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STUDIES ON THE POZZOLANIC AND HYDRAULIC PROPERTIES OF FLY ASHES IN MODEL SYSTEMS

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In this work, the pozzolanic and hydraulic properties of ashes originating from various sources were studied in model systems such as ash and ash-lime pastes. The sources of studied ashes were: fluidized combustion of brown coal, pulverized combustion of brown coal and pulverized combustion of hard coal. This article is a continuation of our previously published studies on cement pastes with mentioned ashes.

The following experimental techniques were applied: calorimetry, thermal analysis (TG, DTG) and infrared absorption (IR). Previously drawn conclusions relating to the reactivity of ashes in an environment containing Ca^{2+} ions were confirmed. According to these conclusions, an ash originating from fluidized combustion of coal exhibited higher reactivity compared to other ashes from pulverized combustion. Pozzolanic and hydraulic properties of this ash were also confirmed. Differences in the behaviour of ashes originating from pulverized combustion of various types of coal in the presence of water and Ca^{2+} rich environment were demonstrated.

Keywords: *fly ash, hydration, hydraulic activity, pozzolana*

Introduction

The studies on the utilization of various waste products in cement composition, influence of these waste products on the processes of cement hydration and on the properties of final material, have been carried out for many years. The examples of materials that are chemically active in the system of hydrating cement are: silica fume [1–3], spent fluidized catalytic cracking catalysts [4–7], fly ashes of various types [2, 8–12].

Fly ashes have been used for many years in building engineering, for instance as a component of cements, and their influence on the processes of hydration of Portland cement was a subject of many studies. Many factors influence the physico-chemical properties of these ashes, being a waste product of power plants. These factors include the type of coal, its grain size, conditions of combustion, etc. Therefore, ashes of various origin can significantly differ in physico-chemical properties and in consequence in activity in the environment of hydrating cement, which is confirmed by experimental results presented in [8]. Large part of ashes does not meet the standard requirements for the components of cement or concrete and therefore they can not be utilized in this way. Such ashes attract special attention of the researchers.

The action of ashes in cement compositions is a complex one. As a rule, they exhibit pozzolanic or pozzolana-hydraulic properties, influencing the amount of $Ca(OH)_2$ and binding phases in the system. In the beginning phases of hydration, small ash grains can act as centers for precipitating products of cement hydration. Soluble constituents of the ashes can also influence the early hydration of cement. The grains of additive that did not take part in a reaction, act as micro-fillers.

Pozzolanic activity means the ability to react with $Ca(OH)_2$, including calcium hydroxide liberated during hydration of cement. The products of pozzolanic reaction between the active phases of the ash and $Ca(OH)_2$ are compounds similar to those that are formed during the hydration of cement – hydrated calcium silicates (so-called C–S–H phase) and hydrated aluminate phases. Pozzolanic materials contain active silica but do not contain significant amounts of calcium compounds and that is why they do not exhibit intrinsic binding properties in the presence of water. Contrary to the materials of this type, hydraulic additives contain bigger amounts of calcium compounds, enabling the binding reactions.

Our earlier works [8, 13] present the influence of addition of ash from fluidized combustion of brown coal, compared to ashes originating from pulverized combustion, on the hydration of cement. Differences in physico-chemical properties of these waste products were confirmed, resulting in different activity of ashes. It was demonstrated that the ash from the fluidized combustion contains highest amounts of calcium and sulphur compounds, compared to other samples. Chemical

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composition of studied ash from fluidized combustion suggests, that in a cement system, it can exhibit pozzolanic and hydraulic properties. Thermal analysis studies on cement pastes conducted during 90 days of hydration showed that the ash from fluidized combustion exhibited higher pozzolanic activity compared to the other studied wastes. For cement pastes containing more active ash originating from fluidized combustion, higher amounts of water bound in hydrates and lower concentration of $Ca(OH)_2$ were observed, compared to the samples of pastes containing other ashes [8]. Calorimetric and IR absorption studies carried out during 48 h of hydration confirmed that this ash exhibits higher activity already in the first period of hydration [8, 13].

This work is a continuation of above presented studies. The aim of this study was an attempt of more precise analysis of pozzolanic and hydraulic properties of ashes in model systems, such as ash and ash-lime pastes.

