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CALORIMETRIC STUDIES OF REFRACTORY CORUNDUM
Calcium aluminate composites

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Abstract

Calorimetry has been used in the investigations of calcium aluminate materials produced as a binder for aluminate–corundum composites of high refractoriness. The kinetics and of hydration process was thus characterized and the optimum compositions of initial binders and cement–corundum refractory filler blends could be selected for further tests.

The acceleration of heat evolution – the shortening of so-called induction period and relatively high heat output in the presence of corundum was observed. It means the acceleration of hydration process, that is early crystallisation of hydration products and subsequent further dissolution of initial anhydrous aluminate phases. In the presence of fine grained corundum particles these phenomena should be attributed to the nucleating effect of fine corundum particles.

Keywords: calcium aluminate cement, heat of hydration, refractory concrete

Introduction

Calcium aluminates are the constituents of calcium aluminate cements produced usually by melting or sintering of bauxite and lime containing mixtures [1]. The concretes based on calcium aluminate cements have very high performance in specific applications. They are used in many industrial structures exposed to high temperatures and this is one major field of calcium aluminate cements production and use.

There are different compositional ranges for calcium aluminate cements, ranging from about 40 to over 80% Al_2O_3 [2, 3]. Those with higher alumina content are produced for refractory purposes. Monocalcium aluminate phase $CaO \cdot Al_2O_3$–CA (notation commonly used in cement chemistry: C=CaO, A=Al_2O_3, H=H_2O) is the principal phase in aluminate cements. Among the other calcium aluminate phases, $12CaO \cdot 7Al_2O_3$–$C_{12}A_7$ and $CaO \cdot 2Al_2O_3$–CA_2 can be produced. On reaction with water at ambient temperature a setting and hardening of calcium aluminate paste is observed and the hydrated calcium aluminate phases, such as $CaO \cdot Al_2O_3 \cdot 10H_2O$–$CAH_{10}$, $2CaO \cdot Al_2O_3 \cdot 8H_2O$–$C_2AH_8$ (hexagonal hydrates) and aluminium hydroxide (AH) are

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formed [4]. The reaction of calcium aluminate cements (denoted CAC) with water occurs with heat evolution and followed by calorimetry gives two strong peaks with so-called induction period between them; there is a few hours lasting latent period in which a dissolution of initial substance to attain the supersaturation of liquid phase and slow nucleation of less soluble hydration products takes place [2, 5]. The hexagonal calcium aluminate hydrate phases formed as a first, intermediate product are unstable and convert to $3CaO \cdot Al_2O_3 \cdot 6H_2O$–$C_3AH_6$ (cubic, hydrogarnet type) and aluminium hydroxide. The excess water is available for further hydration [2–4].

In this work the calorimetric measurements were used in the studies of refractory corundum–calcium aluminate composites. The series of synthetic calcium aluminate cements was produced as a first step. The phase composition of sinters and the cementitious properties of ground materials were thoroughly determined and subsequently the aluminate–corundum mixtures were prepared from the selected aluminate materials. These mixtures were used in the production of refractory composites, that is corundum–aluminate concretes. Alumina is known as a refractory agent, affecting the hydration process of aluminate composites owing to its specific surface area and the presence of some impurities. Alumina does not take part itself in the chemical reactions but its role cannot be neglected and every time must be thoroughly controlled [6]. The hydration progress in the corundum-aluminate mixtures was followed using microcalorimetry and X-ray diffraction; the hydration products were characterized and evaluated. The standard tests including setting time, compressive strength and refractoriness of materials were carried out, as well as the tests on selected samples heated at high temperature. Finally, the product of thermal treatment was examined.

Experimental

The research work aimed with the production of high refractory corundum–calcium aluminate composites has been carried out ‘step by step’, from the synthesis of several sinters, through the studies of phase composition and hydration kinetics to the proportioning of mixtures and their standard characteristics. In this report the most significant ones, leading to the final concrete composites will be given, with special emphasis on calorimetry, which played a decisive role in selection of the best solutions [7, 8].

