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; CaO/(SiO₂ + Al₂O₃) = 0.55; Al₂O₃/(SiO₂ + Al₂O₃) = 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 C₃S 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 CaO–Al₂O₃–SiO₂–H₂O 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 CaO–Al₂O₃–SiO₂–H₂O 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 Al₂O₃ additive.
In previous work [35] the influence of $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ ($\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.15$). 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 ($\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.55; \text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.15$) as an additive affects the 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: $\text{SiO}_2$-$\text{H}_2\text{O}$ (“Reaktiv,” Russia) was ground for 3 min in a vibrating cup “Pulverisette 9” mill (speed: 950 rpm) and sieved through a sieve with a mesh size of 80 $\mu$m, $S_n = 1047$ m$^2$/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 for 2 h, ground for 30 s in a vibrating cup “Pulverisette 9” mill (speed: 650 rpm), and sieved through a sieve with a mesh size of 80 $\mu$m; the quantity of free CaO is equal to 99 wt.%, $S_n = 961$ m$^2$/kg. $\gamma$-$\text{Al}_2\text{O}_3$ was produced by burning aluminium hydroxide (“Sigma-Aldrich,” Germany) at 475°C for 4 h, $S_n = 822$ m$^2$/kg.

#### 2.2. Synthetic CAH Samples Preparation

Dry primary mixtures with CaO/(SiO$_2$ + Al$_2$O$_3$) = 0.55 and Al$_2$O$_3$/(SiO$_2$ + Al$_2$O$_3$) = 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 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 $\mu$m. 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 $S_n = 450$ m$^2$/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 (($\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.55, \text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.1)$) and OPC-CAH2 ($\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.55, \text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.15$) 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$_\alpha$ 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 2$\theta = 3–70^\circ$ 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...
10°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 2-3 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 ± 5°C, and put through a sieve with an 80 μm 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 W g⁻¹ to 0.011 W g⁻¹ (OPC-CAH2) and 0.018 W g⁻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 ~1.8 h (Figure 1(b)). However, the accelerating effect begun earlier: from 1.9 h
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 ∼271°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 105–135°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) were obtained in the mixtures with additives by prolonging the duration of OPC hydration.

In this report, the amounts of C₃S that have reacted after heat evolution experiments at different time period under normal conditions were determined by the quantitative analysis (QXRD). The quantity of C₃S 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 ±2% from the mean (Figure 3). C₃S 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 C₃S reacts in pure OPC samples and the further reduction of its quantity depends on duration of hydration (Figure 3).
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 C₃S 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, 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

### Table 2: The main characteristics of thermal effects typical of CAH.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hydration time (h)</th>
<th>Onset, °C</th>
<th>Peak, °C</th>
<th>Heat of process, J/g</th>
<th>Unreacted CAH, wt.%</th>
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<tbody>
<tr>
<td>OPC-CAH2</td>
<td>0</td>
<td>250.2</td>
<td>268.6</td>
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<td>100</td>
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<td></td>
<td>1.8</td>
<td>253.8</td>
<td>271.0</td>
<td>14.65</td>
<td>67.17</td>
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<tr>
<td></td>
<td>3</td>
<td>254.5</td>
<td>273.3</td>
<td>14.51</td>
<td>66.53</td>
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<tr>
<td></td>
<td>5.5</td>
<td>256.7</td>
<td>276.3</td>
<td>13.67</td>
<td>62.68</td>
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<tr>
<td></td>
<td>9.5</td>
<td>261.6</td>
<td>280.5</td>
<td>12.24</td>
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<tr>
<td></td>
<td>13</td>
<td>265.2</td>
<td>282.5</td>
<td>11.94</td>
<td>54.75</td>
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<td></td>
<td>16.5</td>
<td>264.1</td>
<td>286.0</td>
<td>11.71</td>
<td>53.69</td>
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<td></td>
<td>24</td>
<td>267.7</td>
<td>286.8</td>
<td>10.39</td>
<td>47.64</td>
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### Table 3: The main characteristics of thermal effects typical of CSH and gypsum by DSC method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hydration time (h)</th>
<th>CSH</th>
<th>Gypsum</th>
</tr>
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<tr>
<td></td>
<td>Onset, °C</td>
<td>Peak, °C</td>
<td>Heat of process, J/g</td>
</tr>
<tr>
<td>OPC</td>
<td>1.8</td>
<td>45.8</td>
<td>66.7</td>
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<tr>
<td></td>
<td>3</td>
<td>48.0</td>
<td>64.4</td>
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<td></td>
<td>5.5</td>
<td>52.4</td>
<td>73.6</td>
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<td>9.5</td>
<td>54.7</td>
<td>76.9</td>
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<td>57.5</td>
<td>82.0</td>
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<td>16.5</td>
<td>61.0</td>
<td>87.8</td>
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<td></td>
<td>24</td>
<td>58.8</td>
<td>86.3</td>
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<tr>
<td>OPC-CAH1</td>
<td>1.8</td>
<td>49.0</td>
<td>66.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>48.4</td>
<td>68.0</td>
</tr>
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<td>16.5</td>
<td>59.5</td>
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<td>OPC-CAH2</td>
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<td>44.4</td>
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<td>49.4</td>
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<td></td>
<td>24</td>
<td>60.2</td>
<td>86.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hydration time (h)</th>
<th>0</th>
<th>1.8</th>
<th>3</th>
<th>5.5</th>
<th>9.5</th>
<th>13</th>
<th>16.5</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>—</td>
<td>0.14</td>
<td>0.15</td>
<td>0.26</td>
<td>0.40</td>
<td>0.60</td>
<td>1.00</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>OPC-CAH1</td>
<td>—</td>
<td>0.15</td>
<td>0.37</td>
<td>0.42</td>
<td>0.89</td>
<td>0.90</td>
<td>1.18</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>OPC-CAH2</td>
<td>—</td>
<td>0.21</td>
<td>0.22</td>
<td>0.54</td>
<td>0.51</td>
<td>1.03</td>
<td>1.18</td>
<td>1.30</td>
<td></td>
</tr>
</tbody>
</table>
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 began 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 CaS hydration (5.5–16.5 h): after 5.5 h of hydration, only 9% of CaS 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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