The main experimental methods used in this work were thermal analysis (TG, DTG), and infrared absorption (IR). Additionally, for ash pastes calorimetric studies were carried out in the period between addition of water and 48th hour of hydration.

Experimental

Materials

The materials used in this work were ashes originating from different sources: fluidized combustion of brown coal (denominated as PF ash), pulverized combustion of brown coal (PP ash) and pulverized combustion of hard coal (PM ash). Main properties of PF, PP and PM ashes are presented in Table 1. Other properties of these ashes were shown in the article [8].

Ash pastes were prepared by mixing ash and water (with the mass ratio water/ash=0.7). Pastes were tightly enclosed in plastic bags and stored in room temperature for the given period of time. Then the samples were removed from plastic bags, processes of hydration were inhibited with acetone, the samples were dried and thermal analysis (TG, DTG) as well as infrared absorption (IR) studies were carried out. In the case of calorimetric studies, hydration was carried out in a calorimeter in the temperature of 25°C.

Ash-lime pastes were prepared in the following way: ash was mixed with $Ca(OH)_2$ (70 mass% of ash and 30% $Ca(OH)_2$). Then water was added to this mixture (mass ratio: water/(ash+$Ca(OH)_2$)=0.7). Prepared pastes were enclosed in hermetic plastic bags and stored in room temperature. On a given day of hydration, samples were removed from the bags. Then hydration was inhibited in the same way as for ash pastes. Dried samples were investigated by means of TG, DTG and IR methods.

Table 1 Selected properties of PF, PP and PM ashes [8]

Property	Fly ashes		
	PF	PP	PM
Oxide chemical composition (the main components)/mass%			
SiO_2	39.4	44.8	51.4
Al_2O_3	30.0	33.8	30.0
Fe_2O_3	2.16	2.30	4.19
CaO	11.64	3.75	1.33
SO_3	3.75	0.94	0.61
Na_2O+K_2O	3.33	3.58	3.44
phase composition*			
SiO_2 (quartz)	+	+	+
$Al_6Si_2O_{13}$ (mullite)		+	+
$CaSO_4$	+	+	
CaO	+	+	
Fe_2O_3	+		
$CaAl_2Si_2O_8$	+		
Loss of ignition**/mass%	1.9	1.3	3.5

*mark (+) means, that presence of a component was confirmed by X-ray analysis,
**total mass loss in temperature range up to 1000°C

Methods

Calorimetry

Differential calorimeter BMR, constructed at the Institute of Physical Chemistry in Warsaw was used. The results of analysis of first 48 h of hydration, in the form of heat release rate curves and the amount of released heat, were calculated by means of computer software [14].

Thermal analysis (TG, DTG)

SDT 2960 Thermoanalyser, produced by TA Instruments was used. Studies were conducted in the temperatures to 1000°C, heating rate 10°C min^{-1}, mass of samples 9–13 mg.

Infrared absorption

FTIR spectrophotometer Genesis II, produced by Mattson was used. Wavenumber range 4000–400 cm^{-1}, sample preparation – pelletizing with KBr.

Results and discussion

Studies on ash pastes

Experimental results obtained for ash pastes are presented in Figs 1–5. As it could be predicted, studied ashes exhibit low reactivity in water, especially when compared to the results obtained for Portland cement or Portland cement with the addition of ash. However, higher reactivity of PF ash, compared to PM and PP is clearly seen, confirming its hydraulic properties.

In Fig. 1, the curves of heat release rate for ash pastes and amounts of released heat during 48 h of hydration are presented. These results show that in the first min after the addition of water to the ashes, quick release of heat takes place, related to the wetting of grains and transfer of soluble components into the solution. This phenomenon is most intensive for PF ash, probably because of higher porosity of grains and presence of CaO which exothermally reacts with water. The least intensive wetting effect was observed for PM ash. In the case of PM ash, except for wetting, no other thermal effects related to the reaction with water, were observed. As it could be predicted, this ash does not exhibit hydraulic properties, which is related to the low concentration of calcium compounds in its composition. Different course of heat release rate is observed for PF ash paste, where after about 16 and 35 h two additional effects of heat release can be observed. Such behaviour of this waste product suggests its hydraulic character, manifesting itself already during the first 48 h.

