Research Article

The Effect of Synthetic Hydrated Calcium Aluminate Additive on the Hydration Properties of OPC

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The effect of synthetic CAH (130°C; 8 h; $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.55$; $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.1, 0.15$) with different crystallinity on the hydration kinetics of OPC at early stages of hydration was investigated. Also, the formation mechanism of compounds during OPC hydration was highlighted. It was determined that the synthetic CAH accelerated the initial reaction and shortened the induction period. Also, the second and third exothermic reactions begun earlier, and, during the latter reaction, the higher values of the heat flow were obtained in comparison with pure OPC samples. At later stages of hydration, synthetic CAH affect the OPC hydration as the usual pozzolanic additives; moreover, the larger values of cumulative heat were reached. It should be noted that the nature of synthetic CAH samples accelerated the dissolution of gypsum and stimulates the earliest C_3S hydration.

1. Introduction

Supplementary cementitious materials (SCMs), including fly ash, ground granulated blast furnace slag, silica fume, calcined clays, and natural pozzolans, are commonly blended with clinker to make Portland cement or are used as a partial replacement of this component in concrete [1–6]. The practice of using SCMs is increasing, with the world average percent clinker in cement having decreased from 85% in 2003 to 77% in 2010, and it is projected to further decrease to 71% in the future [7]. The use of SCMs is favorable to the industry, generally resulting in concrete with lower cost, lower environmental impact, higher long-term strength, and improved long-term durability [8–10].

It is known that SCMs can be of natural and synthetic origin or used as industrial by-products [11–20]. However, the application of natural minerals or industrial by-products in cement or concrete production is limited by the energy demanding processing of mentioned materials, which includes crushing, grinding, and size separation and, in some cases, it may also involve thermal activation. The latter process is applied for SCMs, which do not have or reach the required pozzolanic activity and also to alter their physical and chemical properties [11–13, 21].

For this reason, due to the high early strength, thermal and chemical stability, and excellent durability with respect to ordinary Portland cement (OPC) the synthetic SCMs have attracted a great scientific attention, when employed in building and ceramic industries [11, 22–29]. The one group of these compounds can be located in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system. During hydrothermal synthesis the interreaction between silica, alumina, and calcium ions results in the formation of compounds such as calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH), and calcium aluminium silicate hydrates (CASH). For this reason, many researchers keep their focus on tailoring the final structural and physical properties of mentioned materials mainly by changing the synthesis conditions (using different raw materials and changing C/S ratio of primary mixture or the duration and temperature of isothermal curing) [30–35]. In Baltakys et al. work, when the duration of hydrothermal synthesis (175°C; 0–24 h) was extended, a lower amount of CASH was obtained [35]. Meanwhile, in Meller et al. work [31–34] the stability of obtained phases in $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system was highlighted. It was found that the latter parameter and the formation mechanism of such compounds were significantly influenced by the synthesis temperature (from 200 to 350°C) and even small amounts of Al_2O_3 additive.

TABLE 1: Chemical and mineralogical composition of clinker.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃ ²⁻	Ignition of losses	Insoluble particles
Amount, %	19.72	5.41	4.21	62.76	3.41	0.16	1.08	2.08	0.93	0.24
Minerals	3CaO·SiO ₂		2CaO·SiO ₂		3CaO·Al ₂ O ₃		4CaO·Al ₂ O ₃ ·Fe ₂ O ₃			
Amount, %	63.19		8.89		7.21		12.81			

In previous work [35] the influence of Al₂O₃ on the formation of calcium aluminium silicate hydrates under hydrothermal conditions was also examined. It was determined that the largest amount of calcium aluminium silicate hydrates was obtained after 8 h of hydrothermal treatment at 130°C, in the mixtures with a higher amount of Al₂O₃ (Al₂O₃/(SiO₂ + Al₂O₃) = 0.15). Meanwhile, the formation of mentioned compounds is inhibited, when the duration of isothermal curing is extended from 16 to 72 h.

