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INVESTIGATIONS OF CEMENT EARLY HYDRATION IN THE PRESENCE OF CHEMICALLY ACTIVATED FLY ASH

Use of calorimetry and infrared absorption methods

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The paper describes an attempt of chemical activation of fly ash and claims the usefulness of combination of such investigation methods as calorimetry and infrared absorption for investigations of early periods of cement hydration. The research samples were cement pastes made with an addition of fly ash and admixtures of chemical activators, $CaCl_2$, Na_2SO_4 and NaOH, whereas a cement paste without fly ash addition and a cement–fly ash paste (both without admixtures) were used as reference samples. In order to investigate early periods of cement pastes hydration, the amount and rate of heat release were registered, and IR spectrums were checked at appointed hydration moments.

As a result, it was shown that the combination of calorimetric and IR absorption methods in the investigations of early periods of cement hydration was useful. It was confirmed that the use of chemical activators $CaCl_2$, Na_2SO_4 and NaOH accelerated the hydration of cement pastes containing fly ash additive in early hours after adding water. The action of activators on hydrating cement system is different for each of investigated compounds.

Keywords: *activation, cement, chemical admixtures, fly ash*

Introduction

Physical and chemical processes that occur after adding water into cement influence its binding properties. The hydration of cement is a long-term process. However, the most intensive transformations occur in initial periods after water is added to binder. A lot of elementary processes overlap during the hydration. Their mechanism becomes more complicated if additional active materials (e.g. silica fume [1], spent fluidised catalytic cracking catalyst [2, 3]) are introduced into the system. An example of component that is introduced into cement at the stage of its production, or as an additive into cement concrete, is fly ash. In order to be able to use the fly ash, its properties should meet adequate standard conditions.

Fly ashes show pozzolanic or pozzolana-hydraulic properties in hydrating cement environment, and in this way they influence the amount of $Ca(OH)_2$ and binding phases. It should be emphasized that fly ashes coming from different sources may significantly differ in their physical and chemical properties [4, 5]. An effect of these differences of fly ash is diverse and not always has a favourable influence on cement hydration, and, in consequence, on features of accomplished composite.

An example is fly ashes coming from fluidised combustion of coal. Such fly ashes differ in chemical and phase composition as well as grain morphology from the fly ashes produced during pulverized coal combustion. Fluidised fly ash in cement paste shows better activity, in comparison to conventional fly ash [5]. Fly ash from conventional coal combustion methods shows pozzolanic activity in subsequent hydration period. For this reason, early strength of composite is decreased, especially when large amounts of fly ash are introduced as a replacement for a part of cement [6, 7]. It limits the possibility of fly ash application as an additive into cement composites in cases when high parameters of young cement mortars, or concretes, are required. Various methods of fly ash activation may be used in order to counteract the reduction of early strengths and improve the pozzolanic activity of fly ash. One of the methods is chemical activation consisting in introduction of admixtures of chemical activators into hydrating cement.

There is a lot of literature that describes these processes, and, mainly, they refer to the influence of ash activation on properties of cement composites. Investigations of products that are created in the presence of activators frequently deal with subsequent hydration periods. There is relatively little research on early hydration, that is, the initial hours after

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adding water, and chemical compounds created at this point. Various hypotheses concerning the action of chemical activators in cement paste are being put forward, and this problem still stirs up controversies.

The aim of this paper is to attempt activation of fly ash and to claim the usefulness of combination of such investigation methods as calorimetry and infrared absorption for investigations of early periods of cement hydration.

Experimental

The research material was fly ash (further marked as PM) obtained from pulverized combustion of hard coal. Physical and chemical properties of the ash are presented in the paper [5]. Approximately, the ash oxide chemical composition (the main components) was the following: 50% SiO_2, 30% Al_2O_3, 4% Fe_2O_3, 1% CaO, less than 1% SO_3, and more than 3 % of K_2O+Na_2O [mass% in all cases]. It was decided that the PM fly ash was selected for the research on activity improvement, based on prior investigations of three fly ashes of different origin [5]. Those investigations proved that PM ash revealed low activity in initial hydration periods of the cement system.

