A study of the early hydration processes and properties of fly ash-slag binders

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Abstract. The results of a study on the early hydration process of pastes composed of ground granulated blast furnace slag and fly ash from fluidized bed combustion of brown coal are presented here. The results of the tests concerning setting time, hydration processes (spectroscopy, calorimetry and thermogravimetry) and mechanical strength confirm that the hydration process occurs and solid microstructures and hydration products (hydrated calcium silicates and aluminosilicates, sulphoaluminates and calcium hydroxide) are formed. The presence of calcium carbonate was confirmed. Increasing the amount of fly ash in pastes intensifies the process of early hydration, thereby accelerating the initial setting time and increasing the amount of water bound in hydration products. The early compressive strength is also improved. For example, the specimen containing the highest amount of fly ash showed a decrease in the initial setting time by about 20% and an increase in the 2-day compressive strength by 22%, compared to the specimen containing the lowest amount of fly ash.

Keywords. Slag–fly ash pastes; CFBC fly ash; granulated blast–furnace slag; calorimetry; spectroscopy; thermal analysis.

1. Introduction

Nowadays, in countries where the power industry mostly burns coal, great emphasis is put on the utilization of the waste from coal combustion in cement composites. This is the result of the necessity of limiting CO₂ atmospheric emissions from among other sources i.e., the cement production process. Such production generates annual emissions of about 800 kg Mg^{−1} of clinker [1]. Hence, the use of by-products instead of cement allows for a limiting of CO₂ emissions. Moreover, economic reasons have also forced a search for alternative (non-clinker) binders which can be used in concrete technology. Thus, the growing amount of by-products of coal combustion (slags and fly ashes) calls out for their use in accordance with the best climatic and circular economy policies.

Fly ashes produced during the conventional (pulverized) coal combustion process are well-understood. These have been used in cement and concrete production for many decades [2,3]. In coal combustion, the process of circulating fluidized bed combustion (CFBC) is now more often applied because of ecological advantages, but it generates a fly ash (CFBC fly ash) of different, specific properties (e.g., high water demand and great specific surface of ash grains) compared to typical, conventional fly ash coming from the pulverized combustion of coal. Such differences limit the

possibilities of using CFBC fly ash in cement and concrete technology. High amounts of calcium compounds, including anhydrous CaSO₄, bring about a situation wherein CFBC fly ash shows binding properties when mixed with water [4–7].

Ground granulated blast furnace slag (ggbf) is a valuable binding material used for portland slag cement production. When appropriately chemically activated, it reveals hydraulic properties in time of curing and phases that share the characteristics of portland cement [8]. In addition, slag composites show high water tightness and resistance to the impact of aggressive agents [9,10].

The papers presented in the literature [11–13] show the possibility of using a combination of slag and fly ash to compose pastes, but such combinations require the addition of highly alkaline chemical activators. The production of such composites is problematic due to safety needs and environmental impacts (contamination).

There are examples in the literature of the activation of slag by the addition of fluidized fly ash containing significant amounts of CaO and SO₃ [14], and also of recommended mixes of this type of fly ash with slag [15]. Indeed, promising results were obtained in our previous research concerning the hydration products and properties of CFBC fly ash–ggbf pastes and mortars after 28 and 90 days of hardening [16,17].

Considering the above, this paper presents the results of research into the early hydration process and the selected

properties of pastes composed of non-clinker binders and water. In this study, the binding reaction of ggbfs was induced by the addition of CFBC fly ash. According to the standard [2], this type of fly ash is not approved to be used for cement and concrete production. However, the mixture reveals suitable pozzolanic and hydraulic properties and seems to be a good non-clinker binder component. The aim of mixing these two components was to obtain a material with limited heat of hydration that may be used in mass concrete production where an increase in temperature within the element may be the main cause of microcracks in a binder matrix. A further aim was to ascertain the effect of utilizing the greatest possible amount of fly ash, so as to minimize the portland clinker as the binder component. The tests conducted within the previous experiment revealed that during the hydration process of non-clinker pastes containing ggbfs and CFBC fly ash from brown coal combustion, hydration products presenting good binding characteristics are formed which have a favourable development of compressive strength even before 28 days of curing [16]. The study confirms that the investigation of the properties of such pastes and their mechanisms of physicochemical changes during setting and early hardening is well-grounded. For this reason, the very early hydration period, i.e., the first 2 days after the addition of water to the binder, was selected for investigation in this particular paper.

