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MICROCALORIMETRIC STUDIES OF SOME CEMENTITIOUS MATERIALS

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The Al doped tricalcium silicate hydration in the presence of active silica was studied by means of calorimetry, DTA, TG, XRD and conductometry of the hydrating suspension.

Keywords: cementitious materials, microcalorimetry

Introduction

The tricalcium silicate $Ca_3(SiO_4)O$ solid solutions known as alites are the main constituents of portland cement clinkers. Their hydraulic properties are influenced not only by their fineness and the presence of impurities or other defects, but also by the admixtures added to the hydrating paste, viz. inorganic and organic soluble compounds or solid additions [1–3].

The pure active silica represents the group of the very effective admixtures known as the condensed silica fumes. The active silicenous components react quickly with the calcium ions from the tricalcium silicate hydrolysis and the so-called calcium silicate hydrate (C–S–H) amorphous product is formed with the rate substantially higher than the rate of C–S–H phase formation from the tricalcium silicate only. This effect can be explained in terms of the nucleation barrier [4].

Experimental and discussion

The studies of alites containing different Al_2O_3 admixtures hydrated in the presence of pure active silica were carried out. The alite samples have been synthesized from the homogenized $CaCO_3$+SiO_2 gel+$Al(OH)_3$ mixture calcined preliminary and then heated at 1550°C. The synthetized material was ground to the specific surface 3500 cm^2/g. The Al_2O_3 contents on Ca_3SiO_5 were 0.25% (sam-

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ple A0.25) and 1.5% (sample A1.5) respectively to obtain the two different polymorphs with two kinds of substitution [5]. The alite samples were mixed with 5 to 20% SiO_2 (Aerosil–Degussa). The hydraulic behaviour was studied by means of calorimetry (BMR differential microcalorimeter constructed in the Institute of Physical Chemistry, Warsaw, Poland), differential thermal analysis and thermogravimetry (Derivatograph Q 1500 D), conductometry of the hydrating suspension and X-ray diffraction.

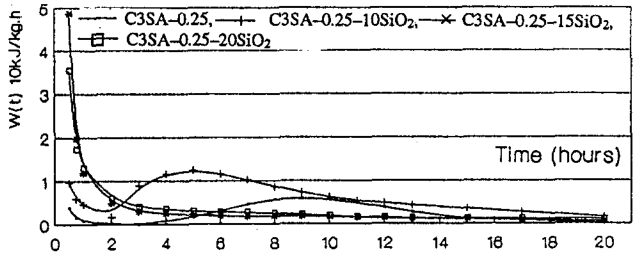

Fig. 1 Calorimetric curves of 0.25% Al_2O_3 doped tricalcium silicate hydrated in the presence of 10–20% SiO_2 addition.

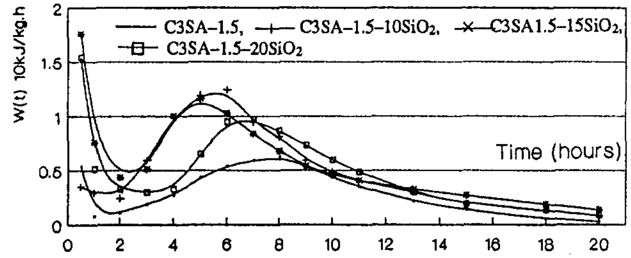

Fig. 2 Calorimetric curves of 1.5% Al_2O_3 doped tricalcium silicate hydrated in the presence of 10–20% SiO_2 addition.

The samples were hydrated in the calorimeter at 25°C, water to alite ratio 0.5. The heat evolution curves are listed in Figs 1, 2. The heat evolved values during 24 h hydration are presented in Table 1. The data relating to the alite hydration degree, bound water content and calcium hydroxide content after subsequent 7 days hydration are listed in Table 2. The conductivity curves representing the concentrations of ions in hydrating suspensions are shown in Fig. 3.

As it was found earlier [6] the alumina addition in alite brings about the change of heat evolution kinetics at early stages. At the presence of active silica the changes of the heat evolution curves shape are evident. At lower alumina content the acceleration of heat evolution leads to the superposition of the second peak on the first one, without any induction period, characteristic for the alite hydration. At higher alumina content only the shortening of the induction period occurs with increasing silica content. It is also noticeable that the highest amounts of silica addition are less effective. This is probably the consequence of the thick layer of product formation, as a result of the reaction between the silica and Ca ions from the alite hydrolysis.