Analysis of the amount of heat released during 48 h of hydration gives a reason to conclude that in the reaction with water higher reactivity is demonstrated by ashes originating from the combustion of brown coal (PF and PP ashes) than from hard coal (PM ash). For the PM ash, total, small amount of heat released in the reaction with water was evolved during the first hour of hydration. In the case of PP ash, a release of slightly bigger amount of heat is observed, which increases gradually during the whole time of analysis. Whereas, in the case of PF ash, the largest amount of released heat with relatively significant increase during 48 h, is observed. Obtained results permit to ascertain that PP ash exhibits certain reactivity in contact with water. Heat release in this period should not be related and probably can not only to the processes of wetting and dissolving of ash components. Higher concentration of calcium compounds than the in case of PM ash, can be one of the causes of this initial, low reactivity of PP ash [15].

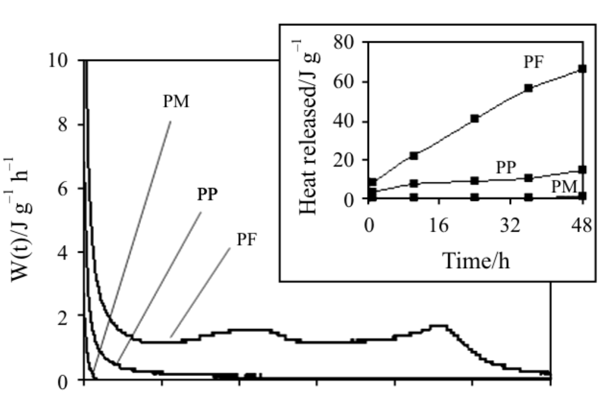

Fig. 1 Heat evolution curves and heat released for ash pastes prepared with PF, PP and PM ashes

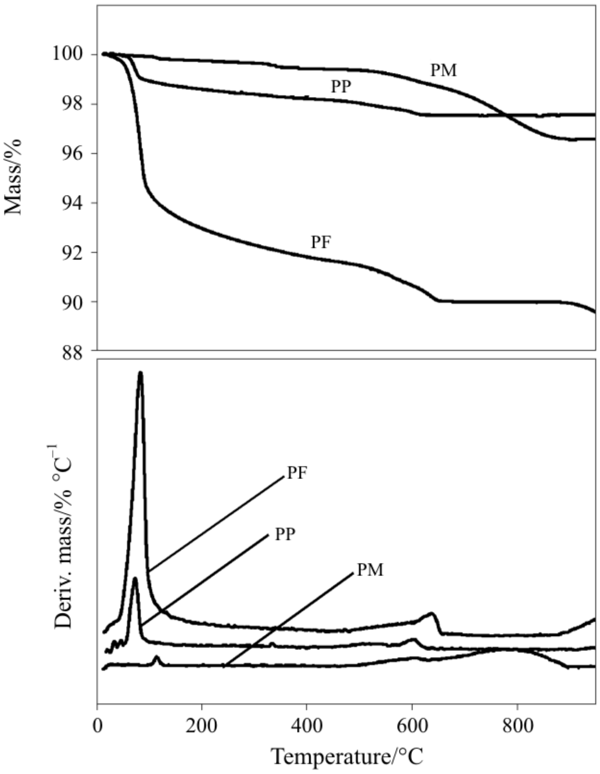

Fig. 2 TG and DTG curves for ash pastes prepared with PF, PP and PM ashes (28th day of hydration)

However, it should be noted that even in the case of PF ash, observed thermal effects are much lower than those observed during hydration of a hydraulic binder, such as Portland cement.

Similar conclusions relating to the reactivity of ashes towards water, can be drawn from the results of thermal analysis. In Fig. 2 a comparison of TG and DTG curves obtained after 28 days of hydration is presented. After 90 days similar results were procured. The main mass loss relating to the dehydration of ash and water reaction products takes place in the temperatures up to 200°C. It is clearly seen that in the case of PM ash, this mass loss practically does not happen and the total mass loss is similar to the value of loss on ignition of this ash. Largest amounts of hydrates are formed during hydration of PF ash. In the case of PF ash, mass loss recorded to the temperature of 500°C is about 8.5%, over four times more than the loss on ignition of this ash (Table 1). Consequently, its hydraulic properties, manifesting themselves by the formation of phases of hydrated compounds, are confirmed. It should be noted, however, that in a measure, the amount of mass loss can be influenced also by the porous structure of PF ash, resulting in an incomplete removal of chemically unbound water in the conditions of hydration inhibition.

