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# HYDRATION BEHAVIOUR OF SULPHOALUMINATE BELITE CEMENT IN THE PRESENCE OF VARIOUS CALCIUM SULPHATES

S. SAHU, J. HAVLICA[*], V. TOMKOVÁ, J. MAJLING

Department of Chemical Technology of Silicates, Slovak
Technical University, 812 37 Bratislava, Czechoslovakia

[*]Institute of Inorganic Chemistry,
Slovak Academy of sciences, 842 36 Bratislava, Czechoslovakia

## SUMMARY

The Sulphoaluminate belite cement clinker with the main phases $C_2S$, $C_4A_3\bar{S}$, $C_4AF$, was synthesised from limestone, fly ash and gypsum. Its hydration was studied in the presence of different admixed calcium sulphates (anhydrites calcined at 750 °C, 1200 °C, hemidrate, gypsum) by differential calorimetry at room temperature.

Results show that predominantly the solubility and to lesser extent the content of calcium sulphate influences the early period of hydration process.

## INTRODUCTION

In recent times a lot of attention has been paid to the development of some modified special cement clinkers, leading to energy saving. One of such cements containing main phases $C_2S$, $C_4A_3\bar{S}$, $C_4AF$ and $C\bar{S}$, was developed recently (refs. 1–4). Instead of $C_3S$, the main silicate phase in ordinary portland cement, which requires a high temperature for its formation, this cement contains two sulphate phases, i.e. $C_4A_3\bar{S}$ and $C\bar{S}$.

The interaction of $C_4A_3\bar{S}$ and $C_4AF$ with $C\bar{S}$ in the presence of water plays an important role in the intial period of hydration, leading to the formation of ettringite.

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Cement chemists' notations

$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$, $H = H_2O$,
$C_3S = 3\ CaO \cdot SiO_2$, $C_2S = 2\ CaO \cdot SiO_2$, $C_3A = 3\ CaO \cdot Al_2O_3$,
$C_4A_3\bar{S} = 4\ CaO \cdot 3\ Al_2O_3 \cdot SO_3$, $C_4AF = 4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$,
$C\bar{S} = CaSO_4$, $C\bar{S}H_2 = CaSO_4 2H_2O$.

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Depending on the ratios of $C_4A_3\bar{S}$ and $C_4AF$ to $C\bar{S}$, formation of monosulphate or ettringite takes place as was shown by heat evolution curves (refs. 5,6). The conversion of ettringite to monosulphate is delayed if anhydrite, rather than hemihydrate or gypsum, is used as $SO_3$ source (ref. 7). Similarly the calcination temperature of anhydrite affects the reactivity and formation of ettringite (ref. 8). The presence of gypsum influences the induction period in ordinary portland cement containing $C_3A$ (ref. 9). The hydration reaction kinetics and the mechanism of formation of different hydrated products depending on the ratios of different phases in the system $C_4A_3\bar{S}$-$C\bar{S}$-CaO-$H_2O$ has been dealt with (ref. 10).

In this work the emphasis has been given to the kinetics of the formation of ettringite in the presence of different kinds of anhydrites, hemihydrate and gypsum taken in their various quantities.

The course of hydration was followed by differential calorimetry, which is very useful in evalution of the heat of hydration.

## EXPERIMENTAL

The clinker was prepared from limestone, fly ash and gypsum by sintering the raw mix for 40 minutes at 1200 °C. Its phase composition was computed according to method (ref. 11). The presence of different phases were identified by X-ray analysis. The quantity of $C_2S$ was estimated by maleic acid extraction method (ref. 12) and free lime by ethyl glycol extraction method.
The computed and estimated values of different phases are given in Table 1. Anhydrites were prepared by calcination of reagent grade gypsum for 1 hour at 1200 °C, 750 °C, and 200 °C. The product calcined at 200 °C was identified as hemihydrate.

TABLE 1
Phase composition of sulphoaluminate belite clinker

| Phase | Wt. % (Cal.) | Wt. % (Est.) |
|---|---|---|
| $C_2S$ | 67.00 | 66.5 |
| C | 0.90 | 1.2 |
| $C_4A_3\bar{S}$ | 19.00 | - |
| $C_4AF$ | 8.5 | - |
| $C\bar{S}$ | 4.6 | - |

To 30 g of clinker was mixed, 2.85 g, 5.70 g and 11.20 g, respectively, of different anhydrites and hemihydrate, and 3.60 g, 7.20 g, and 14.40 g, respectively, of gypsum. The mixtures were vibromilled to a fineness of 350 ± 20 $m^2.kg^{-1}$. The following combinations of mixtures were prepared (Table 2)