Table 1 The heat evolved during the 24h hydration of Al doped alites

SiO_2 content / weight %	Alite doped with 0.25% Al_2O_3 ΔH /kJ·kg^{-1}	Alite doped with 1.5% Al_2O_3 ΔH /kJ·kg^{-1}
0	138.6	163.6
10	234.9	294.2
15	178.0	300.5
20	208.3	263.4

Table 2 The properties of hydrating pastes

a) Hydration degree after 7 days hydration

Alite doped with 0.25% Al_2O_3		Alite doped with 1.5% Al_2O_3	
0% SiO_2	10% SiO_2	0% SiO_2	10% SiO_2
85	75	82	77

b) DTA/TG data for 7 days hydrating samples

	Alite doped with 0.25% Al_2O_3		Alite doped with 1.5% Al_2O_3	
contents:	H_2O / %	$Ca(OH)_2$ / %	H_2O / %	$Ca(OH)_2$ / %
0% SiO_2	17.5	18.5	17.5	17.3
10% SiO_2	14.9	4.4	12.2	10.4
15% SiO_2	25.4	—	21.0	—
20% SiO_2	24.5	—	29.0	—

The conductivity data which in fact give the Ca ions concentration changes *vs.* time can explain the quick hydration of A0.25 sample with silica and slower reaction of A1.5 sample. The concentration of ionic species in A0.25 suspension increases rapidly from the beginning of reaction, reaches the maximum and falls down. In A1.5 sample the slow dissolution within the first hours takes place and subsequently the concentration increase occurs later. Therefore the consumption of calcium by silica is relatively slow and the calorimetric data confirm this fact too. As one can notice, the XRD and TG data relating to the 'older' samples seem to show that the alumina addition does not involve any significant changes after a few days hydration. Consequently, these results for both series with silica are similar. The bound water increase and the calcium hydroxide decreases with the silica content are evident.

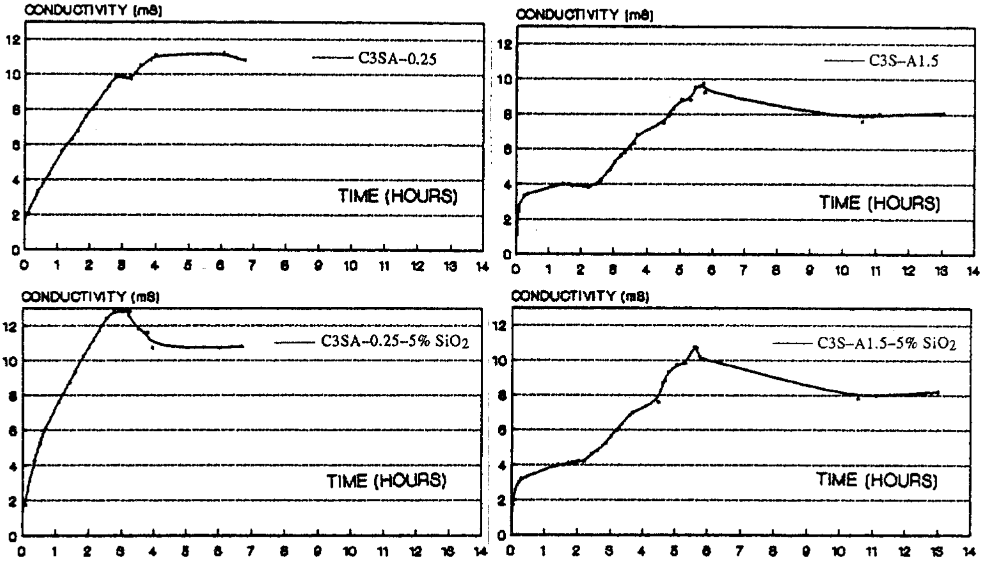

Fig. 3 Conductivity of hydrating alite–silica suspensions

Summarizing the data presented above it is to be underlined that the microcalorimetric method gives the possibility to visualize the subtle differences between the hydration of alite polymorphs, though there is no substantial differences between the final hydration products. This early heat evolution differences are not without practical importance in concrete technology.

References

1 H. F. W. Taylor, Cement Chemistry, Academic Press, London, New York 1990.
2 V. S. Ramachandran, Il Cemento, 83 (1986) 13.
3 Proc. of the 3rd Int. Conf. Fly Ash, Silica Fume, Slag and Natural, Pozzolans in Concrete, Trondheim Norway, 1989.
4 W. Kurdowski, W. Nocun-Wczelik, K. Miškiewicz and J. Szuba, Proc. of the 8th Int. Cong. on the Chemistry of Cements, Rio de Janeiro 1986, Vol.2, p. 179.
5 I. Maki, Il Cemento, 85 (1988) 89.
6 W. Nocun-Wczelik and B. Trybalska, J. Thermal Anal., 32 (1987) 1719.

Zusammenfassung Mittels Kalorimetrie, DTA, TG, Röntgendiffraktion und Konduktometrie der Hydratierungssuspension wurde in Gegenwart von aktivem Silizium-dioxid die Hydratation von mit Al versetztem Tricalciumsilikat untersucht.