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# EFFECT OF THE "POZZOLIT" ACTIVE MINERAL ADMIXTURE ON THE PROPERTIES OF CEMENT MORTARS AND CONCRETES PART 2: POZZOLANIC ACTIVITY

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## ABSTRACT

The results from investigations on the pozzolanic activity of the Pozzolit mineral admixture and its components - silica fume and low calcium content fly ash, are regarded in the present paper. The pozzolanic activity of these materials in hydrating cement pastes in the course of one year has been determined by means of physical, chemical and structural methods. It has been established that the Pozzolit mineral admixture has a high pozzolanic activity, comparable to that of silica fume, which is displayed at all ages of cement hydration and exerts a favourable effect on cement strength characteristics. The pozzolanic properties of the admixture are determined mainly by the silica fume during the early stages of hydration and by the fly ash ingredient - at later stages of hydration.

## Introduction

"Pozzolans" are substances of natural or artificial origin, reacting with $Ca^{2+}$ or $Ca(OH)_2$ in the presence of water, and their pozzolanic activity is defined as an index reflecting the degree of proceeding of the chemical reaction (1). There are different methods for the pozzolanic activity determination - physical, chemical and combined ones (2). The obtained quantity of the $Ca(OH)_2$ bound by the admixture does not provide an objective assessment of the admixture pozzolanic properties. Pozzolans accelerate the clinker minerals hydration in many cases, so that two competitive reactions take place in the course of cement hydration: one of them leading to the increase of calcium hydroxide amount, and the other one - leading to its decrease. These reactions proceed with a different intensity at the different stages of hydration. Thus, the methods for pozzolanic activity determination by the quantity of the calcium hydroxide bound by the admixtures, provide ambiguous characteristics of the admixture qualities. For this reason it is also necessary to determine the quantity of the other newly formed hydration products in cement stone.

It is known that cement stone properties do not directly depend on the quantity of the admixture-bound calcium hydroxide. Strength, for example, is strongly affected by the type, shape, size and distribution of the hydration products and pores and there is no direct relationship between strength and degree of chemical reaction completion. The mechanical

TABLE 1
Granulometric Analysis of Fly Ashes

| Fly ash No | Residue on sieve, % | | | Particle content (%) under 63 μm | Note |
|---|---|---|---|---|---|
| | 200 μm | 90 μm | 63 μm | | |
| 1 | 13.87 | 21.37 | 16.91 | 47.85 | unclassified |
| 2 | 10.28 | 14.28 | 4.49 | 70.95 | unclassified |
| 3 | 0.57 | 4.74 | 2.50 | 92.19 | |
| 4 | 0.00 | 1.50 | 4.70 | 93.80 | classified 75 % under 45 μm |
| 5 | 0.00 | 0.00 | 0.00 | 100.00 | classified 100% under 20 μm |
| 6 | 0.00 | 0.00 | 0.00 | 100.00 | classified 100% under 63 μm |

strength tests and the structural investigations should therefore supplement the chemical methods for pozzolanic activity assessment (3).

The pozzolanic activity of the Pozzolit mineral admixture and its ingredients has been evaluated in the present work by means of a combination of structural and physical and chemical methods and an attempt is made to determine its contribution to the strength of cement stone.

## Materials and Methods

Portland cement PC 45 (C) and the admixtures described in part I were used in this investigation: silica fume (SF) - a by-product from the ferro-silicon steel production in the "Kremikovtsi" State Co. (about 93% amorphous silica content), low calcium content fly ash (FA) from the "Bobov Dol" Thermal Power Generation Plant (Bulgaria) and Pozzolit (Pz) mineral admixture, obtained on the basis of silica fume and fly ash. Different fly ash fractions as well as silica fume and fly ash mixtures in the proportions FA:SF = 75:25 (Pozzolit A) and FA:SF = 50:50 (Pozzolit B), were used initially for the determination of pozzolanic activity according to British Standard (BS) (4). The granulometric composition of the used fly ashes is shown in Table 1. Table 2 presents the compositions of the cement mortars tested according to BS to determine the coefficient of pozzolanic activity.

The coefficient of pozzolanic activity was tested according to the Bulgarian standard BSS-166-72 too. The pozzolanic activity is determined from the quantity of calcium hydroxide in mg, consumed by 1 g of admixture for a specified time and is called chemical hydraulic activity.

