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Investigation of early hydration of high aluminate cement-based binder at different ambient temperatures

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Bretsznajder Special Chapter

Abstract The effect of spent FCC catalyst on early hydration (up to 48 h) of high aluminate cement (Al_2O_3 $>70\%$) at different ambient temperatures (10, 20, and 30 °C) was investigated. Cement pastes with constant ratio of water/binder = 0.35 (binder = cement + addition) and containing 0, 5, 10, and 15% mass of addition as replacement of cement were studied. The hydration kinetics was determined by calorimetric measurements and the structure of hardened binders after 2 days of curing at an appropriate temperature was also investigated using X-ray, SEM, and thermal analysis methods. Due to the fact that hydration of aluminate cements is highly sensitive to temperature conditions as well as certain changes of temperature are inevitable in practice, the evaluation of the impact of the waste catalyst addition in such conditions is justified. On the basis of obtained results, it was stated that the temperature determines the early hydration of high aluminate cement and decides about the influence of waste aluminosilicate. The introduction of the discussed addition has a big impact on the kinetics of cement hydration closely related to the curing temperature. The presence of spent catalyst accelerates the hydration at the temperatures of 20 and 30 °C, but at the temperature of 10 °C this waste aluminosilicate acts as a retarding agent. The effect of the addition on the microstructure of hardened binders after 48 h of hydration is rather insignificant, especially at 20 °C, compared to the influence of the temperature on hydration. At the temperature of 10 °C, a formation of low amount of C_2AH_8 can be observed because of the presence of spent catalyst, while at the temperature of 30 °C the introduction of the mineral addition prevents the hydrogarnet formation.

Keywords High aluminate cement · Spent FCC catalyst · Hydration · Curing temperature · Calorimetry

Introduction

Calcium aluminate cements (CAC) are special hydraulic binders, especially used in refractory concretes. Castable refractories containing CAC are used in different furnaces lining applications in ceramic, cement, glass, iron and steel, petrochemical and others industries [1]. Special properties including high early strength, resistance to chemical attack, fire resistance or resistance to abrasion are the reasons for applying these types of cement also in construction [2].

Different new additives (including nano-sized) are used for developing new materials with CAC (binders, mortars, concretes). The developed materials can be significant for their enhanced properties [3]. However, the modern refractory castables are built by multi-composites systems, the CAC compound plays still a fundamental role to achieve sufficient strength and to create a microstructure which is responsible for final characteristic and application of the concrete at high temperatures [4]. Preparation of such quality product based on aluminate cement requires extensive studies. It is difficult to predict the hydration process of new cement-based materials, because not only the influence of addition on hydration of this cement is

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important, but also the hydration process of such materials is very sensitive to manufacturing conditions: ambient temperature, mixing parameters, water quantity and quality, etc., therefore sometimes producers fail to make so quality product [1, 4].

It is well-known that the hydration process of CAC is involved hydroxylation of the cement surface followed by dissolution of an anhydrous clinker phases with liberation of calcium and aluminum ions, nucleation and then precipitation of the hydrates from solution. There are four hydrates which can be formed during hydration: CAH_{10}, C_2AH_8, AH_3, and C_3AH_6 (according to abbreviations used in cement chemistry and thereby in this work: C—CaO, A—Al_2O_3, H—H_2O) [2, 4–8]. One of the most significant conditions deciding about the kind of created products is the temperature of hydration. Below ca., 15 °C, CA—the main hydraulic phase of aluminate cements, hydrates to give CAH_{10}; at the temperature of ca., 15–25 °C, mixtures of CAH_{10} and C_2AH_8 are produced with an increase in the quantity of C_2AH_8 when the temperature rises. Above ca., 25 °C to at least 40 °C, C_2AH_8 is the main hydration product formed together with hydrous alumina, firstly as alumina gel, which crystallizes with time to gibbsite AH_3. When temperature rises above 40 °C and especially up to 60 °C, the hydrogarnet phase C_3AH_6 is formed, alongside hydrous alumina which gradually changes to gibbsite [5]. However, it should be noticed that the temperature ranges are not exact and some divergent information especially at about ambient temperatures is stated in literature; for example in [4], author proposed that the C_3AH_6 and AH_3 are formed above 27 °C. The structure of hydrating CAC matrix is very complicated and effected not only by the curing temperature. Moreover, the CAH_{10} and C_2AH_8 are metastable products and inevitably convert to the stable C_3AH_6 and AH_3 phases depending on time, temperature, humidity or pH [2, 8–10].

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, exhibits zeolite-type structure and pozzolanic properties [10–20]. It was confirmed that the presence of the waste catalyst modifies the hydration of CACs at ambient temperature by the formation gehlenite hydrate also called strätlingite, which is clearly visible after long time of hydration. Although the reactivity of addition is strongly dependent on the kind of aluminate cement used [10]. At early ages this addition accelerates the hydration at the temperature of 25 °C of various kinds of CAC [17, 20]. The usage of spent FCC catalyst in refractory applications [18] as well as the influence of the heat-treated zeolite waste on hydration of high aluminate cement [17, 19] was also considered.

