



Investigation of different ways of activation of fly ash–cement mixtures

Part 1. Chemical activation by Na_2SO_4 and $\text{Ca}(\text{OH})_2$

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Abstract

Cement industry emits large amount of CO_2 . One of the ways to reduce this emission is to use cement replacements, such as fly ash, in binding mixtures. Blends containing fly ash exhibit different properties compared to typical portland cement. In the case of very high amount of fly ash used as substitute of cement, setting and hardening are elongated, and early compressive strength and also often ultimate strength are reduced. Thus, such blends require activation. The aim of the work was to clarify the influence of chemical activators ($\text{Ca}(\text{OH})_2$ and Na_2SO_4 used together) on hydration/activation of fly ash–cement mixtures containing about 80% of fly ash. Activated mixtures containing inert filler instead of fly ash or cement were also investigated to better understand the influence of chemical activators on each component of the blend. The research included early hydration periods (3 and 24 h) and subsequent days (till 90th day of hydration). Several methods were used: calorimetry, TG/DTG, FTIR, X-ray diffraction and SEM microscopy.

Keywords Fly ash · Cement · Activation · Hydration · Calorimetry · TG/DTG

Introduction

It is well known that cement industry emits large amount of CO_2 , mainly as an effect of decarbonation of limestone [1, 2]. One of the ways to reduce this CO_2 emission is the use of cement replacements because of which the demand for portland cement clinker should be lower. Commonly used cements containing fly ash, slag, pozzolans and other components are commercially available [3]. Nowadays, binding “green” mixtures containing ecologically friendly non-clinker components arouse interest and they are the subject of research works, e.g., [4–9]. Some industry by-products can be used for this purpose. Thus, additional

ecological benefit can be obtained resulting in utilization of these materials.

The amount of fly ash used as replacement of cement usually does not exceed 35%. However, composites containing much higher quantity of fly ash in the binding material arouse interest [8, 10–15]. Portland cement in low-cement mixtures acts as hydraulic component and activator for fly ash. However, in the case of very high amount of conventional fly ash (70 mass% and more) and small amount of cement, the properties of early and final hardened composite are rather not satisfactory. It happens because conventional fly ash contains very low amount of calcium compounds and, for this reason, it cannot harden in the presence of water. Such kind of fly ash exhibits pozzolanic properties. It means that active forms of silica and alumina from fly ash can react with $\text{Ca}(\text{OH})_2$ in the presence of water. $\text{Ca}(\text{OH})_2$ is generated from hydration of cement, in the discussed case. Products of pozzolanic reaction are similar to those that are formed during portland cement hydration [16]. However, in the case of very high volume fly ash (VHVFA) blends, the amount of cement may be insufficient to fully

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develop fly ash activity and to obtain the required properties of the final material. In such case, setting and hardening are extended, and early compressive strength and often also ultimate strength are significantly reduced. This limits the applicability of the material.

There are several methods to activate the system and to enhance its properties [17]. Recently, using some inorganic salts (sulfates or carbonates, e.g., Na_2SO_4 , Na_2CO_3) as chemical activators was proposed [10, 12–15, 18]. Their impact on fly ash grains consists of increasing pH of reaction environment. It happens because these compounds can react with $\text{Ca}(\text{OH})_2$ arising in cement hydration. Solid products of the reaction are precipitated (CaSO_4 or CaCO_3 depending on the kind of activator) and alkaline hydroxide (e.g., NaOH in the case of sodium salts) is formed. In this way, pH increases and aluminosilicate fly ash grains can faster dissolve and react. Na_2SO_4 is often proposed as chemical activator for VHVFA mixtures, and discussions about mechanism of its action can be found in the literature [10, 12, 14]. Other chemical compounds, including organic salts [13], were also investigated.

Results of our previous research show that some activating effect for VHVFA pastes can be also observed in the case of exchange of small amount of fly ash by more active aluminosilicate pozzolanic material [19]. Influence of selected chemical activators on pozzolanic and hydraulic activities of fly ash [20] and on cement pastes containing typical (30%) [21] and higher [22] amount of fly ash was also presented.

Results of preliminary investigation of early hydration of fly ash–cement mixtures, recently published by us [17, 23], show that it is possible to activate them by mechanical or chemical way. Interesting results were obtained in the case of combined mechanical and chemical activation based on grinding together all dry components, i.e., fly ash, portland cement, $\text{Ca}(\text{OH})_2$ and Na_2SO_4 [17, 23]. All this encouraged us to take more exhaustive research on the mechanism of chemical–mechanical activation of VHVFA mixtures. For better understanding of processes of this combined activation, research on the chemical activation (no milling process) and mechanical activation alone (without additional chemical activators) was also undertaken. Such studies are important, taking into account that hydration/activation processes are long term and formed products influence properties of the materials. Moreover, recognition of these processes can be useful in modifying and developing new activation procedures to enhance properties of fly ash–cement blends.

This work is the first part of the series of publications relating to investigation of the proposed different ways of activation of VHVFA mixtures. The aim of this research was to clarify the influence of chemical activators ($\text{Ca}(\text{OH})_2$ and Na_2SO_4) on hydration/activation of fly ash–cement mixtures, including products formed on different stages of the process

and microstructure of hardened material. Na_2SO_4 was used as known accelerator of cement hardening, providing: increase in pH (as a result of reaction with $\text{Ca}(\text{OH})_2$), better solubility of fly ash grains, increase in pozzolanic reactivity as well as additional amount of sulfate for further reactions. $\text{Ca}(\text{OH})_2$ was proposed as additional component of the mixture to make Ca^{2+} available earlier for activating reaction. Moreover, excess of $\text{Ca}(\text{OH})_2$ can react in pozzolanic reaction in further periods. Pozzolanic activity of fly ash can be developed more, and additional amount of binding phases, such as C–S–H and C–A–S–H,¹ can be formed. Thus, enhancement of properties of fly ash–cement composites can be expected.

Activated mixtures containing inert filler instead of fly ash or cement were also investigated in this work to better understand the influence of chemical activators on each component of VHVFA blend.