Aluminium readily enters the calcium silicate hydrate phase (C–S–H) of Portland cement, and this substitution is expected to play a significant role in many aspects of the chemical behavior of cement paste, including the cation and anion exchange behavior, solubility, and the progress of the reactions that occur during delayed ettringite formation [36–42].

In previous work [35] it was proved that the synthetic CAH (CaO/(SiO₂ + Al₂O₃) = 0.55; Al₂O₃/(SiO₂ + Al₂O₃) = 0.15) as an additive affects the early hydration of OPC. This compound effectively shortens the induction period and accelerates the second and the third exothermic reactions.

For this reason, the main objective of this study was to determine the effect of synthetic CAH with different crystallinity on the hydration kinetics of OPC at early stages of hydration. Also, the compound formation mechanism is highlighted.

2. Materials and Methods

2.1. Materials. In this paper the following reagents were used: SiO₂·nH₂O (“Reaktiv,” Russia) was grinded for 3 min in a vibrating cup “Pulverisette 9” mill (speed: 950 rpm) and sieved through a sieve with a mesh size of 80 μm, S_a = 1047 m²/kg by CILAS LD 1090 granulometer, the loss of ignition, 7.0 wt.%. Calcium oxide from Ca(OH)₂ (“Reaktiv,” Russia) was additionally burned at 500°C temperature for 2 h, grinded for 30 s in a vibrating cup “Pulverisette 9” mill (speed: 650 rpm), and sieved through a sieve with a mesh size of 80 μm; the quantity of free CaO is equal to 99 wt.%, S_a = 961 m²/kg. γ-Al₂O₃ was produced by burning aluminium hydroxide (“Sigma-Aldrich,” Germany) at 475°C for 4 h, S_a = 822 m²/kg.

2.2. Synthetic CAH Samples Preparation. Dry primary mixtures with CaO/(SiO₂ + Al₂O₃) = 0.55 and Al₂O₃/(SiO₂ + Al₂O₃) = 0.1; 0.15 were mixed with water to reach the water/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis has been carried out in unstirred suspensions in 25 mL volume PTFE cells, which were placed in “Parr instruments” (Germany) autoclave, under saturated

steam pressure at 130°C temperature for 8 h (the temperature was reached within 2 h). After hydrothermal treatments, the autoclave was quenched to room temperature. The suspensions after synthesis were filtered and products were rinsed with ethanol to prevent carbonization of materials, dried at 50 ± 5°C temperature for 24 h, and sieved through a sieve with a width of 80 μm. These synthesis conditions were chosen according to previously published data [35].

2.3. Cementitious Admixtures with Synthetic CAH Samples. Samples of OPC were prepared in a laboratory grinding mill by grinding cement clinker (JSC “Akmenes cementas,” Lithuania) with a 4.5% additive of gypsum (“Sigma-Aldrich,” Germany) up to S_a = 450 m²/kg. The chemical analysis and phase composition of clinker are shown in Table 1. Synthetic CAH sample was added as a partial replacement of the OPC at levels of 10% by weight of the total cementitious material. Therefore the water and cement ratio (W/C) of all OPC samples was equal to 0.5.

In the next stage of experiment, synthesized CAH samples were added as a partial replacement of the OPC at levels of 10% by weight of the total cementitious material. The additives of hydrated calcium aluminate were labeled as OPC-CAH1 ((CaO/(SiO₂ + Al₂O₃) = 0.55, Al₂O₃/(SiO₂ + Al₂O₃) = 0.1)) and OPC-CAH2 (CaO/(SiO₂ + Al₂O₃) = 0.55, Al₂O₃/(SiO₂ + Al₂O₃) = 0.15) depending on the composition of primary mixtures.

2.4. Test Methods. The X-ray powder analysis (XRD) was performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with Ni 0.02 mm filter to select the CuK_α wavelength. Diffraction patterns were recorded in a Bragg-Brentano geometry using a fast counting detector Bruker LynxEye based on silicon strip technology. The specimens were scanned over the range 2θ = 3–70° at a scanning speed of 6°C min⁻¹ using a coupled two-theta/theta scan type.