The aim of this work was to investigate the influence of spent FCC catalyst on the hydration of high aluminate cement (commonly used in refractory concretes—Al_2O_3 >70%) at first 2 days of hardening at different ambient temperatures (10, 20, and 30 °C). The effect of the addition on hydration kinetics was studied by calorimetric measurements and the structure of such hardened binders by X-ray, SEM, and thermal analysis methods was also investigated. Taking into account a changing temperature in practical working conditions in moderate climate and temperature-dependence of hydration of aluminate cement, the evaluation of the impact of the waste catalyst addition under the conditions proposed in this work is needful.

Experimental

Materials

The studied samples were prepared with:

- *High aluminate cement* of grade Górkal-70 produced by the Górka company (Poland). Its chemical composition is (mass%): Al_2O_3 70.2, Fe_2O_3 up to 0.3, CaO 28.0. The main minerals are CA ($CaO \cdot Al_2O_3$) and CA_2 ($CaO \cdot 2Al_2O_3$), the additional phases are $C_{12}A_7$ and α-Al_2O_3. Its refractoriness is 1690 °C, its specific surface area 0.42–0.45 m^2/g, and bulk density 1.1 g/cm^3 [21].
- *Fine-grained spent catalyst* waste (sizes of particles 20-100 μm, average particles size is ~42 μm). It exhibits zeolitic structure. Its chemical composition is (mass%): Al_2O_3 39.4, SiO_2 50.1, Fe_2O_3 1.3, SO_x 2.3, CaO 0.5, MgO 0.49, Na_2O 0.2, K_2O 0.07, Mn_2O_3 0.06. Bulk density 945 kg/m^3. Its specific surface area is ~100 m^2/g. Calcination loss at 1000 °C temperature is about 5% [10, 19].
- *Distilled water*

Cement pastes were made with constant water/binder ratio = 0.35 (binder = cement + addition). Spent catalyst was introduced as 0, 5, 10, or 15% by mass of binder.

Methods

The following experimental equipment was used:

- For the calorimetric measurements—a differential isothermal calorimeter ToniCAL III—the mixes (35 g distilled water and 100 g of solid substance) were studied at the appropriate temperature (10, 20, or 30 °C) and the heat evolution curves were registered up to 48 h of hydration;
- For thermoanalytical studies—thermoanalyser STA PT-1600, operating at temperatures ranging up to 1000 °C in air, at heating rate of 10°C min^{-1}, sample

mass of $\sim$55 mg. The TG and DTG curves of each sample after 48 h of hydration were registered;

- For the X-ray phase analyses—DRON-7 diffractometer (anticathode—cooper, anode voltage 30 kV, anode current 12 mA). The phase composition of each sample after 48 h of hydration was identified using data from the ICDD database;
- For SEM tests—JEOL JSM-7600 F—the microstructure of each prepared sample after 48 h of hydration was observed.

Results

Determination of the kinetics of the hydration process by calorimetric measurements

Calorimetric measurements constitute a very useful method for examining the kinetics of the hydration process. After adding water to cement, a sequence of physiochemical transformations occur which condition the binding and hardening of cement, inter alia wetting of cement particles, dissolving anhydrous phases of clinker, their hydrolysis, and then nucleation and crystallization of hydrated products. 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. The initial minor increase in the amount of heat release 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 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 [17, 22–24].

The calorimetric results of pastes of high aluminate cement, in which part of cement was replaced with an additive of waste aluminosilicate (0, 5, 10, 15%, respectively), conducted at various hydration temperatures (10, 20, and 30 °C), are presented in the form of curves of a heat released rate (dQ/dt [Jg^{-1} h^{-1}]) in Fig. 1. Moreover, the characteristic of the quantity of heat released (Q [J/g]) at specific times of the process (1, 6, 12, 18, 24, and 48 h) is shown in Fig. 2.

On the basis of data presented it may be noticed that temperature is crucial for the kinetics of hydration of all the samples under examination. The change of temperature from 10 to 30 °C results in sudden changes of the values of heat released, as well as it influences the heat released rate both for samples with, and without the additive of the waste catalyst. The increase of the curing temperature results in a significant increase of the heat released irrespective of the presence of the additive. The samples hydrated at the temperature of 30 °C show the highest values of heat released and even when 15% of cement is replaced with spent catalyst the amount of Q [J/g] are higher than for the hydration of pure aluminate cement pastes, which was conducted at 20 or 10 °C. After 48 h, the highest amount of heat, i.e., 405 [J/g] is released by the pure cement paste hydrated at 30 °C, whereas the lowest values of Q refer to samples cured at the temperature of 10 °C with 10 and 15% of a mineral addition, $Q = 252$ [J/g] and $Q = 255$ [J/g], respectively. In the case of samples without spent FCC catalyst, the increase of temperature from 10 to 20 °C results in an increase of the total amount of heat released after 48 h by only 22 [J/g], whereas in the case of a temperature increase from 20 to 30 °C difference Q amounts to as much as 108 [J/g]. This trend is also visible in the case of appropriate pastes of which the part of

