EFFECTS OF SULPHATE, CALCIUM AND ALUMINUM IONS UPON THE HYDRATION OF SULPHOALUMINATE BELITE CEMENT

M. T. Palou and J. Majling

Department of Ceramics, Glass and Cement, Faculty of Chemical Technology, Slovak Technical University, 812 37 Bratislava, Slovak Republic

Abstract

In the model sulphoaluminate belite cement, the process of hydration is governed by the diffusion and transport phenomena of the main ionic species. The sulphate components and combined sulphate and aluminium ions, exert an accelerating effect upon the kinetics of sulphoaluminate belite cement hydration. Aluminium and calcium ions delay the hydration by creating a retarding layer which can be considered a co-precipitate of aluminium and calcium hydroxides. This is revealed in the calorimetric curves by the duration of induction period and also by the intensities of the main peaks. The appearance of small additional peaks characterizes the formation of 'primary ettringite', due to the presence of sulphate ions in aqueous solution. The intensities of these peaks depend on the ion concentration too.

Keywords: accelerators, hydration, sulphoaluminate belite cement

Introduction

The mechanism and kinetics of the hydration of calcium sulphoaluminate belite cement (SAB) have been investigated [1–3] and some progress has been made towards an understanding of the main factors governing the hydration process. In this system, hydration of the sulphoaluminate phase in the presence of anhydrite results in the formation of ettringite [3, 8]. It has been reported that the process of dissolution of anhydrite could affect the mechanism of ettringite formation to a great extent [5]. The conditions under which ettringite forms, and its stability, are of importance with regard to the setting of SAB paste and the durability of concrete made from this type of binding material. Numerous studies [3–7] indicate that the factors influencing the conditions of ettringite formation in the SAB system include the *pH* of the liquid phase, the specific surface (possibly the particle size of the individual clinker minerals), admixtures, etc. There are two main theories for the hydration mechanism: the topochemical and the through-solution mechanism. According to the former,

ettringite is formed on the surface of $C_4A_3\bar{S}$* and grows as slender needles [3]. According to the latter, ettringite is formed from the liquid supersaturated with respect to Ca^{2+}, Al^{3+} and SO_4^{2-}. The process of Al^{3+} transfer into solution and the solubility of the $C_4A_3\bar{S}$ phase depend on the *pH* of the surrounding liquid. Aluminium oxides are amphoteric compounds. Al^{3+} is stable only in an environment of suitable *pH*. On increase of the *pH* of the surrounding liquid, the hydrolytic reaction leading to $Al(OH)_4^-$ formation occurs, with precipitation in the form $Al(OH)_3$ as the *pH* decreases. This fact demonstrates the important role played by the *pH*. On the other hand, studies of chemical admixtures as controllers (retardants or accelerators) of the setting of SAB paste have not yet been performed. Optimal control of the microstructure development would lead to a more adequate utilization of SAB. Even though the ettringite present in portland cement (PC) is considered to be a setting regulator, it plays another role in the case of SAB cement (a promoter of the early strength).

Studies were earlier made [4, 7, 10] of the effects of setting-modifying admixtures (generally inorganic or organic electrolytes) on the hydration of PC. These affect the length of the induction period, the time of maximum rate of heat evolution, or the total heat evolution. Despite the long and intensive use of $CaCl_2$ as a commercial accelerator in PC, very little is known about its influence upon the hydration of SAB.

Ettringite is always precipitated when Ca^{2+}, SO_4^{2-} and Al^{3+} are present in the stoichiometric ratio:

$$6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^- + 4OH^- + 26H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$$
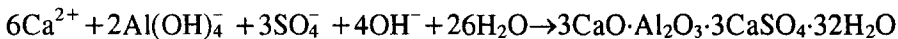
As the dissolution kinetics (which depends on the specific surface of each clinker mineral) to a large extent governs the initial phenomena in the starting period, the input of ions into the solution plays a significant role. Ca^{2+} comes from the dissolution of $C_4A_3\bar{S}$, $C\bar{S}$ and C_2S, $C_4A_3\bar{S}$ is the only source of $Al(OH)_4^-$, while SO_4^{2-} comes from $C_4A_3\bar{S}$ leading to the formation of ettringite is known to give rise to expansional properties in cements, and the controlled crystallization of ettringite during SAB cement hydration forms the basis of the expansive cements. The slow hydration of C_2S guarantees long-term strength development.