TABLE 2
Composition of Cement Mortars Tested According to BS, g

| Component | Portland cement | Sand | Admixture | Water |
|---|---|---|---|---|
| Reference samples | 450 | 1350 | | 225 |
| Test samples | 315 | 1350 | 135 | spread ± 5 mm of the reference sample |

TABLE 3
Chemical Hydraulic Activity According to BSS

| Mineral admixture | CaO bound by 1 g of admixture for days, mg | |
|---|---|---|
| | 7 days | 28 days |
| Silica fume | 84.59 | 211.58 |
| Fly ash No 1 | 23.52 | 41.60 |
| Pozzolit A | 38.64 | 164.50 |
| Pozzolit B | 87.64 | 205.34 |

The complex thermal analysis was carried out parallelly on samples without and with admixture of silica fume, fly ash and Pozzolit, where 10% of the mass of cement were replaced. Cement was mixed with distilled water to obtain a paste of water/solid ratio W/S = 0.33, which was intensively stirred in a high-speed homogenizer for 10 min. The samples were sealed in plastic containers and cured at a temperature of 20°C till the age of testing. The specimens were dried at a temperature of 105°C for 6 hours before testing. The investigations were carried out on a MOM 3427 derivatograph (Hungary) at the age of 1, 2, 3, 7, 28, 90, 180 and 360 days of hydration on samples with mass of 200 mg, temperature rise of up to 1000°C and heating rate of 10°C/min. The quantity of water, released during portlandite dehydration, termed CH-water, was determined in the temperature range of 460-520°C and the total mass loss of the samples was obtained in the range of 105-1000°C.

The so called Breakdown-method (5), developed for active mineral admixtures (6), was used for the assessment of the Pozzolit admixture contribution to the strength of cement stone. It is based on the comparison of the strengths of mortars with the same water/cement ratios with and without mineral admixture. Five series of samples with different water/cement ratios, each of them comprising six specimens - 4 × 4 × 16 cm prisms, were prepared from two types of cements - a reference one (100% C) and a test one with 25% of the mass of cement replaced by Pozzolit. The compressive and flexural strengths were tested at different stages of hydration, the experimental results being plotted as the logarithm of cement stone strength versus water/cement ratio.

## Experimental Results and Discussion

Pozzolanic Activity According to BS and BSS. The pozzolanic activity coefficient is determined according to BSS for some of the admixtures (Table 3). It is seen that silica fume has a much higher activity than the unclassified fly ash No 1 and Pozzolit B, obtained from the same fly ash exhibits a chemical activity comparable to that of silica fume.

The results from the determination of the pozzolanic activity coefficient according to BS are presented in Table 4. The highest value is that of silica fume - 192 %, the lowest one of 73% - for fly ash No 1, which has the coarsest granulometry. Fly ash pozzolanic activity coefficient is increased with the decrease of the mean particle diameter.

Mixing with silica fume increases the activity, which is most pronounced for fly ash No 1 - two times. This effect of silica fume is not so strongly expressed when the fineness of fly ash is increased. The highest pozzolanic activity according to BS is displayed by the Pozzolit B admixture (SF:FA = 50:50) with fly ash No 6 (177%). This composition has been used in the further studies.

TABLE 4
Coefficient of Pozzolanic Activity According to BS, %

| Mineral admixture | Initial mate-rials | Pz A | Pz B |
|---|---|---|---|
| Silica fume | 192 | - | - |
| Fly ash No 1 | 73 | 109 | 150 |
| Fly ash No 2 | 81 | 129 | 142 |
| Fly ash No 3 | 99 | 152 | 155 |
| Fly ash No 4 | 136 | 155 | 144 |
| Fly ash No 5 | 146 | 157 | 161 |
| Fly ash No 6 | 110 | - | 177 |

Complex Thermal Analysis. It is known that silica fume accelerates cement hydration and that the pozzolanic reaction between the amorphous silica of the admixture and the portlandite obtained in the course of hydration starts as early as on the first day of mixing cement with water. These processes progress with different intensity at the different stages of hydration and depend on the admixture amount and on water/cement ratio (7). For this reason the comparison between portlandite quantities in cement pastes with and without mineral admixtures cannot be the only indication of occurring or absent pozzolanic reaction. The total amount of the newly formed hydration products in cement stone should also be taken under consideration. It has been established however, that at the later stages of hydration water is released in cement pastes due to the processes of hydrosilicate recrystallization, this process being more intensive in cements containing active silica (8) and hence the chemically bound water is not a sufficiently reliable criterion for the determination of the degree of hydration. The parallel determination of portlandite as well as of hydrosilicate and hydroaluminate quantities in cement pastes (8,9) is therefore assumed as a measure for the result of the reactions between cement and the admixtures. The latter quantity, called H-water, is obtained as the difference between the total mass loss at heating from 105 to 1000°C and the CH-water. The additional interpretation of the results by relating them to the mass of cement in the investigated samples provides the possibility of more exact defining the start and rate of the pozzolanic reaction.

