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# HYDRATION PROCESS OF CEMENT CONTAINING FLY ASH AND SILICA FUME: THE FIRST 24 HOURS

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## ABSTRACT

Results from studies on the early hydration (till the 24th hour) of cements mixed with fly ash, silica fume or a combination of both, called Pozzolit, are presented. The active role of the Pozzolit mineral additive was revealled by DTA, XRD and IRS analyses. The effect of the additive is expressed in increased total amount of hydration products and decreased portlandite content. © *1997 Elsevier Science Ltd*

## Introduction

The incorporation of silica fume-fly ash blend in the form of an additive in cement compositions is potentially very useful as it results in decreased corrosion and permeability and increased strength of cement stone (1-4). The individual effect of fly ash (5-8) and silica fume (9-14) on cement hydration have been thoroughly studied and no substantial controversy regarding the mechanism of their action has been found. The hydration of cement in the presence of a mixture of pozzolanic additives differing in specific surface, chemical and granulometric composition, as is the case of silica fume-fly ash blend has not yet been sufficiently well described. The present work considers the results from studies on the hydration process of cement containing silica fume and low-calcium fly ash.

## Materials and Methods

Portland cement, PC 45, is the test material in the present study. The silica fume (SF) is a by-product from the ferro-silicon steel production in "Kremikovtsi" State Co. (Bulgaria). The fly ash (FA) is a low-calcium one, class F, from the "Bobov Dol" Thermal Power Generation Plant (Bulgaria) (1). The blend of the two mineral additives called Pozzolit (Pz) (4) is prepared from equal quantities of FA and SF and has a density of about 610 kg/m$^3$. The specific surface of SF, FA, and Pz determined by the BET-method is 19.2, 2.83, and 8.9 m$^2$/g, respectively. Four cements were studied-without additives (#1) and with addition of SF (#2), FA (#3), and Pz (#4) amounting 10% of the initial cement mass.

The differential particle size distribution of the used cements and compositions was investigated by laser granulometric analysis in a liquid medium of pure ethyl alcohol to avoid the dissociation and agglomeration of cement particles during contact with water. The measurements were carried out on a Laser Particle Sizer Analyssette-22, Fritsch, based on He-Ne laser wavelength of 632 nm and 5 mW radiant power and a multielement detector with 32 channels. The apparatus is capable of measuring particle size distribution over the 0.3 μm-110 μm range assuming a spherical form of the particles. The duration of one measurement was about 1 min.

Electron micrographs were performed on a "JEOL" scanning electron microscope in a mode of secondary electron emission.

The cement pastes (water/solid ratio of 0.33) were cured in plastic containers at a temperature of 20 (±2)°C. The hydration was stopped at the respective time by a consecutive soaking in acetone and ether and the samples were subsequently dried at 105°C for 3 hours in vacuum.

The DTA studies were performed on a MOM-3427 derivatograph (Hungary) at a heating rate of 10°C/min in the range 20-1000°C. The test samples were of equal mass of 200 mg each. The amount of non-evaporable water (the mass loss in the temperature interval 105-1000°C) was the estimate for the quantity of the hydration products in the cement pastes. The quantity of water released during portlandite dehydration, termed CH-water was determined in the

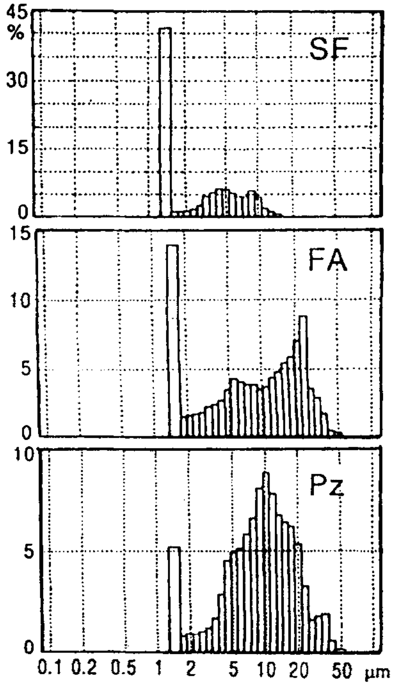

FIG. 1.
Differential particle size distribution of SF, FA and PZ.

