



Article The Role of Pozzolanic Activity of Siliceous Fly Ash in the Formation of the Structure of Sustainable Cementitious Composites

Grzegorz Ludwik Golewski D

Department of Structural Engineering, Faculty of Civil Engineering and Architecture, Lublin University of Technology, Nadbystrzycka 40 Str., 20-618 Lublin, Poland; g.golewski@pollub.pl; Tel.: +48-81-538-4394

Abstract: The following article introduces, in a thorough manner, how the chemical pozzolanic reaction takes place in cement composites containing the fly ash (FA) additive. In the research part, however, the development of phases in the structure of the cement paste in the initial period of its curing and after 28 days from its preparation was traced. For this purpose, a Scanning Electron Microscope (SEM) was used. In order to accurately highlight all the characteristic stages of the formation of the structure of the composite containing FA, an analysis of the cement matrix was carried out between 0.5 and 28 days of their curing. Microstructural studies were complemented by tests of pozzolanic activity of FAs used. In order to conduct a full analysis of this feature, experiments were carried out using two types of research methods, i.e., chemical and physical. On the basis on the conducted studies it was found that: in cement composites with the addition of FA, in the period until the third day of curing, the development of the material structure is mainly the result of the hydration reaction, and between the seventh and fourteenth day after sample preparation, the first signs of the pozzolanic reaction on FA grains are visible; however, in the period between 14 and 28 days, there is a clear homogenization of the structure of the cement composite with the addition of FA, resulting from the change of disordered phases into compact and homogeneous forms and filling in the composite of porous places with pozzolanic reaction products. The use of cement composites based on materials whose application makes it possible to reduce GHG emissions to the atmosphere, reduce energy consumption, and reduce industrial waste landfills leads towards the development of ecological and sustainable building engineering.

Keywords: siliceous fly ash (FA); pozzolanic activity; cement matrix; scanning electron microscope (SEM); microstructure; C-S-H phase; strength activity index (SAI); sustainable concrete structures

1. Introduction

The goal of producing environmentally sustainable concrete is primarily to reduce the consumption of pure OPC in the technology of manufacturing these composites by replacing it with other useful mineral-based materials [1–12]. In practice, such materials are referred to as Supplementary Cementitious Materials (SCMs), and their large group consists of various types of industrial, agricultural, and other waste [13–20].

It should be stated that industrial waste such as fly ash (FA) or silica fume (SF) are characterized by the so-called pozzolanic activity [21–29]. Thanks to this property, which causes complex chemical reactions in the cement paste, the concrete structure is filled with additional products that are able to seal and strengthen it [30–34]. However, the time of initiation of the pozzolanic reaction and its intensity of interaction depends on numerous factors, such as, for example:

- chemical composition of SCMs,
- content of active oxides contained in SCMs, mainly SiO₂ and Al₂O₃,
 - the content and type of glass and the chemical composition of the glass phase of the material used,



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- fineness, particle size distribution, and specific surface area of the OPC substitute used,
- proportions of water to the solid phase occurring in the cement paste with SCMs,
- thermal and humidity conditions prevailing in the area of the modified composition cement matrix.

Of all the industrial wastes that are pozzolanically active, SF has the highest activity. This is due to, among other things: very high content of active SiO_2 in SF, its high specific surface area, and very fine particle size distribution [35–39]. Similarly high activity is also characterized by nanoadditives [40–45].

On the other hand, FAs exhibit significantly lower pozzolanic activity. However, even if this material is used in cement composites, this feature brings measurable benefits in terms of additional homogenization of the matrix structure [46,47]. Unfortunately, based on previous research, it has not been clearly determined at what point the pozzolanic reaction in the FA-modified cement paste begins. However, such knowledge is of great importance in the process of forecasting the strength of composites based on OPC-FA binders, both early and late in the curing period. On the other hand, FAs are now a basic substitute for cement binder [48–50]. Therefore, one should strive to obtain the most accurate data on the processes occurring in the structure of cement composites from FA, as this affects their mechanical parameters.

Therefore, the following article introduces, in a thorough manner, how the chemical pozzolanic reaction takes place in cement composites containing the FA SCM. The main factors concerning the composition and morphology of FA grains, which have a decisive influence on its final effect, are also given. In the research part, however, the development of phases in the structure of the cement paste in the initial period of its curing and after 28 days from its preparation was traced. For this purpose, a Scanning Electron Microscope (SEM) was used. In order to accurately highlight all the characteristic stages of the formation of the structure of the composite containing FA, an analysis of the cement matrix was carried out between 12 and 678 h of their curing.