The hydration processes of non-clinker binders are different from the well-known hydration process of portland cement, despite the fact that the products are often similar. Thus, an investigation of the hydration process (including its early stages) of new, atypical binders is important for broadening the knowledge and application possibilities, to determine the development of essential binder properties and for assessing the possibilities of their modification.

2. Materials and methods

2.1 Materials

In this work, pastes were prepared by mixing fly ash (CFBC fly ash) from the CFBC of brown coal and ggbfs with water. Prior to this, the fly ash underwent the process of mechanical activation. This resulted in separating the conglomerates of ash fractions and refreshing the grain surfaces without the change of their dimensions [18]. Both CFBC fly ash and ggbfs were analysed prior to the experiment. The results are as follows: the Blaine fineness of CFBC fly ash is equal to $4700 \text{ cm}^2 \text{ g}^{-1}$ and that of ggbfs is $3150 \text{ cm}^2 \text{ g}^{-1}$. The density of CFBC fly ash is 2.44 g cm^{-3} , and that of ggbfs is 3.17 g cm^{-3} . Figure 1 presents the particle size distribution of CFBC fly ash and ggbfs. The oxide composition of the applied materials (% by mass) is given in table 1.

These materials are composed of both amorphous and crystalline phases. The phase composition of CFBC fly ash (crystalline compounds identified with the X-ray diffraction method) revealed the presence of anhydrite, calcium oxide,

Figure 1. Particle size distribution of CFBC fly ash and ggbfs.

Table 1. Oxide composition of CFBC fly ash and ggbfs (according to EN 197-1 [19]).

Component (%) by mass or property	ggbfs	CFBC fly ash
SiO ₂ tot.	36.27	34.87
SiO ₂ react.	34.40	19.50
CaO tot.	45.15	21.10
CaO free	0.80	7.00
CaO react.	40.10	13.90
Fe ₂ O ₃	1.55	4.82
Al ₂ O ₃	9.15	23.09
MgO	5.86	1.69
SO ₃	0.67	5.66
Na ₂ O	0.01	0.02
K ₂ O	0.05	0.01
P ₂ O ₅	0.69	3.81
Cl ⁻	0.11	0.04
Loss on ignition	0.01	3.15

quartz, calcite, portlandite and hematite [16]. ggbfs is mainly amorphous (glassy). Small amounts of crystalline phases identified in ggbfs are: calcite, quartz and calcium silicate oxide [16]. CFBC fly ash is rich in pozzolanic and hydraulic components that are active in a aqueous environment. This results in the formation of a solid microstructure of CFBC fly ash composites.

As revealed in table 1, the total amount of CaO in CFBC fly ash is about 21% by mass, including free CaO (7%) (marked accordingly to EN 197-1 [19]). As a comparison, in ggbfs, the total amount of CaO is about 45% (free CaO is <1%). Furthermore, the total amount of SiO₂ is similar in both components and equals to about 35% by mass. With regard to aluminium compounds (as Al₂O₃)—much more can be found in CFBC fly ash (about 23% by mass) than in ggbfs (about 9% by mass). In addition, Fe₂O₃ is present in CFBC fly ash to an amount of about 5%, and in ggbfs, to about 1.5% by mass. Finally, sulphur compounds marked as SO₃ are present in CFBC fly ash to an amount of 6%, and in slag, to about 0.7% by mass.

Table 2. Proportions of ggbfs and CFBC fly ash in the binder of particular formulae (% by mass).

Formula number	Code of specimen	ggbfs, % by mass	CFBC fly ash, % by mass
1	70S/30FA	70	30
2	60S/40FA	60	40
3	50S/50FA	50	50
4	40S/60FA	40	60
5	30S/70FA	30	70

The pH of aqueous extracts of CFBC fly ash and ggbfs is equal to 12.7 and 12.4, respectively.