TABLE 1

Particle Size Distribution of the Additives

| additive | % of additive particles of size smaller than, μm | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | <1 | <2.5 | <5 | <10 | <15 | <20 | <25 | <35 |
| Silica fume | 28 | 46 | 70 | 95 | 99.6 | 100 | 100 | 100 |
| Fly ash | 8.5 | 18.5 | 31 | 51 | 63 | 72 | 90 | 97 |
| Pozzolit | 3.5 | 8 | 23 | 58 | 76.5 | 88 | 95 | 98.5 |

temperature range 460-520°C (15). The results are presented for a unit mass of cement in the investigated samples so that the contribution of the mineral additive can be more clearly expressed.

The IR spectroscopic test was performed by spectrometer "Specord 75 IR" (Germany) in the range 400-4000 cm$^{-1}$. The samples (1 mg mass, 0.5 mm thickness) were mixed with 300 mg KBr. The recording time per sample was 4.4 min.

The powder X-ray diffraction (XRD) phase analyses of the cement samples were performed on a DRON 3M diffractometer with Ni-filtered Cu-α radiation. The patterns were recorded

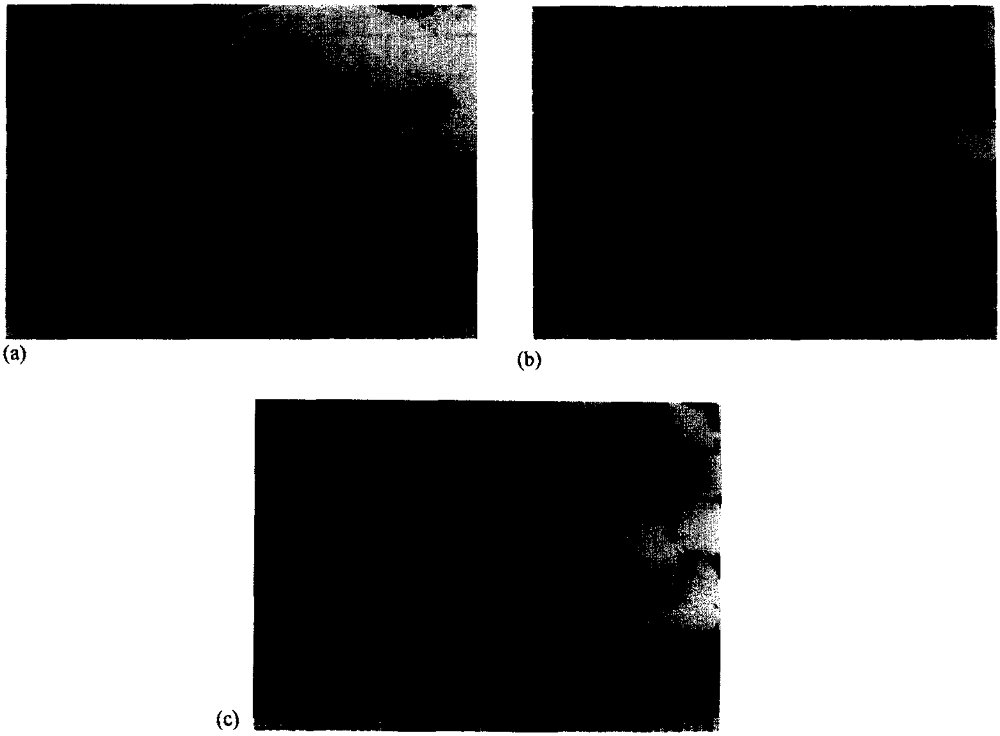

FIG. 2.
SEM micrograph of FA (a) and Pz (b,c) particles.

in the range 10-55° 2-theta. Before XRD measurements the samples were dried, ground and pressed in standard holders.