The research samples were cement pastes prepared from Portland cement CEM I 32,5R and PM ash, whereas $CaCl_2$, $Na_2SO_4\cdot 10H_2O$ as well as NaOH were used as chemical activators. The mixture of 70 mass% of cement and 30 mass% of PM was used to prepare cement pastes.

Activators were introduced in the amount of 2 mass% of the mass of binder (cement+fly ash) as a solution in make-up water. Water/(cement+fly ash) ratio was 0.5 in all cases. Water coming from hydrated salts was included into calculations as part of the total amount of water in cement paste. For comparison reasons, cement pastes containing 0 and 30 mass% of PM (reference A and B, respectively) without the activators were also performed.

Calorimetric measurements of cement pastes were conducted using a differential calorimeter BMR, constructed at the Physical Chemistry Institute of Polish Academy of Sciences. Within 48 h from the moment of adding water into the binder, heat release and its rate were measured. The results were calculated using computer software [8].

Infrared absorption measurements were carried out for the samples of cement pastes in given moments of their hydration. Cement pastes were sealed in polyethylene bags right after their preparation. At the given moment, the samples were taken out of the bags and, next, their hydration process was being stopped by means of acetone. A spectrometer Genesis II FTIR (Mattson) was used. The investigations were conducted in 4000–400 cm^{-1} wave number ranges, using KBr pellets preparation.

Results and discussion

Calorimetric measurements

The results of calorimetric measurements of chemically activated cement pastes are shown in Fig. 1. The curves illustrating the rate of heat release are typical for cement pastes. In initial minutes after adding water, fast heat releasing takes place. This is the effect of binder grains wetting, their partial dissolving of the surface, and the initial stage of ettringite formation. Then, the process is slowed down (induction period), which is caused by the covering of cement grains with thin layer of hydrates. After the induction period is finished, there follows another fast release of heat, which is connected with crystallization of cement hydration products [9]. An introduction of PM ash into cement paste (reference B) makes the amount of released heat get reduced, and the curve of heat release rate of the sample is becoming flatter in comparison

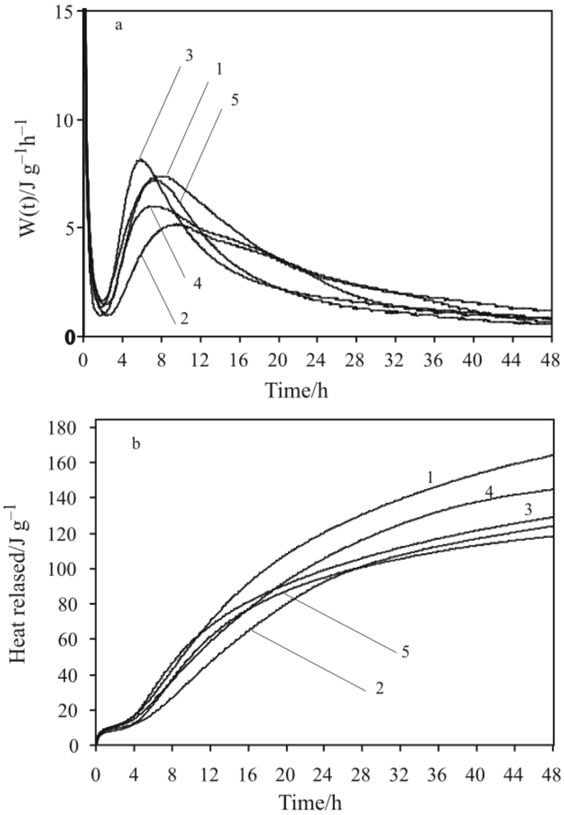

Fig. 1 a – Heat evolution curves for cement pastes and b – heat released during hydration; 1 – reference A; 2 – reference B; 3 – cement paste containing fly ash and $CaCl_2$ admixture; 4 – cement paste containing fly ash and Na_2SO_4 admixture; 5 – cement paste containing fly ash and NaOH admixture

with cement pastes without the ash. It confirms earlier findings [5]. The effect is caused mainly by the replacement of part of the cement with a less reactive material. The addition of fly ash extends the induction period compared with reference A as well as it shifts the second heat effect maximum from about 8 h of hydration for the cement paste without the ash to about 10 h for the samples containing additive. Therefore, it can be expected that the start and end time of set of the binder get extended.