Materials and methods

Commercially available portland cement CEM I 32,5R and fly ash from conventional pulverized combustion of hard coal in energy industry were used. Average oxide composition (main components) of fly ash is presented in Fig. 1. Size of fly ash grains does not exceed 345 μm , dimensions of 90% of grains are below 150 μm , and mean grain diameter equals 64 μm . Grains are mostly spherically shaped.

Blend containing 80 mass% of fly ash (FA) and 20 mass% of portland cement (PC) was made. Chemical reagents, Na_2SO_4 and $\text{Ca}(\text{OH})_2$, of analytical purity were used as activators. They were introduced as dry powders into dry fly ash–cement mix in amount 4 and 10%, respectively, calculated with reference to fly ash + cement mass. TG/DTG curves, IR spectra and X-ray diffraction pattern for such dry mixture (0 day of hydration) are presented in Figs. 2–4. Mixtures containing fine sand (S), as inert component, instead of FA or PC were also made. Distilled water was added into dry components in an amount providing water/binder = 0.5. Compositions of samples are presented in Table 1.

Pastes were closed in small polyethylene bags immediately after mixing, and then they were stored at room temperature. After 3 h, 24 h, 7, 28 and 90 days of hydration, the samples were removed from the bags. They were crushed, and hydration processes were stopped using acetone [19]. The samples were investigated by TG/DTG, FTIR and XRD. SEM observations were carried out on small pieces of pastes. Samples subjected to calorimetric measurements were hydrated in calorimeter at 25 °C.

The following research methods, apparatus and conditions were used:

¹ Abbreviations used in cement chemistry: C–CaO, S– SiO_2 , A– Al_2O_3 , H– H_2O .

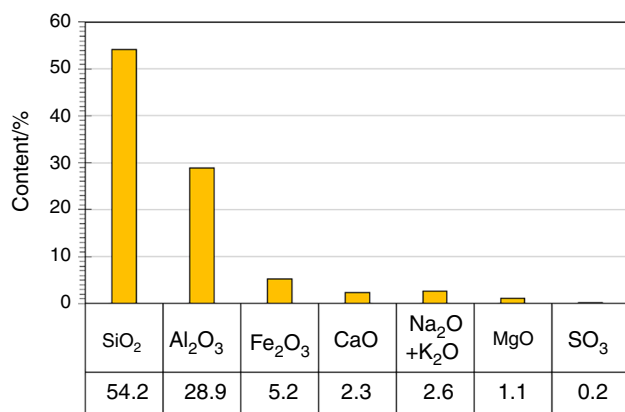


Fig. 1 Average oxide composition of fly ash

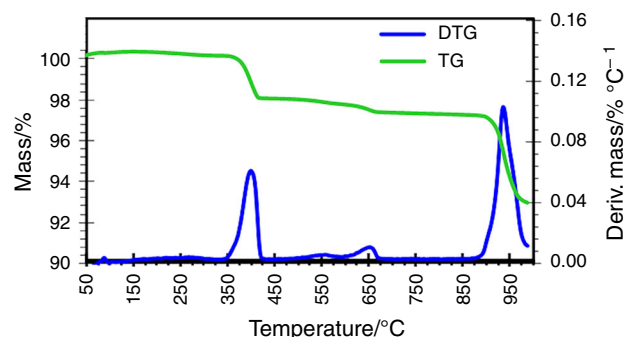


Fig. 2 TG and DTG curves for fly ash–cement mixture containing Na₂SO₄ and Ca(OH)₂ (before addition of water)

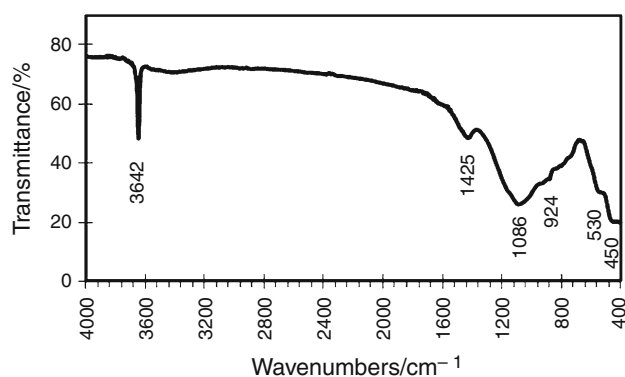
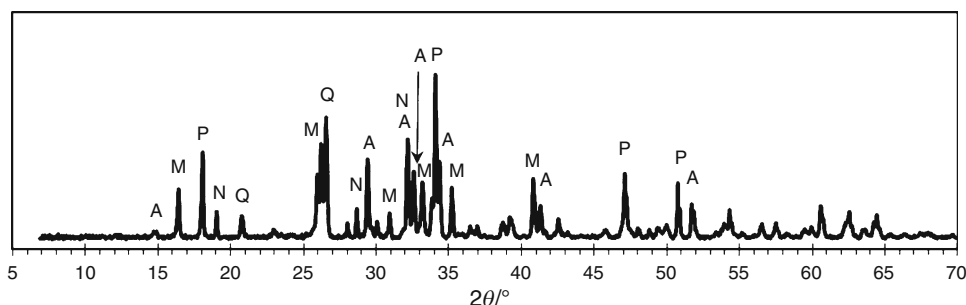


Fig. 3 IR spectra for fly ash–cement mixture containing Na₂SO₄ and Ca(OH)₂ (before addition of water)

Fig. 4 X-ray diffraction pattern for fly ash–cement mixture containing Na₂SO₄ and Ca(OH)₂ (before addition of water), A—alite, M—mullite, N—Na₂SO₄, Q—quartz, P—portlandite



- calorimetric measurements—BMR calorimeter constructed at the Institute of Physical Chemistry, Polish Academy of Sciences, was used, and the results were calculated using computer software [24],
- thermogravimetry—SDT 2960 Thermoanalyzer (TA Instruments) was used, heating rate was 10 °C min^{−1}, nitrogen atmosphere, and the mass of sample was 15–25 mg,
- infrared spectroscopy—FTIR spectrophotometer Genesis II (Mattson) was used, and the samples were prepared as KBr pellets,
- X-ray diffraction—Bruker D8 Advance diffractometer, Cu-Kα radiation, was used
- SEM/EDS analysis—scanning electron microscope JEOL with an X-ray microanalyzer EDS was used.