TABLE 2

Composition of mixes

| Mix No | SAB Wt. % | $C\bar{S}/C\bar{S}H_2$ Wt. % | Type of $C\bar{S}$ |
|---|---|---|---|
| 1 | 91.32 | 8.68 | $C\bar{S}H_{0.5}$ |
| 2 | 84.04 | 15.96 | " |
| 3 | 72.82 | 27.18 | " |
| 4 | 91.32 | 8.68 | $C\bar{S}$ (750 °C) |
| 5 | 84.04 | 15.96 | " |
| 6 | 72.82 | 27.18 | " |
| 7 | 91.32 | 8.68 | $C\bar{S}$ (1200 °C) |
| 8 | 84.04 | 15.96 | " |
| 9 | 72.82 | 27.18 | " |
| 10 | 89.30 | 10.70 | $CSH_2$ |
| 11 | 80.65 | 19.35 | " |
| 12 | 67.57 | 32.43 | " |

The hydration experiments were perfermed at room temperature using differential calorimetric system ZIAC - GDR (refs. 13, 14). A cuvette with distilled water was used as the reference sample. In each case 2 g of the sample from the above mixtures were taken and put into the calorimeter and tempered for 2 hours. Then 1 ml of distilled water was injected into the sample, maintaining W/C = 0.5. The heat-evolution data were collected and evaluated by a microcomputer.

* SAB = Sulphoaluminate Belite Cement (Tab. 2).

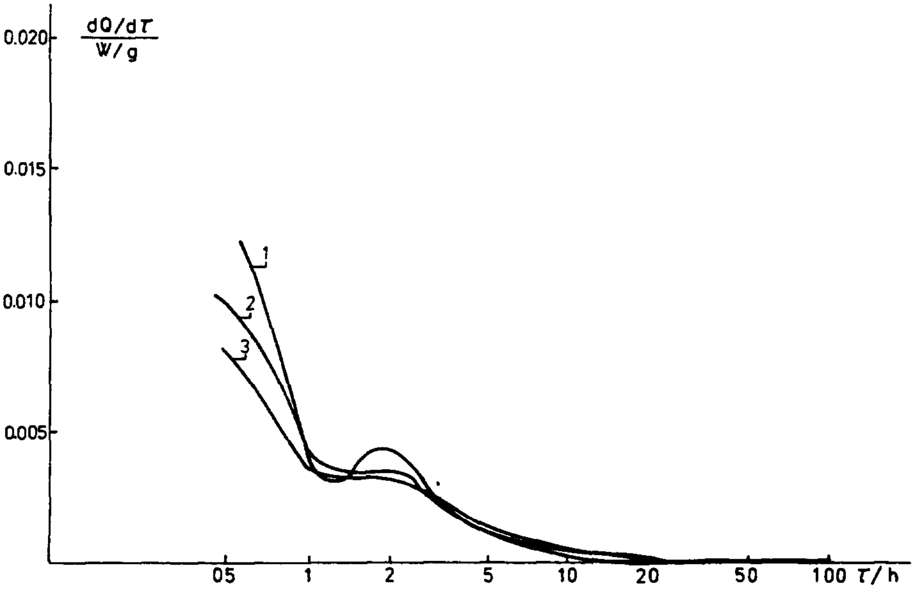

Fig. 1 The trends in heat evolution of Sulphoaluminate belite cement in the presence of $C\bar{S}H_{0.5}$ (Mix no. 1,2,3)