## Results and Discussion

The differential particle size distribution of SF, FA and Pz is presented in Fig. 1. As seen from this Figure and Table 1, the maximum size of the SF particles practically does not exceed 10-12 μm and 50-60 μm for the cases of FA and Pz. Half of the SF particles are with size <3 μm, this value being 9 μm for FA and Pz. If SF and FA particles slightly interact with each other, they should be disaggregated initially by the mechanical and subsequently by ultrasonic treatment of the suspensions prior to the measurement, and hence the maxima of particle size distribution of Pz must be shifted towards <10 μm sizes. Table 1 does not confirm this assumption. Fig. 2a

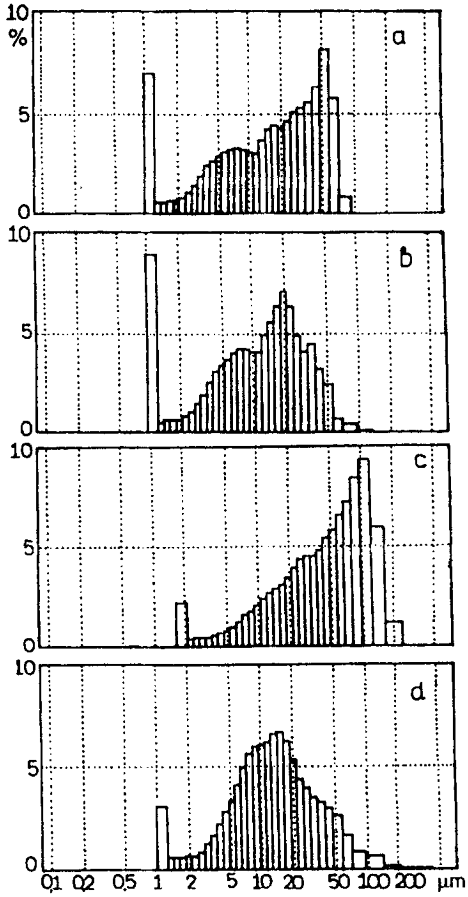

FIG. 3.
Differential particle size distribution of initial cement (a) and cement mixtures with SF (b), FA (c), and Pz (d).

shows FA particles and Fig. 2b,c-the Pz ones. The large FA grains are observed separately in the FA-SF mixture, while the smaller ones (size of up to 10 µm) are covered by fine SF particles. This is an evidence that a strong tendency exists for the FA and SF particles to adhere to each other, thus forming stable complexes of small particles while part of the SF particles stuck to the coarser FA grains are set apart in the suspension.

The differential particle size distribution of the used cements (Fig. 3) shows that the SF additive increases the fraction <1 µm by 2% and the relative part of the particles with sizes <10 µm grows by 7.5% (Fig. 3b). There are no particles of size greater than the maximum one in the intial cement and the distribution curve peak is shifted towards smaller sizes which allows one to conclude that SF and cement particles have no affinity to stick together. The great difference in their density is probably the reason for this fact. In the case of cement-FA blend the portion of the particles with sizes <1 µm is 1.1% compared to 6% in the initial cement. The particles with sizes <10 µm are 12.5% respectively compared to 38%. The maximum of the size distribution curve is shifted in the region 80-100 µm. Particles >100 µm are not observed in the plain cement, while in the cement-FA blend their content is 16%, some of them reaching 200 µm size (Fig. 3c). Probably the fine cement particles cover the FA ones attracted on the