Microstructural studies were complemented by tests of pozzolanic activity of FAs used. In order to conduct a full analysis of this feature, experiments were carried out using two types of research methods, i.e., chemical and physical. Thanks to the second method, it was also possible to assess the results obtained with the SEM method in the scope of diagnostics of the initial stage of the pozzolanic reaction initiation in cement composites with the addition of FA.

Thanks to this research, the obtained conclusions may have both utilitarian and proenvironmental significance [51–54]. The practical use of the research results contained in the following article may be helpful in the case of forecasting the early strengths of FA-modified cement composites, which are used with increasing frequency. Such knowledge can be applied to structures that require knowledge of concrete strength at an early or very early age, e.g., prestressed or composite structures [55–57]. In addition, activities consisting of limiting GHG emissions in the atmosphere, reducing energy consumption, and limiting industrial waste in landfills, along with their efficient and useful application, lead to the development of ecological and sustainable construction [58,59].

2. Pozzolanic Activity of Siliceous Fly Ash and Formation of the Structure of Composites in the OPC-FA System

The introduction of FA into the cement paste changes the chemical and physical structure of the cement matrix. FA grains bind with calcium hydroxide, Ca(OH)₂ (CH), forming a calcium silicate hydrate (C-S-H) phase, both on the surface of FA grains and in the pores of the paste [60–62]. The pozzolanic reaction does not generally change the hydration of cement but complements and integrates the hydration process by reducing the CH content while increasing the content of the C-S-H type phase with a lower C/S ratio than in the paste based only on OPC [63]. The course of this reaction is mainly determined by six factors characterized in Section 1 [64–69].

However, the analysis of the properties of pastes with the addition of FA in various fractions shows that more fine-grained FA and better pozzolanic properties contribute to the following: an increase in concrete strength with those additives, shorter bonding time, and smaller quantity of water necessary to obtain the paste of standard consistency. In general, materials having such properties are said to have the ability to bind at room temperature and in the presence of water and calcium hydroxide (CH) to form durable calcium silicate hydrate (C-S-H) as well as calcium aluminate silicate hydrate (C-A-S-H) hydraulic phases [70]. Apart from C-S-H and C-A-S-H, the pozzolanic reaction also produces hydrated calcium aluminates (C_4AH_{13} , C_2AH_8), and hydrated calcium aluminosilicates of the hydro gehlenite (C_2ASH_8) and hydrogarnet ($C_3AS_3-C_3AH_6$) types. The course of the pozzolanic reaction is given in Equation (1).

$$\begin{cases} \operatorname{SiO}_{2}(\operatorname{active}) \\ \operatorname{Al}_{2}\operatorname{O}_{3}(\operatorname{active}) \end{cases} + \operatorname{Ca}(\operatorname{OH})_{2} \xrightarrow{\operatorname{H}_{2}\operatorname{O}} \begin{cases} \operatorname{C}-\operatorname{S}-\operatorname{H} \\ \operatorname{C}-\operatorname{A}-\operatorname{S}-\operatorname{H} \\ \operatorname{C}_{4}\operatorname{AH}_{13}, \\ \operatorname{C}_{2}\operatorname{AH}_{8}, \\ \operatorname{C}_{2}\operatorname{ASH}_{8}, \\ \operatorname{C}_{3}\operatorname{AS}_{3}-\operatorname{C}_{3}\operatorname{AH}_{6} \end{cases}$$
(1)

Due to high pozzolanic activity of finer FA fractions and their ability to significantly reduce water demand, we can obtain composites with more uniform structure, greater homogeneity, and higher strength. The results of the research presented in papers [71,72] show that more fine-grained FA causes:

- increase in composite compressive strength,
- refinement of the pore microstructure in concrete by decreasing the general porosity, pore size distribution, and pore diameter and increasing the number of gelled pores, the size of which ranges from 5.7 to 10 nm,
- limitation of the content of CH phase after 28, 60, and 90 days of curing, which brings forth a reduction in intensity of reflections in diffractograms and changes in microstructure visible in SEM images,
- intensification of the hydration reaction, pozzolanic reaction, and the formation of the nuclei of hydrates,
- significant improvement in concrete microstructure density.

To support the fourth of the above statements, this paper presents SEM images of pastes containing the addition of fine FA fractions in short periods of their curing (see Section 4).

