Early Hydration of Calcium Aluminate Cement Blended with Spent FCC Catalyst at Two Temperatures

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Abstract

The early hydration (up to 24h) of calcium aluminate cement (Al\textsubscript{2}O\textsubscript{3} min. 40%) blended with spent FCC catalyst at two temperatures i.e. 10 °C and 25 °C was investigated. The calorimetric measurements were used to study cement pastes with constant ratio of water/binder = 0.5 (binder = cement + addition) and containing 0, 5 and 25% mass of mineral waste as replacement part of cement. In addition the kind of created products using X-ray diffraction method was identified. On the basis of obtained results it was found that the influence of spent FCC catalyst on early hydration of calcium aluminate cement strictly depends on temperature of hydration process. At the temperature of 25 °C this waste aluminosilicate accelerates setting and hardening of cement, but at the temperature of 10 °C acts as retarder. These changes are realized by variation of duration of the induction period and the bigger content of FBCC the bigger the effect is regardless of the temperature of hydration. The presence of this mineral waste causes a minor effect on the crystalline hydrates produced after 1 day of hardening although it clearly increases degree of CA hydration.

Keywords: calcium aluminate cement, spent FCC catalyst, calorimetry measurements, X-ray diffraction, temperature.

1. Introduction

Calcium aluminate cements are specific hydraulic binders, especially recommend for refractory materials. However because of such special properties as high early strength, resistance to chemical attack, or resistance to abrasion also used in construction [1], [2]. Their relatively high cost (CAC is more expensive than Portland cement) and possibility of deterioration of strength properties occurring with time related with a process of conversion of aluminate hydrates, even leading to building collapse (e.g. collapsing of the roofs in England in years 1973–74) [3], [1], CACs are often blended with different additions to improve the properties [4], [5]. The most popular are additions which exhibit pozzolanic activity i.e. microsilica, ground granulated blast furnace slag, fly ash or natural pozzolans [6–8]. Silica component of these minerals introduced into hydrating calcium aluminate cement system gives possibility of alternative way of hydration by formation of certain C-A-S-H phases [9], [10], [2], [4]. It is difficult to predict the exact effect of addition on aluminate cement hydration, because the hydration process is very complicated and depends on many different factors e.g. kind of aluminate cement, temperature or mixing parameters [11].

In general the hydration process of calcium aluminate cement can produce four main temperature-dependent hydrates: CAH\textsubscript{10}, C\textsubscript{2}AH\textsubscript{8}, AH\textsubscript{3} and C\textsubscript{3}AH\textsubscript{6} (according to abbreviations used in cement chemistry: C-CaO, A-Al\textsubscript{2}O\textsubscript{3}, H-H\textsubscript{2}O) [3], [12].

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Below ca. 15 °C – CAH<sub>10</sub> is formed, at the temperature of ca. 15–25 °C, mixtures of CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub> are produced with an increase in the quantity of C<sub>2</sub>AH<sub>8</sub> when the temperature rises. Above ca. 25 °C to at least 40 °C, C<sub>2</sub>AH<sub>8</sub> is the main hydration product formed together with hydrous alumina, firstly as alumina gel, which crystallizes with time to gibbsite AH<sub>3</sub>. When temperature rises above 40 °C and especially 60 °C, the hydrogarnet phase C<sub>2</sub>AH<sub>6</sub> is formed, alongside hydrous alumina that gradually changes to gibbsite [3]. However the temperature ranges are not precise and in literature some divergent information especially at about ambient temperatures are stated.

Spent catalyst from the fluidized catalytic cracking installation (named here as FBCC) is a fine grained aluminosilicate material, porous and of well developed specific surface, zeolite-type structure and pozzolanic properties [13–15]. Profitable influence of this waste material on hydration of Portland cement was proved [16], [17]. Our investigations concerning its effect on aluminates cements delivered that the waste aluminosilicate influences also the hydration of aluminate cements. At ambient temperature the formation of gehlenite hydrate also called strätlingite after long time of hydration by the presence of FBCC was found, although the reactivity of addition strongly depends on the kind of aluminate cements [4]. At early ages this addition accelerates the hydration at the temperature of 25 °C of various kinds of calcium aluminate cements [18], however in case of high aluminous cement at the temperature of 10 °C acts as a retarding agent [11]. The usage of spent FCC catalyst in refractory applications [19] as well as the influence the heat-treated zeolite waste on hydration of high aluminous cement [20], [21], was also considered.