Experimental

$C_4A_3\bar{S}$ was synthesized by heating a homogenized stoichiometric mixture of $CaCO_3$, $CaSO_4{\cdot}2H_2O$ and $Al(OH)_3$ of analytical reagent quality at 1300°C dur-

---

* Cement chemistry notation is used, where C = CaO, S = SiO$_2$, A = Al$_2$O$_3$, $\bar{S}$ = SO$_3$ and H = H$_2$O.

ing 3 h. $C\overline{S}$ was obtained by annealing gypsum at 1200°C for 1 h. C_2S was synthesized likewise from a stoichiometric mixture of $CaCO_3$ and pure quartz (99.99% SiO_2). All prepared minerals were ground and air-separated into the fractions 0–5 μm, 5–20 μm and 20–40 μm. For the present studies, the following mineral combination was chosen: 45% C_2S (0–5 μm), 35% $C\overline{S}$ (5–20 μm) and 19% $C_4A_3\overline{S}$ (5–20 μm). This combination allows the formation and stability of ettringite, and leads to calorimetric hydration curves with good characteristics.

Results and discussion

Influence of CaCl₂

From the calorimetric curves in Fig. 1, $CaCl_2$ evidently delays the formation of ettringite in SAB cement, whereas it is considered an accelerator of PC hydration. Indeed, the hydration of PC is often related to that of the major mineral phase (C_3S). In this condition, the accelerator effect is attributed to the highly mobile ions Cl^-, which penetrate the initial protective layer to the underlying C_3S, forcing the diffusion of other ionic species to maintain electroneutrality, thereby accelerating hydration. For a SAB cement, however, where C_3S is absent, it is generally agreed that $CaCl_2$ accelerates β-C_2S hydration, but to a

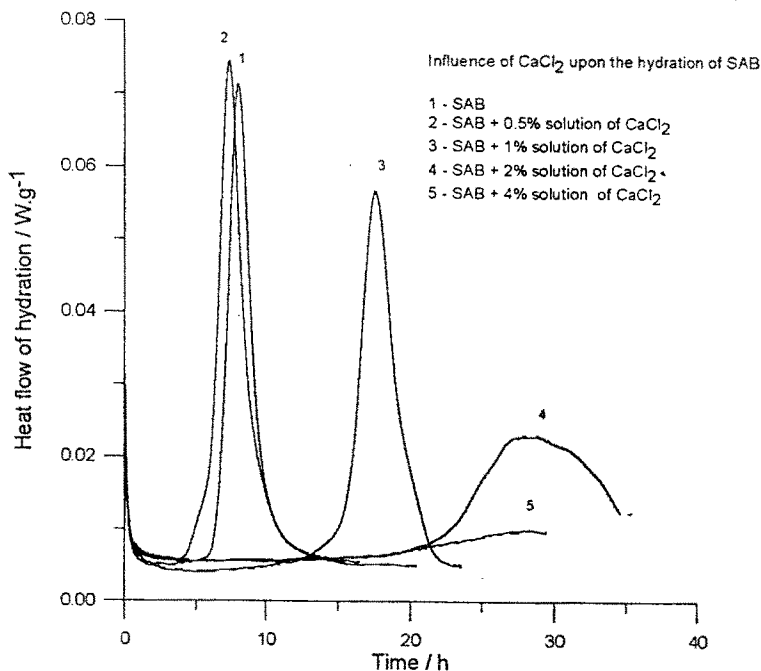Influence of CaCl₂ upon the hydration of SAB

1 - SAB
2 - SAB + 0.5% solution of CaCl₂
3 - SAB + 1% solution of CaCl₂
4 - SAB + 2% solution of CaCl₂
5 - SAB + 4% solution of CaCl₂