In the case of PP ash discussed mass loss is slightly higher than loss on ignition, which indicates the formation of new products of reaction between this ash and water in small amounts.

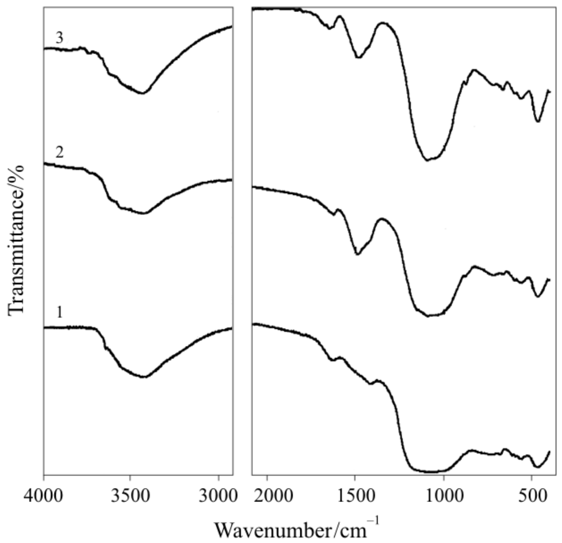

Fig. 3 IR spectra of 1 – PF ash and ash paste prepared with PF (2 – 28th and 3 – 90th day of hydration)

Formation of hydrates in studied ash pastes is practically finished before 28th day of the experiment, which is confirmed by the fact that the elongation of hydration time to 90 days does not cause the increase of the amount of bound water (lack of significant differences in the shape of TG and DTG curves after 28 and 90 days of hydration) [15].

In Figs 3–5, recorded earlier IR spectra of dry PF, PP and PM ashes [8], and IR spectra of studied ash pastes, are presented for the comparison. It can be ascertained that the IR spectra of ash pastes differ only slightly from the spectra of dry ashes, particularly in the case of PM ash. It confirms that studied ashes only to a limited extent undergo hydration in water with the formation of phases of new hydrates.

Detailed analysis of IR spectra shape demonstrates that in the case of PF ash, changes in the wide band of water molecules stretching vibrations (3700–3100 cm^{-1} [16]) take place during hydration. Additional, weak absorption bands appear at 3730 and 3636 cm^{-1}, which can indicate the formation of new silicate or aluminate hydrates. The absorption band of O–H in H–O–H deformation vibrations, located at 1627 cm^{-1} is slightly more intensive. Appearing in the spectrum of ash paste PF, absorption bands at 1485 and 877 cm^{-1}, evidence the presence of carbonates [17], probably formed as a result of carbonatization of hydration products. In the case of PF ash paste, also the change of shape of an absorption band having the maximum at 1092 cm^{-1} (Si–O and Al–O vibrations [18]) can be noticed after 28 days of hydration, compared to the spectrum recorded for a dry ash. Noticeable narrowing of this band with the time of hydration and the shift of its maximum towards higher wavenumbers indicates the change of structure of silicate and aluminate phases.

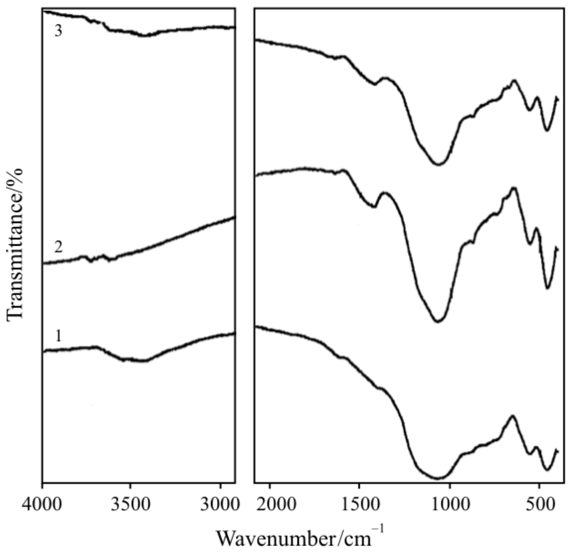

Fig. 4 IR spectra of 1 – PP ash and ash paste prepared with PP (2 – 28th and 3 – 90th day of hydration)