Pastes were prepared by mixing CFBC fly ash and ggbfs with water. In doing so, no chemical activators were used to induce the binding reaction of ggbfs. The proportions of components of pastes were chosen in such a way, to ascertain the possibility of mixing CFBC fly ash with ggbfs and to reveal the properties of the obtained pastes (table 2).

Specimens of pastes for early hydration investigation were prepared according to the presented formulae, utilizing a constant water/binder ratio equal to 0.5. Pastes for thermogravimetric analysis (TG/DTG) and Fourier transform infrared spectroscopy (FTIR) investigation were prepared manually by mixing the binder with water. These were placed into tightly closed polyethylene bags and kept at room temperature. After 2 days of curing, the pastes were taken out from the bags, ground and the process of hydration was stopped by the use of acetone.

Specimens for calorimetry studies were hydrated in a calorimeter for 48 h. Herein, measurements were conducted constantly beginning from the moment of addition of water to the dry binder.

The specimens for the mechanical strength tests were cast in prismatic moulds of $40 \times 40 \times 160$ mm, at the constant value of the water/binder ratio equal to 0.5. After setting (24 h), the specimens were taken out of the moulds and placed in a water bath of temperature $20 \pm 1^\circ\text{C}$ for one day until they reached 48 h of curing. Prior to the tests, the specimens were taken out of the water, wiped dry, measured and weighed.

The specimens used to investigate the setting time and soundness of CFBC fly ash–slag binders were prepared according to the standard EN 196-3 [20]. The amount of added water was varied to ensure that the pastes presented a standard consistency (water/binder ratios are presented in table 3).

2.2 Methods

The following tests were conducted on the obtained pastes:

- Initial and final setting time of pastes of standard consistency, *via* a Vicat apparatus, according to EN 196-3 [20];
- Soundness: according to EN 196-3 [20];

- Flexural and compressive strength: according to EN 196-1 [21];
- Infrared (IR) spectroscopy tests: by way of utilizing a spectrophotometer Genesis II FTIR (Mattson); the range of spectra: $4000\text{--}400\text{ cm}^{-1}$, specimens prepared in the form of KBr pellets;
- Calorimetry tests: *via* the BMR calorimeter constructed at the Institute of Physical Chemistry of Polish Academy of Sciences; temperature of thermostat: 25°C , binder mass: 10 g, water mass: 5 g; tests performed 48 h from the moment of adding water to the binder; the results presented as the amount and rate of heat emission were calculated by means of computer software; [22]
- Thermogravimetry (TG/DTG) tests: using a thermoanalyser SDT 2960 (TA Instruments); specimen mass: 10–17 mg, atmosphere: nitrogen and temperature rise: $10^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1 Setting time and soundness

The results of the initial and final setting times and soundness investigation of the obtained slag–fly ash pastes are presented in table 3.

The period between the initial and final setting time of all five formulae is about 80 min. It is noted that the more of CFBC fly ash and the less of slag that are added to the pastes, the shorter is the initial setting time. This decreases to an extent of 94 min from a maximum of 472 min for the 1st formula (70S/30FA) to 378 min for the 5th formula (30S/70FA) (table 3). Such results indicate that the more of CFBC fly ash is added, the faster the hydration reaction of CFBC fly ash–slag pastes is initiated. Hence, increasing the amount of CFBC fly ash, which exhibits some binding properties, results in accelerating the binding reaction. Synergy effects can be expected. Compounds such as CaO, $\text{Ca}(\text{OH})_2$ and CaSO_4 , the amount of which increase with the higher amount of CFBC fly ash in the test pastes, activate the slag, inducing its binding properties [23–25]. Of note, it is known that a good slag activator is a mix of gypsum and $\text{Ca}(\text{OH})_2$ [23].

The effects of CFBC fly ash and slag hydration are the first portions of products shaping the microstructure and transforming a ductile paste into its bound, solid form. In the case of time between the initial and final settings, the differences between pastes are quite minute, thus, the influence of CFBC fly ash addition on that parameter cannot be ascertained. With regard to water demand, certainly an increase in the CFBC fly ash amount results in a higher water demand (table 3).