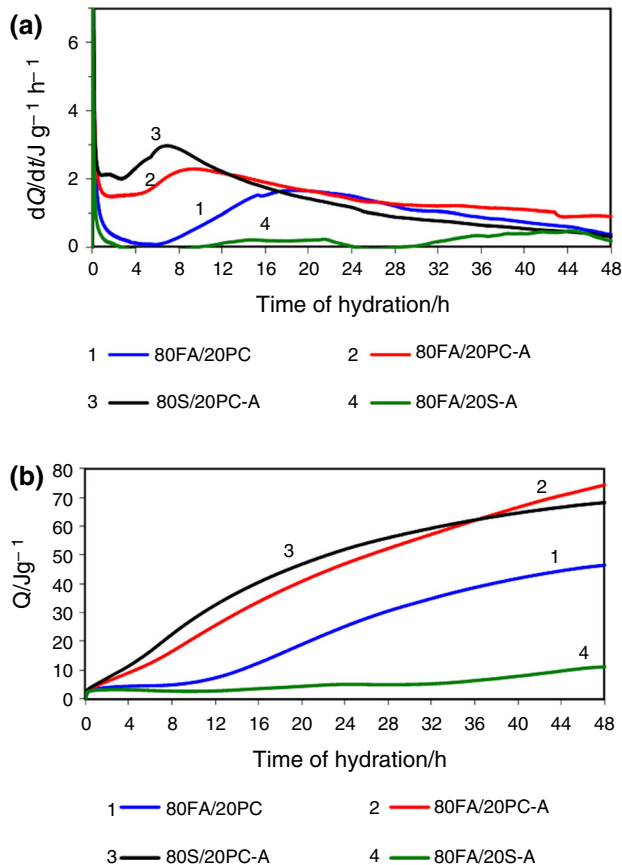
Results and discussion

Early hydration/activation periods

Results of calorimetric measurements (Fig. 5) present kinetics of heat evolution for hydrating pastes. It is a known fact that the course of calorimetric curve and the amount of heat released are strictly associated with chemical processes taking place in the paste and, consequently, with some properties of binder [16, 25, 26]. Thus, influence of fly ash on binder reactivity and properties can be estimated. Delay of hydration, slow setting and hardening are especially visible when high amount of cement is substituted by low-calcium conventional fly ash [19]. Such phenomenon was confirmed once again in this work. Results for non-activated paste containing 80% of fly ash in the mix (80FA/20PC) show as follows: long induction period lasting almost up to 8th hour of hydration, small intensity and elongated period related to precipitation of C–S–H-type product, relatively low total amount of heat released after 48 h (Fig. 5 line 1). Low reaction degree of the fly ash–cement composition results from the fact that fly ash (used in this work) is poor in calcium and has no self-cementing properties. Cement can activate it.

Table 1 Compositions of the investigated samples

Samples	Quantity of the components/g					
	Portland cement (PC)	Fly ash (FA)	Sand (S)	Na ₂ SO ₄	Ca(OH) ₂	Water
80FA/20PC (reference)	20	80	0	0	0	50
80FA/20PC—A	20	80	0	4	10	50
80S/20PC—A	20	0	80	4	10	50
80FA/20S—A	0	80	20	4	10	50

**Fig. 5** Heat evolution curves (a) and total heat released (b) for investigated pastes

However, cement also needs some time to form $Ca(OH)_2$ for pozzolanic reaction, and then fly ash needs time to react with this hydroxide. Thus, at early hydration period, setting and hardening depend mainly on cement hydration which is delayed by significant dilution effect of cement due to fly ash.

Introduction of Na_2SO_4 and $Ca(OH)_2$ into fly ash–cement mixture (80FA/20PC-A) causes intensification of heat release rate, which indicates acceleration of early hydration processes (Fig. 5 line 2). Induction period is reduced (it ends about 5 h after the moment of water adding), and the next period of heat release is more intense compared to the result for reference (80FA/20PC). As a consequence,

shorter initial setting time can be expected compared to non-activated sample. The total heat released after 48 h of measurement is also higher compared to result received for the non-activated sample. Thus, in general, tendency of changes of heat release observed previously [23] was confirmed in this work.

Comparison of the results registered for activated fly ash–cement paste (80FA/20PC-A) and those for samples containing sand instead of fly ash or cement (80S/20PC-A or 80FA/20S-A, respectively) disclosed that, in early period of hydration, activating effect is mainly caused by acceleration of cement hydration. However, some influence of chemical activators on fly ash reactivity is not excluded despite the short time of hydration. Na_2SO_4 is easily soluble in water and can react with $Ca(OH)_2$ increasing pH of solution. Cement minerals can be more soluble in such conditions and undergo hydration earlier. Fly ash grains need more time and high pH to dissolve. It is visible that in the case of activated sample containing sand instead of fly ash (80S/20PC-A) activating effect is higher compared to result for fly ash–cement blend (80FA/20PC-A). However, starting from 36 h of hydration, total heat released for activated fly ash–cement paste is higher and increases continuously compared to result for sand–cement sample. It indicates the development of fly ash–cement activity. This conclusion is confirmed by calorimetric results registered for mixtures without cement (80FA/20S-A). In this case, fly ash slowly and with low intensity undergoes activation. The first stage of fly ash activity development takes place between 12 and 24 h, while the second, slightly more intense, after 30 h.

TG and DTG curves (Figs. 6 and 7) show a few stages of mass losses:

- up to about 380 °C—dehydration of products such as: C–S–H phase, hydrated sulfoaluminates, hydrated aluminates, and, on very early hydration periods, also unreacted gypsum (Δm_1 —Fig. 8);
- from about 380 °C to about 460 °C—dehydroxylation of $Ca(OH)_2$ (Δm_2 —Fig. 9);
- from about 600 °C to about 680 °C—decomposition of carbonates;
- above 800 °C—reduction of sulfates with non-burned carbon [27] (only for samples containing fly ash).

