MICROCALORIMETRIC STUDY ON CALCIUM ALUMINATE CEMENT HYDRATION

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Abstract

Calcium aluminate cement (CAC) is very versatile special cement used for specific applications. During the hydration of CAC a large quantity of heat is liberated within one day that causes a considerable increase of temperature in material.

This paper examines the hydration of three samples (A, B and aged B) of commercial CAC ISTRA 40 (producer: Istra Cement, Pula, Croatia). The rate of heat generation of cement pastes due to the hydration reactions was measured at several temperatures with differential micro-calorimeter. In the experiments water to cement ratio was also varied and in one sample quartz sand was added.

When CAC and water first come in contact far less heat is liberated, than for Portland cement. Higher water to cement ratio increases the heat evolved at later ages due to higher quantity of water available for hydration. Cement mortar prepared with milled quartz sand showed 1.2 h shorter setting time than corresponding neat CAC paste. This could be explained by more germination sites available for the nuclei to start the hydration precipitation. Except for the change in the setting time there are no other significant differences in the kinetics of hydration when compared to original cement sample. Due to a water and CO_2 uptake from the environment the aged sample has a greater weight loss on ignition, shorter setting time, lower hydration rate and lower heat of hydration evolved in comparison to original sample. Contrary to previous reports in literature acceleration of CAH_{10} formation was observed in 5 to 10 ^{o}C temperature range. Heat generation data obtained could not be satisfactory fitted by the Avrami-Erofe'ev nucleation and growth kinetic model.

Keywords: calcium aluminate cement, calorimetry, heat of hydration, kinetics.

1 Introduction

Due mainly to their higher cost, calcium aluminate cement (CAC) do not compete directly with Portland cements. Despite the well documented construction failures in the 1970's, if CAC is used correctly as recommended ($w/c < 0.4$, adequate curing), it is a good constructional material to be advantageously employed with high performance in specific applications (resistance to chemical attack, high early strength, refractory, resistance to abrasion, low ambient temperature) [1,2]. Although the hydration of CAC represents a process of commercial and industrial importance, the physical and chemical processes involved during hydration are not yet well understood [1-5]. Hydraulic hardening of CAC is primarily due to the hydration of $CaAl_2O_4$, but other compounds may also participate in the hardening process especially in long term strength development. The hydration of CAC is temperature dependent, yielding CAH_{10} (cement notation: C[CaO], A[Al_2O_3], H[H_2O]) as main products at temperatures less than 20 °C, C_2AH_8 and AH_3 at about 30 °C and C_3AH_6 and AH_3 at temperatures greater than 55 °C. CAH_{10} and C_2AH_8 are known to be metastable at ambient temperature and convert to the more stable C_3AH_6 and AH_3 with consequent material porosity increase and loss of strength. The conversion is accelerated by temperature and moisture availability for the dissolution and re-precipitation processes to take place [2]. During the hydration of CAC a large quantity of heat is liberated in a short period (first 24 h) that can cause a considerable increase in material temperature. It is important to ensure adequate curing during the initial hardening stage. This may be achieved by spraying with cold water during the 24 hour period after placing or by the use of a curing membrane, or wet sacking to prevent excessive heating and water loss.

By means of the heat released, it is possible to determine the degree of hydration relative to hydration duration according to the equation:

$$\alpha(t) = \frac{Q(t)}{Q_{\max}} \tag{3}$$

where $Q(t)$ is heat released by time t, and $Q_{\max}$ represents the total heat a sample can release. The rate of heat generation, q can thus be expressed proportional to the rate of reaction:

$$q(t) = Q_{\max} \frac{d\alpha(t)}{dt} \tag{4}$$

The data of pure Portland cement minerals usually fit [6] the Avrami-Erofe'ev nucleation and growth kinetic model:

$$\frac{d\alpha}{dt} = nKt^{n-1} \exp(-Kt)^n \tag{5}$$

where K is a rate parameter and n is a power law index. However, the hydration rate is controlled by dissolution process, mass transfer, nucleation and growth of crystals and rate of reaction between water and cement at its boundary.

This paper presents results of calorimetric study on calcium aluminate cement hydration for the sake of elaboration of the hydration model which would predict the hydration rate, $d\alpha/dt$ relative to the hydration degree, α and temperature, T. In cement application, the model will enable a real simulation of temperature distribution in material and better planning of curing during early age of hydration to obtain better durability and functionality.