An analysis of the results of the soundness test (table 3) indicates that pastes with the highest amount of CFBC fly ash exhibit the highest soundness (0.5 mm), and conversely, the pastes with the lowest amount of CFBC fly ash demonstrate

Table 3. The results of initial and final setting times and soundness tests conducted according to EN 196-3 [20] on five formulae of fly ash–slag pastes.

Formula	Code of specimen	Water/binder ratio	Initial setting time (min)	Final setting time (min)	Soundness, (mm)
1	70S/30FA	0.417	472	555	0.2
2	60S/40FA	0.435	465	548	0.3
3	50S/50FA	0.455	440	518	0.4
4	40S/60FA	0.501	387	470	0.4
5	30S/70FA	0.529	378	463	0.5

Figure 2. Heat released during 48 h of hydration of slag–fly ash binders (1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA).

the lowest soundness (0.2 mm). Therefore, it can be stated that the changes in the volume of the investigated pastes are induced by the CFBC fly ash addition, and occur because of the expansive phases that emerge during the hydration process. This may be the effect of the free CaO presence in the CFBC fly ash. Hence, the process of hydration results in a significant change in volume. Moreover, the increase in the amount of CaSO_4 promotes the formation of expansive ettringite [26]. Expansion may also be caused by MgO [23,27]. However, it needs to be emphasized that the soundness test results of all five formulae of fly ash–slag pastes do not exceed 10 mm, hence according to the EN 196-3 standard, the pastes are considered to be non-expanding.

3.2 Calorimetry

Calorimetry tests were conducted to evaluate the influence of the composition of the non-clinker binder on the kinetics of early hydration. The results are shown in figure 2 (total amount of heat emitted in a certain period of time) and figure 3 (rate of heat emission). As a comparison, in figure 4, the calorimetric curve of portland cement is shown.

In the case of portland cement hydration, the typical curve of the heat emission rate is well-known and described in the literature, for example, refs [28–30]. Five characteristic

Figure 3. Calorimetric curves of the rate of heat release during 48 h of hydration of slag–fly ash binders (1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA). **Figure 4.** Example of the heat emission rate curve of portland cement (periods I–V: explanation in text).

stages of hydration may be found (figure 4): I: stage of wetting, when fast emittance of relatively little amounts of heat is observed, II: induction period, III: period of an increase in the heat release rate connected with the precipitation of hydration products, IV and V: periods of a gradual decrease of heat emission and stabilization (paste is in a solid state form).

The replacement of cement by a material of lower activity, e.g., fly ash from the conventional process of coal combustion, depending on the amount of the entered additive, may lead to a longer induction period and a lower intensity of heat emission during the stage of hydration product precipitation, and a reduction in the total amount of heat emitted after 48 h of hydration [30,31]. The change in intensity of heat emission and duration of characteristic periods are particularly visible when the binder consists of a significant amount of pozzolanic substitutes of cement with little amounts of the clinker, as shown in the paper [31]. In some cases of such binders, period III may not be visibly separated within the curve.

In comparing the results shown in figures 2–4, it can be observed that with regard to the investigated non-clinker binders, the shape of the calorimetric curves is different from the typical curve known for cement. This indicates the existence of different kinetics of the hydration reaction and differences in chemical processes that are taking place.

On analysing figures 2 and 3, it can be observed that above all, with the slag–fly ash binder, an intense heat emission occurs in the first stage of wetting. This suggests that the most intense process of hydration occurs during the first 4 h. Moreover, when the effect is more intense, more CFBC fly ash is present in the binder. Such an effect is most probably caused by the high amount of CaO and anhydrite in CFBC fly ash and the high porosity of its grains. An increase in the heat emission rate observed within the first minute after adding water to the binder is the result of the wetting of the CFBC fly ash grains, the dissolution of components (mainly CaO exothermal hydration) and the beginning of the process of hydration. In the case of the investigated pastes, their induction period and the following period of the heat emission rate are very slightly distinguishable in contrast to the result for portland cement. It can be noticed that after the intense heat emission during the first few hours of hydration, further emission is at a moderate and almost constant rate. However, the continuity of the process during the investigated period of time indicates the progression of chemical processes in the tested configurations. Still, the kinetics of hydration is different from that of portland cement.