Application of small amounts of chemical activators causes a distinct change of a course of calorimetric curves. In the cement system activated with $CaCl_2$ it is clearly seen that the induction period is shorter, and the intensity of heat stream in initial hydration hours is increased, compared with cement–fly ash paste without the activator (B). Duration of the induction period of activated cement paste containing ash is similar to the induction period for plain cement paste without fly ash addition (A). The second period of heat release time is shorter, more intensive, and it achieves its maximum faster. It is a well-known effect of $CaCl_2$ activity as an admixture accelerating the setting and hardening of cement.

The Na_2SO_4 acts in a cement paste in a different way. The accelerating activity of Na_2SO_4 is not so intensive as in the case of $CaCl_2$. Comparing the above results with those obtained for the reference B one may state that the introduction of Na_2SO_4 admixture into cement paste containing ash causes the induction period to shorten, and the release of heat to become more intensive in the following period. As a result, the second period maximum on calorimetric curve is shifted to about 7 h of hydration. Similar, however, to reference B is the extended time period of heat release in the period of crystallization of products. Yet, it has to be noted that the induction period is longer than in the case of reference sample A, and the calorimetric curve is flatter.

The cement paste activated with NaOH behaves in a manner which is in between the two previous activators. Acceleration of the start of binding is nearly identical to the one of Na_2SO_4. The period of intensive heat release has also a similar duration; yet, around the 10th hour of the process, a sudden fall of heat release rate takes place and the curve develops in a similar way as the curve for cement paste containing $CaCl_2$. The analysis of calorimetric curve leads to a conclusion that NaOH becomes most active after the induction period.

After the induction period, from among activated cement pastes, the highest values of released heat in the first hours are observed for cement paste containing $CaCl_2$, in later hours – for the sample admixtured with Na_2SO_4. This observation confirms that the $CaCl_2$ admixture in the initial hours after water addition has the most accelerating influence, whereas the Na_2SO_4 acts in a more moderate way and is extended in time, compared to $CaCl_2$. In case of cement paste containing NaOH, the most intensive release of heat, indicating acceleration of the hydration, takes place between 4th and 25th hour from the moment of adding water.

Infrared absorption findings

The results presented above confirm that calorimetry is a very good method for comparative investigations, and helps to draw conclusions about the processes occurring in the initial, most intensive hydration periods. Nevertheless, this method does not give a direct answer about the products being formed in given periods.

In order to find out about composition of cement pastes in individual moments of their hydration, one can use infrared (IR) absorption method, on condition the hydration is stopped after a given time period. The results of IR investigations of cement pastes in time periods up to 24 h of hydration are presented in Figs 2–5. The periods for investigations were selected on the basis of calorimetric curves; after 25 min (this is after initial wetting period), after 3 h (finished induction period), after 8 h (second heat effect maximum for reference A), and after 24 h.

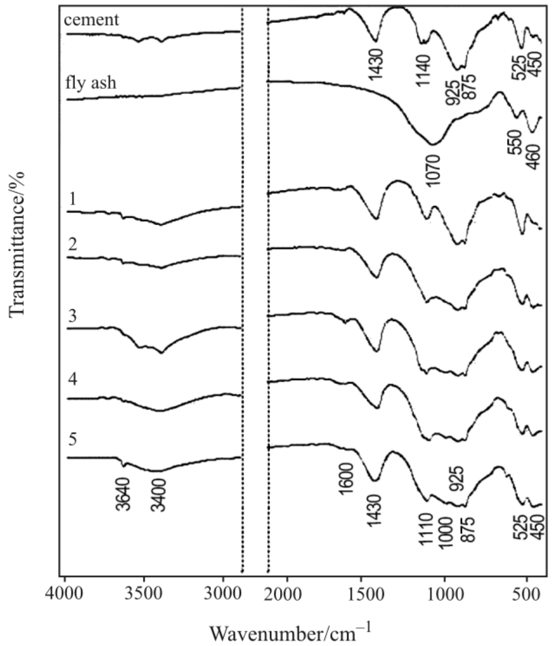

Fig. 2 IR spectra of cement pastes after 25 min of hydration and components of cement pastes (cement and fly ash); 1 – reference A; 2 – reference B; 3 – cement paste containing fly ash and $CaCl_2$ admixture; 4 – cement paste containing fly ash and Na_2SO_4 admixture; 5 – cement paste containing fly ash and NaOH admixture

