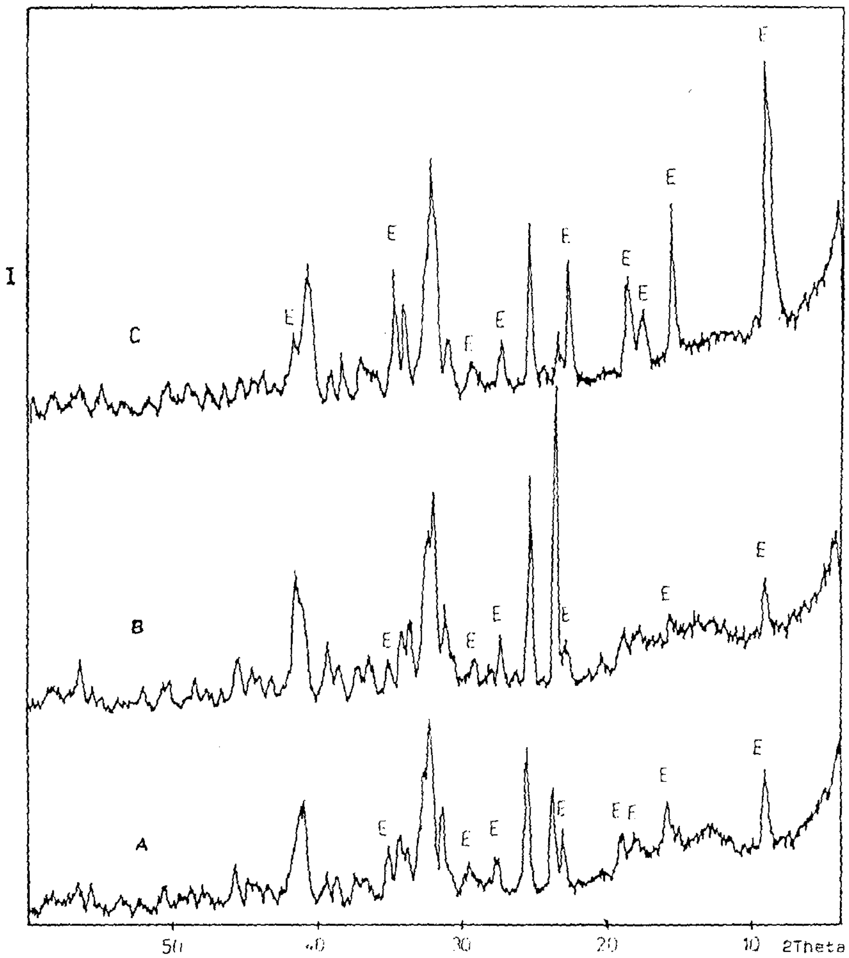

Fig. 5 X-ray diffraction patterns (using radiation CuK_{α_1}) of hydrated samples at 5 min of hydration (A), 90 min of hydration (B), 24 h of hydration (C); C_2S synthesized at 1100°C; E – ettringite

was interrupted at different intervals of time by washing in acetone, then in diethyl ether, with subsequent drying at room temperature.

Results and discussion

When the composition of other initial phases of the system and the measurement conditions are maintained constant, the effect of the ignition temperature upon the reactivity of dicalcium silicate is evident from the calorimetric curves.

Calorimetric measurements on samples of C_2S prepared in the temperature range 900–1100°C during 1 and 2 h are depicted in Figs 2 and 3. The positions of the peaks are the same, but the peak intensities differ due to the crystallinity of the dicalcium silicate.