An increase in the released heat amount along with an increase in the amount of incorporated CFBC fly ash indicates that during the early period of hydration, CFBC fly ash is a more active binder component. Such an effect is consistent with the results of setting time tests. The blast furnace slag exhibits latent hydraulic properties, when mixed with water and a chemical activator, it undergoes the process of hydration. In the investigated pastes, the CFBC fly ash plays the role of a slag activator. CFBC fly ash also shows some binding properties by itself and it is mainly responsible for early hydration. A high alkalinity of the reaction environment (the pH values of aqueous extracts of ggbs and CFBC fly ash are 12.4 and 12.7, respectively) favours the activation. High alkalinity is responsible for the dissolution of aluminosilicate species. As a result, silicate and aluminate ions are transferred to the solution and undergo further reactions, resulting

Figure 5. (a) IR spectra of dry binders before water addition and (b) pastes after 2 days of hydration; formulae numbers are placed on the right side of diagrams (1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA).

in forming products similar to the C–S–H phase or hydrated aluminates and sulphoaluminates. In the liquid phase, wherein the pH is equal to 12.5, alumina compounds are significantly dissolved [23].

3.3 FTIR

To assess the composition of investigated pastes after 2 days of hydration, FTIR tests (figure 5) and thermal analysis (subsection 3.4) were conducted. Herein, the IR spectra of pastes after 2 days of hydration are compared with the spectra of dry CFBC fly ash–slag binders before the addition of water (zero time of hydration). For comparative purposes, figure 6 shows the CFBC fly ash and slag spectra. The apparent differences in the spectral shape registered for the dry binder as fly ash–slag mixes (figure 5a) and pastes (figure 5b) confirm that during

Figure 6. IR spectra of CFBC fly ash and slag.

the 2 days of hydration, particular physicochemical processes had taken place and new products were formed.

In the analysis of the dry component spectra (figure 6), it is evident that the main absorption bands are maximal at about 1000 and 500 cm^{-1} . Generally, the shape of the dry binder IR band spectra (figure 5a) is broadly similar to those of the slag and CFBC fly ash IR spectra, and the changes in the intensities of particular bands are the result of differences in the amounts of added component (according to table 2). It should be noted that the location of the most intense main band is different in the case of CFBC fly ash and slag. Such a locational difference indicates the differences in the composition of the aluminosilicate phases that result from different crystal and amorphous (glassy) phase proportions and differences in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

In the slag IR spectra (figure 6), the following absorption bands (and their characterization) may be observed:

- the main band being broad and intense within the range of 1300–800 cm^{-1} , with an extreme value at 960 cm^{-1} . The effect is related to the antisymmetric stretching vibrations of $\text{Si}(\text{Al})\text{--O}$. The band location at a relatively low wavenumber indicates the vibrations of the $[\text{Si}_2\text{O}_7]^{6-}$ units that are typical to the melilite silicate phases [32]. Such effects may also be due to the high amount of aluminium in the aluminosilicate phases (in the resulting tetrahedral structure, Si^{4+} is partly replaced with Al^{3+}). A significant band half-width is due to the presence of the glassy phase [32,33];
- a band of an extreme value at 507 cm^{-1} . This is because of the bending vibrations of the O--Si--O bonds in the tetrahedral arrangement. This is probably also connected with the effects induced by $[\text{Si}_2\text{O}_7]^{6-}$ units [32];
- a moderately intense broad band near 710 cm^{-1} . This is due to the symmetric stretching vibrations of $\text{Si--O--Si}(\text{Al})$ units [31]. This band may overlap with a band that typifies the presence of carbonates (712 cm^{-1}). Minute amounts of carbonates in the slag are also confirmed

by the slight band at 1420 cm^{-1} due to the vibrations of CO_3^{2-} ;

- a broad, slightly intense band of an extreme value near 3390 cm^{-1} (typical to the stretching vibrations of water molecules) and a slight shoulder at 1630 cm^{-1} (induced by the deformation vibration bands of H--O--H) which indicate the minor presence of water in the specimen.