Table 5 presents the results from the determination of the CH-water content at different ages of hydration. It is obvious that it is lower in cement pastes with mineral admixtures than in the reference plain cement at all ages. The CH-water content of cement pastes containing silica fume and Pozzolit increases till the 28th and 90th day respectively, its decrease with time being

TABLE 5
Changes of Portlandite Quantity in Cement Pastes

| | CH-water content, mg/g of cement, for age of hydration, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Age<br>Cem. paste | 1 | 2 | 3 | 7 | 28 | 90 | 180 | 360 |
| C = 100% | 22.2 | 28.7 | 31.0 | 36.6 | 39.9 | 43.2 | 41.9 | 42.6 |
| C = 90%, SF = 10% | 19.7 | 22.2 | 27.2 | 32.1 | 34.4 | 32.1 | 29.6 | 28.7 |
| C = 90%, FA = 10% | 14.8 | 19.7 | 22.2 | 25.9 | 30.7 | 33.7 | 34.4 | 35.0 |
| C = 90%, Pz = 10% | 18.5 | 24.6 | 26.0 | 28.7 | 32.1 | 34.4 | 30.7 | 29.6 |

TABLE 6
Changes of Hydrosilicate and Hydroaluminate Quantities in the Cement Pastes

| Age<br>Cem. paste | H-water content, mg/g of cement, for age of hydration, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 7 | 28 | 90 | 180 | 360 |
| C = 100% | 63.2 | 66.7 | 73.2 | 92.5 | 130.8 | 224.2 | 230.8 | 234.7 |
| C = 90%, SF = 10% | 93.7 | 119.4 | 121.8 | 152.7 | 177.3 | 273.8 | 278.3 | 280.0 |
| C = 90%, FA = 10% | 83.9 | 103.4 | 108.3 | 145.3 | 203.2 | 261.9 | 266.1 | 267.6 |
| C = 90%, Pz = 10% | 99.7 | 118.2 | 121.8 | 164.0 | 195.8 | 263.6 | 270.4 | 273.4 |

clearly observed subsequently. It should be specially noted that portlandite content in fly ash containing cement pastes is low till the 28th day of hydration and that the character of changes in portlandite quantity is identical to that in plain cement pastes.

Table 6 presents the results from the determination of the H-water content for all ages of hydration. The H-water content preserves the tendency of growth with time for all tested specimens and at each age it is higher in the pastes with admixtures than in the plain cement ones. The hydrosilicate and hydroaluminate content in the Pozzolit containing cement pastes is higher than that of the silica fume containing pastes till the 28th day of hydration, this relation turning to be the opposite till the 360th day of hydration. The paste with fly ash admixture has the lowest H-water content of all admixture-containing pastes, except for the age of 28 days, which results from the sharp increase in the hydrosilicate and hydroaluminate quantity during the interval between the 7th and 28th day of hydration.

The ratio CH/H-water content has been chosen as a quantitative criterion for the relation between the processes leading to portlandite formation on one hand and hydrosilicate and hydroaluminate formation on the other hand. Table 7 shows the variation of this ratio with time.

The ratio of the plain cement paste is higher than the ratio of all other pastes at all investigated ages of hydration, which is an evidence for the pozzolanic activity of the admixtures. A clearly expressed diminution of this parameter is observed between the 3rd and the 90th day of hydration for all studied cements (about 2 times for cement pastes without and with silica fume admixture), the values being very slightly decreased afterwards till the 180th