25th minute of hydration

After 25 min of hydration, there are still visible bands characteristic for components of the cement (Fig. 2). An intensive band with a maximum at about 925 cm^{-1}, and bands at about 525 and 450 cm^{-1}, are connected with vibrations of Si–O in alite (the bands of alite are generally broader than belite bands and they overlap) [10]. In the case of cement pastes containing PM ash, the latter two bands overlap with bands characteristic for PM (at about 550 and 460 cm^{-1} – the bands of vibration of Al–O and Si–O [11]). Intensity of the band at about 450 cm^{-1} for cement–fly ash pastes (compared with IR spectrums of dry cement, PM and reference A) indicates that it originates form ash. A sharp band of middle intensity at about 1430 cm^{-1} and a sharp, intensive band at about 875 cm^{-1} as well as a very weak band at about 1790 cm^{-1} are connected with the presence of carbonates [10, 12] (location of the second of the bands is similar to silicate bands, and they overlap). Distinct changes observed in a short time after water addition to cement are connected first and foremost with sulfate and silicate phases. Already after 25 min of hydration, a triple band, characteristic for dry cement, of sulfates (gypsum) at range of 1100–1150 cm^{-1} transforms into a single band located at the bottom part of the bracket. It confirms early forming of ettringite [13]. In case of cement–fly ash pastes this band may partially overlap with the main band characteristic for PM (about 1070 cm^{-1}). Conversions of sulfate phases to ettringite formation are also confirmed by changes of shape of stretching and bending bands of water molecules vibrations. In case of a complex, broad band at 3000–3800 cm^{-1}, it is observed that two bands characteristic for $CaSO_4$ hydrate (gypsum) at about 3550 and 3400 cm^{-1} [14] disappear, and a broad band with one, main maximum is being formed. At about 1600 cm^{-1}, a weak doublet appears.

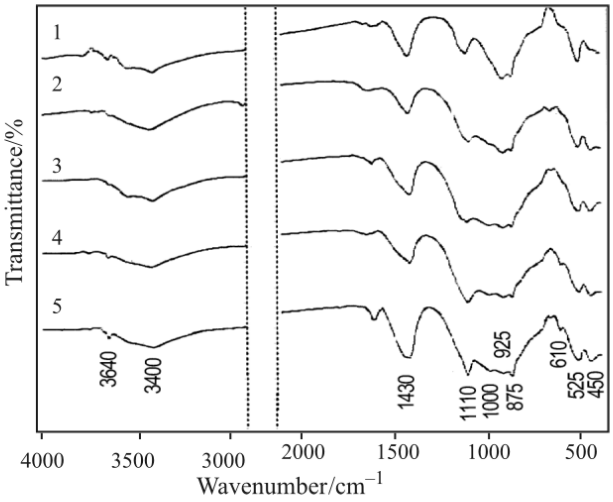

Fig. 3 IR spectra of cement pastes after 3 h of hydration; 1 – reference A; 2 – reference B; 3 – cement paste containing fly ash and $CaCl_2$ admixture; 4 – cement paste containing fly ash and Na_2SO_4 admixture; 5 – cement paste containing fly ash and NaOH admixture

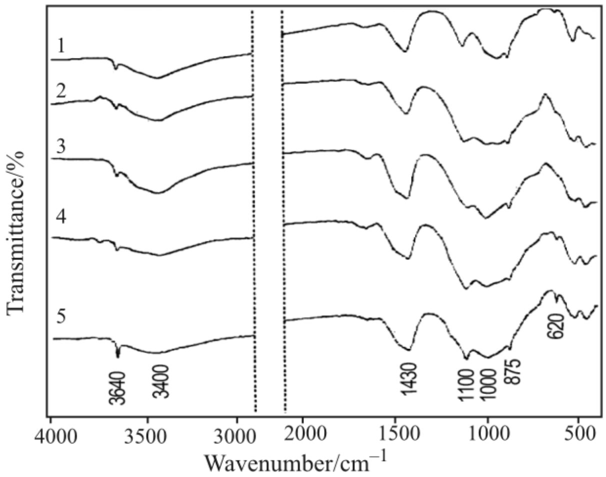

Fig. 4 IR spectra of cement pastes after 8 h of hydration; 1 – reference A; 2 – reference B; 3 – cement paste containing fly ash and $CaCl_2$ admixture; 4 – cement paste containing fly ash and Na_2SO_4 admixture; 5 – cement paste containing fly ash and NaOH admixture