Synthesis of calcium aluminate materials

In order to produce synthetic calcium aluminate cementitious material of fairly good hydraulic activity the aluminate cements were laboratory made from pure 99.5% Al_2O_3 (commercial alumina) of high fineness, ca. 3 $m^2 g^{-1}$ (BET) and $CaCO_3$ (99.6%) containing raw mixtures. The Al_2O_3 content was 64.4 and 65.1%, respectively. Thus the latter one exhibits an excess of alumina as compared to the former one, being stoichiometric CA. The mixtures were sintered at 1500°C within 2 h. The phase composition of synthetic calcium aluminate clinkers was evaluated using Rietveld’s method [9] (precision estimated for ±0.3%); the contents of particular components are given in Table 1.

Table 1 Phase composition of calcium aluminate clinkers

Sample code/Al_2O_3 content in initial mixture/%	Composition of calcium aluminate clinker		
	CA content/%	$C_{12}A_7$ content/%	CA_2 content/%
CAC1/65.21	92.5	–	7.5
CAC2/64.40	82.8	7.7	9.6

Taking into account the results presented in Table 1 one can find that some excess of alumina component promoted the CA synthesis. In a stoichiometric mixture the formation of CA was not completed and the reaction between $C_{12}A_7$ and CA_2 could be continued for example at higher temperature. On the other side some amount of $C_{12}A_7$ present was assumed to accelerate the hydration process further on.

The sinters thus produced were subsequently ground to the Blaine fineness of 0.32 $m^2 g^{-1}$.

Studies of calcium aluminate cements hydration process

The two calcium aluminate cements were hydrated within 24 h at water to solid ratio 0.45. After this period of time the degree of hydration was calculated with help of Rietveld method (precision in this case estimated for ±3%), used for evaluation of initial phases consumption [7]. The rate of heat evolution was followed by calorimetry. For this purpose a differential BMR microcalorimeter, constructed in the Institute of Physical Chemistry, Polish Academy of Science, was used. Hydrating pastes were prepared at water to solid ratio 0.5; the initial temperature was kept constant at 25°C. The heat evolved values (measured with accuracy of ±5 J g^{-1}) are given together with degrees of hydration in Table 2; the heat evolution curves are shown in Fig. 1 as curves CAC1 and CAC2.

Table 2 Properties of two calcium aluminate cements

Sample code	Degree of hydration after 24 h	Total heat evolved/J g^{-1}
CAC1 (CA with CA_2)	15%	367
CAC2 (CA with $C_{12}A_7$ and CA_2)	42%	330

As it can be noticed in heat evolution curves the maximum of heat evolution rate in case of sample CAC2 is achieved within ca. 22 h, while for CAC1 sample – after ca. 25 h. The so-called 'induction period' is very prolonged. However, the heat evolved value is higher, than in case of 'stoichiometric' material. From these data one can conclude that the hydration process of CA main constituent is strongly accelerated in the presence of $C_{12}A_7$. The authors presume also that CA itself, formed in the presence of excess alumina may exhibit more disordered structure, with some defects.

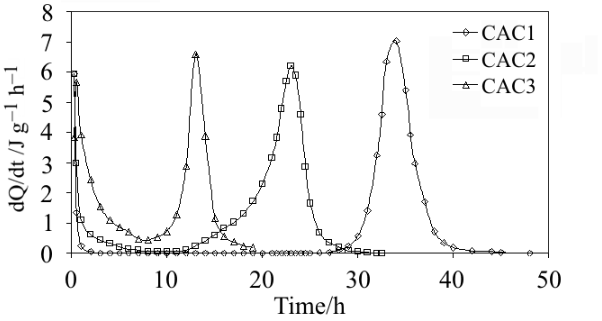

Fig. 1 Heat evolution curves for samples CAC1, CAC2 and CAC3

Synthesis and properties of active, multicomponent, cementitious aluminate material

As it has been found in the experiments with the two cements CAC1 and CAC2 the 'intermediate' $C_{12}A_7$ phase modifies strongly the hydration of calcium aluminate cement. The same result may be attained as a consequence of highly disordered structure, which is formed when material is heated quickly to the assumed temperature of synthesis and kept far from equilibrium. Therefore in order to produce even more active material the third initial mixture of containing 64.8% Al_2O_3 was prepared from the same components and quickly heated up to 1550°C and cooled. Final components of this CAC3 cement (XRD measurements) are as follows:

$$59.2\%\ CA+23.9\%\ C_{12}A_7+10.6\%\ \alpha\text{-}Al_2O_3+6.3\%\ CA_2$$

It is clearly seen that the CA synthesis has not been completed, but there is a significant $C_{12}A_7$ content together with CA_2 and unreacted corundum.