The aim of this work was to study the early hydration (up to 24 h) of calcium aluminate cement (Al<sub>2</sub>O<sub>3</sub> min. 40%) blended with spent FCC catalyst at two temperatures i.e. 10 °C and 25 °C. The study is a continuation of our investigations of the effect of waste aluminosilicate on high aluminous cement hydration presented in [11]. Due to the fact that hydration of all kinds of aluminate cements is highly sensitive to temperature as well as certain changes of hydration for the sake of type of aluminate cement can occur, evaluation of the influence of spent FCC catalyst on the hydration of calcium aluminates cement is well-founded.

The calorimetric measurements were used to study cement pastes with constant ratio of water/binder = 0.5 (binder = cement + additive) and containing 0, 5 and 25% mass of mineral waste as replacement part of cement. In addition the kind of created products using X-ray diffraction method was identified.

2. Materials and methods

The studies were carried out with calcium aluminate cement – Górkal 40 (called further as CAC 40) produced by Górka Cement Sp. z o.o., Poland, and waste petrochemical fluid catalytic cracking catalyst (FBCC) as an addition.

- For CAC40 the content of components recalculated into oxides is (according to information from webpage of cement producer): Al<sub>2</sub>O<sub>3</sub> min.40%, CaO min. 36%, SiO<sub>2</sub> 24%, Fe<sub>2</sub>O<sub>3</sub> max.14 mass%, and mineralogical composition is: CA as a primary phase and C<sub>3</sub>A<sub>f</sub>, C<sub>12</sub>A<sub>7</sub> and C<sub>2</sub>A<sub>8</sub> as concurrent phases (Fig. 1), its specific surface area 0.31–0.38 m<sup>2</sup>/g, and bulk density 1.1 g/cm<sup>3</sup>.
- (According to abbreviations used in cement chemistry: C-CaO, A-Al<sub>2</sub>O<sub>3</sub>, S-SiO<sub>2</sub>, F - Fe<sub>2</sub>O<sub>3</sub>, H-H<sub>2</sub>O)
- Fine-grained spent catalyst waste (sizes of particles 20–100 μm, average particles size is ~44 μm) (Table 1 and Fig. 2). It exhibits zeolite structure (Fig. 1). Its chemical composition marked by XRF is (mass.%): Al<sub>2</sub>O<sub>3</sub> – 39.32±0.35, SiO<sub>2</sub> 52.86±0.27, Fe<sub>2</sub>O<sub>3</sub> 0.81±0.15, SO<sub>3</sub> 0.2±0.12. Bulk density 945 kg/m<sup>3</sup>. Its specific surface area is ~100 m<sup>2</sup>/g. Calcination loss at 1000 °C temperature is about 5%.

Cement pastes were made with water/binder ratio = 0.5 (binder = cement + additive) containing 0, 5 and 25% mass of mineral waste as replacement part of cement. In addition the kind of created products using X-ray diffraction method was identified.

The following experimental equipment was used:

- For the calorimetric measurements:
  - differential isothermal calorimeter ToniCAL III – the mixes (50 g distilled water and 100 g of solid substance) were studied at the temperature of 10 °C and the heat evolution curves were registered up to 24h of hardening,
  - BMR calorimeter produced by the Institute of Physical Chemistry, Polish Academy of Science – the mixes (5 g distilled water and 10 g of solid substance) were studied at the temperature of 25 °C and the heat evolution curves were registered up to 24 h of hardening.
- For the X-ray phase analyses – HZG–4 diffractometer (anticathode cooper, anode voltage 35 kV, anode current 25 mA).
- For SEM tests – JEOL JSM-7600F.
- For particle size analysis – laser size analyser Cilas 1090 LD (Cilas, France).
3. Results and discussion

The characteristics of materials used in this study are presented in Fig. 1 and 2 and in Table 1 as well as the results of investigations of cement pastes are shown in Figs. 3–6.