Fig. 6 TG curves for investigated pastes after different periods of hydration

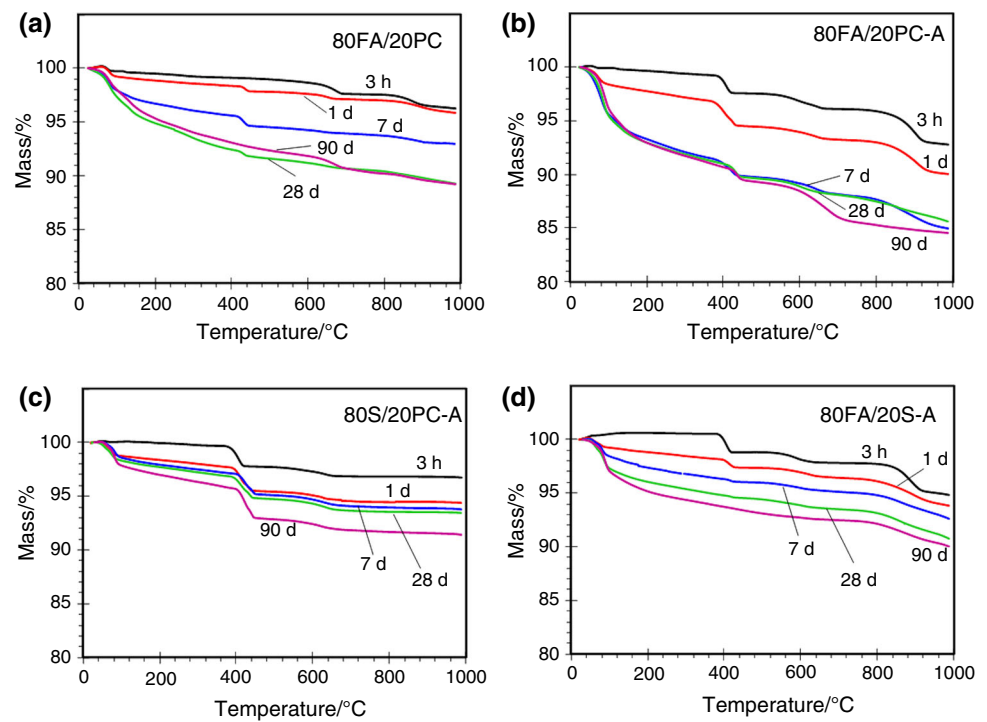
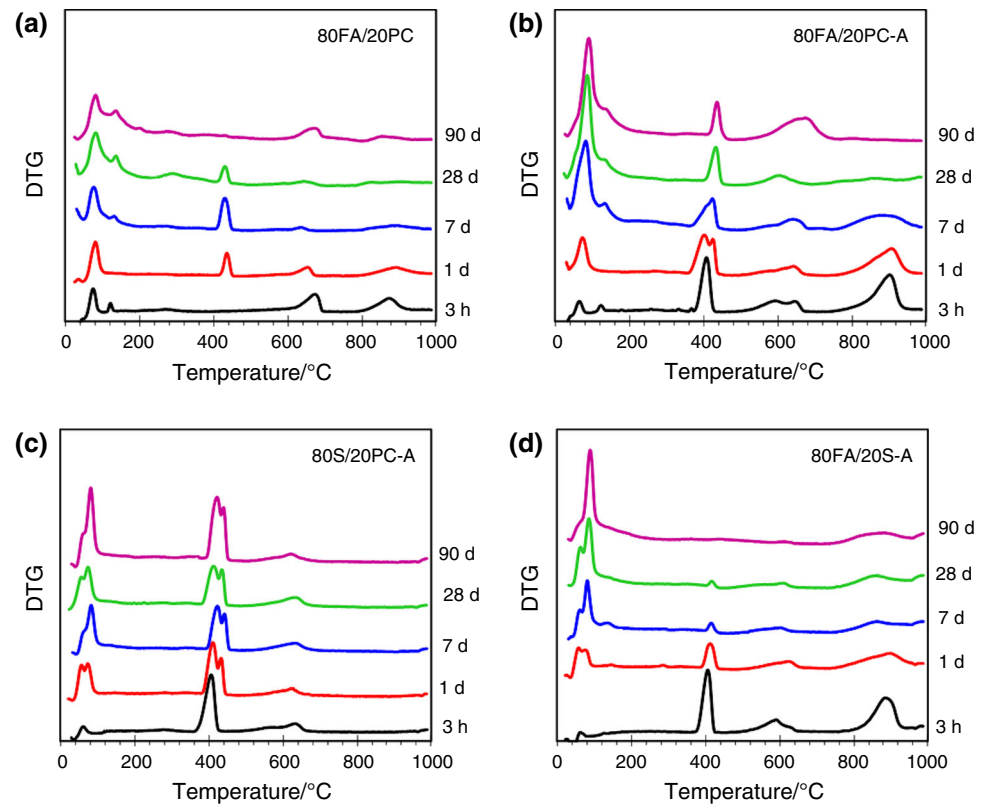


Fig. 7 DTG curves for investigated pastes after different periods of hydration



After early hydration period (3 h), the pastes bound a very low amount of water (estimated as Δm_1 , Fig. 8). Results registered for non-activated reference show that Ca(OH)_2 is not precipitated at this early stage. Its presence

as well as small increase in bound water is visible after 1st day. Two peaks on DTG (up to 150 °C) after 3 h of hydration likely indicate the presence of small amount of

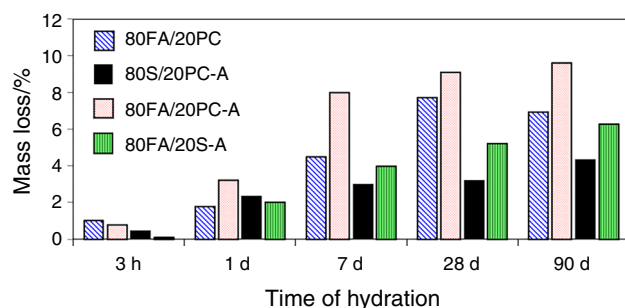


Fig. 8 Mass loss relating to water bound in hydrates (Δm_1)