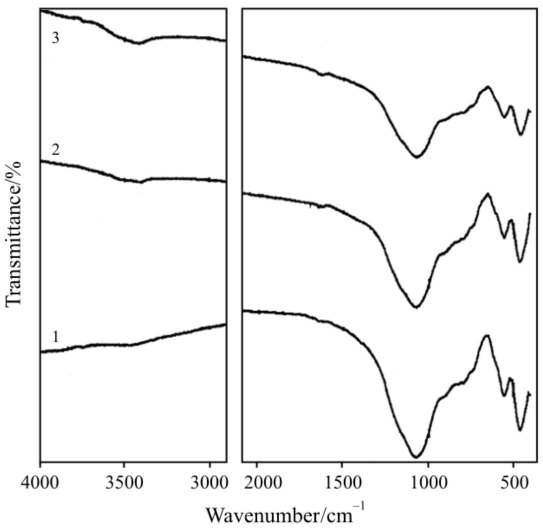

Fig. 5 IR spectra of 1 – PM ash and ash paste prepared with PM (2 – 28th and 3 – 90th day of hydration)

Similar changes in IR spectra of ash pastes, particularly relating to the ranges of wavenumbers characteristic for the vibrations of carbonate groups as well as silicate and aluminate phases, are also visible for the paste of PP ash.

On the other hand, in the case of paste made of PM ash, after 28 and 90 days of hydration, no distinct changes in the shape of bands in the analyzed range can be noticed, which confirms earlier drawn conclusions, that this ash does not react with water [15].

Studies on ash-lime pastes

Results obtained for ash-lime pastes are presented in Figs 6–10. These results confirm that in the presence of adequate amount of $Ca(OH)_2$ and water, studied ashes exhibit pozzolanic properties. Depending on the origin of the ash, determining its physico-chemical properties, the activity of ashes in an environment containing Ca^{2+} ions is different.

In Fig. 6 exemplary TG and DTG curves of ash-lime pastes are presented, recorded after 28 days of hydration. Three characteristic effects of mass loss are observed:

- to about 400°C (on DTG curve two main peaks to the temperature of 200°C) – release of water from the formed C–S–H hydrates, hydrated calcium aluminates and aluminosulphates
- in the range of 400–480°C – decomposition of $Ca(OH)_2$
- over 500°C – decomposition of carbonates ($CaCO_3$) formed as a result of carbonization with carbon dioxide from air as well as introduced with $Ca(OH)_2$ used for the preparation of pastes

The values of the above mentioned mass losses after 28 and 90 days of hydration are presented in Fig. 7.

Similar shape of the curves obtained for all studied pastes means that the nature of the reactions taking place in the systems up to 28th day and products of these reactions are similar.

Significant differences in the intensity of observed effects indicate the varied quantitative composition of studied samples resulting from the differences in the activity of ashes. All three studied wastes undergo pozzolanic reaction in an ash-lime paste already during the first 28 days. The analysis of mass losses of pastes recorded up to temperature of 400°C confirms high reactivity of PF ash, manifested by the largest amount of water bound in the products of pozzolanic reaction. In the case of PM ash, also the increase of amount of phases decomposing below 400°C in time is observed, however it is lowest among all studied ashes. It has to be noticed that for the paste containing PF ash, the amount of water bound in hydrates practically does not change since the 28th day of hydration, while for PP and PM ashes it increases between the 28th and 90th day. It confirms higher activity of PF ash in the beginning days of hydration and gradual development of pozzolanic activity in time in the case of ashes originating from conventional combustion.

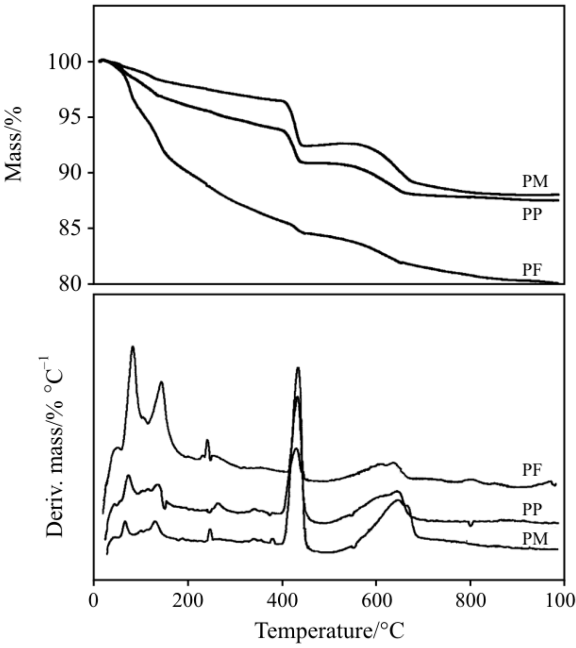

Fig. 6 TG and DTG curves for ash-lime pastes prepared with PF, PP and PM ashes (28th day of hydration)