This multicomponent cementitious material was ground to the Blaine fineness of 0.57 $m^2\ g^{-1}$. Such a high specific surface is and additional factor enhancing the hydraulic activity of binder.

The degree of hydration of this CAC3 cement, after 24 h reaction with water was 44.7% (XRD). The heat evolved – 340 $J\ g^{-1}$ was similar to the values for former cements CAC1 and CAC2, but the maximum rate of heat evolution occurred earlier – after 13 h (Fig. 1; heat evolution curve of cement CAC3 is added to the former ones). The properties of CAC3 calcium aluminate cement – flexural strength at 1 day – 8.3 MPa and compressive strength at 1 day – 46.6 MPa comply very well with standard requirements.

Calorimetry and other properties of corundum–calcium aluminate binders

The three calcium aluminate cements reported above, that is of alumina content 65.21% (CAC1), 64.40% (CAC2) and 64.80% (CAC3) respectively, were used together with very fine grained corundum to produce cementitious mixtures of high refractoriness. The three different corundum materials were used:

Corundum1 with specific surface 1 $m^2\ g^{-1}$ (BET)

Corundum2 with specific surface 2.1 $m^2\ g^{-1}$ (BET)

Corundum3 with specific surface 3.4 m^2 g^{-1} (BET)

Different mixtures with calcium aluminate cement content from 18 to 25% and corundum content from 82 to 75% respectively were produced. The heat evolved values are given in Table 3. The sets of calorimetric curves (examples) are shown as Figs 2–6; the heat evolved values are given in Table 3.

Table 3 Heat evolved values in hydrated corundum–calcium aluminate systems

Series of samples (Fig. No)	Composition of mixture/%	Heat evolved/J g^{-1}
CAC1/Corundum2 (Fig. 2)	22 CAC1+78 Corundum2	184
	20 CAC1+80 Corundum2	146
	18 CAC1+82 Corundum2	149
CAC2/Corundum1 (Fig. 3)	22 CAC2+78 Corundum1	147
	20 CAC2+80 Corundum1	139
	18 CAC2+82 Corundum1	137
CAC2/Corundum2 (Fig. 4)	22 CAC2+78 Corundum2	162
	20 CAC2+80 Corundum2	139
	18 CAC2+82 Corundum2	143
CAC3/Corundum2 (Fig. 5)	25 CAC3+75 Corundum2	130
	22 CAC3+78 Corundum2	108
	20 CAC3+80 Corundum2	138
CAC3/Corundum3 (Fig. 6)	25 CAC3+75 Corundum3	157
	22 CAC3+78 Corundum3	141
	20 CAC1+80 Corundum3	139

The hydrated pastes were examined by XRD. Different phases were detected: the residual corundum and cement calcium aluminate components (CA, CA_2, CA_{10} – so-called 'β'-A), as well as the hydration products, such as so-called hexagonal calcium aluminates C_2AH_8, CAH_{10} and hydrogarnets type C_3AH_x. Burning at high temperature 1650–1800°C resulted in the formation of highly refractory corundum – calcium aluminate product. The characteristics of concrete produced from 20% CAC3 cement

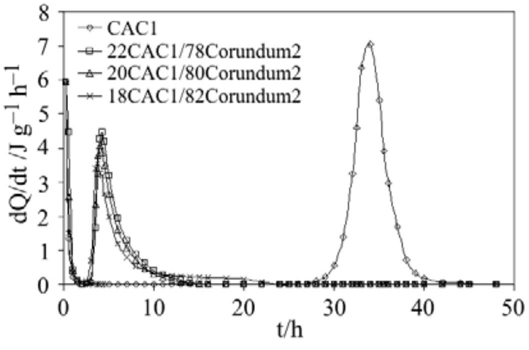

Fig. 2 Heat evolution curves for samples CAC1 with varying amount of Corundum2 fine aggregate

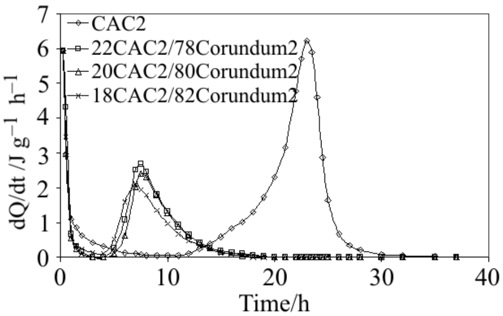

Fig. 3 Heat evolution curves for samples CAC2 with varying amount of Corundum1 fine aggregate