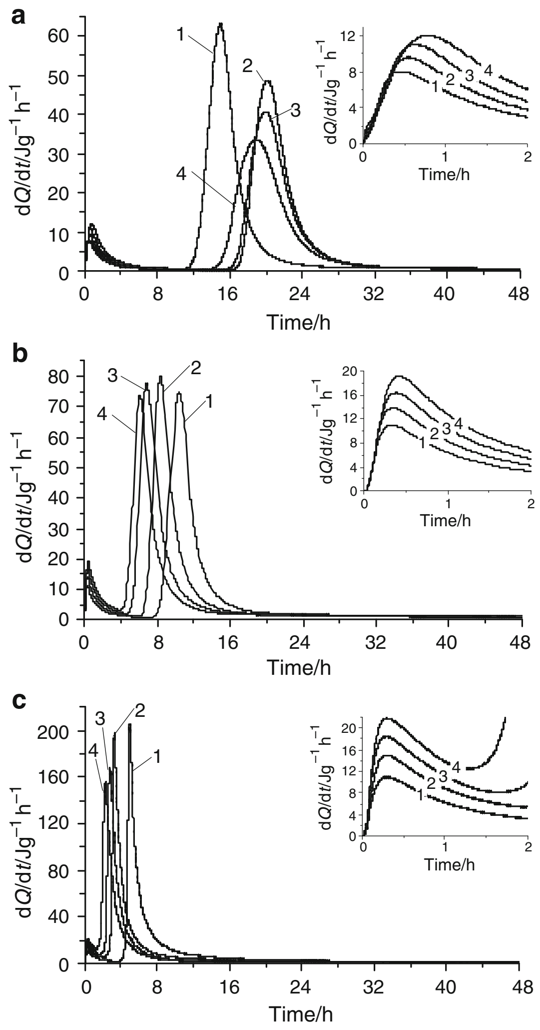


Fig. 1 Heat evolution curves for high aluminate pastes hydrated at temperature **a** 10 °C, **b** 20 °C, and **c** 30 °C and containing *1* —0%, *2*—5%, *3*—10%, and *4*—15% addition of waste aluminosilicate

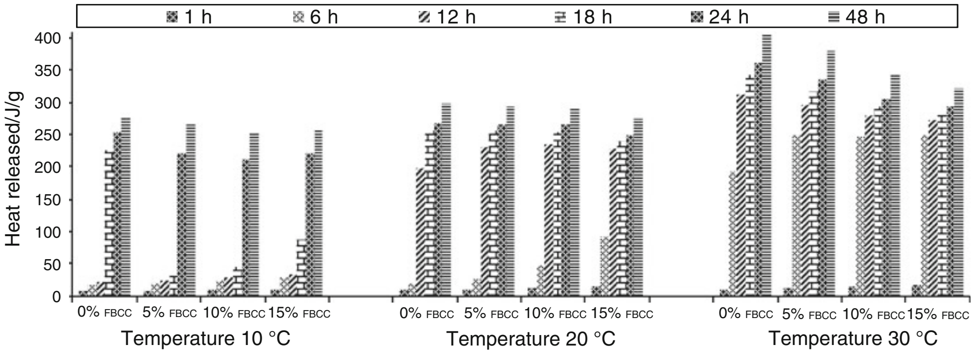


Fig. 2 Characteristic of the heat released during hydration of studied high aluminate-based binders at different ambient temperatures

cement was replaced by waste aluminosilicate. The differences of hydration temperature change not only the amount of heat released, but they also result in considerable differences in heat released rate (Fig. 1). Although the first maximum reached at the wetting stage does not show significant differences in the case of pure cement pastes neither regarding its occurrence, nor regarding the value along with the temperature increase, the second maximum undergoes significant changes. Along with the temperature increase, the moment of massive precipitation of hydrates, obtained through the shortening of the induction stage, takes place much more rapidly. At the temperature of 10 °C, this second maximum occurs 15 h after contact cement with water and with the value of $\mathrm{d}Q/\mathrm{d}t = 63$ $[\mathrm{J\ g^{-1}\ h^{-1}}]$, whereas at the temperature of 20 °C, it is obtained after 10.5 h with the value of $\mathrm{d}Q/\mathrm{d}t = 75$ $[\mathrm{J\ g^{-1}\ h^{-1}}]$, and at the temperature of 30 °C as early as after 5 h, with the value of $\mathrm{d}Q/\mathrm{d}t = 206$ $[\mathrm{J\ g^{-1}\ h^{-1}}]$.