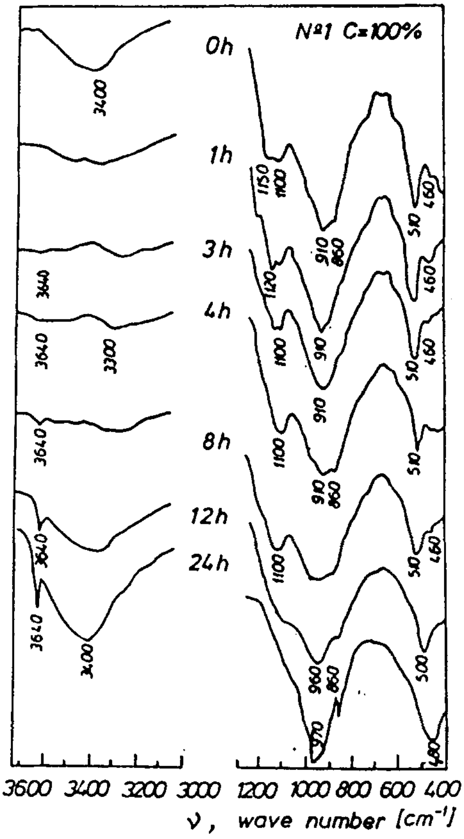

FIG. 4.
IR spectra of plain cement.

defect regions on their surface. The maximum in the differential size spectrum of cement-Pz blend is shifted to smaller sizes (Fig. 3d). Single 200 μm grains are observed (1% of the total amount) and the portion of those <1 μm is reduced 2.5 times.

The IR spectra of all nonhydrated cements (0 h) (Figs. 4-7) contain the bands of the basic clinker minerals [15,17]: alite-ν = 460 and 910 $cm^{-1}$; belite-ν = 510 and 860 $cm^{-1}$ and gypsum-ν = 465, 805, and 1100 $cm^{-1}$. The main changes in the plain cement spectrum in the first hours of hydration (Fig. 4) are outlined in a decreased intensity of the gypsum and alite bands and emerging of the band characteristic for calcium hydroxide (ν = 3640 $cm^{-1}$). The C-S-H band at ν = 960-970 $cm^{-1}$ gradually formed after the 4th hour. In parallel, the intensity of the portlandite band increased and after the 8th hour the sulphoaluminate band with maximum at ν = 3400 $cm^{-1}$ was formed. The IR spectra of FA-containing cement (Fig. 5) repeat the above regularities for the plain paste, the only difference being that the C-S-H band was formed earlier (between the 1st and 3rd hour) while the bands of portlandite and ettringite were not so clearly expressed. All the bands of the main hydration products (Fig. 5) are wider than those in the plain cement which is, probably, due to the presence of distorted Si-tetrahedra in the fly ash plain cement part causing variable frequency (18). The spectra in Figs. 6 and 7 taken from SF-

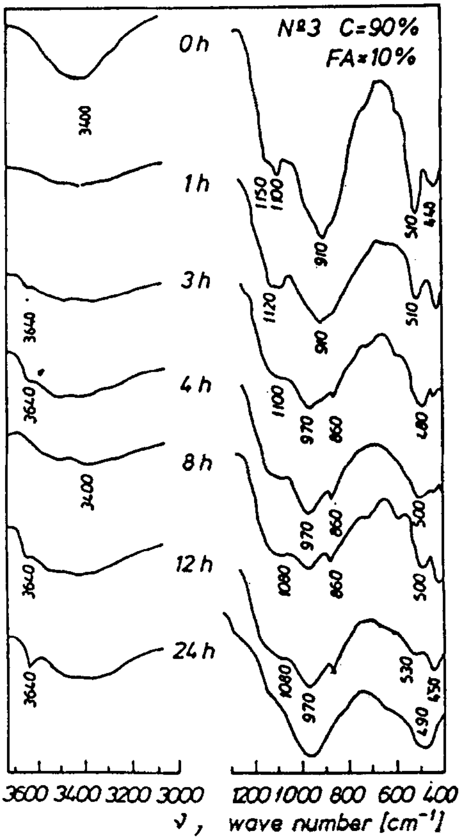

FIG. 5.
IR spectra of FA-containing cement paste.