Simultaneous thermal analysis (STA: differential scanning calorimetry, DSC, and thermogravimetry, TG) was also employed for measuring the thermal stability and phase transformation of samples at a heating rate of 15°C min⁻¹; the temperature ranged from 30°C up to 900°C under air atmosphere. The test was carried out on a Linseis instrument STA PT1000. The ceramic sample handlers and crucibles of Pt were used.

Differential scanning calorimetry (DSC) analysis was performed by a Netzsch DSC 214 Polyma instrument. This method was employed for measuring the thermal stability and phase transformation of samples at a heating rate of

FIGURE 1: The heat evolution rate (a–c) and cumulative heat (d) of OPC (1), OPC-CAH1 (2), and OPC-CAH2 (3) samples during the early stage of hydration.

$10^{\circ}\text{C min}^{-1}$, and the temperature ranged from 30°C up to 600°C under air atmosphere. Ceramic sample handlers and Al crucibles were used.

An eight-channel TAM Air III isothermal calorimeter was used to investigate the heat evolution rate of the samples. Glass ampoules (20 mL) each containing 3 g dry cementitious material were placed in the calorimeter and the injection units for each ampoule filled with amounts of water equivalent to a W/(OPC and additive) ratio of 0.5. After a steady temperature of 25°C had been reached, the water was injected into the ampoules and mixed inside the calorimeter with the dry material for 20 s (frequency $2\text{--}3\text{ s}^{-1}$). The heat evolution rate was then measured over a period of 72 h. Repetition of the measurements showed deviations in total heat below 3% for samples of similar type. Apart from the first minutes of water additive and mixing, the heat evolution rates were essentially identical. The rate of heat evolution was calculated on the basis of a unit weight of OPC.

In order to investigate the mineralogy and chemical composition of compounds formed during hydration, the heat evolution experiments were repeated at 25°C for different time periods (1.8, 3, 9.5, 13, and 24 h), which corresponded to the onset/peak/end duration of different early hydration periods. Hydration of samples was stopped by using acetone. Later on, the samples were crushed to powder, dried at

the temperature of $50 \pm 5^{\circ}\text{C}$, and put through a sieve with an $80\text{ }\mu\text{m}$ mesh.

3. Results and Discussion

3.1. Heat Evolution in Hydrated Cementitious Admixtures with Synthetic CAH Samples. The data of cumulative heat of hydration as well as the rate of heat evolution of the binary blended pastes are presented in Figure 1.

The heat of hydration curves for pure OPC and OPC with additives shows the typical five stages of the hydration reaction (the initial reaction, the induction period, the acceleratory period, the deceleratory period, and the period of slow continued reaction) as described in the literature [43–45].

It was determined that the additives of synthetic CAH samples in OPC samples accelerated the initial reaction (1–2 min) because an increase in the maximum heat evolution rate was observed from 0.005 Wg^{-1} to 0.011 Wg^{-1} (OPC-CAH2) and 0.018 Wg^{-1} (OPC-CAH1) (Figure 1(a)). And also, the induction period, which is assigned to the growing C-S-H and CH on the surface of the particles of primary compounds, was effectively shortened. In pure OPC samples, the mentioned process continued after 3 h, while in a case of OPC-CAH1 and OPC-CAH1 only after $\sim 1.8\text{ h}$ (Figure 1(b)). However, the accelerating effect begun earlier: from 1.9 h

FIGURE 2: DSC curves OPC with 10 wt.% additive after 1.8 h (a) and 16.5 h (b): 1, OPC; 2, OPC-CAH1; 3, OPC-CAH2.

in the samples with an additive and from 3.2 h in pure OPC samples (Figure 1(c)). Moreover, the lower values of the heat flow of the second exothermic reaction, typical to the dissolution of C_3S , were reached in OPC mixtures with additives: 0.0023 Wg^{-1} at 5.02 h for OPC-CAH1 and 0.0023 Wg^{-1} at 6.02 h for OPC-CAH2. Meanwhile, during the third exothermic reaction, which is characteristic to the dissolution of C_3A and the formation of ettringite, the highest value of the heat flow (0.0032 Wg^{-1}) at 13.1 h was obtained in OPC-CAH2 sample (Figure 1(c)).