Similar conclusions related to the evaluation of pozzolanic activity can be drawn basing on the mass losses caused by the decomposition of $Ca(OH)_2$ (value proportional to the amount of $Ca(OH)_2$ in the sample). It is noticeable that calcium hydroxide present in the system is expended in the pozzolanic reaction with ashes. This process runs slowest in the system containing PM ash and fastest in the system with PF ash. In the case of PF ash the amount of calcium hydroxide in the sample changes only slightly between 28th and 90th day of hydration, which allows to conclude that active towards calcium hydroxide components of PF ash reacted almost completely during first 28 days of hydration. On the other hand, in the case of PP and PM ashes, the amount of hydroxide in pastes decreases in time, which is an evidence for pozzolanic reaction taking place in the systems containing these ashes in later periods compared to the PF ash.

Mass losses of ash-lime pastes recorded in the range of temperatures from 500 to 1000°C corresponding to the decomposition of carbonates, do not differ significantly both after 28 and 90 days of hydration. Only in the case of paste containing PF ash slight increase of mass loss is observed.

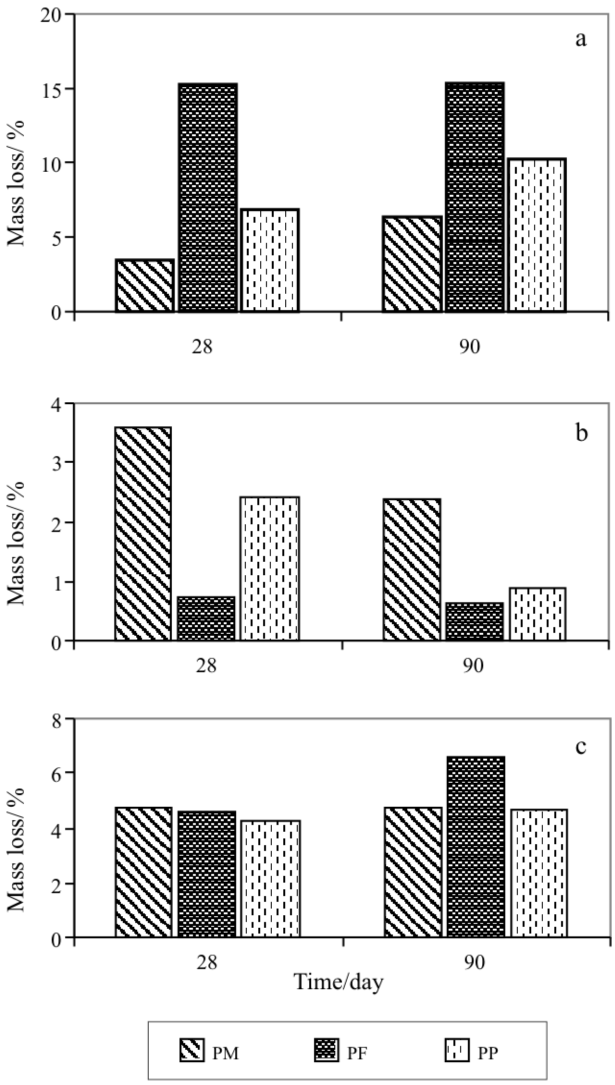

Fig. 7 Mass losses for ash-lime pastes prepared with PF, PP and PM ashes (a – to about 400°C, b – 400–480°C, c – over 500°C)

The above presented conclusions related to the activity of studied ashes in the environment of Ca^{2+} ions, are also confirmed by the results of infrared absorption studies of ash-lime pastes (Figs 8–10). The formation of phases of new products is particularly visible when, similarly to the ash pastes, a comparison of infrared spectra for ash-lime pastes and dry initial ashes is made.