It should also be added that eliminating corrosive CH from hydration products and creating durable C-S-H connections increases the resistance to corrosion and fracture toughness of pastes, mortars, and concretes made of cement containing FA [73–76]. FAs reduce the heat of cement hydration, increase its water tightness, and reduce shrinkage [77].

Such cement exhibits slow dynamics of early strength growth, but after a longer period of time its strength reaches a value exceeding the strength of Portland cement [78,79]. This is mainly determined by the chemical reactions in the composition of the modified cement matrix, which are characterized below [80].

Hydration of OPC with FA is a complex process due to the mutual influence of reacting cement minerals and FA. Therefore, in order to fully understand the processes occurring in the cement–ash paste, it is necessary to systematize reactions occurring in the pure cement paste during the initial period of its binding. Next, it is possible to identify what role FA plays in the formation of the matrix structure and how this chemically active additive is able to change its final composition [81,82].

Clinker minerals hydrate with water at different rates. The fastest enter into chemical reactions C_3A and C_3S [60,61]. However, the situation is slightly different in the case of pastes with an OPC-FA system because in these, in the initial period of hydration, the FA

addition causes a delay in the early hydration of these two clinker phases. However, the magnitude of the delay increases with the increase of FAs' share in cement [83–85].

Such a phenomenon is confirmed, for example, by the results of the studies of the heat of hydration of the pastes, showing the extension of the induction period in the pastes from cements containing FA [86]. At the chemical level, the delay in the hydration of the C₃S phase is caused by the introduction into the liquid phase of the paste of ions derived from the dissolution of FA, such as aluminate and organic ions. According to [60], these ions may delay the crystallization of the CH and CSH phases. The phenomenon of early delay may also be caused by the adhesion of fine FA particles to the surface of cement grains, thereby hindering the reaction of cement with water. According to another theory [87], the beginning of rapid hydration of C₃S minerals in the ordinary OPC paste coincides with the period in which the maximum degree of saturation of the liquid phase of the paste with CH is reached. The time of saturation of CH in the case of FA addition is delayed. For this reason as well, the hydration of C₃S is also delayed. However, according to [88,89], this phenomenon is related to the adsorption of aluminates on the C₃S surface, leading to the inhibition of its dissolution.

After the induction period, along with the crystallization of CH and C-S-H hydration products, cement hydration in the presence of FA is accelerated. The analysis of the research on the heat of hydration and the review of the resulting structures in SEM-EDS images of cementitious pastes, with and without the addition of FA, shows that FAs in cement delay the hydration of clinker phases over time but, on the other hand, cause an increase in the degree of hydration of these phases in relation to the hydration occurring in the paste based only on OPC [90,91]. This is due to the fact that FA grains are additional surfaces for the precipitation of hydration products. In the pure paste, these products form only on the surface of the C_3S phase and additionally hinder the contact of this phase with water [60].

Although the precipitation of hydration products on FA grains may partially interfere with the pozzolanic reaction in the case of FA-containing pastes, the alkalinity of the resulting solution makes it so that both the FA glassy phase and the hydration products formed on their surface in the initial phase of contact with the paste are activated for subsequent reactions. As a consequence, it facilitates the transition of silicate and aluminate ions to the resulting solution, which ultimately leads to an intensification of the pozzolanic reaction [60,61].

The hydration process of the cement paste can be considered to be based on the elemental reactions of individual clinker components and the analysis of the liquid phase composition of the paste and the type of hydrates formed in the hydration process. The type and speed of hydration products formed as a result of the pozzolanic reaction depends on the composition of the liquid phase of the paste [92]. Particularly important is the stage of initiating the pozzolanic reaction in composites containing FA, due to the possibility of delay in the initial reaction phase of the main clinker phases, as mentioned above.

Therefore, it is very important to determine at which point it is in the structure of the cement matrix containing a certain amount of FA that the process of inducing additional phases as a result of the activation of the pozzolanic reaction begins. There are currently several opinions on this subject.

According to some scientists, the pozzolanic reaction in composites with FA begins quickly, but its impact on the properties of the paste appears relatively late. For example, according to [93], FA after one day is still inactive, and according to [94], in the period from the first to the third day since batch preparation, the first signs of the pozzolanic reaction appear. However, according to [36], the reinforcement of the paste structure with the addition of FA was observed after 7 days.

Other sources suggest that this reaction begins after approx. 10–14 days from the preparation of the paste, and the most extreme opinions on this subject indicate that the reaction of ash glass with CH begins late, and the C-S-H phase is visible in SEM images only after 28 days [60,61].