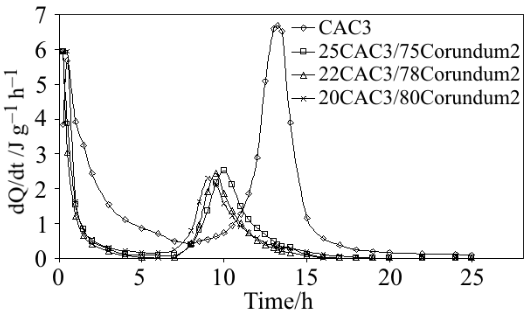

Fig. 4 Heat evolution curves for samples CAC2 with varying amount of Corundum2 fine aggregate

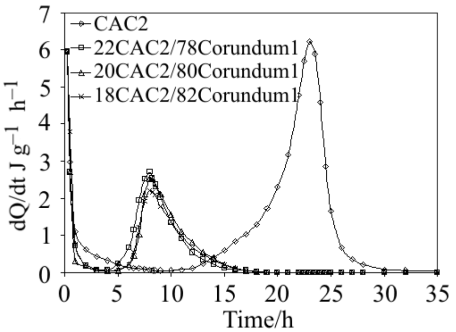

Fig. 5 Heat evolution curves for samples CAC3 with varying amount of Corundum2 fine aggregate

and 80% corundum powder Corundum3 is as follows: refractoriness >1800°C, initial setting – 1 h 55, final setting – 4 h 55, 1 day flexural/compressive strength – 3.2/7.9 MPa, flexural/compressive strength after burning at 1650°C (4 h) – 28.1/77 MPa, shrinkage after burning 0.93–1.50%. These data are given as an example to prove the fairly good properties of composites thus obtained.

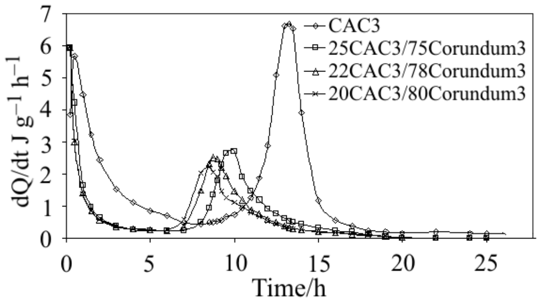

Fig. 6 Heat evolution curves for samples CAC3 with varying amount of Corundum3 fine aggregate

Discussion

As it can be easily seen in Figs 2–6 the heat evolution process in corundum–calcium aluminate mixtures is strongly accelerated; this effect is particularly strong in case of slowly hydrating cement CAC1, of the highest CA content, with no $C_{12}A_7$. At corundum content on ca. 80% level he maximum of heat evolution takes place after 6–7 h instead of more than 30 h and total heat evolved is only 50–60% lower than for cement without corundum. The same situation is for two other cements. It is a little surprising that for more active, from calorimetric point of view samples, this accelerating effect of fine grained corundum admixture is significantly less pronounced. Therefore for CAC2 and CAC3 cement samples the shift of maximum heat evolution rate is in the range of 15 h and 4–6 h, respectively.

The acceleration of heat evolution – the shortening of so-called induction period – means the acceleration of hydration process, that is the crystallisation of products and further dissolution of initial anhydrous aluminate phases. In the presence of fine grained corundum particles this total acceleration should be attributed to the nucleating effect of fine corundum particles.

From the simplified calculation it could be assumed that the inert filler will reduce the heat evolved proportionally to the content in the hydrated mixture. However, the heat evolved values are significantly higher, they are on the level of 30% or more of heat evolved for hydrated cement samples. The role of nucleation process should be thus proved. More over, it seems that the deposition of hydrates on the surface of corundum filler is an exothermic process. For all these reasons the degree of hydration in the presence of corundum should be a little higher.

Conclusions

- Calorimetry shows very clearly the effect of fine grained alumina in calcium aluminate cements hydration acceleration; the shortening of initial dormant period takes place and it means the intensive reactions of dissolution/precipitation after mixing with water.

- Degree of aluminate hydration in CAC-corundum mixtures is approximately 30% higher than in neat cement paste, as it results from heat evolved values.
- Fine corundum nuclei are more compatible with less active calcium aluminate containing cement.

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