Pergamon

Cement and Concrete Research 29 (1999) 3–8

CEMENT AND CONCRETE RESEARCH

# Microscopic and laser granulometric analyses of hydrating cement suspensions

Vili Lilkov [a], Ekaterina Dimitrova [b], Stoyan Gaidardzhiev [a]

[a]*University of Mining and Geology, Department of Physics, Darvenitsa 1100, Sofia, Bulgaria*
[b]*Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Manuscript received 26 January 1998; accepted manuscript 23 September 1998

**Abstract**

The results from microscopic and laser granulometric analyses of hydrating cement suspensions, containing active mineral additives (silica fume, fly ash, and a mixture of both called Pozzolit) are presented. Conclusions are drawn about the specific hydration processes of the cements investigated, as well as the applicability of the laser granulometry method for the study of cement and its hydration products. The investigation is part of a program studying the combined effect of silica fume and fly ash on the hydration process and the physical and mechanical properties of cement mortars and concretes. 

*Keywords:* Laser granulometry; Microscopy; Mineral additives; Cement suspensions; Hydration; Particle size distribution

Laser granulometric analysis has been used in cement research for the study of particle size distribution of unhydrated cements and the assessment of their quality. The scope of the method has been extended to the study of cement clinker mineral activity in contact with water. It has been evaluated according to the variation of particle concentration with time [1], the time dependence of particle size variation for suspensions and cement pastes with different inorganic admixtures [2,3], as well as the specific surface determination of various pozzolanic additives [4] and the effect of chemical admixtures on the dispersity and specific surface of cement particles [5].

The microscopic methods used in their different versions have proved to be universal for the study of various microscopic objects. They provide extremely valuable information based on direct observation of the investigated objects.

This work presents the results obtained from microscopic and laser granulometric research of cements containing active mineral additives (silica fume, fly ash, and a mixture of both) hydrating in the form of suspensions.

## 1. Materials and methods

Portland cement PC45 (C), silica fume (SF) (a by-product material of the production of ferro-silicon steel in the "Kremikovtsi" Metallurgical Plant, Bulgaria, with a content of about 93% of amorphous silica), classified fly ash (FA) from the "Bobov Dol" Thermal Power Generation Plant, Bulgaria, and a Pozzolit (Pz) mineral additive [6] based on a 50:50 mixture of silica fume and fly ash were used in the present investigation. Four different cement compositions, without and with mineral additives, were studied. In three the cement was replaced by 10% silica fume, fly ash, or Pozzolit.

The microscopic analysis was performed using an Image Analyzer developed at the Technical University, Sofia. The device is used to determine the disperse composition of emulsions and suspensions. It includes a Jena 2–Carl Zeiss optical microscope equipped with a CCTV-SSC-8001 video camera and a computer. The average dimension $L_{av}$ and the $\alpha = L_1/L_2$ ratio between the maximal ($L_1$) and the minimal ($L_2$) linear dimensions of each of the observed particles had been determined. The program provides the graphic image and calculation of the effective diameter $D_{eff}$ for the whole group of analyzed particles. The advantage of the method is that the sizes of the particles are obtained directly and that it is possible to work individually with the objects. The suspensions of the cement and mineral particles are investigated in 0.5-mm high glass cells. Adjustment of the device and the recording time for each measurement do not exceed 3 min.

The laser granulometer (Laser Particle Sizer Analysette-22, Fritsch) is based on an He-Ne laser wavelength of 632 nm, power of 5 mW, and a multielement 31-channel detector. The apparatus is capable of measuring particle size distribution over the range from 0.3 to 1100 μm, based on the presumption of a spherical particle. The software offers the

* Corresponding author. Tel.: (359 2) 62 581/347; E-mail: lilkov@staff.mgu.bg.


PII: S0008-8846(98)00173-2

Table 1
Particle size distribution (%) of the additives and of the cements depending on the $\alpha = L_1/L_2$ ratio.

| α in the interval | 1–1.16 | 1.16–1.5 | 1.5–2 | >2 |
|---|---|---|---|---|
| Additives | | | | |
| SF | 54.2 | 18 | 17.5 | 10.3 |
| FA | 46.4 | 26.4 | 20 | 7.2 |
| Pz | 45.1 | 25.6 | 19.3 | 10 |
| Cements | | | | |
| C | 46.5 | 27 | 14.5 | 12 |
| C + SF | 49.5 | 21.9 | 18.6 | 10 |
| C + FA | 47.7 | 22.9 | 20.2 | 9.1 |
| C + Pz | 47.5 | 26 | 15.7 | 10.8 |

$L_1$, maximal and $L_2$, minimal linear dimension of the particles.

possibility of obtaining both frequency size distribution and cumulative size distribution. At the beginning of each test the distance between the cell and the detector had been adjusted, and in all measurements beam obscuration was kept within the limits of 8% to 10%. The duration of one measurement was about 1 min.