2 Experimental

The CAC used was taken from a regular production of Istra Cement International, Pula, Croatia. The cement has the following nominal oxide mass fraction composition: CaO 37-40%, Al_2O_3 39-42%, Fe_2O_3 14-17%, SiO_2 2-5%, MgO<1.2% and SO_3<0.4%. Residue on sieve at 90 µm 4%, fineness (Blaine) 3350 cm^2/g, bulk density 1.15 g/cm^3, specific gravity 3.20 g/cm^3. The main compounds are monocalcium aluminate, CA and ferrite phase (C_4AF-C_6AF_2), with mayenite, $C_{12}A_7$, gehlenite, C_2AS and β-C_2S as minor compounds [2]. The samples A and B were used as received while the third sample aB is cement B aged for one year. About 20 g of sample B is sealed for one year in a little PE bag at laboratory conditions (20 °C and ~55 % r.h.). For preparing cement mortar, quartz sand (99 % SiO_2, size 1 mm) milled for 1 h in planetary mill (Fritsch, Pulverisette 5, *α*-Alumina pot and grinding balls) was used.

The rate of heat generation of the prepared CAC samples has been determined by the differential isoperibolic-conduction microcalorimeter developed at the Technical University of Budapest. It is capable of giving information on heat evolution from the instant the water was injected in cement sample holder. As hydration heat evolves the small temperature difference across a thermopile (consisting of 18 thermocouples) between the sample cell and reference cell produces a voltage that is logged at regular time intervals (10 s) by a microvoltmeter (Data logger Almemo-2390-8, with DC Millivolt Connectors, resolution 1μV). The calorimeter operates under isoperibolic conditions with small temperature difference. The rate of heat generation at time *t*, is calculated applying Tian's equation [7,8]:

$$\frac{dQ}{dt} = \frac{c_p}{m\,g}\left(\frac{dU}{dt} + \beta U\right) \tag{2}$$

where *U* is the voltage difference (referenced to baseline), c_p is effective heat capacity of calorimeter (J/°C), *g* is voltage to temperature conversion constant (μV/°C), *β* is calorimeter cooling constant (s^{-1}), and *m* is cement mass. Small samples, 4g of cement, is used to avoid undesirable temperature rise in the cell. More detailed operation and calibration of the calorimeter is described elsewhere [7]. The cement and appropriate amount of water was left to reach thermal equilibrium (overnight) in an ultrathermostat before the water was injected into the cement sample holder to start the hydration. Results are presented as an average of two measured curves. Uncertainty of the microcalorimetric measurement of heat evolved (Q/Jg^{-1}, with 95% confidence) is evaluated to be ± 3%.

The composition of cement and hydrates formed was investigated by X-ray diffraction (XRD). The cement samples were investigated by loss on ignition determined by firing at 950 °C in laboratory furnace.

First serial of experimental work was done on as received samples A and B for cement pastes and mortars mix proportions given in Table 1. Temperature, *T*, water to cement ratio, *w/c*, and sand-cement ratio, *s/c* was varied. High *w/c* ratios were used in order to assure good wetting of the cement. Second serial was conducted on aged sample, Table 2.

3 Results and discusion

XRD on samples hydrated at appropriate temperature for 30 h confirmed the hydrate compositions expected from the literature. At 5 °C only CAH_{10} was observed, while at 20 °C a small quantity of C_2AH_8 and AH_3 could be detected. At 30 °C C_2AH_8 and AH_3 are main products with appearance of C_3AH_6 but no CAH_{10} was observed.

Results of investigations of CAC sample A and B hydration by microcalorimeter are given in Figures 1-3 and Table 3. In Figures 1 and 3a only rate of heat generation ($q=dQ/dt$, J $h^{-1}g^{-1}$) is presented while in others heat evolution obtained by integration of (1), Q, Jg^{-1} is also added.

Times of initial and final set were established from the microcalorimetry results. Initial set is acquired from the intersection of two straight lines [6,9]: one fitted through the induction period of the curve and the other fitted through the inflection point of the rising slope of main peak ($tg\alpha_{i.p.}$). The final set can be approximated at the point of maximal heat generation $t_{q\max}$. Unlike calorimetry, the Vicat initial setting time is significantly affected by *w/c* due to the consistency of the paste being tested [6]. In a more fluid paste longer time is needed to reach the required resistance to penetration.

Table 1. First serial of cement pastes and mortars mix proportions.