![Figure 1: X-ray diffraction patterns of raw materials: waste catalyst (FBCC) and calcium aluminate cement (CAC 40)]

![Figure 2: SEM image of waste FCC catalyst](image)

Table 1. The particle size analysis of spent FCC catalyst

<table>
<thead>
<tr>
<th>Fractions of particles [µm]</th>
<th>Percentage of particular fractions [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2–10</td>
<td>4.41</td>
</tr>
<tr>
<td>11–30</td>
<td>7.79</td>
</tr>
<tr>
<td>31–50</td>
<td>48.41</td>
</tr>
<tr>
<td>51–71</td>
<td>32.71</td>
</tr>
<tr>
<td>75–112</td>
<td>6.68</td>
</tr>
</tbody>
</table>

Calorimetry is a very important experimental method widely applied in cement and concrete chemistry and technology. The changes of the course of the heat release rate allow us to distinguish particular stages of hydration process, and to determine the influence of the curing conditions, or the presence of various additives [22–24]. After adding water to cement, a sequence of physiochemical transformations occur which condition the binding and hardening of cement and can be distinguished on calorimetric curves [12]. The initial minor increase in the amount of heat release rate corresponding to the wetting period undergo into the induction stage, which is characterized by the lack of thermal effects, and the subsequent sudden increase in the amount of heat release rate is strictly connected with exothermic massive precipitation of hydrates, followed by further hydration and transformation of products, related with a decrease in the heat evolved [11], [18].
The calorimetric curves for mixes made of calcium aluninate cement and 0%, 5% or 25% mass of waste aluminosilicate as replacement part of cement with 0.5 water/binder ratio (binder=cement + addition) registered during first 24 h of hydration at temperature of 10 °C and at temperature of 25 °C were presented in Fig. 3 and 4, respectively.

![Fig. 3. Calorimetric curves for mixes made of calcium aluninate cement and various amount of waste aluminosilicate with 0.5 water/binder ratio (binder=cement + addition) hydrated at temperature of 10 °C](image)

Just after addition of water to aluninate cement the hydroxylation of cement grains, surface dissolution and hydrolysis of clinker phases lead to release of $\text{Ca}^{2+}$ and $\text{Al(OH)}_4^-$ ions into solution with the simultaneous increase of pH [25]. As a result the small exothermic effect on calorimetric curves at wetting period is registered.

![Fig. 4. Calorimetric curves for mixes made of calcium aluninate cement and various amount of waste aluminosilicate with 0.5 water/binder ratio (binder=cement + addition) hydrated at temperature of 25 °C](image)
In case of samples with waste FCC catalyst a considerable increase of this effect is observed. Due to a very big specific surface of spent FCC catalyst, the bigger the amount of the aluminosilicate the more intensive the effect is, regardless of the temperature of hydration.

At the subsequent stage of induction, in which the heat released is inhibited, the following dissolution of anhydrous calcium aluminates and nucleation of hydrates progress. The rates of dissolution and precipitation being approximately equal. When the nuclei are grown to a critical size and quantity a rapid and massive precipitation of hydrates occurs and it is followed by a strong exothermic effect and maximum of the rate of heat released. However, it should be noticed that within the dissolution process the anhydrous cement particles exposed to water are consumed and the nucleation takes places at the surface of anhydrous grains rather than in solution, so the layer of hydrated products formed around cement particles hinders the penetration of water.

Comparing the pastes which contain the spent FCC catalyst and without the addition it is noticeable that the waste aluminosilicate strongly influences the duration of induction period both at temperature of 10 °C and at temperature of 25 °C. The higher the content of the addition, the greater the influence is, although the presence of studied waste exhibits the reverse effect at these two temperatures of hydration. Whereas the shortening of the induction stage with simultaneous acceleration of precipitation of hydrated products caused by the presence of spent catalyst occurs at the temperature of 25 °C, at the temperature of 10 °C the addition of waste aluminosilicate results in prolongation of the induction period and inhibition of the moment of hydrates precipitation.