Cement suspensions were prepared with 400 mg of cement and 100 mL of distilled water mixed in a magnetic stirrer (5 min) and subsequently stored until the moment of measurement. The suspensions were ultrasonically dispersed for 1 min immediately before measurement. The water-to-solid ratio of the suspensions investigated was determined experimentally in the range of maximum sensitivity of the laser granulometer.

The differential particle size distribution of the materials used and of the cements was investigated in a liquid medium of pure ethyl alcohol to avoid the dissociation and agglomeration of cement particles that occur upon contact with water.

## 2. Results and discussion

The microscopic analysis proved that about 54% of the SF particles and more than 45% of the FA, Pz, and initial cement particles are of a close to spherical form, with the α ratio being less than 1.16. Addition of the additives to the initial cement does not change significantly the form of the particles (Table 1).

The results from the microscopic and laser granulometric analyses of the initial materials (Fig. 1) are very close because the materials investigated are characterized by a greater share of the spherical particles.

When mixing fly ash and silica fume the share of particles smaller than 2 μm is decreased whereas the share of particles with an average size larger than 5 μm is increased. The effective diameters of the SF, FA, and Pz particles are 1.9, 7.9, and 9.5 μm, respectively. The graphic images and the SEM micrographs of the mineral additives particles are shown in Figs. 2 and 3, respectively.

The graphic images of the particles of the cements investigated are shown in Fig. 4. The effective diameter of the particles is 5.4 μm for the initial cement and 5.0, 7.1, and 7.7 μm for the cements with silica fume, fly ash, and Pozzolit, respectively.

The results confirm that the silica fume and fly ash particles, as well as the cement and additive particles, are susceptible to sticking to one another, forming complexes of heterogeneous particles that exist in the mixtures together with the particles of the initial materials.

The graphic images of the particles of the cement suspensions investigated at the fourth hour of hydration are presented in Fig. 5.

In the process of hydration of all the cement suspensions, the number of particles with a close to spherical shape decreases. This is especially well expressed for the silica fume and Pozzolit containing cement suspensions (Table 2). The silica fume particles obviously serve as links between the single hydrating particles, uniting them in complexes of particles of irregular shape.

During the first hour of hydration, the average dimension of the particles in the pure cement suspensions decreases as a result of the dissolution of particles larger than 5 μm, thus increasing the share of particles with average dimension less than 1 μm (Fig. 6a). In the case of cement suspensions with mineral additives, the share of the finest and the most coarse particles is diminished during the same period,

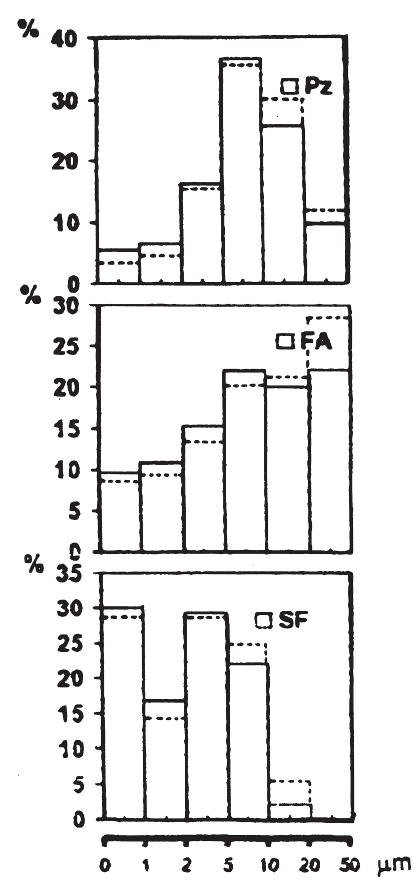


Fig. 1. Differential particle size distribution of the SF, FA, and Pz particles: (—), microscopic study; (- - - -), laser granulometric study.