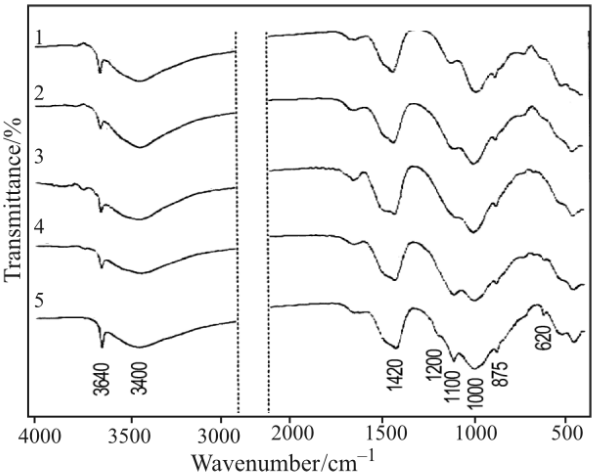

Fig. 5 IR spectra of cement pastes after 24 h of hydration; 1 – reference A; 2 – reference B; 3 – cement paste containing fly ash and $CaCl_2$ admixture; 4 – cement paste containing fly ash and Na_2SO_4 admixture; 5 – cement paste containing fly ash and NaOH admixture

Observed changes occur with the most intensity for cement pastes activated with NaOH, and are the slowest for the sample with $CaCl_2$. It may be an effect of decreased dissolution of $CaSO_4$ in the presence of $CaCl_2$ (influence of common ion). When applying Na_2SO_4 as an activator, the amount of available SO_4^{2-} ions increases and it gives a possibility to form a larger amount of ettringite.

Active influence of used admixtures on early hydration of silicate phases is visible in the bands range, characteristic for these phases. A distinct band at about

1000 cm^{-1} is observed, which indicates some acceleration of forming of C–S–H phase[**]. This band is not visible for reference samples A and B. Simultaneously, with the exception of the paste admixtured with NaOH, the formation of $Ca(OH)_2$ is practically not observed (very weak band of vibration of OH in $Ca(OH)_2$ at about 3640 cm^{-1}).

3rd hour of hydration

The IR spectrums of investigated cement pastes after the third hour of hydration (Fig. 3) do not show any significant changes compared to those registered after 25 min. It confirms that chemical conversions in the induction period are slowed down. In case of reference A cement paste, the spectrum after the 3rd hour of hydration is similar to the one registered earlier. It is similar in the case of non-activated cement paste containing PM (reference B). However, in the case of sample B after the 3rd hour of its hydration, a weak band, already at about 1000 cm^{-1}, begins to appear. It indicates a formation of the first amount of C–S–H phase, probably as a result of nucleation acting onto the finest grains of the ash and/or accelerating the action of Na^+ and K^+ ions from the ash. After the 3rd hour of hydration, in the case of cement pastes activated with Na_2SO_4, the band at about 1110 cm^{-1} undergoes some intensification, and a band of SO_4^{2-} vibration at about 610 cm^{-1} forms. It suggests a more complete reaction to ettringite. The IR spectrums of the other cement pastes do not differ significantly from those registered after 25 min.

