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THE STUDIES OF Al-DOPED TRICALCIUM SILICATE HYDRATION

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The hydration of tricalcium silicate containing Al_2O_3 admixture has been investigated using calorimetry, DTA, TG and XRD methods.

The tricalcium silicate solid solutions known as alites are the main constituent phase of portland cement clinkers. Polymorphism, structure and hydraulic activity of different alites have been widely studied for a long time and they are not fully explained till now [1–3]. The sequence of Ca_3SiO_5 polymorphic transitions can be presented as follows:

$$T_I \xrightarrow{620} T_{II} \xrightarrow{920} T_{III} \xrightarrow{980} M_{Ia} \xrightarrow{990} M_{IIa} \xrightarrow{1060} M_{IIb} \xrightarrow{1070} R$$

The effect of aluminium on the alite structure and properties was studied by many authors. Up to 1% the Al_2O_3 admixture forms the solid solution with Ca_3SiO_5. Introducing of more than 0.45% Al_2O_3 favours the T_{II} modification stabilization. As the Al_2O_3 concentration in solid solution increases, the temperatures of Ca_3SiO_5 polymorphic transition become lower. Al^{3+} cation can substitute Si^{4+} in the structure while the Al_2O_3 content does not exceed 0.45%. At higher Al_2O_3 concentrations Al^{3+} occupies also the positions of Ca^{2+}. The Al_2O_3 admixture to Ca_3SiO_5 higher than 0.7% brings about the formation of liquid phase microscopically detectable during heating at 1550°.

The modification of structure, liquid phase formation, crystal defects and other effects resulting from Al_2O_3 admixture influence also the hydraulic behavior of alites containing different Al_2O_3 content.

The comparative studies of alites containing Al_2O_3 admixtures have been carried out. The alite samples have been synthesized from the homogenized $CaCO_3 + SiO_2$ gel + $Al(OH)_3$ mixtures calcined preliminary and then heated at 1550°. The Al_2O_3 contents in Ca_3SiO_5 were 0.25% (sample A 0.25) and 1.5% (sample A 1.5) respectively. The 0.25% Al_2O_3 content ensured the T_I modification formation and one kind of substitution. The 1.5% Al_2O_3 content gave the stabilization of T_{II}

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polymorph, two kinds of ionic substitution in the structure and acceleration of sintering process due to the liquid phase formation.

Two kinds of samples were prepared by grinding: samples of the high fineness in the range of 0–10 μm and samples with the grain size distribution corresponding to the cement of good quality i.e. 0–60 μm and the specific surface of 3500 cm^2/g.

The hydraulic activity has been studied by means of calorimetry (BMR differential microcalorimeter constructed by Institute of Physical Chemistry—Warsaw, Poland), differential thermal analysis and thermogravimetry (Derivatograph Q 1500 D) and X-ray diffraction (Tur M62 diffractometer).

The samples were hydrated in the calorimeter at 25° with the water to solid ratio of 0.5. After 72 hours calorimetric measurements the samples were removed from the calorimeter and the hydration process was stopped. The dried samples were subjected to quantitative X-ray diffraction analysis in order to estimate the unhydrated alite residue and to the DTA and TG studies to measure the bound water content in the hydration products. The results are presented in Figs 1, 2 and Tables 1, 2, 3.

The increasing Al_2O_3 content in Ca_3SiO_5 phase brings about the hydraulic activity augmentation as it has been proved by means of calorimetry, TG and QXRD. The rate of heat evolution, particularly at early stages, becomes higher. The calorimetric data are confirmed by QXRD. Almost identical values of total heat evolved for the 0–60 μm alite fraction, referred to the 1 g of hydrated alite seem to

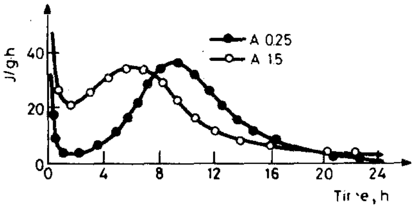

Fig. 1 Calorimetric curves of hydrated Al-doped alites (fraction 0–60 μm). ●—— A 0.25, ○——A 1.5

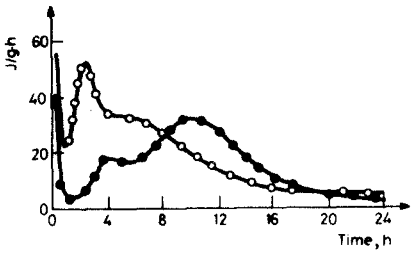

Fig. 2 Calorimetric curves of hydrated Al-doped alites (fraction 0–10 μm). ●—— A 0.25, ○——A 1.5

Table 1 The hydration degree of Al-doped alites after 3 days reaction with water

Samples		Hydration degree, %
C_3S A 0.25	0–10 μm	69
C_3S A 1.5	0–10 μm	78
C_3S A 0.25	0–60 μm	61
C_3S A 1.5	0–60 μm	70

C = CaO, S = SiO_2, A = Al_2O_3

Table 2 The total heat evolved during the 3 days hydration of Al-doped alites

Samples		Heat referred to alite content in anhydrous sample (heat referred to alite hydrated J/g)
C_3S A 0.25	0–10 μm	432/708
C_3S A 1.5	0–10 μm	497/681
C_3S A 0.25	0–60 μm	361/694
C_3S A 1.5	0–60 μm	436/692

Table 3 The bound water content in CSH phase and the calcium hydroxide content in hydrated alite pastes after 3 days hydration

Samples		H_2O, % in CSH	$Ca(OH)_2$, % in paste after drying
C_3S A 0.25	0–10 μm	12.0	21.6
C_3S A 1.5	0–10 μm	13.5	18.0
C_3S A 0.25	0–60 μm	11.6	18.5
C_3S A 1.5	0–60 μm	12.0	19.5

indicate the same reaction mechanism and the similar nature of hydration products. The rate of heat evolution increase in the samples with higher Al_2O_3 content is caused by the additional crystal defects. In the case of very fine alite fraction the total heat evolved per 1 g of hydrated 1.5% Al_2O_3 containing alite sample reduces and this fact seems to indicate that the modification of hydration process takes place. Presumably the rapid small grains dissolution and CSH phase precipitation occur. This can be derived from the shape of the calorimetric curves and from the hydration degree values combined with the $Ca(OH)_2$ contents. The differences between H_2O in CSH and $Ca(OH)_2$ contents in the hydration products of very fine fraction suggest that the "excess" of hydrated alite formed the CSH phase.

References

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Zusammenfassung — Mittels kalorimetrischer, DTA-, TG- und XRD-Methoden wurde die Hydratierung von Trikalziumsilikat unter Zusatz von Al_2O_3 untersucht.

Резюме — Методом ДТА, ТГ, рентгеноструктурным и калориметрическим методом изучена гидратация трикальций силиката, содержащего окись алюминия в качестве добавки.