TABLE 7
Changes of the Ratio Between CH- and H-Water in Cement Pastes

| Age<br>Cem. paste | CH/H-water content, % , for age of hydration, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 7 | 28 | 90 | 180 | 360 |
| C = 100% | 35.2 | 43.1 | 42.4 | 39.6 | 30.5 | 19.3 | 18.15 | 18.14 |
| C = 90%, SF = 10% | 21.0 | 18.6 | 22.3 | 21.0 | 19.42 | 11.71 | 10.62 | 10.24 |
| C = 90%, FA = 10% | 17.6 | 19.0 | 20.5 | 17.8 | 15.13 | 12.87 | 12.94 | 13.08 |
| C = 90%, Pz = 10% | 18.05 | 20.9 | 21.4 | 17.5 | 16.38 | 13.06 | 11.37 | 10.81 |

day of hydration, reaching a constant value subsequently. The only exception is the fly ash containing cement paste, where the equilibrium between CH- and H-water content is achieved as early as the 90th day of hydration. The maximum of this ratio is observed at the age of 3 days for cements with admixture and at the age of 2 days - for plain cement. The CH/H ratio for the silica fume containing cement paste is higher than the ratio of fly ash and Pozzolit containing pastes (except for the 2nd day) till the 28th day of hydration, the relation turning to be the opposite later on.

Taking into consideration the dynamics of alteration of the portlandite quantities as well as of the hydrosilicate and hydroaluminate ones, it can be concluded that the reactions of portlandite consumption prevail over the reactions of its formation after the 3rd day of hydration, although its total quantity continues to grow at later ages too as a result of the proceeding hydration. As far as the effect of silica fume is concerned, it can be noted that during the first days of hydration its influence consists in acceleration of the clinker minerals hydration and in consumption of portlandite in the cement paste. The rest unreacted part of silica fume after the 28th day of hydration mainly bounds portlandite in insoluble hydrosilicates. Fly ash is not so active with respect to cement hydration and $Ca(OH)_2$ consumption till the 7th day of hydration, but is activated in the period between the 7th and the 90th day of hydration, the pozzolanic reactions of fly ash being the dominant ones.

The effect of the Pozzolit mineral admixture depends on the silica fume component during the first 7 days of hydration, which is expressed in accelerating cement hydration and binding of portlandite. The main processes in the Pozzolit containing paste later on depend on the fly ash component.

The above mentioned considerations concerning the effect of the mineral admixtures are confirmed by the investigation on the alteration of the differences in the portlandite content ($CH-CH_0$) and in the hydroaluminate and hydrosilicate content ($H-H_0$) with time for plain and admixture containing cement pastes (Fig. 1).

Breakdown Method. Fig. 2 presents the results from the compressive and flexural strength tests, which have been carried out to determine the contribution of the Pozzolit mineral admixture to the strength of cement stone.

The data are plotted as the logarithm of cement stone strength $\sigma$ versus water/cement ratio W/C, since the Abrams formula $\sigma = A/B^{W/C}$ is valid (A and B are constants). The full lines show the values for the reference sample (plain cement) and are the closest approximation obtained by the least squares method according to the Abrams formula. The corresponding symbols represent experimental data for the strength of cement stone, containing 25% of Pozzolit from the mass of cement. It is seen in the figures that the mineral admixture exerts a favourable effect on the strength of cement, which is more pronounced for the case of the flexural strength. The contribution to the compressive strength is better displayed at the 2nd day of hydration and at the 7th day the test composition strength does not differ from the reference one. The experiments for the determination of the pozzolanic activity show that the pozzolanic reaction at this age is very clearly expressed, which proves that there is no direct relationship between the pozzolanic reaction degree and strength. It is obvious that regardless of the chemical activity of the admixture, the contribution to the strength at the early ages results rather from the high specific surface of the admixture particles and their ability to fill larger pores in cement stone, whose quantity is directly related to its strength. The strength of the Pozzolit containing samples at the age of 28 and 90 days of hydration is higher than the strength of the reference ones, which proves that Pozzolit has a positive effect on cement stone strength.