8th hour of hydration

Shapes of IR spectrums after the 8th hour of hydration (Fig. 4) confirm an occurrence of intensive changes in cement pastes after the induction period completion. It is visible that a broad band of H–O–H vibration with a maximum at about 3400 cm^{-1} intensifies. There appears a distinct band of $Ca(OH)_2$ at about 3640 cm^{-1}. This band is the most intensive one for the cement paste containing NaOH. In case of reference A, some widening and a shifting of asymmetric stretching vibrations of Si–O from 925 cm^{-1} to slightly higher values of wave numbers is observed. It indicates a formation of C–S–H phase. In case of reference sample B, the forming of C–S–H is confirmed by a presence of the band at around 990 cm^{-1} beside the band of not-reacted alite at 927 cm^{-1}. In case of cement pastes activated with Na_2SO_4 and NaOH, there are two bands visible; a distinct band of vibration of SiO_4 in C–S–H phase at about 1000 cm^{-1} and a weak alite band at about 930 cm^{-1}. It confirms accelerating action of these compounds. In the two latter cases, the SO_4^{2-} band at about 620 cm^{-1} is clearer. $CaCl_2$ shows the fastest acceleration of hydration between the 3rd and 8th hour after adding water to binder, which confirms the results of calorimetric findings (greatest amounts of released heat in this period). After 8 h of hydration in cement paste containing $CaCl_2$, the initial components of Portland clinker are practically not visible (main absorption band of alite has disappeared, and the intensity of a band at about 520 cm^{-1} has much decreased). However, the C–S–H band is distinct. The band at about 1100 cm^{-1} is decreasing, which is an indication of a beginning of further transformation of sulfate phases.

24th hour of hydration

After 24 h of hydration, shapes of IR spectrums of investigated cement pastes are already quite similar (Fig. 5). Practically, there are no visible bands that would indicate any presence of alite. Moreover, there is more evidence that indicates hydration progress, namely: increasing intensity of $Ca(OH)_2$ band at 3640 cm^{-1} (the most intensive for sample with NaOH), intensification of the broad absorption band of hydrates between 3200 and 3600 cm^{-1}, and the presence of intensive band of C–S–H phase. In case of the reference A, the maximum of C–S–H band is at around 980 cm^{-1}, that is in a typical place for this product [13], whereas for cement pastes containing PM the maximum is shifted to slightly higher values of wave numbers. It may indicate a higher degree of silicate polymerization or a formation of the C–S–H phase, richer in silica, in the presence of ash [15]. The band at about 1100 cm^{-1} is the most intensive in case of cement pastes containing Na_2SO_4 and NaOH, and this suggests the largest content of ettringite in these samples, whereas in case of cement paste with $CaCl_2$ the band is hardly visible. Probably, in case of cement paste containing $CaCl_2$ most of the SO_4^{2-} ions available got combined in ettringite before the 24th hour of hydration, and then a conversion in the direction of chloroaluminates and monosulfate was started. It has to be pointed out, however, that in research [16] a formation of compounds of hydrated calcium chloroaluminates type in pastes containing $Ca(OH)_2$, ash and $CaCl_2$ was observed only on the 7th day of hydration.

In case of cement paste containing NaOH, there is a presence of weak band at about 1200 cm^{-1} which, together with a band at 1100 cm^{-1}, suggests conversions towards monosulfate formation.

[**] Abbreviations used in cement chemistry : C–S–H – hydrated calcium silicates of different chemical composition, the main product of cement hydration, also the product of pozzolanic reaction between active silica and $Ca(OH)_2$. Other abbreviations used in this paper: C_3S – tricalcium silicate, alite, $3CaO\cdot SiO_2$; C_3A - tricalcium aluminate, $3CaO\cdot Al_2O_3$; C_3F – ferrite phases, $3CaO\cdot Fe_2O_3$

The band characteristic for carbonates at around 1420 cm^{-1} starts changing its shape parallel to its loss of symmetry (most visible in case of the sample admixtured with $CaCl_2$). It indicates a beginning of transformations of carbonate phases.

Mechanism of chemical activation of cement pastes containing fly ash

$CaCl_2$

Findings presented in this paper confirm the accelerating effect of $CaCl_2$ on hydration of cement–fly ash paste. In the presence of $CaCl_2$ a shortening of induction period takes place, and an intensive hydration period follows. As a result, shortening of setting and hardening times may be expected. The acceleration is connected with a release of greater amounts of heat, especially in initial hours of the hydration. The admixture of $CaCl_2$ eliminates the retarding effect of the ash – duration of induction period for cement–fly ash paste containing $CaCl_2$ was similar to the value registered for reference A, while the effect of heat release that followed (connected with crystallization of hydration products) was even more intensive.