At later stages of hydration, synthetic CAH samples affect the OPC hydration as the usual pozzolanic additive; moreover, the largest value of cumulative heat was reached in the OPC-CAH2 sample (Figure 1(d)).

3.2. Quantity of Compounds in the Cement Paste. It was determined that, during early OPC hydration, the stability and reactivity of OPC-CAH1 and OPC-CAH2 significantly depend on the primary mixture composition used for hydrothermal synthesis. OPC-CAH1 additive fully reacted already after 1.8 h of hydration; meanwhile, in a case of OPC-CAH2, only 33% (14.65 J/g) of calcium aluminium hydrate reacted (Figure 2(a): endothermic effect at $\sim 271^\circ\text{C}$; Table 2).

However, when the duration of OPC hydration was extended to 24 h, the amount of unreactive compounds was decreased (Figure 2; Table 2).

It should be noted that the nature of CAH accelerated the dissolution of gypsum. In the pure system, the latter compound fully reacted only after 16.5 hours of hydration, whereas in the samples with additives it fully reacted already after 13 h. It is clearly visible in DSC curve: the endothermic effect in a $105\text{--}135^\circ\text{C}$ temperature range, which corresponded to the dehydration of gypsum, disappeared (Figure 2; Table 3). Moreover, in comparison with pure OPC samples, only a smaller amount of semicrystalline C-S-H (Figure 2: endothermic effect at 67°C ; Table 3) as well as portlandite (Figure 2: endothermic effect at 440°C ; Table 3)

FIGURE 3: The quantity of unreactive C_3S in pure OPC, OPC-CAH1, and OPC-CAH2 samples after different duration of hydration.

were obtained in the mixtures with additives by prolonging the duration of OPC hydration.

In this report, the amounts of C_3S that have reacted after heat evolution experiments at different time period under normal conditions were determined by the quantitative analysis (QXRD). The quantity of C_3S was calculated from the intensity change of the basic reflection (d -spacing, 0.2604 nm). Each calculation was done five times, and it was determined that their data declined no more than $\pm 2\%$ from the mean (Figure 3). C_3S quantity in the mixtures of pure OPC and OPC with additives (before hydration) was equal to 100%.

It was determined that after 5.5 h of hydration, only 9% of C_3S reacts in pure OPC samples and the further reduction of its quantity depends on duration of hydration (Figure 3).

TABLE 2: The main characteristics of thermal effects typical of CAH.

Composition	Hydration time (h)	Onset, °C	Peak, °C	Heat of process, J/g	Unreacted CAH, wt. %
OPC-CAH2	0	250.2	268.6	21.81	100
	1.8	253.8	271.0	14.65	67.17
	3	254.5	273.3	14.51	66.53
	5.5	256.7	276.3	13.67	62.68
	9.5	261.6	280.5	12.24	56.12
	13	265.2	282.5	11.94	54.75
	16.5	264.1	286.0	11.71	53.69
	24	267.7	286.8	10.39	47.64

TABLE 3: The main characteristics of thermal effects typical of CSH and gypsum by DSC method.