Label	**Sample**	***w/c***	***s/c***	***T*/°C**
A20C0.4	A	0.4	-	20
A20C0.5	A	0.5	-	20
A20C1.0	A	1.0	-	20
A20C0.5S	A	0.5	1,0	20
B20C0.4	B	0.4	-	20
B20C0.5	B	0.5	-	20
B5C0.4	B	0.4	-	5
B5C0.5	B	0.5	-	5
B10C0.4	B	0.4	-	10
B10C0.5	B	0.5	-	10
B10C1.0	B	1.0	-	10
B30C0.4	B	0.4	-	30
B30C0.5	B	0.5	-	30

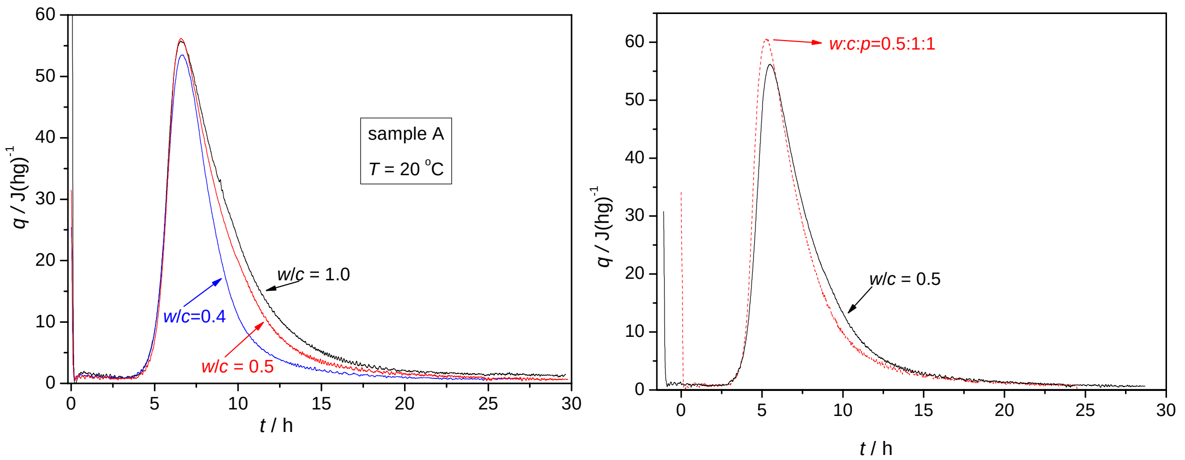
Table 2. Second serial of cement pastes mix proportions for the study of aged cement sample.

Label	**Sample**	***w/c***	***T*/°C**
aB14C0.4	aB	0.4	14
aB14C0.5	aB	0.5	14
aB20C0.5	aB	0.5	20

Far less heat is liberated when cement and water first come in contact than for Portland cement. This heat is attributed mainly to the cement wetting and dissolution processes occurring during the first minutes of hydration. During the induction period a small rate of heat generation is observed (~1 J(h g)$^{-1}$), whose length is determined by temperature, water content and cement composition. Induction period is followed by the onset of the accelerated stage of reaction due to massive precipitation of hydrates. The maximum of heat generation amounts up to 55 J(h g)$^{-1}$ and is reached in only few hours after the onset of the accelerated stage. In comparison to PC that is up to six time greater rate of maximal heat generation.

Influence of the water to cement ratio, *w/c* on CAC hydration at 20 °C is shown in Figure 1a. Samples prepared at higher *w/c* show greater rate of heat generation at later ages. From the comparison of the *w/c* impact in Figure 1a it can be concluded that the limiting reactant is water. Due to water consumption, hydration reaction is slowing down. This principal influence of *w/c* is also visible immediately before the maximum of the main peak with higher values of $q_{\max}$ for higher *w/c*. We argue that this can be the case only if the reaction i.e. interaction on cement boundary is the main rate limiting mechanism.

In Figure 1b a comparison of mortar (A20C0.5s) and paste hydration (A20C0.5) is presented by translating paste hydration to overlap the onset of the main peak. Cement sets faster (Table 3, Δt_v = 1.2 h) in the form of the sand-cement mortar than neat paste. The massive hydrate precipitation begins after nuclei germination from the saturated solution. The reason for slower activity in the neat paste could be explained by the lack of germination sites for the nuclei to start the hydration precipitation. After the onset of the main peak the hydration rate is faster for the sand-cement mortar due to more germination sites. A little time past the maximal rate, with higher value for mortar, the hydration continues slower in comparison to neat paste.



a) b)

Figure 1. Heat generation during hydration at 20 ^{o}C: a) influence of *w/c*, and b) comparison of mortar (A20C0.5s) and paste hydration (A20C0.5 – translated hydration start).