After introducing waste catalyst of fluid catalytic cracking into paste its influence on the course of calorimetric curves is determined mostly by the value of the curing temperature, and not by the amount of introduced additive. Whereas the shortening of the induction process with simultaneous acceleration of the precipitation of hydrated products caused by the presence of catalyst occurs at the temperature of 20 and 30 °C, at the temperature of 10 °C the additive of waste aluminosilicate exhibits adverse performance thus prolonging the induction stage, and inhibiting the precipitation of hydrates. Moreover, the higher the content of the additive, the greater the effect of accelerating hydration by the catalyst at 20 and 30 °C, whereas at the temperature of 10 °C, the inhibition of hydration is the lowest with the biggest quantity of aluminosilicate. At the stage of wetting the addition of FBCC causes increase of the value of the first maximum on the $\mathrm{d}Q/\mathrm{d}t$ curves, the bigger the increase, the bigger the additive content and the higher the curing temperature, although only at 30 °C this maximum occurs after 0.3 h regardless of the presence of waste, whereas at lower temperatures this effect slows down slightly, the greater the content of the catalyst and lower hydration temperature, the more it decelerates. The second maximum on the $\mathrm{d}Q/\mathrm{d}t$ curve undergoes a shift towards shorten hydration times at both 20 and 30 °C, and the more cement was replaced by the catalyst, the greater the extent of this shift is. In the case of hydration at the temperature of 30 °C, this acceleration of the second maximum is combined with decrease in its value along with an increase of the additive content. For the paste with 15% FBCC, this maximum occurs at 2.3 h with $\mathrm{d}Q/\mathrm{d}t$ equals 156 $[\mathrm{J\ g^{-1}\ h^{-1}}]$, while in case of pure cement paste it is reached after 5 h and amounts to 206 $[\mathrm{J\ g^{-1}\ h^{-1}}]$) (Fig. 1c). The more additive the binder contains, the lower the total value of heat released after 48 h was obtained (Fig. 2). When hydration was conducted at the temperature of 20 °C, the shift of the second maximum on the $\mathrm{d}Q/\mathrm{d}t$ curve towards shorten hydration times is combined with an increase of its value for 5 and 10% of aluminosilicate, and for 15% of the content of waste remains at a comparable level to a sample without the additive (Fig. 1b). The amount of heat evolved after 48 h for pastes with 5 and 10% of the FBCC does not practically differ from the reference sample, and for 15% of spent catalyst it is only slight lower than for pure cement paste (Fig. 2). At the temperature of 10 °C, the value of the second maximum $\mathrm{d}Q/\mathrm{d}t$ becomes smaller along with an increase in the amount of the mineral addition into paste similar as at 30 °C, but at 10 °C the maximum shifts towards later hydration times. For a sample with 5% catalyst content, it is reached at the latest—over 20 h after adding water to binder and for 15% of the additive it is earlier—18.8 h but still later in comparison to pure cement paste (Fig. 1a). The total amount of Q after 48 h in case of pastes with waste aluminosilicate is only insignificant lower than the reference sample (Fig. 2).

Determination of the microstructure of hardened binders by XRD, SEM, and TG/DTG analysis

The results of the XRD, TG/DTG, and SEM analyses obtained for the samples under examination after 2 days of hydration are presented in Figs. 3, 4, and 5 respectively.

Fig. 3 X-ray diffraction patterns of cement pastes made of high aluminate cement and containing *1*—0%, *2*—5%, *3*—10%, and *4*—15% addition of FBCC after 2 days of hydration at temperature of: **a** 10 °C, **b** 20 °C, and **c** 30 °C

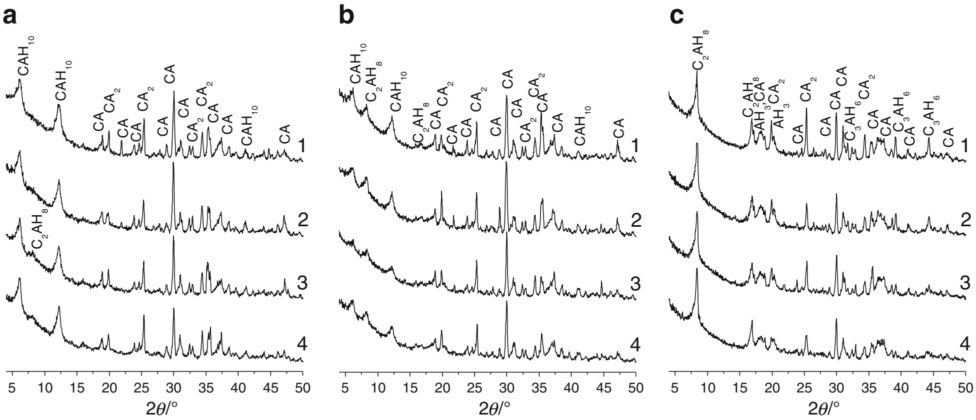
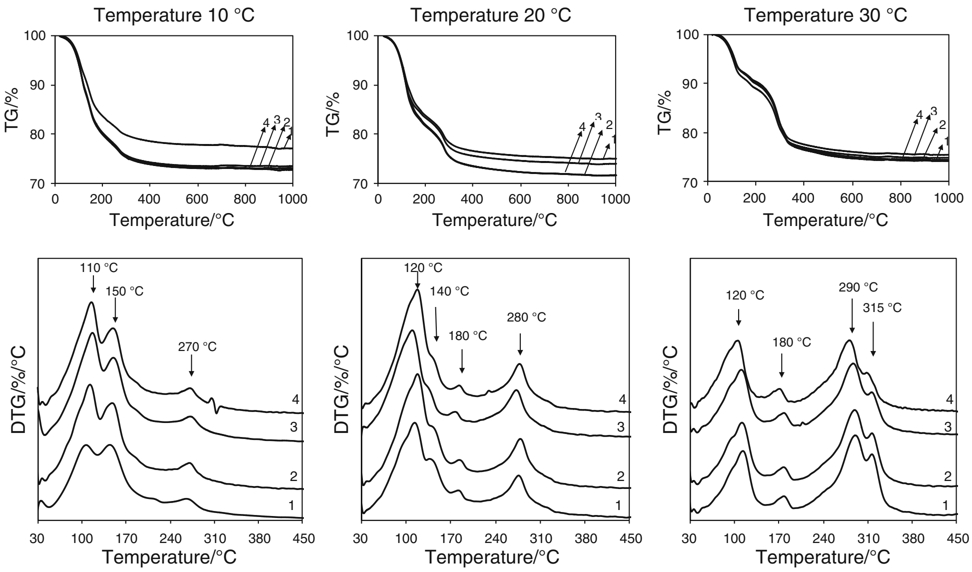