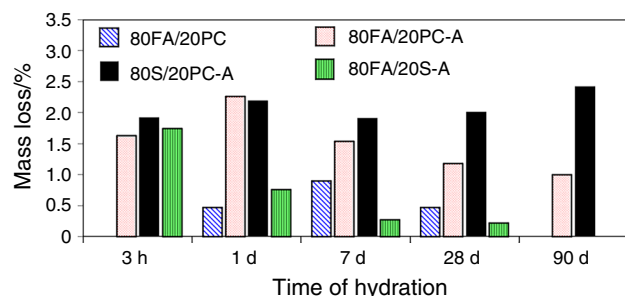


Fig. 9 Mass loss relating to decomposition of Ca(OH)_2 (Δm_2)

gypsum which undergoes reaction during the next hydration periods (Fig. 7a).

The courses of TG/DTG curves (Figs. 6, 7) of activated mixtures after 3 h of hydration are similar to those obtained for non-activated one (80FA/20PC). The obvious difference is the pronounced effect of dehydroxylation of Ca(OH)_2 which was introduced as an activator (on DTG, clear peak with an extreme at about 400°C is visible for all activated samples). Because Na_2SO_4 is the second component of the activating mixture, TG/DTG curves for samples 80FA/20PC-A and 80FA/20S-A (Figs. 6b, d, 7b, d) exhibit more clear mass loss above 800°C compared to result for non-activated reference. This effect is not visible for activated sample composed without fly ash (80S/20PC-A) as this blend does not contain the carbon necessary for high-temperature reduction of sulfate.

On the 1st day of hydration, DTG curves registered for samples containing cement and chemical activators (Fig. 7b, c), i.e., 80FA/20PC-A and 80S/20PC-A, show untypical shape from about 360°C to 460°C . Two peaks are visible at this temperature range. Ca(OH)_2 from cement hydration appears (DTG peaks with extreme at about 430°C visible for all samples containing cement). The results evidence that Ca(OH)_2 , which precipitated during cement hydration, has different morphology and, resulting from this, different thermal stability compared to Ca(OH)_2 which was introduced as an activator. TG results show that mass loss resulting from dehydration of hydrated silicate, aluminate and sulfoaluminate phases (Δm_1) is the largest

for activated fly ash–cement paste 80FA/20PC-A. Thus, this composition bound the greatest amount of water during 24 h of hydration.

TG and DTG curves for activated sample without cement (80FA/20S-A) exhibit significant reduction in the effect of decomposition of Ca(OH)_2 . Such results indicate that Ca(OH)_2 quickly undergoes reaction in the system (reaction of Ca(OH)_2 with Na_2SO_4 and start of pozzolanic reaction). Thus, conclusions based on the results of calorimetric measurements regarding the development of fly ash activity in the presence of chemical activators were confirmed.

For most samples, IR spectra (Fig. 10) after 3 h are similar (sample 80S/20PC-A is an exception, because of the absence of fly ash in its composition) and confirm low reaction degree. Intense and broad band with an extreme at about 1100 cm^{-1} is the main band of fly ash (asymmetric stretching vibrations of Si(Al)-O bonds [28] in silica and aluminosilicate phases such as quartz, mullite and amorphous silica (overlapped bands)). The effects at about 545 cm^{-1} and about 450 cm^{-1} also come from the presence of fly ash in the mixture. The bands with extremes at $3420\text{--}3440$ and $1620\text{--}1650\text{ cm}^{-1}$ are related to the presence of water (stretching and bending vibrations of H-O-H), while bands at about 1420 and 875 cm^{-1} indicate the presence of carbonates. Some new bands for activated blends (Fig. 10b–d), compared to IR spectra for reference mixture (Fig. 10a), are associated with the presence of additional amounts of sulfate compound and Ca(OH)_2 . There is an intense sharp band at 3643 cm^{-1} related to vibrations of OH in Ca(OH)_2 . The main band related to SO_4^{2-} vibrations overlaps with the most intense band of fly ash and sand as it is placed at about 1100 cm^{-1} . Sharp band at 617 cm^{-1} is connected with the presence of sulfates.

IR spectra collected after 1st day show that during this short time of hydration the first portions of hydrated products were precipitated and activating processes also started. In the case of activated fly ash–cement paste (80FA/20PC-A, Fig. 10b), the band at 1105 cm^{-1} and a shoulder at lower wavenumbers (about 1035 cm^{-1}) are separated. It confirms transformations in aluminosilicate structure of fly ash. Similar effects were observed for sample without cement (80FA/20S-A, Fig. 10d). Moreover, significantly lower intensity of the Ca(OH)_2 band confirms that this component undergoes reaction with the formation of new products. Precipitation of ettringite is not excluded as the bands typical for this product have similar position as the sulfates and some bands of fly ash. Thus, the effects overlap, for example the main intense band for ettringite is located at about 1120 cm^{-1} [29], another band at 620 cm^{-1} [30]. Presence of this component may be confirmed by X-ray diffraction results presented in Fig. 11