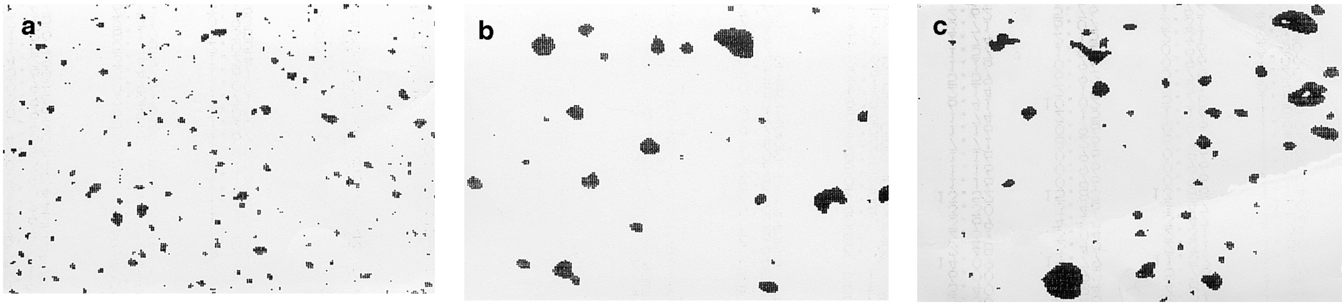


Fig. 2. Graphic images of the SF (a), FA (b), and Pz (c) particles.

whereas the share of the middle-size particles (2–10 μm) is increased (Figs. 6b–6d).

At the fourth hour of hydration of pure cement suspensions, the share of particles with an average size less than 2 μm is decreased and the share of particles larger than 5 μm is increased (Fig. 6a), whereas in the silica fume and Pozzolit containing cement suspensions the share of particles larger than 10 μm is increased more than twice at the expense of the decreased share of particles in the range from 1 to 10 μm (Figs. 6b and d).

At this stage of hydration, strong growth of the share of particles larger than 20 μm is observed for the fly ash containing cement suspensions (Fig. 6c).

Compared to the results from microscopic investigations, the average particle sizes obtained from laser granulometric analysis are shifted in the direction of larger particle diameters (Fig. 7). The reason for this difference is in the object recording principle of laser granulometry, as well as in the alterations of particle shape that occur during the course of hydration. The unequal friction forces on the surface of solid particles of irregular shape suspended in a viscous fluid result in pressure fluctuations leading to vortex drag (turbulence resistance) [7], thus causing oscillatory and rotary movement of the particles in the stream that is superposed on their oriented flow in the suspension. The record-

Table 2
Particle size distribution (%) of the hydrating cement suspensions depending on the $\alpha = L_1/L_2$ ratio

| Cements | α in the interval (h) | 1–1.16 | 1.16–1.5 | 1.5–2 | >2 |
|---|---|---|---|---|---|
| C | 0 | 46.5 | 27 | 14.5 | 12 |
| | 1 | 36.4 | 36.4 | 18.1 | 9.1 |
| | 4 | 36.0 | 31.2 | 19.5 | 13.3 |
| C + SF | 0 | 49.5 | 21.9 | 18.6 | 10 |
| | 1 | 25 | 35.5 | 22.1 | 17.4 |
| | 4 | 30.1 | 28.5 | 23 | 18.4 |
| C + FA | 0 | 47.7 | 22.9 | 20.2 | 9.2 |
| | 1 | 35.7 | 30.9 | 22.6 | 10.8 |
| | 4 | 34.8 | 29.8 | 23.2 | 12.2 |
| C + PZ | 0 | 47.5 | 26 | 15.7 | 10.8 |
| | 1 | 30.0 | 34.7 | 20.2 | 15.1 |
| | 4 | 29 | 30.1 | 23.1 | 17.8 |

$L_1$, maximal and $L_2$, minimal linear dimensions of the particles.