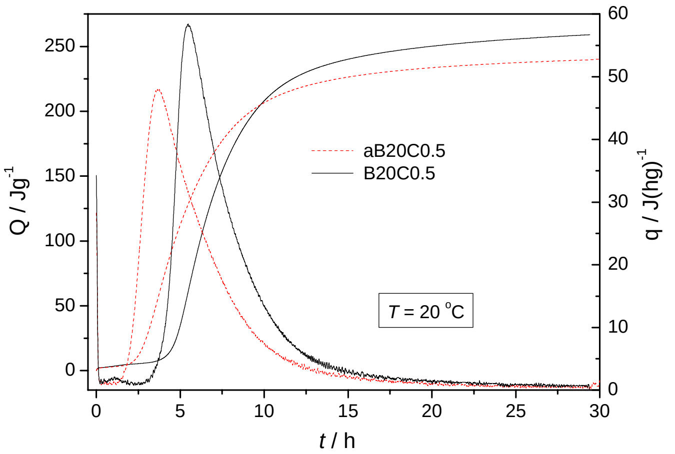
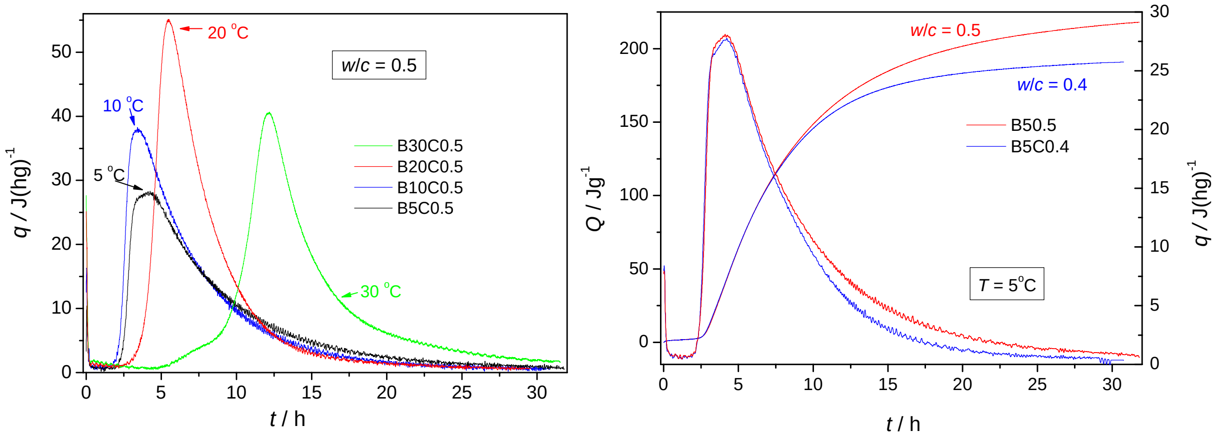


Figure 2. Comparison of sample B and sample aB (one year sealed in a little PE bag at 20 ^{o}C and 55% r.h) hydration.



a) b)

Figure 3. Heat generation during hydration: a) Influence of temperature on hydration, and b) influence of *w/c* on hydration at 5 ^{o}C.

Table 3. Results of the investigations by microcalorimeter: hydration heat evolved after 24.5 h ($Q_{t=24.5\text{h}}$), maximal rising slope at inflection point of main peak ($tg\alpha_{i.p.}$), main peak maximal heat generation (q_{max}) at time $t_{q\max}$, and initial setting time (t_{set}).

Label	$Q_{t=24.5\text{ h}}$ / Jg^{-1}	$tg\alpha_{i.p.}$/ $\text{Jh}^{-2}\text{g}^{-1}$	q_{max} / mWg^{-1}	$t_{q\max}$ / h	t_{set} / h
A20C0.4	204.3	41.5	14.9	6.6	5.0
A20C0.5	250.0	48.5	15.6	6.5	5.1
A20C1.0	287.6	51.3	15.7	6.5	5.1
A20C0.5S	243.5	62.7	16.9	5.2	3.9
B20C0.4	207.7	45.0	15.1	5.5	3.9
B20C0.5	253.3	46.8	15.3	5.5	4.0
B5C0.4	187.5	42.2	7.7	4.2	2.4
B5C0.5	210.2	40.9	7.8	4.2	2.5
B10C0.4	196.5	49.7	10.6	3.6	2.3
B10C0.5	225.2	50.3	10.5	3.4	2.2
B10C1.0	253.4	32.3	9.3	3.4	1.7
B30C0.4	216.1	26.6	13.1	12.2	9.6
B30C0.5	243.3	19.3	11.3	11.6	9.7
aB14C0.4	190.8	27.6	10.1	3.5	1.6
aB14C0.5	236.1	26.0	10.4	3.6	1.6
aB20C0.5	237.2	35.4	13.3	3.6	2.0