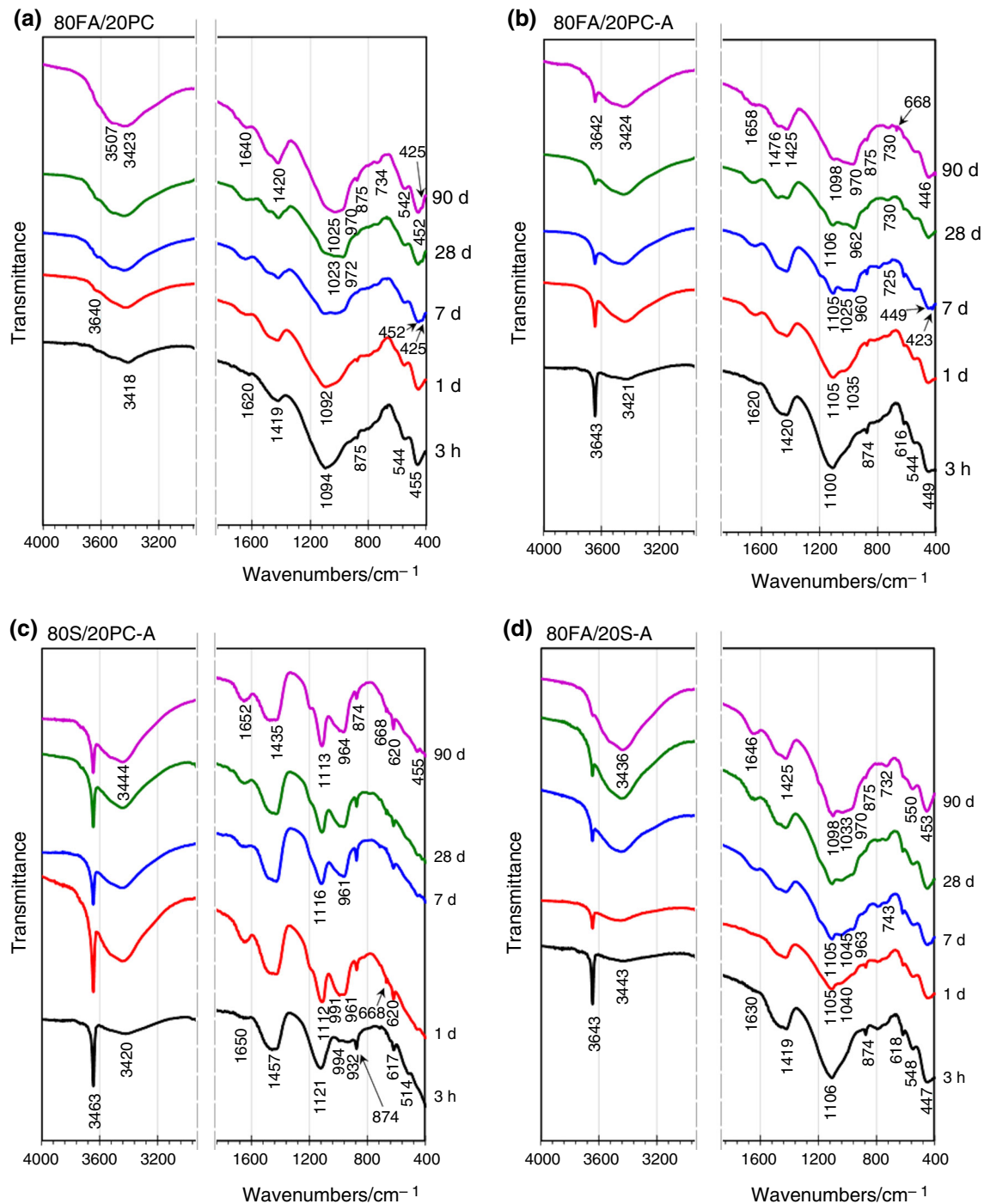


Fig. 10 IR spectra for investigated pastes after different periods of hydration

(very low intensity peaks for ettringite are visible for activated blend). Hydration/activation products formed at this early hydration period are amorphous. X-ray diffraction pattern shows the presence of a few crystalline components of fly ash–cement mix: quartz, mullite (from fly ash), calcite, calcium silicate C_3S (from cement) as well as effects related to activators ($Ca(OH)_2$, Na_2SO_4).

For comparison, in the case of non-activated blend, FTIR spectrum collected after 1st day has almost the same shape as spectrum after 3 h. (Only insignificant broadening of the main fly ash band toward lower wavenumbers was observed.) Thus, conclusions presented above, based on calorimetric and thermogravimetric measurements, were confirmed. Chemical activators influence fly ash grains and

Fig. 11 X-ray diffraction patterns for investigated pastes after 1st and 28th day of hydration, E—ettringite, M—mullite, Q—quartz, P—portlandite, A—alite, N— Na_2SO_4 , Cc— CaCO_3

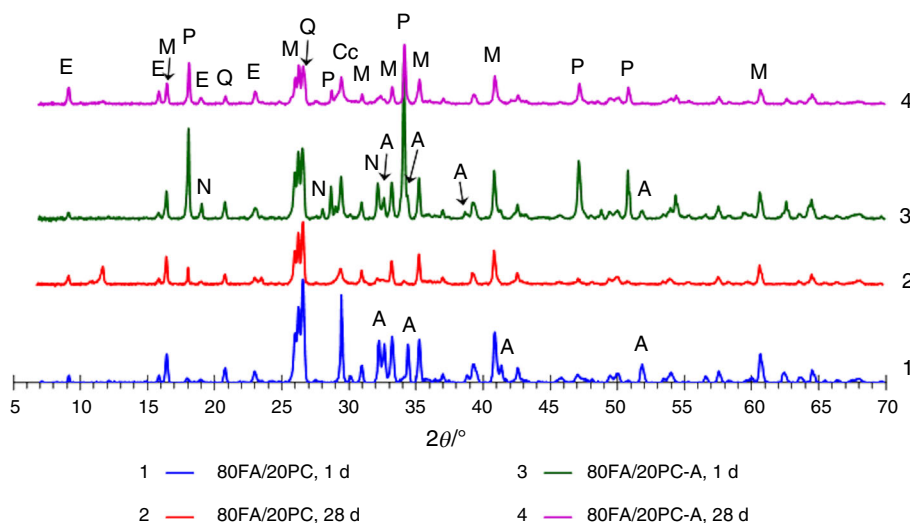
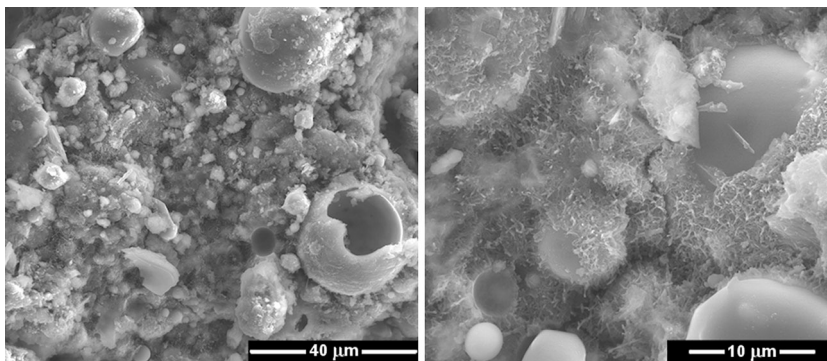


Fig. 12 Exemplary SEM images of microstructure of activated fly ash–cement paste (28th day of hydration)



stimulate their reactivity just after several hours after addition of water.