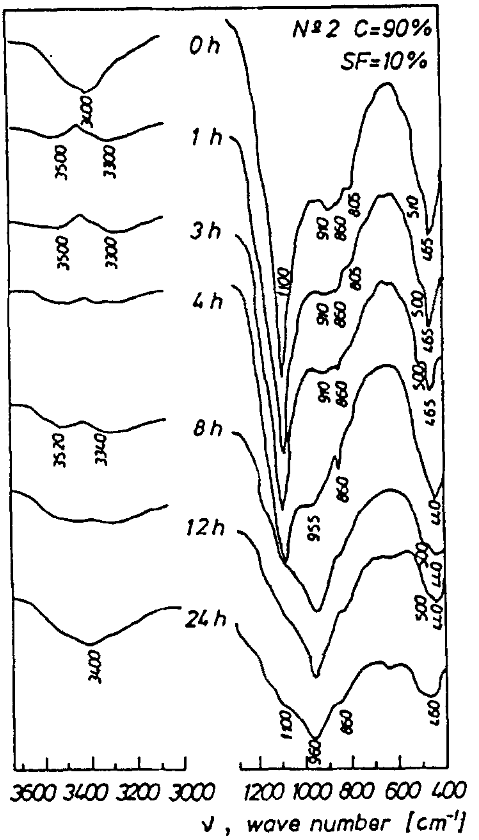

FIG. 6.
IR spectra of SF-containing cement paste.

and Pz-containing cements show that SF participates actively in the hydration process from the first hour after the contact with water-the characteristic bands of amorphous silica at $\nu = 1100$ $cm^{-1}$ fade with time, the spectral bands of C-S-H being formed at the same time (after 1 hour for Pz-containing paste and about the 4th hour for the SF-containing one). $SiO_2$ band of cement #2 is preserved indicating that part of silica had not reacted and remained for further reaction in the later stages of hydration. The same band wasn't observed in paste #4 after the 8th hour which was expected in respect to the lower SF quantity in it. The earlier formation of the C-S-H band in the spectrum of cement #4 is related to the easier C-S-H formation at lower SF-concentrations which confirms the conclusions of Barret (16). The portlandite band is not displayed in the last two figures, probably, because of its small amount in both pastes and the screening effect of the ettringite band which is better shaped in the Pz-containing paste.

Summarized diffraction patterns of cement pastes (##1-4) showing the phase changes in the first 24 hours of hydration are given in Fig. 8. The lowest pattern in each case is of cement before hydration start. In the plain cement paste the portlandite (CH) formation detected by XRD is found to start around the 3-4th hour of hydration with gradual increasing crystallization followed up to the 24th hour. The most intensive diffraction peak of CH (d = 4.90 Å) in the

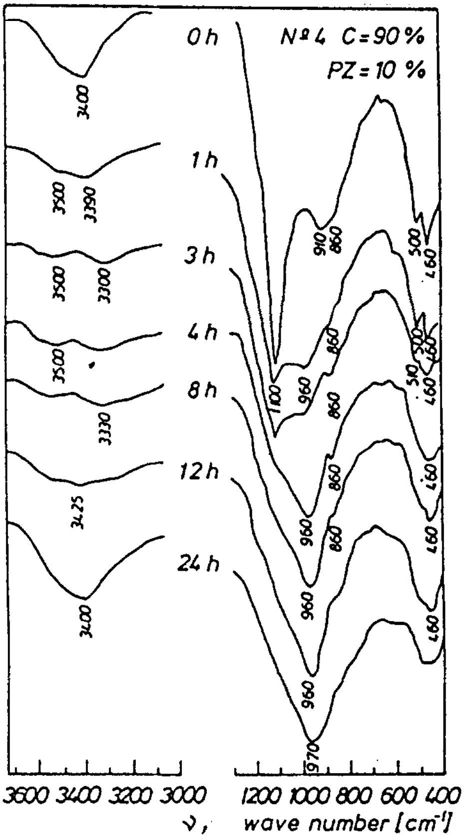

FIG. 7.
IR spectra of Pz-containing cement paste.

pattern of FA-containing paste first was detected after the 6th hour of hydration then followed by a gradual intensity increase. For the case of SF-containing paste the formation of CH was obstructed up to the 12th hour (except a very small intensity trace at the 6th hour). Between the 12th and 24th hour the content of portlandite in this sample rapidly increased. For the cement paste with Pozzolit the crystallization of CH with time very much resembles that of cement #2- up to the 12th hour of hydration no portlandite was detected.