There is a hypothesis concerning the shortening of induction period of cement paste admixtured with $CaCl_2$ that claims that initial decrease of $Ca(OH)_2$ solubility is a result of great saturation with Ca^{2+}, which may contribute to earlier crystallization of $Ca(OH)_2$ [17]. This accelerating of $Ca(OH)_2$ crystallization, however, was not observed in conditions of experiment for this paper findings. In the initial hydration hours some reduction of $CaSO_4$ solubility was observed, probably as a result of common ion, and acceleration of hydration of clinker phases by $CaCl_2$. Smaller amounts of SO_4^{2-} ions moving in the initial minutes to solution may result in the formation of smaller amounts of ettringite and a faster hydration of aluminates. In consequence, a thinner ettringite layer is formed on clinker grains, and this results in considerable shortening of induction period.

Simultaneously, fast appearing of the first portions of C–S–H phase, already after 25 min, may suggest catalytic influence of $CaCl_2$ and/or that it facilitates nucleation. These phenomena are also reported as hypotheses of accelerating effect of $CaCl_2$ [17]. The forming of C–S–H in initial periods is not connected with direct crystallization of $Ca(OH)_2$ despite the presence of larger amounts of Ca^{2+} ions in the solution resulting from admixture introduction. It may indicate that silicate phase that is formed in initial periods is rich in Ca^{2+}.

Obtained results partially confirm research findings of Cheeseman and Asavapisit [18], who observed as early as on the 1st hydration day (in case of cement paste containing small amounts of $CaCl_2$) the formation of $Ca(OH)_2$ in amounts close to the level registered for a cement paste without the activator, and that the formation of $Ca(OH)_2$ got limited after exceeding a certain level of $CaCl_2$.

Moreover, it should be noted that for all investigated cement pastes containing PM ash a mechanism of C–S–H precipitation must be different from an analogous process occuring in the reference A. It was shown clearly in IR spectrums. In case of cement paste without ash, the forming of C–S–H is confirmed by a shifting of the main band of alite vibrations to higher values of wave numbers, which is well recognised in literature [13]. It is different, however, in case of cement pastes containing ash – a presence of C–S–H is initially observed as an additional band at about 1000 cm^{-1} developing beside the alite band at about 925 cm^{-1}. The alite band disappears in subsequent time. After a short induction period, between 3rd and 8th hour of hydration, there occurs a specifically intensive acceleration of reactions. The C–S–H forms very fast. One may expect that for the reason of relatively small amounts of introduced $CaCl_2$, it does not cause new silicate phases to form in a way different from those created in cement hydration. It does, however, accelerate a reaction of tricalcium aluminate (C_3A) and ferrites with gypsum. Probably, the gypsum reacts first and the ettringite arises; after SO_4^{2-} ions consumption, a monochloroaluminate $C_3A\cdot CaCl_2\cdot 10H_2O$ (Friedel's salt) is formed, while after $CaCl_2$ runs low, there occurs a conversion of the ettringite in the monosulfate [17]. In case of ferrite phases, a compound analogous to Friedel's salt is formed $C_3F\cdot CaCl_2\cdot 10H_2O$ [19].

Similar products may be formed in reaction with aluminate ions that are moved into solution from the ash. However, for the reason that chlorides do not show characteristic bands in infrared, while IR spectrum of Friedel's salt [20] does show bands in places where the other components of cement pastes absorb, a presence (or lack) of compounds of the type of Friedel's salt has not been confirmed in our findings. It can be expected, though, that $CaCl_2$ will act as activator also in relation to pozzolana, i.e. fly ash, which was confirmed by some authors [16, 21–23]. Nevertheless, during 24-h hydration, the acting of $CaCl_2$ to improve fly ash activity is not clearly visible. The activation of cement–fly ash paste is basically limited to the influence of $CaCl_2$ on hydration of clinker phases.

Na_2SO_4

Presented results confirm the accelerating acting of Na_2SO_4 in relation to the hydration of cement–fly ash paste. The shortening of the induction period, however, reveals a lower degree intensity than in the presence of

$CaCl_2$. This observation may be linked to the fact that larger amounts of ettringite are formed, which is visible already in the first minutes after adding water to binder. It is confirmed in works of other authors reporting that the forming of ettringite is an important stage of sulfate activation, and it explains improvement in early strength of cement components containing ash [6, 7, 21–23].