There are various techniques for determining the progress of hydration in cement containing mineral additives. It is possible to estimate changes in the structure of the cement matrix based on data from X-ray or calorimetric tests [95]. It is also a good solution to track the progress of the development of individual phases in the paste based on the view of microscopic images taken in subsequent time periods from the moment of preparation of the paste [96]. Pozzolanic activity of FA can also be tested using one of several specially developed methods [97]. In any case, it is beneficial to confirm the obtained results with more than one experimental technique [98].

In the following article, it is therefore proposed to assess the pozzolanic activity of the FAs used and analyze the impact of this feature on changes in the structure of the cement matrix on the basis of:

- tracing the development of significant phases in the structure of the modified FA cement mortar in various periods of its curing,
- analysis of FA pozzolanic activity indicators by two qualitatively different measurement methods [99–101].

3. Experimental Procedure

3.1. Materials

The FA view used in the study is shown in Figure 1. The photo shows the grain dimensions of the SCM used. Their size, oscillating within a few micrometers, proves their fine grain size and probably high pozzolanic activity (see Section 2).



Figure 1. A view of fine fly ash particles.

The oxide and phase composition relevant in the evaluation of FA pozzolanic activity were determined using the XRF and Rietveld methods, respectively. The obtained results are shown in Tables 1 and 2 respectively.

Table 1. Chemical composition of fly ash used.

Component (wt %)													
SCM	CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	P_2O_5	TiO ₂	Cs ₂ O	BaO	SO ₃	LOI *
FA	2.15	50.96	25.88	8.25	2.65	1.26	2.60	0.35	1.36	0.09	0.32	0.65	3.20

* Ignition loss.

Component (wt %)SCMAmorphousQuartzMulliteFA71.519.78.8

Table 2. Phase composition of fly ash used.

Analyzing the results summarized in Tables 1 and 2, it should be stated that both the sum of active FA oxides $(SiO_2 + Al_2O_3 + Fe_2O_3)$ at the level of more than 80% (Table 1) and the content of the vitreous phase in the material in the amount of more than 70% (Table 2) also indicates that the FA applied may have high pozzolanic activity and the ability to create additional phases in the cement composite.

3.2. Methods

3.2.1. Preparation of Samples for Experiments

In order to determine the impact of the FA additive on the processes of formation and development of the main phases of the cement composite in its curing process and to diagnose the role of pozzolanic activity of the mineral additive in question in these processes, samples of mortars in the shape of a cuboid with dimensions of $40 \times 40 \times 160$ mm were made. According to EN-450-1 [102], the cementitious binder in these samples was replaced by FA in the amount of 25%, while the water-bonding index was 0.5. These samples were primarily used for testing the FA pozzolanic activity by the physical method. Then, after the destruction of the samples, a microscopic analysis of pieces of the samples with dimensions of $10 \times 10 \times 3$ mm was carried out in the scope of the assessment of:

- structure of the cement matrix, with particular attention to the development of phases in the area of FA grains,
- changes occurring in the vitreous phase of the additives used.

It should be added that, in the case of samples curing after 0.5, 1, and 2 days, it was necessary to vacuum dry them. In order not to damage the structure of the analyzed material, temperature drying was abandoned.

In addition, in order to supplement the full picture of pozzolanic activity, applied FA, an assessment of this feature, was carried out using the chemical method according to the procedure described in Section 3.2.3.

Samples for microstructural tests and evaluation of pozzolanic activity were made using the following materials which originated Poland:

- ordinary Portland cement CEM I (OPC) from Chełm cement plant,
- siliceous FA (FA) from the Puławy thermal power station,
- pit sand 0–2 mm in size from Markuszów deposit,
- plasticizer Basf Liquol BV-18,
- laboratory pipeline water.

3.2.2. Microstructural Investigations

The microstructure studies of the analyzed composites were carried out using SEM QUANTA FEG 250. Since the moment of actual initiation of FA pozzolanic activity in the cement paste has not yet been clearly defined, the analyses were carried out at quite short and rather unusual time intervals, i.e., between 0.5 and 28 days of curing of the material. It was assumed to take SEM images of the structure of the paste:

- every 12 h until the first day of curing,
- daily until the third day of curing,
- weekly from the seventh to the twenty-eighth day of curing.

During the tests for each curing time, photos were taken on six samples, then 30 images were taken for each sample, from which representative photos were selected. The research methodology chosen in this way was aimed at accurately capturing the moment of FA

activation, which, according to previous findings, should take place in the first two weeks of batch preparation [60,61].