Composition	Hydration time (h)	CSH			Gypsum			Unreacted gypsum, wt. %
		Onset, °C	Peak, °C	Heat of process, J/g	Onset, °C	Peak, °C	Heat of process, J/g	
OPC	1.8	45.8	66.7	14.89	112.5	122.4	16.23	69.01
	3	48.0	64.4	17.22	108.1	118.3	16.69	70.96
	5.5	52.4	73.6	28.12	111.1	119.4	10.97	46.64
	9.5	54.7	76.9	40.88	113.3	119.8	6.86	29.15
	13	57.5	82.0	53.01	116.2	121.3	0.80	3.36
	16.5	61.0	87.8	71.84	—	—	—	—
	24	58.8	86.3	77.42	—	—	—	—
OPC-CAH1	1.8	49.0	66.8	18.61	113.6	121.0	13.63	74.93
	3	48.4	68.0	22.53	112.2	119.4	10.33	43.92
	5.5	54.5	75.7	37.60	115.1	121.0	6.02	25.57
	9.5	58.7	81.5	51.10	116.6	122.7	0.29	1.24
	13	62.7	87.6	63.13	—	—	—	—
	16.5	59.5	84.8	66.49	—	—	—	—
	24	58.5	84.5	71.74	—	—	—	—
OPC-CAH2	1.8	44.4	63.0	17.20	110.5	118.3	13.54	67.60
	3	49.4	69.3	21.10	111.7	119.6	11.15	55.67
	5.5	55.2	76.9	37.32	114.7	120.8	4.74	23.68
	9.5	64.7	85.1	54.86	116	121.8	0.51	2.54
	13	61.9	85.8	64.14	—	—	—	—
	16.5	61.4	85.1	58.51	—	—	—	—
	24	60.2	86.6	66.50	—	—	—	—

Meanwhile, within the same duration of hydration, in the samples with CAH1 and CAH2 additives, 21% and 18% of this compound reacted, respectively (Figure 3). It was noticed that mentioned additives stimulate the earliest C_3S hydration in all samples (5.5–16.5 h) (Figure 3).

Presumably, the synthetic CAH sample also induced the formation mechanism of ettringite.

In order to prove this fact, the intensity change of the basic reflection of ettringite (d -spacing, 0.972 nm) in cement samples was evaluated by X-ray diffraction analysis (XRD) according to the area of mentioned diffraction maximum per shift at different hydration time.

The obtained results showed that after 3 hours of hydration, the area of the main diffraction peak typical to ettringite increased in two times in comparison with the pure OPC samples (Figure 4). The same tendency was also observed,

TABLE 4: The values of the main diffraction peak area of ettringite in OPC, OPC-CAH1, and OPC-CAH2 samples.

Composition	Hydration time (h)							
	0	1.8	3	5.5	9.5	13	16.5	24
OPC	—	0.14	0.15	0.26	0.40	0.60	1.00	1.45
OPC-CAH1	—	0.15	0.37	0.42	0.89	0.90	1.18	1.39
OPC-CAH2	—	0.21	0.22	0.54	0.51	1.03	1.18	1.30

when the duration of hydration was extended to 9.5 hours (Table 4).

In addition, due to the accelerated dissolution of gypsum, a larger amount of formed ettringite was observed in OPC-CAH1 and OPC-CAH2 samples. Meanwhile, in an excess

FIGURE 4: The change of the main diffraction peak of ettringite in samples after 3 h of hydration: 1, OPC; 2, OPC-CAH1; 3, OPC-CAH2.

of gypsum in the pure OPC samples, the area of the main diffraction maximum of ettringite was slightly higher after 24 h of hydration (Table 4).

4. Conclusions

It was examined that the additives accelerated the initial reaction and shortened the induction period. Also, the second and third exothermic reactions begun earlier, and, during the latter reaction, the higher values of the heat flow were obtained in comparison with pure OPC samples. At later stages of hydration, synthetic CAH affect the OPC hydration as the usual pozzolanic additives; moreover, the larger values of cumulative heat were reached.

It was noticed that additives stimulate the earliest C_3S hydration (5.5–16.5 h): after 5.5 h of hydration, only 9% of C_3S reacts in pure OPC samples and the further reduction of its quantity depends on duration of hydration. Meanwhile, in a case of CAH1 and CAH2 additives, 21% and 18% of this compound reacted.

It should be noted that the nature of synthetic CAH samples accelerated the dissolution of gypsum. In the pure system, the latter compound fully reacted only after 16.5 hours of hydration, whereas in the samples with additives it reacted already after 13 h. For this reason, a larger amount of formed ettringite was observed in OPC-CAH1 and OPC-CAH2 samples till 16.5 h of hydration.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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