To start from the very first minutes of hydration, similar to $CaCl_2$, the forming of C–S–H phase is observed. It is an effect of faster dissolving of alite and belite in the presence of activator. Similarly as in the case of cement pastes with $CaCl_2$, the creation of C–S–H in the first minutes of hydration is not connected with a distinct precipitation of $Ca(OH)_2$, which suggests that the C–S–H phase is rich in Ca^{2+}. After induction period, there occurs an acceleration of processes, yet not as intensive as in the case of $CaCl_2$. The period of crystallization of products is extended in time, similarly as in the case of cement–fly ash paste without admixtures. It was noted that the result of extended activity of Na_2SO_4, compared to $CaCl_2$, is a constant increase in the amount of heat released up to 48 h of hydration, during which time the total amount of emitted heat is the greatest. Observed phenomena may be linked with changes of composition of liquid phase, that is, a decrease of Ca^{2+} ions concentration and increase of OH^- ions concentration [17].

In case of activation of cement–fly ash paste with Na_2SO_4, two directions of its acting should be taken into consideration: accelerating of the hydration of alite and belite, and accelerating of dissolving of glass alumina-silicate phases from ash. According to quoted authors [21–23], Na_2SO_4 reacts with $Ca(OH)_2$ in the presence of water, and, as a result, $CaSO_4{\cdot}2H_2O$ precipitates and NaOH arises. The effect of this is a fast increase of pH of the solution, which makes it easier to dissolve alumina-silicate glasses of ash, thereby to accelerate the pozzolanic reaction, mainly in the period controlled by pozzolana dissolving. Probably, such a process takes place also in the analysed case, but in the first 24 h after water addition it was more important to note the acceleration of hydration of clinker phases.

NaOH

The presence of NaOH accelerates the hydration of alite, i.e. the main component of Portland cement. The accelerating acting displays mainly in early periods (up to one day of hydration) [24]. It is consistent with our findings of calorimetric measurements. It was observed that in the presence of NaOH the accelerating of hydration of cement–fly ash paste, similarly as in two other cases, discussed earlier. However, the results show that a mechanism of acting of each of the admixtures is different. In case of the introduction of NaOH into cement system, the amount of heat released in the first minutes of hydration is the lowest. Observed shortening of induction is similar as in the case of Na_2SO_4 but the period of acceleration of processes that follows is more intensive, similar to $CaCl_2$. In given conditions of the experiments the presence of NaOH favours fast ettringite forming. In subsequent hours of hydration the monosulfate arises, and it is possible that a monosulfate phase rich in sodium ions is also formed.

To start from the first minutes after water addition, the acceleration of C–S–H phase forming connected with greatest amounts of $Ca(OH)_2$ precipitation takes place. It is possible that according to reports of authors [24, 25] Na^+ ions build into structure of surface layer of hydrated alite already in the first minutes of hydration. It is most likely that the Na^+ ions build also into other hydration products, which was presented in other papers [26, 27]. Fast ettringite formation and crystallization of $Ca(OH)_2$ may be explained by the increase of gypsum dissolution and reduction of $Ca(OH)_2$ dissolution after NaOH introduction. It is not unlikely that in case of all admixtures used, the main activation acting in the first 24 h is caused by the acceleration of hydration of clinker phases. Distinct improvement of pozzolanic properties of ash may only be visible in subsequent periods of hydration.

Conclusions

- A combination of calorimetry and infrared absorption is a good method to investigate mechanisms of early cement hydration. It is especially important in cases when active materials are introduced into cement components as additives or admixtures.
- The calorimetry enables continuous observations of exothermic reactions occurring after water has been added to binder. It is especially important in case of comparative investigations.
- Infrared absorption enables to draw conclusions about hydration products being formed in definite periods.
- It was confirmed that the application of chemical activators such as $CaCl_2$, Na_2SO_4 and NaOH accelerates the early hydration of cement pastes containing fly ash addition. It has to be noted, however, that the mechanism of activators acts differently for each of them.
- It is claimed that acceleration of chemical processes in cement–fly ash paste (in case of all admixtures used), up to 24 h of hydration, is mainly connected with the acceleration of cement hydration. Only to a small degree it can be the effect of increasing of ash grains dissolving.

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