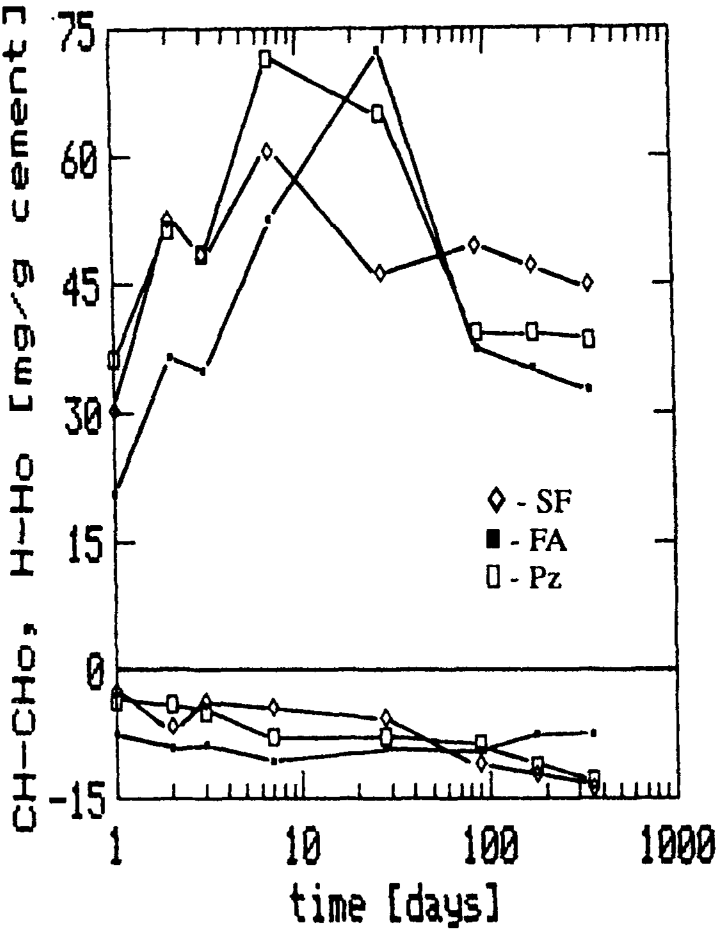


FIG. 1.
Changes with time of the differences in the portlandite and hydrosilicate and hydroaluminate content for cements pastes with and without mineral admixtures.

## Conclusions

1. The Pozzolit mineral admixture comprising the ingredients: silica fume and classified low-calcium fly ash in the proportion 50:50, possesses high pozzolanic activity, comparable to that of silica fume, which is observed from the 1st to the 360th day of hydration.
2. The division of the chemically bound water into two components: the first resulting from portlandite dehydration and the second - from the dehydration of the other hydrates, as well as the investigation of their relationship in the course of time, provide the possibility to understand in more detail the action of the different admixtures at the different stages of hydration.
3. The pozzolanic properties of Pozzolit depend on the silica fume component during the first 7 days of hydration and are displayed as acceleration of cement hydration and binding of portlandite, and later on - on the fly ash component.

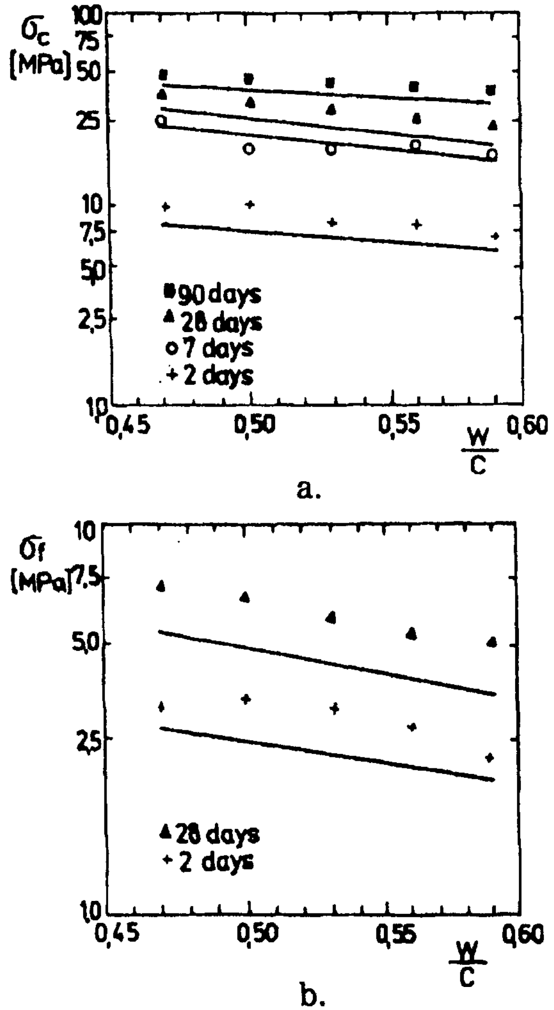


FIG. 2.

Dependence of compressive (a) and flexural (b) strength of cement stone without (full lines) and with Pozzolit mineral admixture (symbols) on the water/cement ratio W/C at different ages of hydration.

4. The Pozzolit mineral admixtures has a high chemical hydraulic activity and exerts a favourable effect on the strength characteristics of cement stone, this effect being stronger for the flexural strength. The admixture successfully substitutes the cement and imparts new properties to cement stone.

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