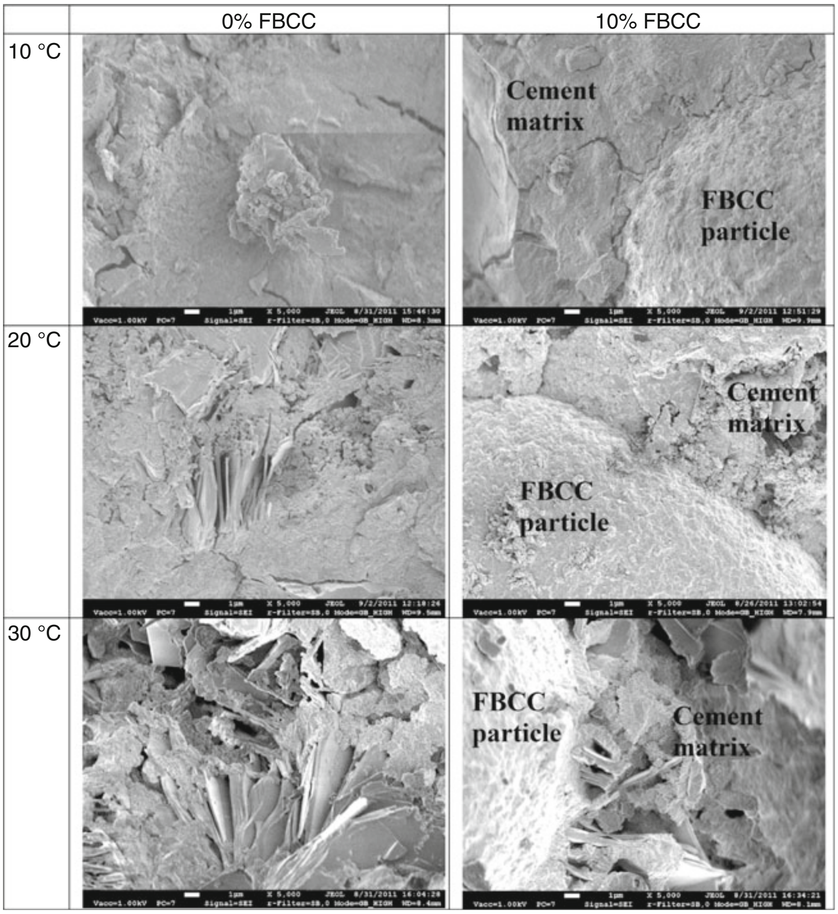
Fig. 4 Thermal analysis (TG/DTG) of cement pastes made of high aluminate cement and containing **1** – 0%, **2** – 5%, **3** – 10% and **4** - 15% addition of FBCC hydrated 2 days at temperature of: 10 °C, 20 °C and 30 °C



The results presented show the quality of the microstructure of the examined binders and confirm the importance of temperature for hydration. Despite the fact that the change in temperature occurs only every 10 °C, this already considerably changes the type of hydrates formed. On the basis of X-ray results, it needs to note that unreacted clinker phases of cement type CA and CA_2 are still present; however, the intensity of the diffraction peaks originating from CA decrease noticeably along with an increase in the hydration temperature (Fig. 3). The XRD analysis indicates that in the case of pure aluminate cement paste, which hydration occurs at the temperature of 10 °C, the only one kind of crystalline hydrate—CAH_{10} is identified. The AH_3 phase (gibbsite), the presence of which in the paste can be related with a peak on the DTG curve at 270 °C (Fig. 4) [9, 10] is probably poorly crystalline. The analysis of SEM images confirms a compact, packed, and amorphous structure of the paste (Fig. 5). An increase in the hydration temperature up to 20 °C results in a decrease in the intensity of the peaks of the CAH_{10} phase on X-ray diffraction patterns, as well as an increase in the value of the AH_3 peak of the DTG curve in comparison to a sample hydrated at 10 °C. Moreover, the diffraction peaks of C_2AH_8 phase (Fig. 3b) are also identified. The presence of C_2AH_8 in this paste is also confirmed by the peak at 180 °C on DTG results (Fig. 4) [9, 10]. Small plates of C_2AH_8 are observe on the SEM pictures (Fig. 5), despite the fact that the structure is still fairly compact. In the case of hydration at the temperature of 30 °C, the CAH_{10} phase does not occur, and besides metastable C_2AH_8 the crystallite gibbsite AH_3 is formed, as well as small amounts of the C_3AH_6 phase, which are confirmed by X-ray patterns as well as the presence of peaks on the DTG curves, at 290 and 315 °C, respectively [9, 10]. The SEM images confirm an increase of crystallinity of the microstructure and the presence of well-formed C_2AH_8 plates.