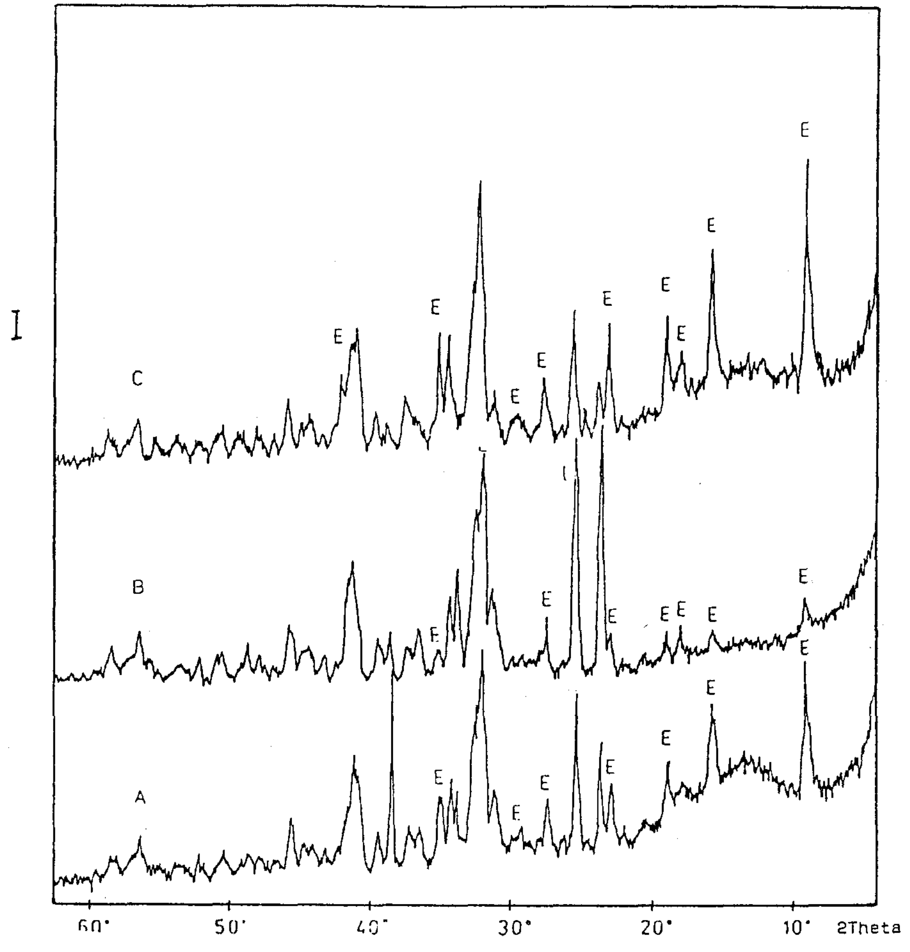

Fig. 6 X-ray diffraction patterns (using radiation CuK_{α_1}) of hydrated samples at 5 min of hydration (A), 90 min of hydration (B), 24 h of hydration (C); C_2S synthesized at 1000°C; E – ettringite

A comparative analysis (Fig. 2) of the calorimetric curves of the hydration process shows that in the early period of hydration, the content of free lime decreases with increasing temperature of ignition of C_2S, and accordingly the intensities of the first peaks decrease. The intensities of the first peak can be attributed not only to the hydration of CaO, but also to the exothermic wetting effect, as mentioned previously.

The results indicate that the maximum time of heat evolution in the hydration system $C_2S-C_4A_3\overline{S}-C\overline{S}-H$ varies from 4 to 10 h. It is evident that the kinetics of the hydration reactions in the system $C_2S-C_4A_3\overline{S}-C\overline{S}-H$ (with different dicalcium silicates) depends on the temperature of ignition of the dicalcium silicate. This is illustrated not only by the duration of the induction period, but particularly by the intensities of the second peaks and by the times corresponding to the maxima.

The X-ray diffraction analyses were carried out on samples that had been hydrated for 5 min, 90 min or 24 h. In Fig. 4, 5 min is the time corresponding to the first maximum, 90 min is the time corresponding to the beginning of the induction period, and 24 h denotes the calorimetric end of the hydration process.

The X-ray powder patterns of the hydrated samples (Figs 5–6) show that only ettringite was observed as a stable hydration product in all diffractograms. Other possible hydration products, such as monosulphate, gibbsite or calcium hydroxide, were not identified. The unmarked peaks represent the unreacted initial phases. Ettringite formation according to Eq. (3) is kinetically quick, because the rates of reaction of CaO with water, $C_4A_3\overline{S}$ and gypsum are higher than that of the reaction in Eq. (2) [6].

The intensity of the characteristic X-ray diffraction for ettringite at a *d*-spacing ($2\theta = 9$) of 0.756 for a 90 min hydration is smaller than that for the 5-min hydration (Figs 5 and 6). This phenomenon is probably caused by ettringite formation in the early period via a topochemical mechanism on the surface of $C_4A_3\overline{S}$, thereby causing a retardation of the hydration. The next hydration reaction will depend on the diffusion of water molecules through the hydrated layer. The diffusion through the crystalline solid or amorphous phase is extremely slow at room temperature, and the ettringite can be partially and congruently dissolved before and during the induction period. The observed phenomenon can also be caused by the formation of ettringite with a gel-like microstructure. It is evident that the crystallinity of C_2S (which depends on the temperature of ignition) influences the reactivity of the system $C_2S-C_4A_3\overline{S}-C\overline{S}-H$ by changing the mechanism and kinetics of ettringite formation.

Conclusion

The hydration reactivity of C_2S (prepared by a sol-gel process) in the system $C_2S-C_4A_3\overline{S}-C\overline{S}$, relevant for belite sulphoaluminate cement, depends on its ignition temperature. With increasing temperature, the lime content decreases and the hydration reactivity of C_2S increases. In accordance with the phase equilibria of C_2S, the effect probably relates to the consecutive transformation of β-C_2S to the α form.

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