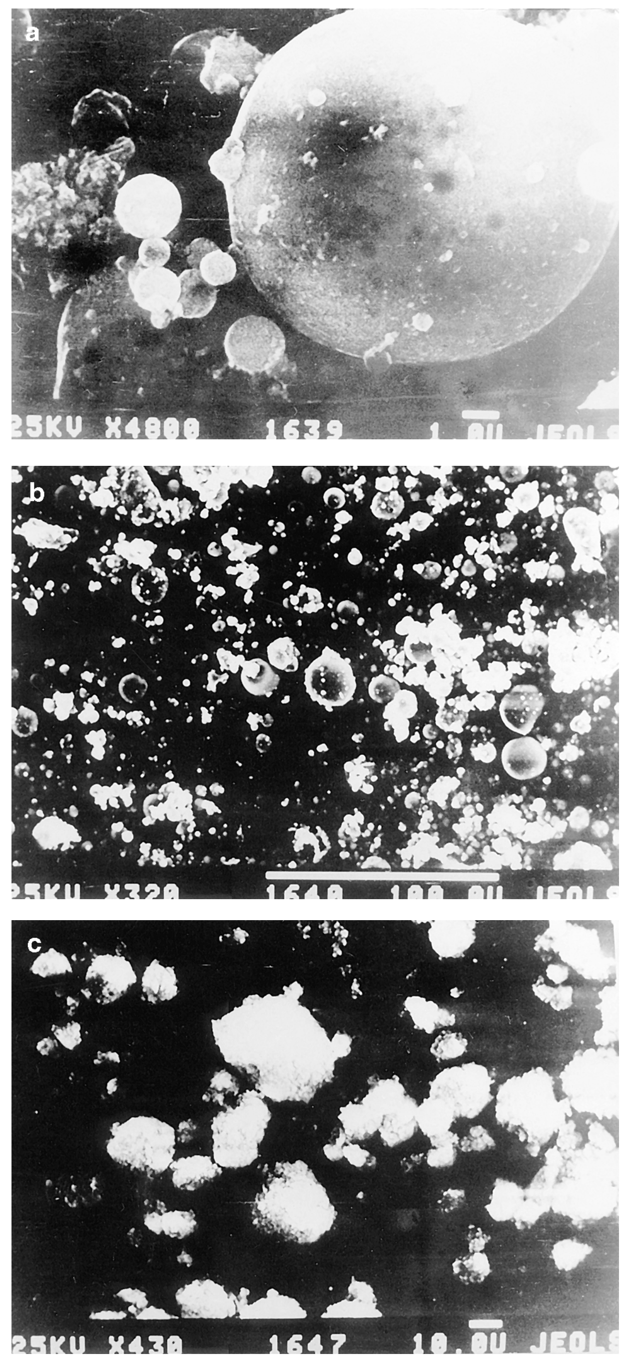


Fig. 3. SEM micrographs of the FA (a) and Pz (b,c) particles.

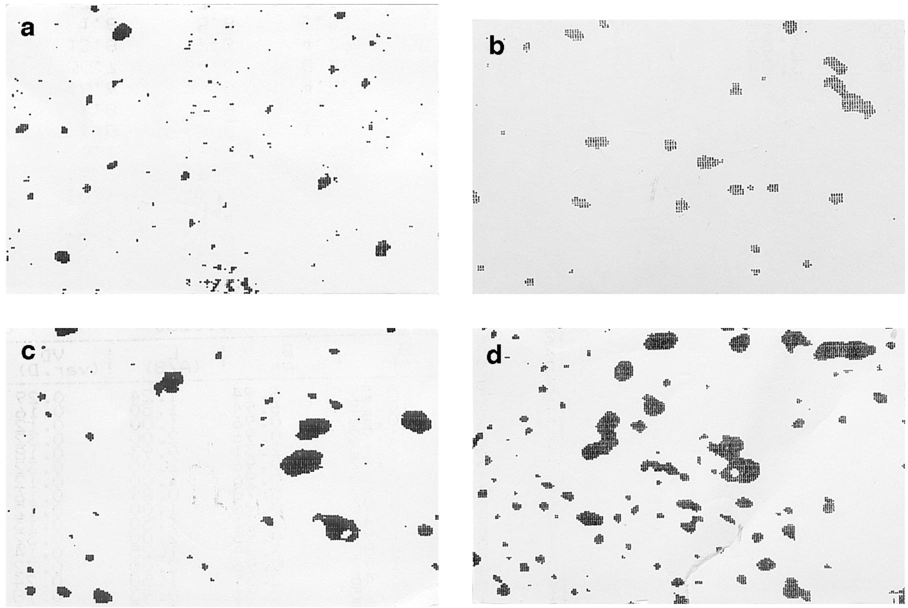

Fig. 4. Graphic images of the particles of the (a) initial cement (C) and cements with (b) SF (C + SF), (c) FA (C + FA), and (d) Pz (C + Pz).