When comparing the pastes which contain an additive of spent FCC catalyst and these without the additive, it is

Fig. 5 SEM images of high aluminate cement pastes with 0 and 10% of spent FCC catalyst after 2 days of hydration at temperature of 10, 20, and 30 °C



noticeable that waste aluminosilicate itself has a slight influence on the structure developed during 2 days of hydration in comparison to the effect of curing temperature. The temperature of the hydration process determines the influence of aluminosilicate, i.e., its ability to “incorporate” into the hardened paste (Fig. 5) and its effect on the quality of hydrates formed (Fig. 3 and 4). At the temperature of 10 °C, a higher value of the catalyst (10 and 15%) can favor the formation of C_2AH_8 (Fig. 3a), whereas at the temperature of 30 °C, the presence of the catalyst inhibits the formation of C_3AH_6, (Fig. 3c, 4). The thermal analysis confirms an increase in the content of hydration products within the range of dehydration temperatures of 30–170 °C, when the paste contains spent catalyst, the bigger amounts of these products the lower temperature of hydration was (Fig. 4). Within this range of dehydration of C–A–H gel and CAH_{10} or C_2AH_8 hydrates occurs and the dehydration of C–S–H or C–A–S–H phases is also possible here, although these phases might occur only in the samples with aluminosilicate additive [10, 19, 24]. However, the samples have not undergone the stopping of the hydration process and the presence of chemically unbounded water needs to be taken into account as well.

Discussion

At the first stage after addition of water to aluminate cement, the hydroxylation of cement grains, dissolution and hydrolysis of clinker phases lead to release of Ca^{2+} and $Al(OH)_4{}^-$ ions into solution with simultaneous increase of pH, as suggested in reactions 1 and 2 [25]:

$$Ca(AlO_2)_2 + 4H_2O \leftrightarrow Ca^{2+} + 2Al(OH)_4^- \tag{1}$$

$$Al(OH)_4^- \leftrightarrow Al^{3+} + 4OH^- \tag{2}$$

As a result a small exothermic effect in the wetting period on calorimetric curves is observed (Fig. 1). At the subsequent stage of induction in which the heat released is inhibited, the following dissolution of anhydrous calcium aluminates as well as nucleation of hydrates progress and the concentrations of ions remain near their maximum values and the rates of dissolution and precipitation thus being approximately equal [8, 25]. This cyclic process of ion dissolution–precipitation proceeds until most (or all) of the anhydrous cement particles exposed to water are consumed. The products nucleate and grow until a saturation point is reached and when the nuclei have grown to a critical size and quantity a rapid and massive precipitation of hydrates occurs. It is followed by a strong exothermic effect and a maximum of the rate of heat released is obtained (Fig. 1). However, the hydration reactions occur by congruent dissolution followed by precipitation it should be noticed that the nucleation takes places rather at the surface of anhydrous grains than in solution and a layer of hydrated products forms around cement particles and hinders the penetration of water [6].

The lower solubility of hydrates compared to the anhydrous cement phases is the driving force of hydration reactions and massive precipitation of hydrates when the solubility limit is reached. In the case of aluminate cement, different products of hydration can arise and these hydrates present the following order of solubility: $C_3AH_6 < C_2AH_8 < CAH_{10} < AH_3$. The formation of less soluble hydrates will mean an increase in the precipitation. In contrast, the most soluble hydrate (AH_3) requires a longer induction period [4, 25]. Moreover, in contrast to Portland cement hydration in which created hydrates remain broadly similar with time and curing temperature, in case of aluminate cements the kind of hydration products is highly dependent on temperature [4]. This fact was confirmed by the analysis of the structure of hardened cement pastes presented in this study (Figs. 3, 4, 5). In addition, the results obtained from calorimetric measurements (Figs. 1, 2) indicate that the temperature decides not only about the hydration products but it also determines the kinetics of the hydration process. The decrease in curing temperature causes retardation of the precipitation of hydrates realized by extension of the nucleation period what can be connected with the type of the hydration products. As suggested in Figs. 3 and 4 in period of early hydration (after 48 h) CAH_{10} is the major hydrate created at temperature of 10 °C, at 20 °C—C_2AH_8 together with CAH_{10} are formed whereas at 30 °C the main hydration products are C_2AH_8 and AH_3 with a small amount of C_3AH_6. According to the solubility series of hydrates, the most soluble is CAH_{10} what probably caused the longest induction stage for sample cured at the lowest studied temperature of hydration (10 °C). If the solubility of hydrates is lower, the precipitation of such kind of products is faster, therefore the formation of C_2AH_8, and especially C_3AH_6 shortens the induction period. The formation of C_2AH_8 at the temperature of 20 °C can be related to the affect of $C_{12}A_7$ phases in cement clinker. The $C_{12}A_7$ enhances the CA reactivity catalytically and reacts with water to produce C_2AH_8 already at lower temperature according to reaction 3 [5]:

$$C_{12}A_7 + 51H \rightarrow 6C_2AH_8 + AH_3 \tag{3}$$

On the other hand, the solubility of anhydrous cement grains increases with an increase in temperature due to the liberation of Ca^{2+} and $Al(OH)_4^-$ ions into solution is more intensive and the solubility limit of C_2AH_8 or C_3AH_6 is rapidly reached. The increase in the total heat released after 48 h of hydration (Fig. 2) as well as the analysis of X-ray diffraction patterns (Fig. 3) confirm the higher degree of CA hydration with an increase in curing temperature.

However, there are opinions in literature about a more complicated relationship between hardening of aluminate phases and curing temperature. The setting time of monocalcium aluminate usually shortens between 0 °C and about 20 °C, but at 28-30 °C it can be up to 8 times as long as at 20 °C. Above 30 °C, it again shortens very rapidly [8]. Authors of work [26] proposed that the anomalous setting behavior is caused by the fact that none of the hydrated calcium aluminates can form readily in the range 25–30 °C. The nucleation of CAH_{10} is no longer favored on thermodynamic grounds, while the rate of formation of C_2AH_8 is very sluggish, and C_3AH_6 can only be formed via conversion of these metastable hydrates in this temperature range. Hence precipitation of the hydrate crystals to produce a set cement takes longer than at other temperatures.