In the IR spectra of ash-lime pastes, most of all the attention is drawn to the changes of shape and intensity of absorption bands located in the range characteristic for the H–O–H valence vibrations (ca. 3700–3200 cm^{-1}, including sharp peak characteristic for the OH group vibrations in $Ca(OH)_2$, located at about 3640 cm^{-1}), and intensive bands appearing at about 1000 cm^{-1}, characteristic for silicate and aluminate phases.

Deterioration in hydration time of sharp, clear absorption band of vibration of OH group in $Ca(OH)_2$ confirms pozzolanic properties of studied ashes. It is visible that the reduction of this band is least intensive for the paste containing PM additive and most intensive for the sample containing PF. It is characteristic that in the case of PF ash, discussed absorption band already in the 28th day of hydration is weak and disappears almost totally after 90 days. Obtained results confirm the thermal analysis results, presented earlier. Moreover, for the paste containing PF ash, formation of higher number of bands in the range 3700–3200 cm^{-1} is observed, suggesting more complex composition of hydrates than for PP and PM ashes.

Changes of the shape of absorption band related to the vibrations of Si–O and Al–O bonds indicate the progress in formation of binding compounds in ash-lime pastes. In the case of paste containing PF ash, certain decrease of intensity of this wide band is observed, in the range of wavenumbers of 1200–900 cm^{-1}, particularly from the side of higher wavenumbers, evidences the disappearance of silicates and aluminates, originating from the ash in the paste. At the same time, already after 28 days of hydration, there is a clearly visible absorption band formed at about 970 cm^{-1}. It evidences that silicate and aluminate phases from the ash fade away in the sample and C–S–H phase is formed as a result of pozzolanic reaction. Between 28th and 90th day, in the discussed range of wavenumbers only slight changes take place, which also confirms earlier ascertainments that PF ash reacts in the presence of Ca^{2+} ions mainly in the first 28 days of hydration. Very similar nature of changes in the discussed range of wavenumbers is exhibited by the pastes made of PP ash. A difference, compared to pastes containing PF ash, is higher

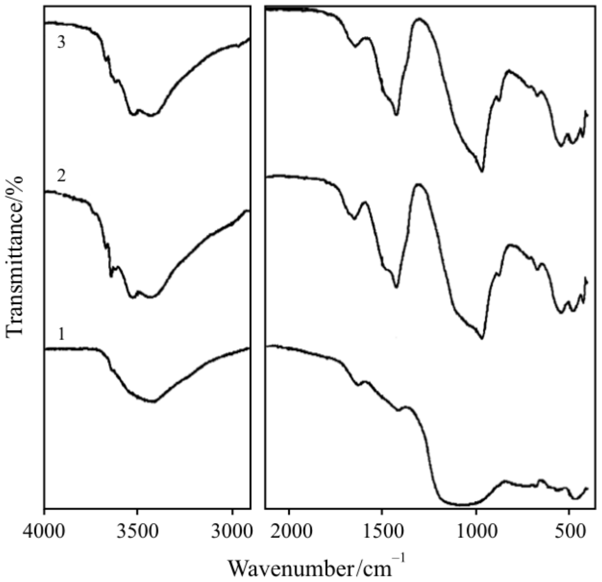

Fig. 8 IR spectra of 1 – PF ash and ash-lime paste prepared with PF (2 – 28th and 3 – 90th day of hydration)

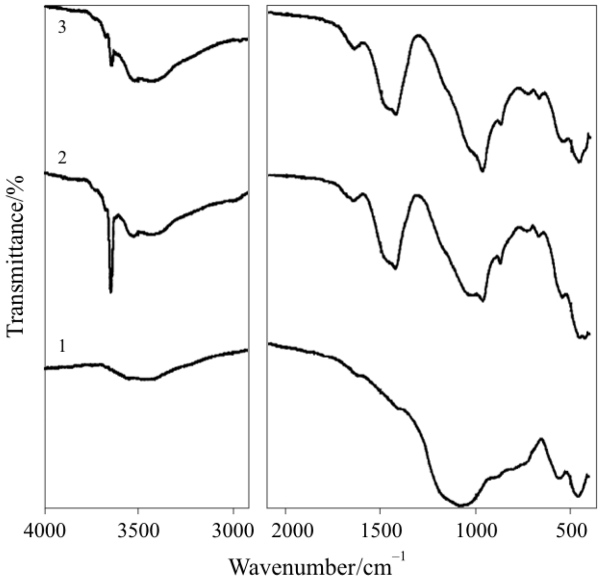

Fig. 9 IR spectra of 1 – PP ash and ash-lime paste prepared with PP (2 – 28th and 3 – 90th day of hydration)