ing principle of operation of the laser granulometer is based on the Frauenhoffer diffraction of the laser beam by the suspended particles [8], when the differently oriented particles in the bulk of the suspension, varying in shape and size, can be "seen" by the detector as identical and vice versa. On the other hand, the larger particle sizes established by laser granulometry, in comparison with the real ones obtained from microscopic investigations, result from their oscillatory and rotary movement during the measuring process when they are "seen" by the detector as spheres with a diameter equal to their maximal linear dimension, because the recording time is considerably longer than the period of particle oscillation in the range of the laser beam.

## 3. Conclusions

1. In the fly ash/silica fume mixtures the silica fume particles cover mainly the fine fly ash grains, forming stable Pozzolit grain complexes.

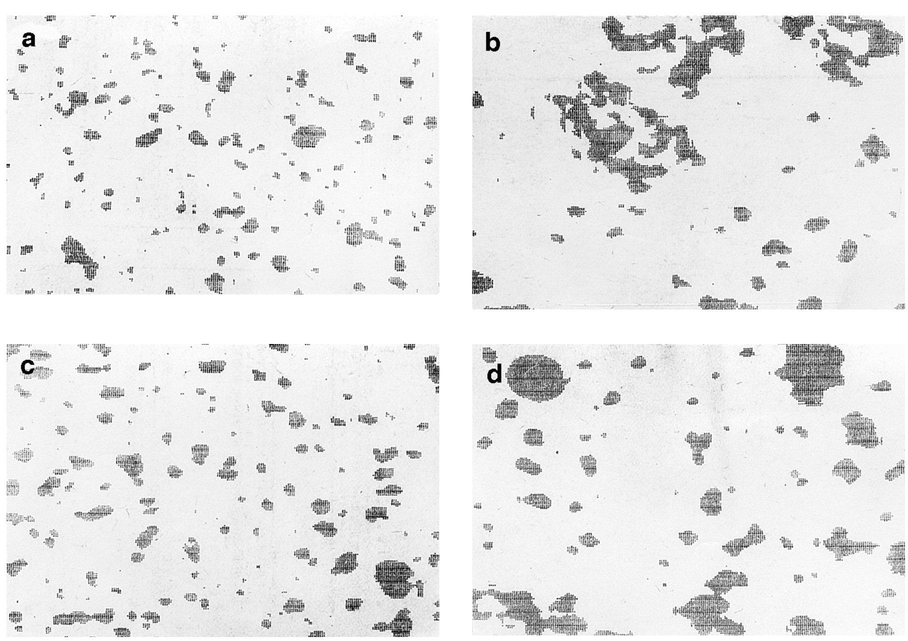

Fig. 5. Graphic images of the particles of (a) the plain cement suspension (C) and cement suspensions with (b) SF (C + SF), (c) FA (C + FA), and (d) Pz (C + Pz) at the fourth hour of hydration.

2. The first hours of hydration of the cements investigated are characterized by variations in the effective particle size and particle size distribution. Several concurrent processes proceed simultaneously: the dissolution of cement particles and diminution of their size on the one hand and aggregation of small particles on the other.
3. Approximately half of the particles of the mineral additives and of the investigated cements have a close to spherical shape. The relative share of these particles diminishes during the course of hydration of the cement suspensions at the expense of the irregularly shaped particles, this being expressed most strongly for the silica fume and Pozzolit containing cements. The fine silica fume particles possessing a great specific surface serve as links between the single hydrating particles.
4. Laser granulometric analysis is applicable to investigation of materials with particles of nearly equal shape, which can be defined unambiguously by the so-called shape parameter of the particles. The most accurate results are obtained for materials with a spherical particle shape in an inert, for them, medium. The method is not applicable to hydrating cement suspensions, because the shape of the particles becomes irregular and is changed greatly during the hydration process.