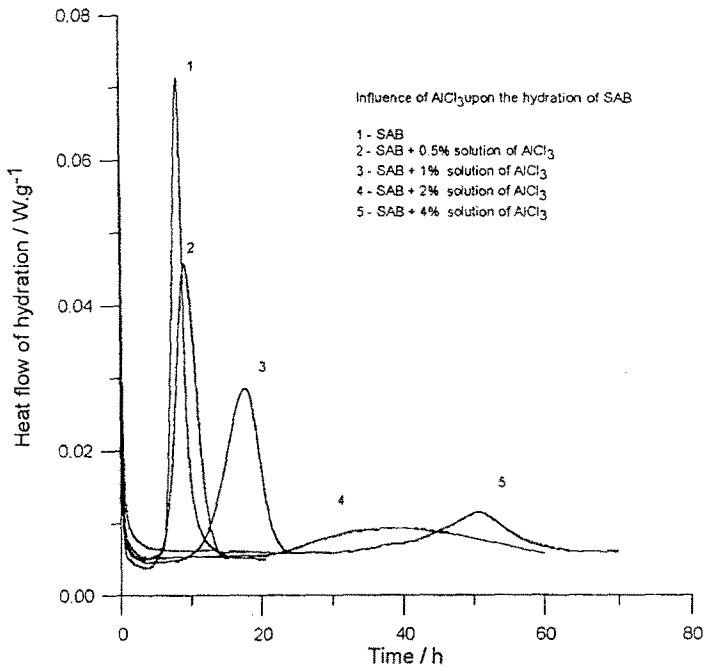**Fig. 1** Influence of CaCl₂ upon kinetics of SAB hydration

Fig. 2a Influence of AlCl₃ upon kinetics of SAB hydration
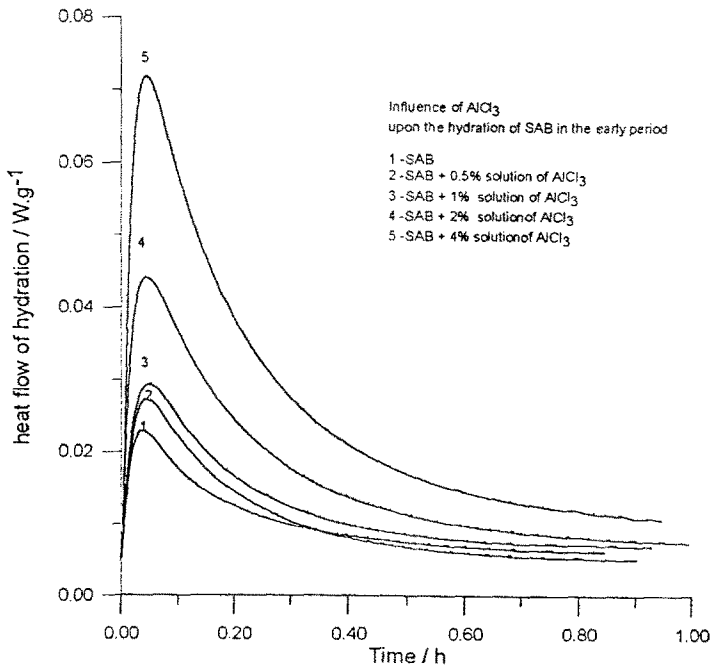

Fig. 2b Influence of AlCl₃ upon kinetics of SAB hydration in early period

lesser degree than that of C_3S. On the other hand, $C_4A_3\bar{S}$ and $C\bar{S}$ undergo the same effects, and input more Ca^{2+} into the solution. This enhances the *pH*, and thus retards ettringite formation. The calorimetric curves demonstrate that the duration of the induction period depends on the concentrations of admixtures.

Influence of AlCl₃

Figure 2b depicts the increasing intensity of the initial peaks with increasing amount of Al^{3+} during the first 50 min. The probable exothermic precipitation of $Al(OH)_3$ in the early period inhibits the formation of ettringite. Indeed, when Al^{3+} precipitates as insoluble hydroxides, retardation is observed. This can be explained in that an impermeable layer of insoluble $Al(OH)_3$ is formed around the hydrating particles. It has been suggested that the precipitation causes the retarding effect by preventing the solution on the liquid–solid boundaries from becoming supersaturated with respect to $Al(OH)_4^-$. It has been claimed [4] that the presence of $Al(OH)_4^-$ in the solution tends to prevent the precipitation of AH_3 and to favour the formation of C_4AH_{12}. The AH_3 retarding layer is then attacked by Ca^{2+} and OH^- in the bulk, and the precipitation of ettringite continues.