The presence of different mineral admixtures in aluminate cements binder influences the kinetics of hydration process at temperature 25 °C and this effect is strongly dependent on quality and quantity of the additions. Presented in work [24], calorimetric curves prove that introduction of 5% as well as 25% of fly ash from fluidized combustion of hard coal or Portland cement as a replacement part of aluminate cements accelerates the hydration at 25 °C to a greater degree when larger amount of additive was applied. In the case of binders containing fly ash from pulverized combustion of hard coal, the 25% amount of the addition accelerates the hydration, whereas 5% of conventional fly ash shows insignificant deceleration effect in comparison with paste without any additions. The calorimetric investigations of influence of spent FCC catalyst on the hydration kinetics of aluminate cements at the temperature of 25 °C [17, 19] or at 20 °C [20] indicate that the waste acts only as an accelerating agent. The impact is greater the larger the mass fraction of waste aluminosilicate and it is retained, even when the catalyst previously treated at high temperature is used [19, 20].

The mechanism of the interaction of discussed waste aluminosilicate on cement hydration stated in literature [10–20] concerns especially Portland cement mixtures [11–16]. Several factors have to be considered around the influence of this mineral addition. Spherical, porous and fine grains of FBCC with a developed specific surface are the additional element next to cement particles which become wetted during the first minutes after adding water to binder [17, 20]. Moreover, this aluminosilicate material exhibits zeolite structure so that it can absorb water [11, 20, 27]. As a result, an increase in the local water/binder ratio might occur. Simultaneously, as suggested in work [14] in the basic media of cement hydration, the aluminosilicate structure present in pozzolanic materials is broken and depolymerized and may be dissolved by reactions 4 and 5.

$$^{3+}\mathrm{Si{-}O{-}Si}^{3+} + 6\mathrm{OH}^- \rightarrow 2\left[\mathrm{SiO(OH)}_3\right]^- \quad (4)$$

$$^{3+}\mathrm{Si{-}O{-}Al}^{3+} + 7\mathrm{OH}^- \rightarrow \left[\mathrm{SiO(OH)}_3\right]^- + \left[\mathrm{Al(OH)}_4\right]^- \quad (5)$$

According to an another theory, spent catalyst has an open framework structure with silicon and aluminum oxides, thus a lot of silicon and aluminum atoms are at the external surface of crystals, giving rise to a high surface energy and indicating the presence of a high quantity of boundary silicon and aluminum atoms, which would act as acidic centers suitable for realization of the pozzolanic reaction [11, 12]. There is most probably that as in case of natural zeolites Si–OH, and Al–OH groups on the zeolite surface are dissociated to $\mathrm{Si{-}O^-}$ and $\mathrm{Al{-}O^-}$ [27]. These ionic centers on the surface of spent catalyst grains can adsorb the Ca^{2+} occurring from dissolution of cement particles [13], so the concentration of Ca^{2+} in bulk solution might decrease by the presence of introduced material and the further hydration reactions of anhydrous phases could be promoted. On the other hand as a fine grained material, FBCC can provide a nucleation center for the precipitation products of cement hydration, thus it can change the rate of the hydration process [11, 12, 17, 19].

A detailed explanation of the mechanism of the interaction of waste aluminosilicate on aluminate cement hydration at 25 °C is proposed in work [17]. The experimental results obtained in this study and presented in Fig. 1 indicate that during the analysis of the effect of the spent catalyst on the kinetics of hydration of alumina cement, the impact of process temperature could not be ignored. The hydration process of high aluminate cement-based binders is accelerated by the presence of the additive only at temperatures of 20 and 30 °C, whereas at 10 °C, the waste aluminosilicate acts as a retardant. 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 spent FCC catalyst results in extension of total surface of wetting thus the duration of the processes in the first stage after the addition of water is prolonged. As an evidence, only at temperature of 10 °C, the slight shift towards later times of first maximum on calorimetric curves is observed (Fig. 1a). The increase in the content of the introduced waste aluminosilicate causes probably greater absorption of water by the catalyst grains and more reduction the value of local *w*/*b* ratio with simultaneously increase of adsorption on the catalyst grains the Ca^{2+} ions from solution. As a result, a moment of supersaturation and mass precipitation of hydrates takes place faster for 15% content of addition replacement part of cement than for an amount of 5 or 10% this aluminosilicate, but it still later than for the paste without FBCC. Formation of little quantity of $\mathrm{C_2AH_8}$ even at 10 °C in binders containing 10 or 15% of addition (Fig. 3a) might also confirm the aforementioned mechanisms of action of spent catalyst. Moreover, the decrease in intensity of diffraction patterns described CA phase in presence of spent FCC catalyst (Fig. 3) as well as insignificant difference in total heat released after 48 h even for 15% substitution of cement compared to pure cement sample (Fig. 2) indicate that on the one hand lower concentration of Ca^{2+} in solution promotes further dissolution of cement clinker, on the other hand the chemical activity of waste aluminosilicate at the first stages of hydration can be supposed. It is possible that the same FBCC participates in the processes of dissolution and depolymerization according to reactions 4 and 5, which is facilitated by high pH and prolonged duration of induction, so the formation of new types of products like CASH or CSH phases next to typical calcium aluminate hydrates could be considered. Although the analysis of DTG curves obtained at the temperature of 10 °C (Fig. 4) seems to confirm this statement, yet the explicit identification of such phases is difficult due to their amorphous and gel form with simultaneously poorly crystalline structure of the pastes (Fig. 5).