In an analysis of the CFBC fly ash IR spectra (figure 6), the following bands and their characteristics can be observed:

- a broad intense main band formed because of the asymmetric stretching vibrations of $\text{Si}(\text{Al})\text{--O}$ (similar as in the case of slag). The extreme value of the band is transferred, in comparison with that of the slag, towards higher wavenumbers (near 1100 cm^{-1}). This effect is indicative of the different compositions of the aluminosilicate phases of both investigated materials. Within the presented wavenumber range, the bands of amorphous silica and crystal compounds are also noticeable. For example, the quartz specific band may be placed at 1150 cm^{-1} [34];
- a band near 468 cm^{-1} . This effect is due to the bending vibrations of O--Si--O when in the tetrahedral structure [35];
- a moderate intense band at an extreme value (1412 cm^{-1}), sharp bands at 875 and 714 cm^{-1} and very weak bands beyond the range of figure 5, near 1798 and 2512 cm^{-1} . These effects are indicative of the presence of carbonates (CaCO_3) [36];
- moderate intense sharp bands near 595, 612 and 680 cm^{-1} . Such effects indicate the presence of anhydrite [35]. The intense main band of S--O vibrations in sulphates, which should be placed near 1100 cm^{-1} , is invisible (non-elicited), because it is overlapped with the main CFBC fly ash band. The shoulder alone (at 1160 cm^{-1}) is visible within the main band, and this effect is possibly connected to the presence of anhydrite;
- a band at extreme value of 3420 cm^{-1} and a slight shoulder at 1625 cm^{-1} . These effects indicate the presence of water;
- a sharp visible band at 3642 cm^{-1} . Such an effect is due to the vibrations of OH in a $\text{Ca}(\text{OH})_2$ compound, and this confirms the minute amount of this component in CFBC fly ash.

As stated above, with regard to the dry mixes of CFBC fly ash and slag (dry binders, figure 5a), bands characteristic to these two components are evident. Moreover, the intensities and location of the bands depend on the proportions of the two components within any mixture. For example, an increase in the amount of CFBC fly ash in a particular binder, results in an increase in the anhydrite amount, and this is reflected by an intensive increase of bands characteristic to this component.

The differences between the IR spectra of the investigated pastes after 2 days of hydration (figure 5b) and the spectra of dry binders (figure 5a) confirm the development of the hydration process and the formation of new products. With regard to such pastes, after 2 days of hydration, new bands can be elicited. First of all, in the main broad band, within the range of $1300\text{--}800\text{ cm}^{-1}$, a visible band is noticeable and this is within the range of $1100\text{--}1120\text{ cm}^{-1}$ (the band location varies depending on the amount of contained CFBC fly ash), with regard to the resulting band, the more CFBC fly ash is added, the sharper, clearer and at higher wavenumber it is. The second band is visible at $980\text{--}1000\text{ cm}^{-1}$. The first mentioned effect may be connected with the presence of sulphate phases (the vibrations of S–O, probably in ettringite). This is indicated by the dependence of the band shape and location on the amount of CFBC fly ash in the binder (near 1120 cm^{-1} , in paste no. 5, 30S/70FA). This band may also be connected with the presence of quartz. The second mentioned band may indicate the formation of aluminosilicate gel, but, herein, the differences in the band location depend on the paste composition, and, hence, reveal the formation of products with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. A significantly intensified band near 3420 cm^{-1} and a clear, moderately intense band near 1635 cm^{-1} confirm the presence of water bound in hydration products. Moreover, a clear increase in the sharp band intensity at 3642 cm^{-1} indicates an increase in the amount of $\text{Ca}(\text{OH})_2$ in any particular paste. When this effect is more intense, the more CFBC fly ash is present within any particular binder. The presence of $\text{Ca}(\text{OH})_2$ is the result of the introduction of that component *via* the CFBC fly ash component. It is also due to the hydration of CaO. It needs to be underlined that probably at this stage of early hydration, the pozzolanic reaction between $\text{Ca}(\text{OH})_2$ and active silica is at a very early stage.