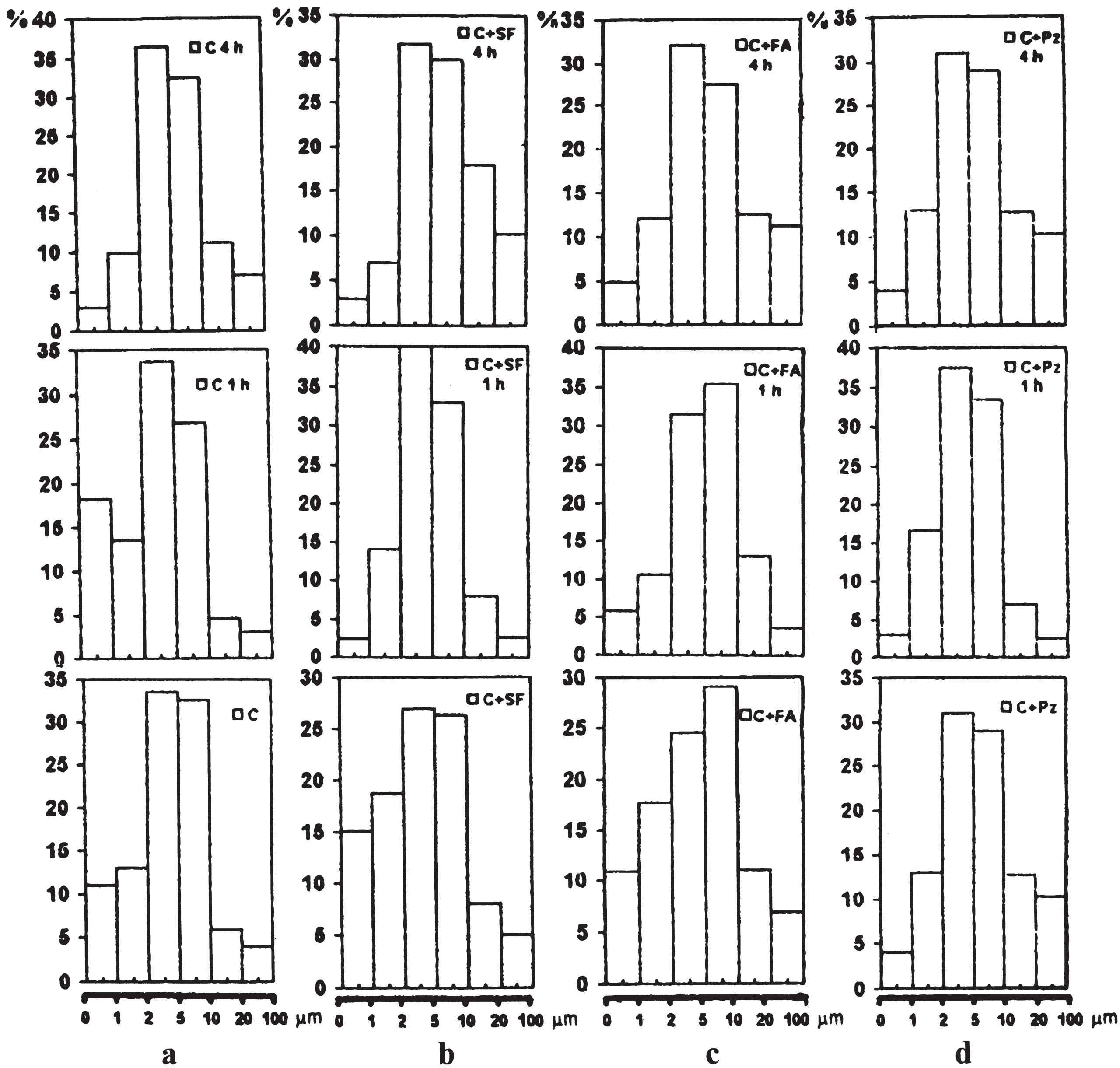


Fig. 6. Differential particle size distribution during hydration of the plain cement suspension (a) and cement suspensions with SF (b), FA (c), and Pz (d) by microscopic investigation.