The results of the X-ray analysis of calcium aluminate cement pastes with and without 25% mass. of spent FCC catalyst and 0.5 water/binder ratio (binder = cement + addition) after 24 h of hydration at temperature of 10 °C and at temperature of 25 °C were illustrated in Figs. 5 and 6, respectively.

According to these findings the presence only of the metastable hydrates (CAH$_{10}$ and C$_2$AH$_8$) as crystalline products of hydration at investigated temperatures were noticed. However, after 1 day of hydration at temperature of 10 °C only CAH$_{10}$ is formed, while at temperature of 25 °C the mixture of CAH$_{10}$ and C$_2$AH$_8$ is created.

The 25mass% content of waste aluminosilicate causes an insignificant changes on the crystalline hydrates produced during first 24 h of hydration at both of the temperatures; only the formation of C$_2$AH$_8$ is slightly promoted by the presence of FBCC. Probably as a result of increase of thermal effect in wetting period. Next to the hydration products, the X-ray diffraction patterns of all of unreacted clinker phases of cement are still registered i.e. monocalcium aluminate, gehlenite and ferrite phases at both of studied temperatures. However, the intensity of the peaks originating from CA decreases noticeably when the spent FCC catalyst is used, especially at temperature of 25 °C.
The mechanism of the interaction of this waste aluminosilicate on early hydration of calcium aluminate cement involves various factors including nucleation action, the ability of the zeolite material to water absorption and adsorption of Ca\(^{2+}\) ions on the surface of addition grains or the liberation of the ions from catalyst into solution. However, during the analysis of the effect of spent FCC catalyst on hydration of calcium aluminate cement, the consideration of the impact of process temperature is necessary as in case of high aluminate cement discussed in detail at our earlier work [11]. Probably at lower temperatures, when the dissolution is less intensive and less mobility of the ions and molecules hinders the water penetration of cement particles, the presence of fine-grained and porous grains of the waste aluminosilicate results in extension of total surface of wetting thus the duration of the processes at the first stages after addition of water is prolonged. The increase in temperature intensifies the processes of hydration and probably, at 25 °C the fine grained FBCC grains with adsorbed Ca\(^{2+}\) ions provide a nucleation centers which are quickly covered with a layer of products and reduce the time of supersaturation and precipitation of hydrates. Moreover adsorption of Ca\(^{2+}\) on an acidic centers on spherical FBCC particles surface (Fig. 2) similar to natural zeolites when Si–OH, and Al–OH groups on the zeolite surface are dissociated to Si–O\(^-\) and Al–O\(^-\) [23] causes a decrease in the concentration of Ca\(^{2+}\) in bulk solution and promotes the further dissolution of monocalcium aluminate. It is possible that the same FBCC participates in the processes of dissolution and depolymerization, which is facilitated by high pH, so the formation of new types of products like CASH or CSH phases next to typical calcium aluminate hydrates might be supposed, however first mostly as an amorphous phases.

4. Conclusions

On the basis of obtained results it can conclude:
• this waste FCC catalyst causes a considerable increase of thermal effect in wetting period of hydration of calcium aluminate cement, the bigger the amount of the aluminosilicate the more intensive the effect is, regardless of the temperature of hydration.
• the influence of spent FCC catalyst on early hydration of calcium aluminate cement strictly depends on temperature of hydration process. At the temperature of 25 °C this waste aluminosilicate accelerates setting and hardening of cement, but at the temperature of 10 °C works as retarder. These changes are realized by variation of duration of the induction period and the bigger content of FBCC the bigger the effect is regardless of the temperature of hydration.
• the presence of this mineral waste causes a minor effect on the crystalline hydrates produced after 1 day of hardening; only the formation of C\(_2\)AH\(_8\) is slightly promoted by the presence of FBCC.
• the introduction of spent FCC catalyst clearly increases degree of CA hydration, especially at temperature of 25 °C.
• the formation of new types of products like CASH or CSH phases next to typical calcium aluminate hydrates is possible, however first mostly as an amorphous phases.