The decaying of bands characteristic to anhydrite (595 , 612 and 680 cm^{-1}) confirms the participation of this component in the binding processes. In pastes with the smallest amount of CFBC fly ash (formulae 1 (70S/30FA) and 2 (60S/40FA)), these bands are not visible, but a weak band at 669 cm^{-1} can be seen. The presence of such a band is probably connected with the C–S–H phase [6]. With regard to pastes with higher amounts of CFBC fly ash (especially formulae 4 (40S/60FA) and 5 (30S/70FA)), there is a visible band near 680 cm^{-1} and a doublet at 612 and 595 cm^{-1} . These effects are due to the presence of CFBC fly ash components, and indicate that after two days of hydration, some CaSO_4 remain within the structure in an unreacted form. Finally, noticeable bands near 1420 (moderately intensive), 712 and 875 cm^{-1} indicate the presence of carbonates (CaCO_3).

3.4 Thermal analysis

The TG/DTG curves of fly ash–slag pastes are presented in figures 7 and 8. In general, the shape of the curves after 2 days of hydration is similar to that of the curves of portland cement

Figure 7. TG curves of fly ash:slag binders after 2 days of hydration (1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA).

Figure 8. DTG curves of fly ash:slag binders after 2 days of hydration (1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA).

pastes presented elsewhere, e.g., refs [37–40] (there are typical three main mass losses on TG curves). Mass losses are presented in figure 9.

On analysing the obtained results, a visible mass loss can be noticed at temperature up to 400°C . This is characteristic of the dehydration process of hydrated forms of the C–S–H type, sulphoaluminates (ettringite), unreacted gypsum (up to 200°C) and hydrated calcium aluminates. Furthermore, a mass loss in temperature of about $400\text{--}450^\circ\text{C}$ is a characteristic of the decomposition of $\text{Ca}(\text{OH})_2$, while a mass loss in temperature of about $600\text{--}700^\circ\text{C}$ is evident for the decomposition of CaCO_3 . In pastes, both mass losses are greater, if the more CFBC fly ash is present. This indicates that the presence of both calcium hydroxide and calcium carbonate is the result of the addition of CFBC fly ash. Moreover, the higher loss of mass is also characteristic of dehydration of water bound within hydrates, and this effect reveals a more

Figure 9. Mass loss (%) of fly ash:slag specimens after 2 days of hydration in a range of temperatures: (A) up to 400°C, (B) 400–450°C and (C) 600–700°C; types of binders: 1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA.

advanced progress of hydration in the presence of CFBC fly ash. However, the increase of water bound in hydrates is not always equivalent to a higher rate of reaction. This is because in the presence of pozzolanic/hydraulic materials, hydrates of different quantitative portions of components may appear (e.g., different CaO/SiO₂ ratios and different amounts of bound water).

A clear mass loss observed within the range of temperature up to 400°C confirms that in the investigated composition, during the first two days of hydration, processes take place during which hydrated phases are produced. In the case of formulae 1 (70S/30FA), 2 (60S/40FA) and 3 (50S/50FA), the amount of water bound in hydrated forms is very similar, while in formulae 4 (40S/60FA) and 5 (30S/70FA), it is higher when the amount of CFBC fly ash contained within the mixture is greater. This effect could be due to a slightly higher activation of the slag after exceeding a particular level in the amount of activating compounds. A similar trend of changes is confirmed by the already presented results of setting time tests (sub-section 3.1). This reveals that the initial setting time is shortened when more CFBC fly ash is present within any particular mixture. Herein, the results obtained for formulae 1 and 2 are close and a visible effect is most noticeable in the cases of formulae 4 and 5. Hence, generally, it can be stated that the greater the addition of CFBC fly ash, the more intense is the hydration process. Such a notion is confirmed by the higher amount of water bound in hydrates and the higher amount of heat released after 48 h of hydration. This assumption is also confirmed by the differences in the initial setting time.

Subsequent to the first two days, a pozzolanic reaction is expected to develop, and thus, additional portions of binding phases are produced *via* reactions between Ca(OH)₂ and the active components of slag and CFBC fly ash. Such effects

Figure 10. Flexural strength f_m and compressive strength f_c of pastes after 2 days of curing; types of binders: 1: 70S/30FA, 2: 60S/40FA, 3: 50S/50FA, 4: 40S/60FA and 5: 30S/70FA.

were confirmed in ref. [16], in the tests conducted after 28 and 90 days of curing.