IR spectra collected for mixture in which fly ash was replaced by sand (80S/20PC-A, Fig. 10c) show influence of chemical activators on cement hydration. Intense bands at 1112 cm^{-1} and about 620 cm^{-1} result probably from ettringite. Bands characteristic for silicates of portland cement change position. Moreover, new band at 668 cm^{-1} appears. It may confirm the formation of C–S–H-type products [31].

Later hydration/activation periods

During the next days of hydration, fly ash develops its activity further and cement undergoes further hydration. As a result, the amount of bound water (presented as the mass loss Δm_1 , Fig. 8) increases with time. In the case of non-activated reference paste (80FA/20PC), $\text{Ca}(\text{OH})_2$ content rises till 7th day which confirms that hydration of cement predominates over pozzolanic reaction. After the 7th day, amount of $\text{Ca}(\text{OH})_2$ decreases (gradual reduction in mass

loss at $410\text{--}460\text{ }^\circ\text{C}$ over time, Fig. 9)² and it is completely invisible after the 90th day. It affirms that pozzolanic activity in non-activated fly ash–cement blend develops after 7 days of hydration. Thus, previous results [19] obtained for fly ash–cement mixture were confirmed. Changes of the DTG shape (Fig. 7a) at temperature range up to $200\text{ }^\circ\text{C}$ indicate that C–S–H is the main product of reference paste on early days of hydration, while, starting from 7th day, hydrated aluminates and aluminosilicates are also present. They are visible by the presence of DTG peak at about $140\text{ }^\circ\text{C}$. A broad peak of small intensity at about $300\text{ }^\circ\text{C}$ is also observed. Intensities of these effects increase with time starting from 7th day of hydration.

Chemically activated fly ash–cement paste (80FA/20PC-A), contrary to the results for reference mix, shows earlier development of reactivity (between 1st and 7th day). In the case of this sample, the amount of $\text{Ca}(\text{OH})_2$ rises till 1st day of hydration. Then, between 1st and 7th day, it starts to

² The amount of $\text{Ca}(\text{OH})_2$ in the sample is proportional to mass loss related to decomposition of $\text{Ca}(\text{OH})_2$.

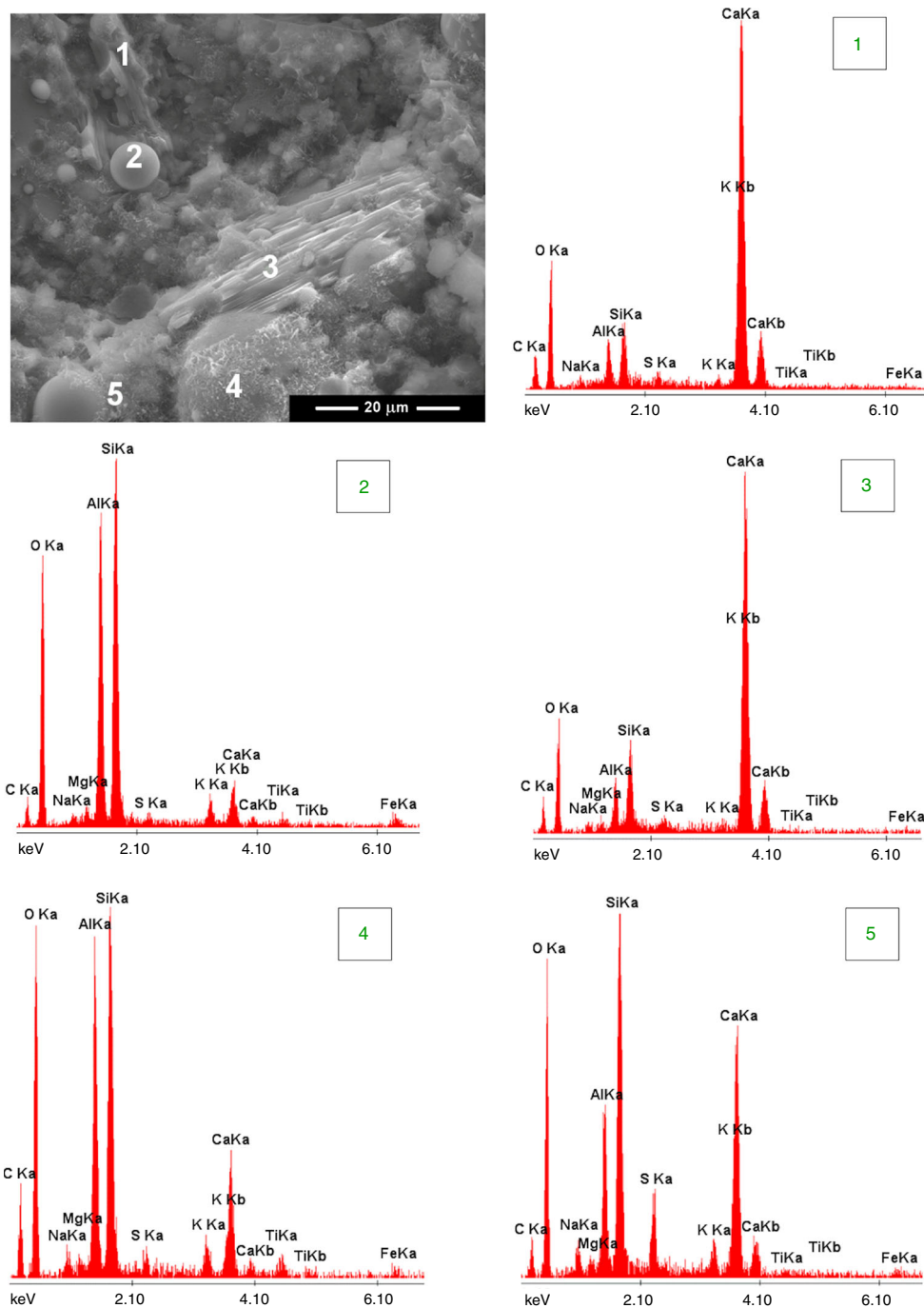


Fig. 13 Exemplary SEM image of microstructure of activated fly ash–cement paste (28th day of hydration) and EDS analysis of selected points (1–5)

reduce, probably partially as a result of reaction with Na_2SO_4 (in early periods) and mainly in pozzolanic reaction (in the following days). The amount of bound water for this mixture is the highest, compared to all investigated blends, through all days of investigation. Larger amount of water was bound between 1st and 7th day. After this time, the amount of water increases only slightly. The DTG curve indicates that