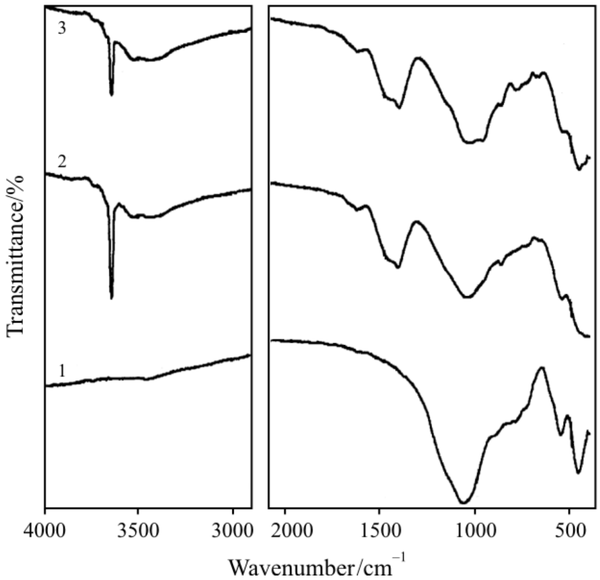

Fig. 10 IR spectra of 1 – PM ash and ash-lime paste prepared with PM (2 – 28th and 3 – 90th day of hydration)

sharpness of a peak located at the side of higher wavenumbers between 28th and 90th day of hydration, indicating that the progress of pozzolanic reaction during this period of time is more significant.

The changes of this absorption band for pastes containing PM ash are different than in the cases of other samples. Wide peak originating from aluminate and silicate groups in the initial ash is visible in the spectra of pastes both after 28 and 90 days of hydration. It indicates that the level of transformation of ash glasses is lower. After 28 days of reaction, no clear band evidencing the formation of C–S–H phase is visible. There is only a slight inflection from the side of lower wavenumbers (below 1000 cm^{-1}). This fact gives a reason to ascertain that pozzolanic reaction takes place and some hydrates of the C–S–H type are formed, however, in smaller amounts than in the presence of PP and PF ashes. In the ash-lime paste containing PM ash, after 90 days the band located below 1000 cm^{-1} is much more distinct and indicates the increase in time of the C–S–H type phases in the sample [15].

Conclusions

Carried out research was a continuation of earlier studies, in which the influence of ashes of various origins on the hydration of Portland cement was investigated [8, 13]. Earlier conclusions were confirmed, relating to the reactivity of ashes in an environment containing Ca^{2+} ions, according to which, PF ash, originating from the fluidized combustion of coal exhibited higher reactivity compared to PP and PM ashes from pulverized combustion. On the other hand, it was demonstrated that while in the earlier studies on cement pastes it was found that the activity of PP and PM ashes is similar, in simpler systems such as ash and ash-lime pastes, certain differences are visible. Studies on ash pastes confirmed that PF ash in the presence of water exhibits some hydraulic properties, which was expected because of highest concentration of calcium compounds in this material. Low reactivity was also observed for PP ash, and PM ash, as it could be predicted, did not exhibit any hydraulic properties.

Clear pozzolanic properties of studied ashes manifested themselves in an environment containing high concentration of Ca^{2+} ions, i.e. in ash-lime pastes. Investigations carried out with the techniques of thermal analysis and infrared absorption confirmed higher pozzolanic activity of PF ash, for which earlier and faster binding of $Ca(OH)_2$ was observed. In the studied paste containing PF, the majority of $Ca(OH)_2$ was bound during first 28 days of hydration, with the formation of binding compounds of the type of hydrated silicates and aluminates. In the other samples pozzolanic reaction went on during the whole experiment, i.e. to the 90th day of hydration, and it was found that PM ash exhibits lower activity compared to PP. Obtained results confirmed that in the case of PP and PM ashes pozzolanic activity develops mainly in the later periods of hydration.

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