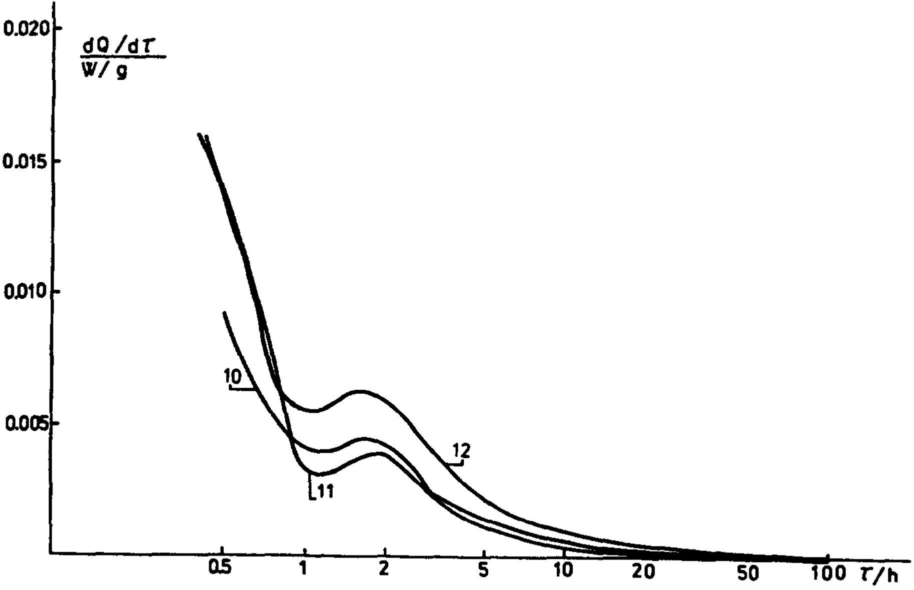

Fig. 2 The trends in heat evolution of Sulphoaluminate belite cement in the presence of $C\bar{S}H_2$ (Mix no. 10, 11, 12)

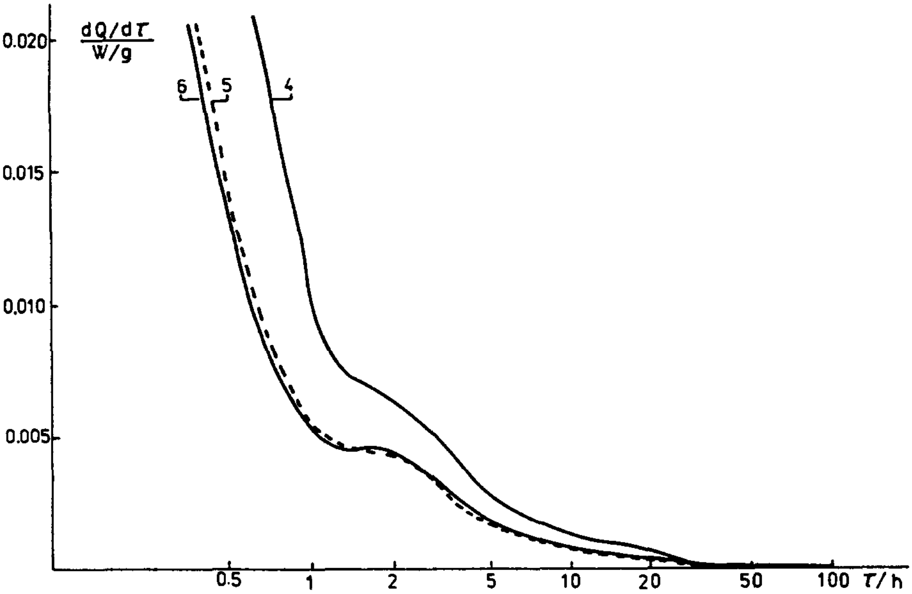

Fig. 3 The trends in heat evolution of Sulphoaluminate belite cement in the presence of $C\overline{S}$, 750 °C (Mix no. 4,5,6)

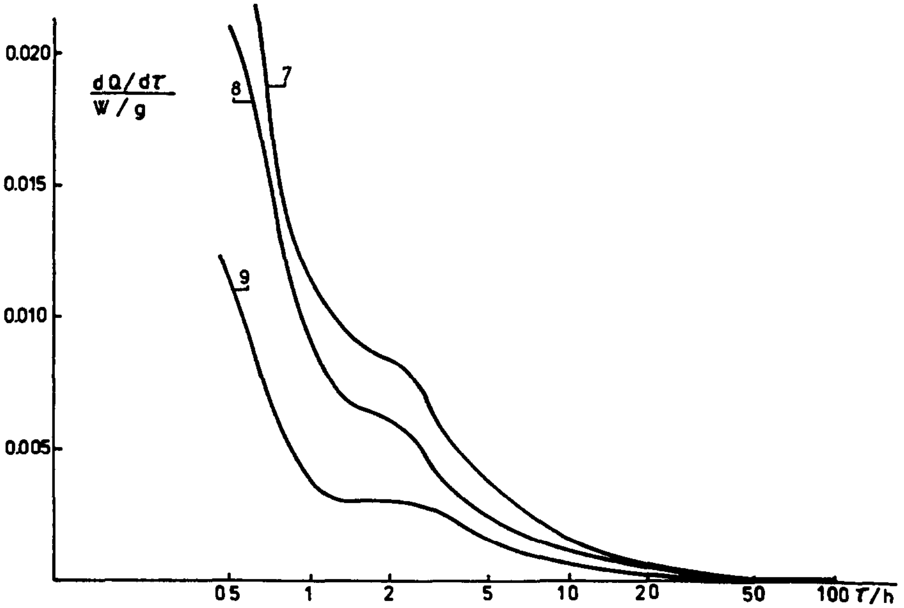

Fig. 4 The trends in heat evolution of Sulphoaluminate belite cement in the presence of $C\overline{S}$, 1200 °C (Mix no. 7,8,9)