$\text{Ca}(\text{OH})_2$, introduced into fly ash–cement mixture as an activator, reacts faster than $\text{Ca}(\text{OH})_2$ which precipitated during cement hydration. The effect visible on DTG, responsible for decomposition of introduced $\text{Ca}(\text{OH})_2$, disappears till 28th day (Fig. 7b). On 90th day, the presence of $\text{Ca}(\text{OH})_2$ (product of hydration) was still visible. It can take part in pozzolanic reaction and form additional binding

products of C–S–H and C–A–S–H type in later days. The effect of mass loss over 800 °C also gradually disappears. It shows that sulfates are bound into other products. (Probably, they are partially incorporated into C–S–H phase.) Shapes of DTG curves at temperature range up to 200 °C indicate that C–S–H phase and ettringite are the main products of reactions. Small effect at about 120 °C can indicate formation of the Afm phase and/or hydrated aluminosilicate products. X-ray diffraction patterns (Fig. 11) confirm the presence of ettringite after 28 days of hydration, which in the form of needles is also visible in SEM images (Figs. 12, 13). Ettringite may be formed as a result of the presence of cement in the mixtures and introduction of gypsum along with it. However, the amount of gypsum from cement is very low. Adding chemical activators, i.e., $\text{Ca}(\text{OH})_2$ and Na_2SO_4 , favors creation of sulfoaluminates. These activators can react with each other in an aqueous environment forming easily soluble NaOH (which increases pH of solution and promotes dissolution of aluminosilicate grains of fly ash) and gypsum which precipitates [10, 12, 14, 18]. According to information given in [10, 12], gypsum created in this way is probably metastable and can be quickly consumed.

TG/DTG results show that the form of $\text{Ca}(\text{OH})_2$ which has lower thermal stability can be relatively fast bound in other compounds. It is especially visible in the case of sample in which the only source of $\text{Ca}(\text{OH})_2$ is the one introduced as an activator (80FA/20S-A). On the other hand, blend containing sand (instead of fly ash) and cement, 80S/20PC-A, shows the presence of both forms of $\text{Ca}(\text{OH})_2$ without its reduction over time. This is because the composition does not contain pozzolan which can react with $\text{Ca}(\text{OH})_2$. Comparison of the TG/DTG results obtained for activated fly ash–cement pastes (Figs. 6b and 7b) with those for samples without cement (Figs. 6d and 7d) show that introduced $\text{Ca}(\text{OH})_2$ was bound up to 90th day of hydration and C–S–H and ettringite are the main products of hydration/activation processes. In the case of 80FA/20S-A sample, hydrated aluminates are probably not formed or only in a small degree, similarly as in the case of sample without fly ash (Figs. 6c and 7c).

Transformation of silica and aluminosilicate components of fly ash over time toward new silicate and aluminosilicate products is also confirmed in IR spectra (Fig. 10). In the case of non-activated fly ash–cement paste (80FA/20PC, Fig. 10a), the main fly ash band widens and gradually forms a new extreme at lower wavenumbers. The extreme visible at about 970 cm^{-1} on 28th day indicates formation of C–S–H phase. Moreover, a new band at about 425 cm^{-1} appears on 7th day of hydration. For activated fly ash–cement blend (80FA/20PC-A, Fig. 10b), the bands confirming formation of new aluminosilicate phases are visible earlier and more clearly. For example, on 28th day

of hydration the band at 1025 cm^{-1} , clear and intense band at 962 cm^{-1} and 730 cm^{-1} are visible.

Figures 12 and 13 present microstructure of activated fly ash–cement binder after 28th day of hydration. There are visible products of hydration/activation formed around grains of fly ash. Figure 13 shows different components which can be found in the microstructure: region enriched in calcium (points 1 and 3), non-reacted aluminosilicate fly ash grains (point 2), C–A–S–H product (point 4) and aluminosilicate product enriched in sulfur (point 5).

Conclusions

1. Chemical compounds, Na_2SO_4 and $\text{Ca}(\text{OH})_2$, can activate fly ash–cement mixture. It is evidenced, compared to non-activated fly ash–cement blend, by: shortening of induction period and intensification of period related to precipitation of C–S–H, increasing total heat released after 48 h of hydration, higher amount of bound water, reduction of $\text{Ca}(\text{OH})_2$ and quicker precipitation of hydrated products resulting from faster development of pozzolanic activity.
2. Ettringite is one of the hydration products, formed in higher amount in chemically activated mix as an effect of introduction of sulfate.
3. Chemical activators accelerate cement hydration and enhance reactivity of fly ash grains. In activated fly ash–cement binder, synergic effect takes place.
4. In early hydration hours, the presence of cement is mainly responsible for activating effect of fly ash–cement mixture. During 24 h of hydration, fly ash starts to react.
5. Two kinds of $\text{Ca}(\text{OH})_2$ can be present in activated fly ash–cement system: hydroxide introduced as component of activating mixture and the one precipitated as cement hydration product.
6. The knowledge about kinetics of chemical and physical processes of hydration/activation and products that are formed is key factor to develop new more ecological binders which could replace cement in the future. Results of investigation on other ways of activation of such systems (i.e., very high volume fly ash mixtures) will be discussed in next works.

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