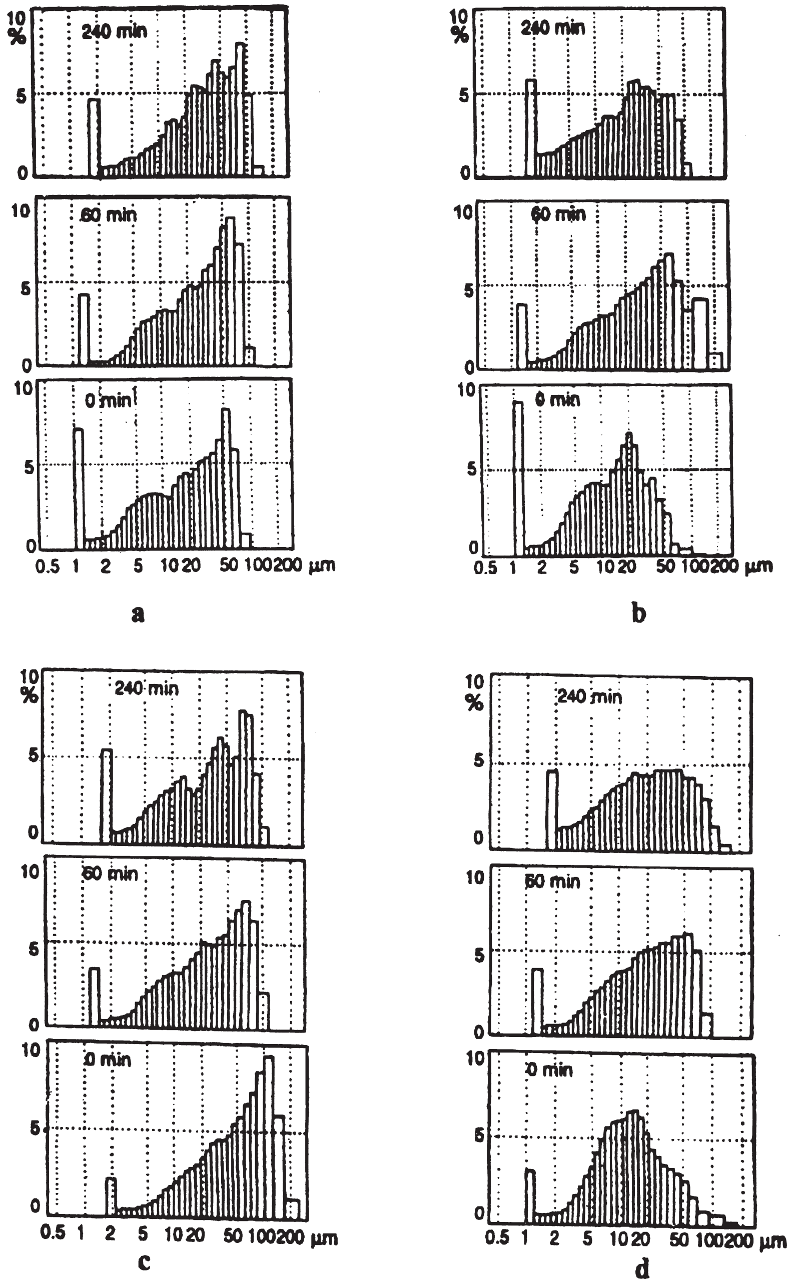


Fig. 7. Differential particle size distribution during hydration of the plain cement suspension (a) and cement suspensions with SF (b), FA (c) and Pz (d) by laser granulometric study.

## Acknowledgments

The present investigation was carried out with financial support from the National Fund “Scientific Investigations” of the Bulgarian Ministry of Education and Science (Project H3-417).

## References

[1] A. Negro, L. Montanaro, A. Bachiorrini, Cem Concr Res 15 (1985) 315.
[2] I. Odler, T. von Borstel, Cem Concr Res 19 (1989) 295.
[3] L. Montanaro, A. Bachiorrini, Il Cemento 82 (1985) 153.
[4] M. Frias, M.I. Sanchez de Rojas, M.P. Luxan, N. Garcia, Cem Concr Res 21 (1991) 709.
[5] I. Masood, S.K. Agarwal, U.N. Sinha, Cem Concr Res 24 (1994) 527.
[6] V. Lilkov, V. Stoitchkov, Cem Concr Res 26(7) (1996) 1073–1081.
[7] L. Landau, E.M. Lipshitz, Theoretical Physics, V. VI. Hydrodynamics. Nauka, Moscow, Russia, 1998 (in Russian).
[8] G. von Bernuth, Laser Partikel-Sizer “Analysette 22.” Ein Labor- und Betriebmessgeraet” zur Messung von Partikelgroessenverteilungen an Mineralischen und Synthetischen Rohstoffen, FRITSCH GmBH, Laborgeratebau D-6580 Idar-Oberstein (published in TiZ 5/88).