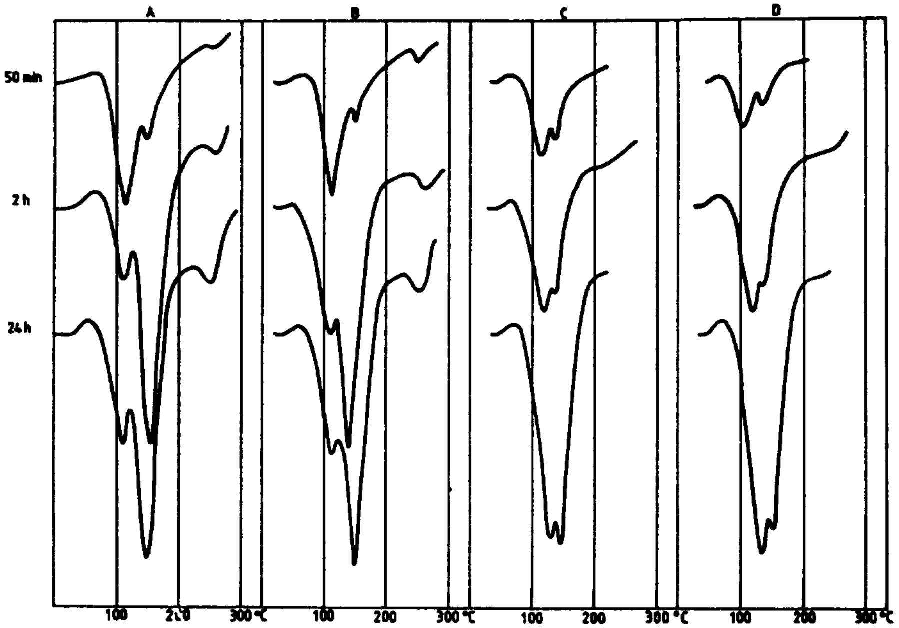

Fig. 5 DTA curves of Samples at various ages of hydration
A = Mix no. 12, B = Mix no. 3,
C = Mix no. 6, D = Mix no. 9.

## RESULTS AND DISCUSSION

The hydrating systems studied differed only in the amount and the kind of admixed calcium sulphates. All other parameters of the systems were kept constant (water to cement ratio, temperature, cement clinker composition). The heat - evolution curves obtained can be classified into two groups. The first group is manifested by the relatively slow decrease in heat evolution after the first period of hydration that takes place approximately from 0,5 - 1 hour, and by the tendency to create a second maximum in the next period of hydration (Figs. 1 and 2).

The second group is manifested by a rapid drop in heat evolution after the first period of hydration and by a further continued but less pronounced heat evolution in the next period of hydration (Figs. 3 and 4).

To the first group of curves belong those obtained by the hydration of clinkers containing more soluble calcium sulphates (hemihydrate and dihydrate). To the second group of curves belong those obtained by the hydration of clinkers which contain less soluble calcium sulphates (anhydrites calcined at 750 °C and

1200 °C).

This difference in shape of the curves can be related to a change in the mechanism of ettringite formation. The more soluble calcium sulphates lead to intensive ettringite formation at the very early period of hydration, which is evident from the DTA Curves Fig. 5. The newly formed ettringite covers the grains of aluminate phases by which the further transport of $Ca^{2+}$ and $SO_4^{2-}$ ions to the surface of aluminate phases is hindered and the hydration is retarded. This is indicated by the end of induction period at the minimum in the hydration curves at approximately 1 hour of hydration.

The less soluble calcium sulphate phases do not create such sudden supersaturation near the surfaces of aluminate phases grains. The precipitated ettringite does not cover the whole surface of aluminate grains and hydration continues further at a slower rate.

The changes in amounts of added calcium sulphate phases do not bring the transition from the first to the second category of curves. However, when the lower amounts of calcium sulphates are present, as necessary for stoichiometric formation of ettringite, then the transition to monosulphate during the next period of hydration will occur. It is expected that the mechanism of ettringite formation will have also significant influence on the next hydration process and development of microstructure.

## CONCLUSION

The solubility of calcium sulphates plays an important role in the hydration of sulphoaluminate belite cement.

The difference in the shape of hydration curves is explained by the difference in the mechanism of ettringite formation and the consequent retardation phenomena.

The variation in the amounts of calcium sulphate phases has only moderate influence in the early period of hydration.

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