Influence of Al₂(SO₄)₃

$Al_2(SO_4)_3$ is known as a chemical with high solubility. It acts similarly to $CaSO_4$ by accelerating the formation of ettringite, and also similarly to $AlCl_3$ by influencing the intensity of the first peak. In the early hydration stage, up to 60 min, Fig. 3a reveals the increase in the initial peak height with the concentration of $Al_2(SO_4)_3$. This can be explained by the exothermic precipitation of $Al(OH)_3$ due to the change in *pH* caused by the presence of Ca^{2+} originating from the dissolution of cement minerals. In general, $Al_2(SO_4)_3$ exerts an appreciable acceleratory effect upon the kinetics of hydration. This effect is mainly due to the presence of SO_4^{2-} .

Influence of Na₂SO₄

The formation of ettringite crystals, or ettringite gel is considered to be a setting regulatory factor in the hydration of PC. The presence of the trisulphate phase in SAB paste contributes to strength development in the early stage of hydration, but its stability is of primary importance. This stability depends on the sulphate concentration. The conditions of ettringite formation in PC paste and in SAB paste have been studied [1], and it has been postulated that the mechanism of ettringite precipitation differs. While the higher *pH* of the solution surrounding C_3A results in a topochemical process in PC, the lower *pH* of the solution near the $C_4A_3\bar{S}$ particles causes the formation of a liquid interlayer be-
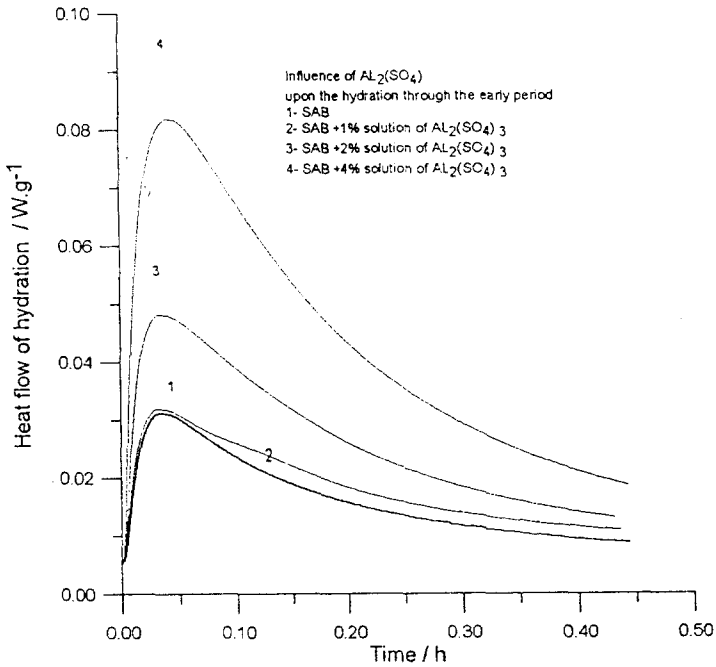
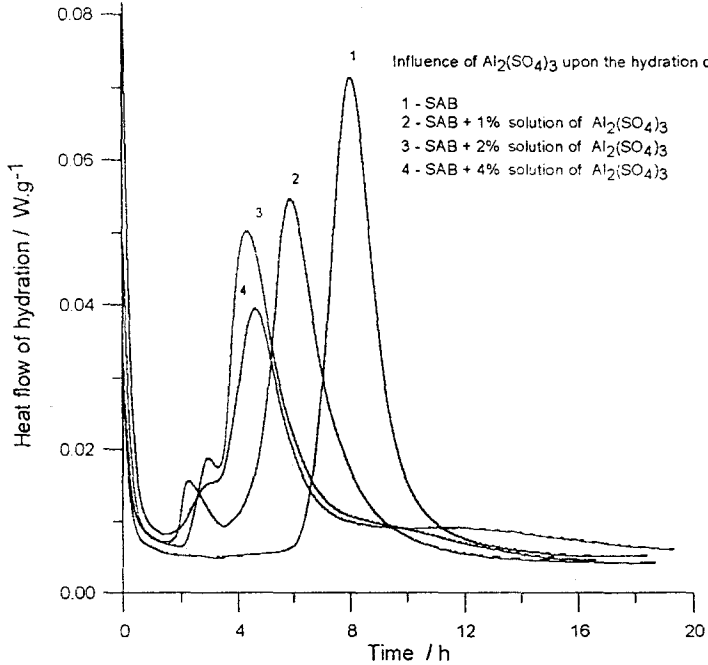**Fig. 3a** Influence of $Al_2(SO_4)_3$ upon kinetics of SAB hydration in early period