3.2.3. Pozzolanic Activity of FA Using Physical Method

The study of FA pozzolanic activity by the physical method was carried out on the basis of the assumptions of EN-450-1 [102]. Based on this, the so-called pozzolanic activity index expressed in (%) is determined as the ratio of the strength of mortar containing 75% OPC and 25% FA to the strength of mortar made on unmodified binder. A material whose Strength Activity Index (SAI) reached a level of at least 75% after 28 days is considered to be pozzolanically active. It should be added that the SAI parameter is also referred to as Pozzolanic Activity Index.

Since the aim of the research was to estimate the moment of initiation of FA pozzolanic activity, the studies determined both the standard 28-day SAI index and estimated its value in the same time periods in which changes in the structure of the cement matrix were assessed. On this basis, an analysis of the changes in the early curing periods of the material was carried out. Thanks to this, it was possible to diagnose when there were clear increments of this parameter, suggesting the beginning of the pozzolanic reaction in the FA area. The conclusions obtained through this research method were then compared with the findings obtained in microstructural research.

3.2.4. Pozzolanic Activity of FA Using Chemical Method

For comparison, a chemical method was also carried out to assess the pozzolanic activity of the FA, according to the ASTM C379-65 standard [103]. The analytical procedure based upon the ASTM C 379-65 standard consists in leaching the active components (SiO₂ and Al₂O₃) from the material. For this purpose, 1 g of analyzed material was introduced into the 100 mL batch of 1 M sodium hydroxide solution and mixed with help of a magnetic stirrer. The suspension was heated during stirring to 80 °C and conditioned at this temperature for 1.5 h. The relatively weak sodium hydroxide solution used in SiO₂ and Al₂O₃ extraction exhibits a pH value similar to that in hydrating cement paste. At the higher temperature of 80 °C, the migration of active components occurs effectively in a short time. The active silica and alumina content are determined in the filtrate thus produced. The oxides are separated by acidification with HCl, resulting in the precipitation of silica. The precipitate is subsequently calcined at temperatures of 1100–1150 °C. The active SiO₂ is determined by the weight method, and the alumina present in the filtrate by titration.

4. Results and Discussion

4.1. Microstructural Analysis

Figure 2 shows the characteristic representative SEM images of the structures of the analyzed OPC-FA cement composites made in eight curing periods in accordance with the underlying methodology in Section 3.2.1. Each of the photographs additionally contains markings or descriptions of characteristic phases formed in the composite or changes observed in the structure of the FA used. The analysis of the photographs focused mainly on the assessment of structures occurring in the close area of FA grains. Therefore, in order to accurately compare the microstructure of composites, we used in the SEM studies the same scale (Figure 2).

Figure 2a–d shows mainly the stages of formation and growth of products of the hydration reaction in the form of a fibrous C-S-H phase of type (I) and C-S-H phase of type (II), which resembles a honeycomb structure [104], around FA grains with diameter of 5 μ m after 0.5, 1, 2, and 3 days of paste curing. No activity has been found in these photos yet in the area of the FA vitreous phase; therefore, it can be concluded that in the period up to the third day of curing of the paste, the pozzolanic reaction in the area of the FA grains had not yet been initiated [93,94]. However, it should be clearly noted that the structure of FA grains is also an excellent place to accumulate hydration reaction products in a short time.

It should be mentioned that according to the data provided in the earlier studies, the C-S-H gel phase is visible in composites with cement matrices after 30 min of paste curing. Further processes bring about the development of C-S-H (I), long-fibered in the first place and then short fibered C-S-H (I), as well as the growth of C-S-H (II) [105]. This can be clearly observed in the period up to the third day of curing of the OPC-FA pastes. During the experiments, shown in the pictures presenting the FA grain, in the subsequent stages of reaction, a rapid and fast growth of C-S-H (I) and C-S-H (II) phase products can be observed. After 2 and 3 days of curing, a single FA grain is entirely covered with the products of the hydration reaction (Figure 2d). In this period, it seems to be fully ready to participate in the next stage of phase development in the structure of the cement composite.

This is clearly visible in the photo from the next stage, performed within one week of curing of the paste (Figure 2e). The structure of the glass in the FA grain, after 7 days, is clearly "stimulated" and activated. It can be presumed that in this particular period, the vitreous phase in the FA is already so active that it is possible to initiate a pozzolanic reaction in this area.