The difference in heat evolved of 2.8 %, Table 3, points out that practically the same hydration degree is achieved after 1 day. The smaller value for mortar could be explained by the wetting of sand. Slope at the inflection point of main peak is 29 % higher for the hydration with sand addition, Table 3 and Figure 1a. Comparison of hydration A and B samples (not depicted in this paper) resulted in difference of heat evolved by 1.8 % and 1.9 % for *w/c* of 0.4 and 0.5, respectively. Considering the measurement uncertainty of measured evolved heat (± 3%) and by comparison of curve shape by translation, it can be concluded that except for the change in the setting time (Δt_{v} = 1.1 h) there are no other significant differences in the kinetics of hydration of samples A and B, Table 3.

Loss on ignition measurement on samples A, B and aB has indicated 0.90, 0.88 and 3.14 % mass reduction, respectively. The aged sample shows greater mass loss due to a water and CO_2 uptake from the environment. It should be noted that only ~ 20 g of sample was aged, and the uptake for larger samples (25 kg in original bag) is expected to be pronounced only on sample periphery.

Results of the investigation of the age impact onto hydration are shown in Figure 2 and Table 3. The aged sample in comparison to original sample B show the quicker setting time, lower hydration rate, the flatter and longer main peak in the heat generation and lower heat evolved.

The influence of temperature on the rate of hydration is presented in Figure 3a. Increasing temperature from 5 to 10 °C increases the rate of formation of CAH_{10} but above 20 °C the low level of supersaturation, sluggish nucleation of CAH_{10} and the massive gel formation retards the setting time and hydration rate. The maximal rate of heat evolution occurs at 20 °C. The flatter and longer main peak in the heat generation at 30 °C than at 20 °C supports the notion of slow growth and crystalisation of C_2AH_8 up to this temperature [9] with the formation of both CAH_{10} and C_2AH_8 in proportions that vary over the temperature range. Contrary to Bushnell and Banfill [6,9], who reported retardation of CAH_{10} formation with increased temperature in the range 5 – 15 ^{o}C, Figure 3 shows clearly acceleration of CAH_{10} formation. Banfill concluded, by applying Avrami-Erofe'ev equation that the maximum rate of heat evolution and the time at which it occurs are reliable kinetic parameters to quantify the hydration rate. In this study heat generation data obtained could not be satisfactory fitted by the Avrami-Erofe'ev nucleation and growth equation. The appropriateness of using Avrami-Erofe'ev analysis for describing whole hydration process is disputable, because the rate of reaction is not solely governed by the nucleation and growth mechanism.

Figure 3b shows the influence of *w/c* on CAC hydration at 5 ^{o}C. With decreasing temperature (20-5 ^{o}C), compare Figures 1a and 3 b, the retardation of hydration rate due to self-desiccation is occurring latter referring to the main maximum.

4 Conclusions

Determining the heat of hydration of cement material will enable, in practice, the realistic simulation of temperature distribution in material and easier planning of curing in the early stage of hydration with the purpose of achieving better durability and functionality of placed material.

Far less heat is liberated when cement and water first come in contact than for PC. Higher *w/c* increases the heat evolved due to higher degree of hydration. Cement sets faster (1.2 h) in the form of the sand-cement mortar than neat pastes. This could be explained by the lack of germination sites for the nuclei to start the hydration precipitation.

Except for the change in the setting time (Δt_v = 1.1 h) there are no other significant differences in the kinetics of hydration of used original cement sample. Due to a water and CO_2 uptake from the environment the aged sample has a quicker setting time, lower hydration rate and lower heat evolved in comparison to original sample.

Contrary to previous reports in literature acceleration of CAH_{10} formation was observed for 5-10 ^{o}C. Obtained heat generation data could not be satisfactory fitted by the Avrami-Erofe'ev nucleation and growth kinetic model due to its non-appropriateness for describing the hydration process in the whole stage.

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