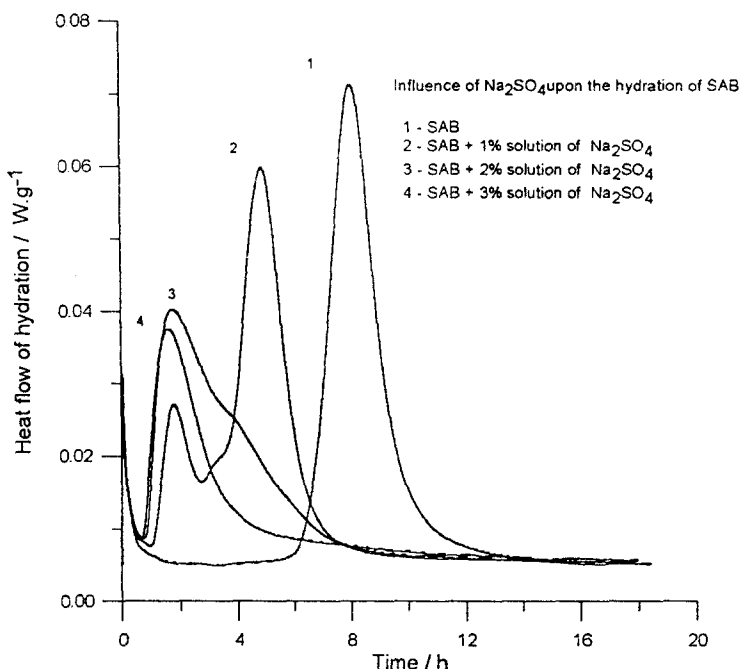**Fig. 3b** Influence of $Al_2(SO_4)_3$ upon kinetics of SAB hydration

Fig. 4 Influence of Na_2SO_4 upon kinetics of SAB hydration

tween $C_4A_3\bar{S}$ and the hydrated products. From the calorimetric curves, therefore, it is expected that the SO_4^{2-} (from either Na_2SO_4 or $Al_2(SO_4)_3$) in the starting solution causes the formation of the 'primary ettringite' detected by IR spectroscopy on the surface of $C_4A_3\bar{S}$. Then, with decreasing SO_4^{2-} concentration, the formation of ettringite stops. Further, owing to the dissolution of the $C_4A_3\bar{S}$ phase, the reaction continues and the second peaks appear (Fig. 4).

Conclusions

Calorimetric methods are useful in examinations of the influence of additives on the acceleration or retardation of the hydration process. The results obtained permit the following conclusions.

1. Calorimetric experiments indicate that the hydration of SAB cement is retarded in the presence of $AlCl_3$ and $CaCl_2$ in the hydrating mixture (though a 0.5% solution has a negligible effect). On increase of the concentrations of these two electrolyte salts, the induction period and the time corresponding to the second maximum heat evolution peak increases. $AlCl_3$ and $CaCl_2$ can be considered to be retarders of SAB cement hydration.

2. With increasing concentration of Na_2SO_4 and $Al_2(SO_4)_3$, the reaction is accelerated and a third peak appears, due to the formation of 'primary et-

tringite', probably on the $C_4A_3\bar{S}$ surface. The intensities of these third peaks increase with the salt concentrations.

References

1 J. Havlica and S. Sahu, Cem. Concr. Res., 22 (1992) 672.
2 A. Gabrišova, J. Havlica and S. Sahu, Cem. Concr. Res., 21 (1991) 1023.
3 K. Ogawa and D. M. Roy, Cem. Concr. Res., 12 (1982) 101.
4 S. Sahu, J. Majling and J. Havlica, 9th ICCC, IV-443 New Delhi 1992.
5 S. Sahu and J. Havlica, 9th ICCC, IV-157 New Delhi 1992.
6 J. Skalny, M. Maretta and J. F. Young, 8th ICCC, II-113, Paris 1980.
7 Deng Min and T. Mingshu, Cem. Concr. Res., 24 (1993) 120.
8 L. Taczuk, J. P. Bayoux, F. Sorrentino and A. Campas, 9th ICCC, III-279 New Delhi 1992.
9 D. M. Roy and M. Dainom, 8th ICCC, II-242, Paris 1980.
10 F. Zhan and Z. Zhon, 8th ICCC, II-88, Paris 1980.