This is confirmed by another SEM photo, taken after 14 days of curing of the paste (Figure 2f). It shows that the structure of the vitreous phase is even more pronounced, with already visible signs of pozzolanic reaction products, which can further strengthen the structure of the matrix. Based on the view of SEM images from Figure 2e,f, it can be concluded that the beginning of the pozzolanic reaction in FA takes place between 7 and 14 days after sample preparation.

In the next photograph taken after 21 days, it can be seen that the structure of the cement matrix is almost dominated by the saturation of additional C-S-H phases. FA glass coatings are still active after this period (Figure 2g).

When the structure of the material reaches the mature period, the intensity of the additional phases decreases, while their morphology changes. The structure of the material is slowly solidified and transformed into an increasingly compact form. Porous zones filled successively by the C-S-H phase or ettringite (E) phase are sealed. Nevertheless, reacting FA grains can still be observed (Figure 2h). According to some sources, they may still be visible in the matrix, in an unreacted form, even after 2 years [36,106].





(b)

(a)

Figure 2. Cont.



Figure 2. Fly ash grain reaction stages between 0.5 and 28 days of curing process: 1—glass matrix of FA grain, 2—exterior glass hull of FA grain; description in the text.

4.2. Pozzolanic Activity Based on the Studies from Physical Method

Figure 3 summarizes the results of the pozzolanic activity tests, applied by FA, determined by the physical method in accordance with EN 450-1 [97]. The figure shows in detail the strength of the pozzolanic activity index and percentage increments of the analyzed parameter for each of the intervals in particular periods of the study (Figure 3).



Figure 3. Changes in pozzolanic activity of fly ash used.

The figure shows that in the period of up to 3 days, the level of FA activity is at a clearly low level, and its increments in each of the measurements are in the range from 7.4 to 12.5%. A clear increase in SAI was recorded for samples after 7 and 14 days, with increments in material activity for each of the periods by more than 20%. These results can therefore be correlated with the clear activation of the vitreous phase in FA observed in the research with the SEM technique (Figure 2e,f).

Further SAI increments after 14 days were already negligible, with the values of only about a few percent after 21 and 28 days. Nevertheless, the pozzolanic activity index after 28 days was 92.13%. This means that its value significantly exceeded the requirements of EN 450-1 [102].

Based on the obtained results, the applied FA can be considered pozzolanically active. The moment of the beginning of the pozzolanic reaction, according to data from the tests of the pozzolanic activity index, falls on the period between 7 and 14 days from the preparation of the paste. Such an observation is therefore a confirmation of the results obtained from microstructural studies and coincides with earlier data, indicating the beginning of this reaction occurring between the tenth and fourteenth day of curing of the paste [63,64].

4.3. Pozzolanic Activity Based on the Studies from Chemical Method

Table 3 shows the average values of the pozzolanic activity obtained from the chemical method, according to the ASTM C379-65 standard [103].

 Table 3. The assessment of pozzolanic activity of fly ash used by chemical method.

Active Components	Results (%)			
SiO ₂	13.31			
Al_2O_3	7.22			
$SiO_2 + Al_2O_3$	20.53			

In the course of experiments, it is established that FA contains more than 20% of active components, i.e., SiO_2 and Al_2O_3 . The obtained results clearly indicate the high pozzolanic activity of the investigated FA [97,107,108]. They also confirm the high pozzolanic activity of the FA, tested by the physical method according to EN 450-1 [102].

5. Conclusions

The article analyzes the impact of the FA pozzolanic reaction (which is their immanent feature) on the processes of creating additional and supplementing existing structures of cement composites containing this mineral additive. From the presented studies, the following conclusions can be drawn:

- (1) In cement composites with the addition of FA, in the period until the third day of curing, the development of the material structure is mainly the result of the hydration reaction.
- (2) Between the seventh and fourteenth day after sample preparation, the first signs of pozzolanic reaction on FA grains are visible.
- (3) There is a clear correlation of the obtained results between the results obtained on the basis of the analysis of the microstructure of the paste with the addition of FA, and the tests of its pozzolanic activity by the physical method.
- (4) The results of the FA pozzolanic activity tests with the chemical method confirm both the high pozzolanic activity of fine-grained FAs assessed by the physical method and the ability of this mineral additive to form additional phases and homogenize the structure of the cement composite within a period of up to 28 days.
- (5) The obtained test results can be helpful in predicting the early strengths of FAmodified cement composites and contribute to their more conscious use in concrete and reinforced concrete structures.

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