DTA data showing the changes in the total amount of the newly formed hydrates in cement pastes during the first 24 hours of hydration are shown in Fig. 9a. The amount of the hydration products for 1g cement in the pastes with SF and Pz is higher than the corresponding amount in the plain cement- and FA-containing pastes. During the first 6 hours of hydration the total amount of the hydration products in the Pz- and FA-containing pastes is the same and later it becomes higher in the paste with Pz. A certain delay in the rate of hydration products formation is observed between the 3rd and the 8th hour for the SF-containing paste and between the 4th and 6th hour for the FA- and Pz-containing ones. This trend is not so clearly expressed for the plain cement paste. The CH-water content in the SF- and Pz-containing pastes till the 6th hour of hydration is in the range of the accuracy of the method-about 1.5 mg per gram cement, and

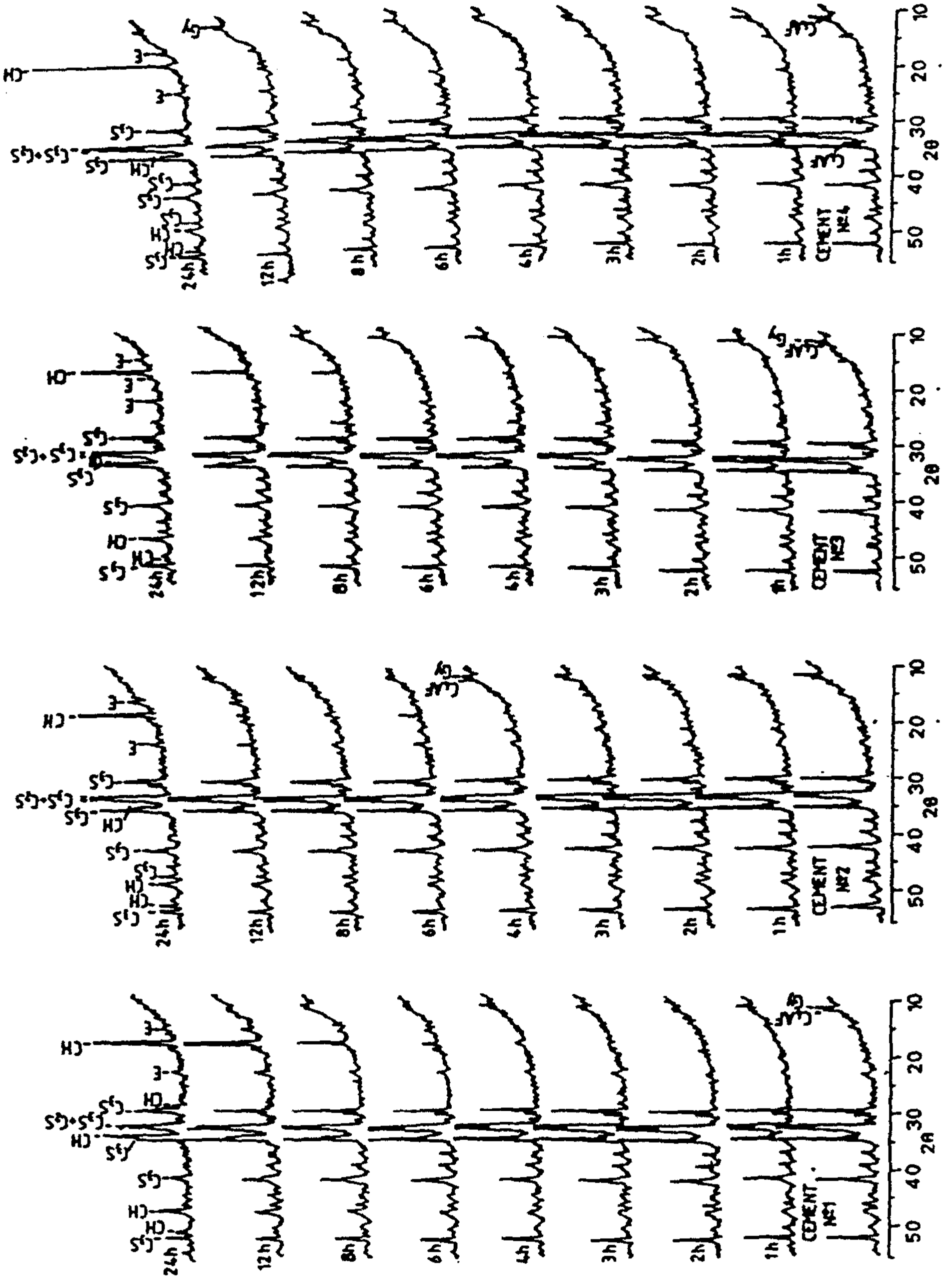

FIG. 8.

XRD patterns of plain cement paste (#1); with SF (#2), FA (#3) and Pz (#4).

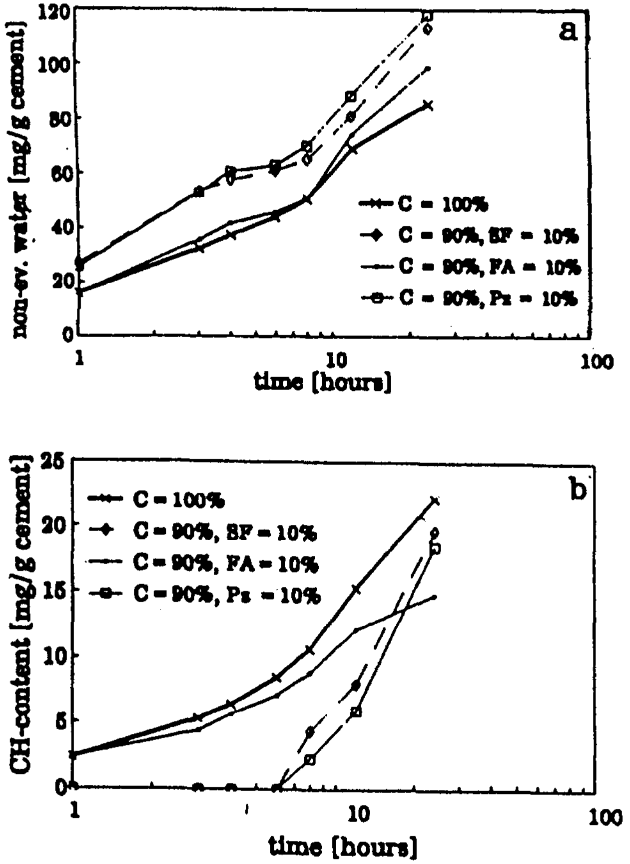

FIG. 9.
Changes in the amount of hydration products (a) and portlandite (b) in the cement pastes.

it increases sharply after this age for both pastes (Fig. 9b). After 1 hour of hydration the CH-quantity in the FA-containing pastes and in the plain cement paste is the same, rising more rapidly in consequence for the additive-free paste, preserving the highest value till the 24th hour. The lowest CH quantity at the same age (24 hours) is recorded in the FA-containing paste, a result due to its delayed formation after the 12th hour. The difference between the non-evaporable water content and the CH-water, called H-water is a measure for the hydrosilicate and hydroaluminate quantity in the cement pastes (19). Fig. 10 shows the changes in the differences between the H- ($H$-$H_0$) and CH-water content ($CH$-$CH_0$) for the pastes with additives on one hand and for plain paste on the other. The periods of accelerated hydration product formation and of relatively delayed hydration process in the additive-containing pastes due to the specific effect of the additives are clearly seen from the curves.