At the curing temperatures of 20 and 30 °C, the acceleration of hydration by the presence of FBCC is clearly visible. The effect is the larger the higher the temperature of hydration and higher content of spent catalyst. The increase in temperature intensifies the processes of hydration and also promotes crystallinity of hydrates. However while at temperature of 20 °C, the presence of waste aluminosilicate causes an insignificant change in the value of heat evolved after 48 h, at 30 °C the effect of “dilution of cement” is seen clear as a reduction in the value of *Q*. The more cement was replaced by the addition the more reduction of *Q* in comparison to a reference sample is observed. On the other hand, if at 20 °C changes in the structure after 48 h of hardening are negligible, at 30 °C introduction the spent catalyst affects more clearly the quality of the products of hydration by limiting formation of $\mathrm{C_3AH_6}$ phase. Probably, at 30 °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 ability of waste aluminosilicate to absorb water. No major changes on the thermal analysis results in 30–170 °C of temperature decomposition of the hydrates (Fig. 4) and favoring the formation of $\mathrm{C_2AH_8}$ instead of $\mathrm{C_3AH_6}$ compared to pure cement paste (Fig. 3) can confirm presented assumption. However, the total value of heat released after 48 h is larger for the sample hydrated at 30 °C even with 15% amount of FBCC than for pastes without the addition cured at lower temperatures.

Although the new CASH crystalline products have not been identified in the experimental findings, the changes of formed structure caused by the presence of FBCC are observed. Based on the experimental results of hydration of aluminate cement pastes containing spent FCC catalyst at temperature of 25 °C published in Ref. [10], a new hydrate described as strätlingite C_2ASH_8 was identified at later curing times. Similar results were presented in works [7, 9, 28] concerning the influence of such mineral addition as ground granulated blast furnace slag, fly ash or silica fume on hydration of aluminate cement. The microstructure of the investigated in this study samples probably also is not stable and over time will be transformed, therefore the complex mechanism of the interaction of waste catalyst in the alumina cement-based binders requires further study.

Conclusions

- The curing temperature decides about the kinetics of the hydration process and also determines the microstructure of hardened aluminate cement paste. The change in temperature of hydration from 10 to 30 °C causes significant differences. When the temperature rises considerably, the increase of total heat released after 48 h of hydration and a clear acceleration of the process realized by the shortening of induction period are observed. Typical hydrates of high aluminate cement are identified as well as unreacted clinker phases still present on the 2nd day of hydration. At lower temperatures only thermodynamically metastable hydrates CAH_{10} and C_2AH_8 are formed whereas at 30 °C a little amount of stable hydrogarnet (C_3AH_6) is already created. The increase in the temperature of hydration promotes the formation of more crystalline gibbsite (AH_3) and causes higher degree of CA hydration.
- The temperature of hydration is the factor deciding about the impact of the spent FCC catalyst on the hydration of high aluminate cement-based binders including its effect on kinetics of process as well as the structure formed after the first 2 days of hardening.
- The introduction of waste aluminosilicate as a replacement part of high aluminate cement modifies the kinetics of hydration of such composite pastes at all studied curing temperatures. In the wetting period, the slight increase in heat released is detected, the higher, the bigger content of FBCC regardless of the temperature of hydration. While, the total heat evolved after 48 h at temperature of 10 and 20 °C shown low differences caused by the presence of spent catalyst, at 30 °C a significant reduction in the value of Q can indicate the effect of "dilution of cement," the bigger the reduction the more of additive was used compared to reference sample. The acceleration of the rate of hydration of high aluminate cement caused by the presence of the mineral addition was confirmed only at the temperatures of 20 and 30 °C. When the temperature of hydration is 10 °C the FBCC acts as a retarding agent. The modification of the kinetics of hydration of the studied binders is realized by variation of the duration of the induction period. The reduction of the induction time and faster precipitation of hydration products are observed at temperatures of 20 and 30 °C, the higher the more amount of spent catalyst was used, while at temperature of 10 °C, the presence of FBCC results in the elongation of the induction stage, the lowest with the largest content of the additive compared to the reference sample. The mechanism of the interaction of this waste aluminosilicate on high aluminate cement hydration kinetics involves several 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.
- The microstructure investigations of high aluminate-based binder on 2nd day of hydration indicate a greater effect of the curing temperature than the presence of the waste aluminosilicate. The introduction of spent FCC catalyst causes rather an inconsiderable influence on the crystalline hydration products. The formation of C_2AH_8 already at lower temperatures is favored and at temperature of 30 °C the formation of C_3AH_6 is prevented by the presence of the addition. These effects could be connected with chemical reactivity of waste aluminosilicate at the early hydration stages of aluminate cement and creation some amorphous CSH or CASH phases.
- The chemical reactivity of spent catalyst from the fluidized cracking installation at the first periods of aluminate cement hydration process is closely related to the kind of hydrates produced. The complex and complicated mechanism of the interaction of the waste aluminosilicate in hydrating aluminate cement matrix requires more research although the influence of curing temperature could not be ignored in such studies.

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