3.5 Compressive and flexural strength

The results of compressive and flexural strength tests of fly ash–slag pastes are presented in figure 10.

In the analysis of the results of mechanical strength tests of pastes after 2 days of curing, a notable trend is that with an increase in the CFBC fly ash amount, compressive strength increases. Herein, the highest compressive strength is seen in formula 5 (30S/70FA), and the lowest in formula 1 (70S/30FA). Moreover, the results of compressive strength tests of specimens of formulae 1 (70S/30FA), 2 (60S/40FA) and 3 (50S/50FA) are quite similar: 1.21, 1.23 and 1.26 MPa, respectively, and the strength is revealed to increase with regard to formula 4 (40S/60FA), at 1.46 MPa, almost 16% higher than the result for formula 3; and formula 5 (30S/70FA), at 1.48 MPa, above 17% higher than for formula 3. Such results confirm the conclusions concerning the hydration process, and the product activation and binding presented in sub-section 3.4.

In the case of flexural strength, its increase is rather slight and can be noticed as being enhanced with an increase in the CFBC fly ash amount in the binder. Formula 5, however, revealed a decrease of strength of 7.9% to that of formula 4.

A comparison with the results obtained for later periods of hardening [16] reveals that a significant increase in mechanical strength, as well as the development of hydration products of fly ash–slag pastes, take place mainly in the period of 28 days of curing (formulae 1: 12.7, 2: 15.6, 3: 18.3, 4: 20.6 and 5: 23.9 MPa). Such effects indicate that the increase of compressive strength between 2nd and 28th day of hydration was

from 10 to 16 times for specimen nos. 1–5, respectively. After this period (28 days), the hydration process is still active, but less intense.

4. Conclusions

This paper presents the results of early hydration investigations of pastes made of CFBC fly ash (derived from brown coal combustion) and of ggbs. The tests conducted within the experiment (mechanical strength, initial and final setting times and hydration process utilizing FTIR, calorimetry and DTG/TG) confirm that hydration takes place and that a solid structure of pastes is formed. Moreover, it indicates that the attributes of each paste are shaped by the products of hydration, i.e., the hydrated silicates, calcium aluminosilicates, sulphoaluminates and calcium hydroxide. The presence of calcium carbonates was also confirmed. Calcium hydroxide was produced with the addition of CFBC fly ash, and was, as well, produced during the hydration process. Of note, its presence enables the pozzolanic reaction to occur in later periods and to form additional binding products, making it a stronger cement.

The addition of CFBC fly ash influences the rate of hydration process and the degree of binder component reaction in a way that the presence of more CFBC fly ash in the binder, the more intense is the hydration process, the earlier the initial setting time and the higher the early compressive strength. For example, the specimen containing the highest amount of CFBC fly ash shows a shortening of initial setting time by about 20% and an increase of 2-day compressive strength by 22%, in comparison with the results for a specimen containing the lowest amount of CFBC fly ash. This is a complex effect resulting from the presence of component with superior binding properties (CFBC fly ash) and greater activating action towards slag. Furthermore, along with the increase in the CFBC fly ash amount in pastes, the increase in water bound in hydration products is enhanced. Such an effect confirms the ability of CFBC fly ash to react with water in a hydration reaction and to bring about a probable acceleration of the hydration reaction of blast furnace slag.

The obtained results compared to previous results [16], are promising, considering the possibility of applying the investigated binders in cement products destined for the construction of structures where fast strength increase in time is not required, and a limitation of hydration heat and its intensity are important. Considering the obtained research results, it can be stated that the development of early properties of binders, such as the initiation of binding processes and compressive strength development, and also the kinetics of heat emission during the reaction with water, as well as the ability to activate slag, and a favourable ration of CFBC fly ash in a fly ash–slag mix, seem to occur in a mixture of about 50–60% of binder by mass. Further research, however, should be conducted to optimize the composition of mixes, so as

to improve the properties of binders in the early periods of hydration. Furthermore, it should be undertaken, so as to analyse the heat emission in fly ash–slag composites to understand them more greatly.

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