The DTA, IRS, and XRD results prove that the manifestation of the chemical nature of the FA is negligible till the 24th hour of hydration and its effect can be considered rather as a physical one-the FA particles behave as a more or less inert material serving as a precipitation nucleus for $Ca(OH)_2$ and C-S-H gel produced from the cement hydration (7). On the other hand

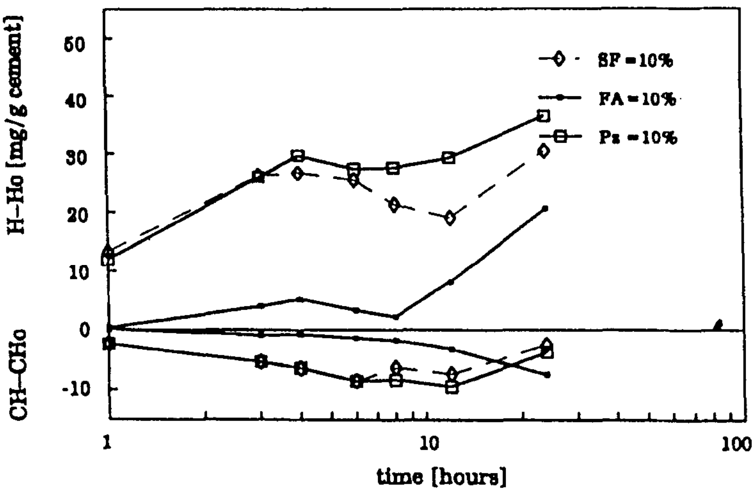

FIG. 10.

Differences between H- and CH- water contents in cement pastes with and without additives.

it is possible that calcium ions in solution react with aluminium associated with FA forming AFt-phase on the surface of the Fa particles (8). The access of Ca2+ to the FA surface is hampered by the increased thickness of these layers thus retarding the clinker minerals dissociation and respectively the rate of hydration. This results in equalization of the hydration products amounts in the plain and FA-containing pastes but does not affect the quantity of portlandite in them. The SF particles participate actively in the hydration process of cement during the first 8 hours. They bind entirely the calcium ions in the solution and for this the amount of calcium hydroxide is low-in the range of the device detection accuracy. The absence of free calcium ions in the solution stimulates the dissolution of cement particles, the latter being gradually covered by SF particles and hydrosilicate gel forming a diffuse layer which hampers their contact with water and slows down the dissolution rate. This period has longer duration in the SF-containing paste because of the high density of the SF particles around the cement grains (12,13). SF, FA particles, and complexes of FA particles surrounded by SF ones exist separately in the Pz-containing paste. The various types of aggregations and the lower SF-concentration in Pz-containing cement paste make diffusion layers around the cement grains more permeable for the water molecules. This is most probably the reason for the shorter period of retardation of the hydration rate in comparison with the SF-containing paste. Hydration is accelerated after the 8th hour due to breaking apart of the gel covers.

## Conclusions

1. The particles of Pz mineral additive have a heterogeneous character-separately existing SF and FA particles and complexes of fine FA particles surrounded by SF grains.
2. The Pz mineral additive actively affects the early hydration of cement: the large FA particles not covered by SF ones serve as precipitation nuclei of hydration products; the

SF grains existing separately or covering finer FA particles enhance cement hydration and bind the hydrating cement grains.

3. The conditions of early hydration in the Pz-containing paste are more favourable in comparison with these of the SF-containing paste where a part of the SF particles remains closed between the forming hydrates on the cement grain surface and do not actively participate in the cement hydration during the first 24 hours.
4. The effect of Pz mineral additive is expressed in increased total amount of hydration products and in a decreased amount of calcium hydroxide.

## Acknowledgements

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