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MICROSTRUCTURAL ALTERATIONS IN FLY ASH MORTARS: STUDY ON PHENOMENA AFFECTING PARTICLE AND PORE SIZE

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ABSTRACT

In the last years, relation among porosity, permeability and durability of mortar has been investigated, and a direct relation among them has been verified. However, these properties (mainly in the case of fly ashes) are influenced by vibration and stirring processes to which cementitious mass is subjected during its elaboration (mixing and moulding). These processes could provoke the breaking of fly ash plenospheres. This fact modifies the behaviour of mortars and concretes with this industrial by-product.

In the present work a laboratory study is carried out. Fly ash granulometric variations provoked by vibration and stirring processes and their influence on mortar properties is shown. © *1997 Elsevier Science Ltd*

Introduction

In most of the cases, mortars containing materials with pozzolanic characteristics have, porosity values equal or superior to that of reference mortars (1,2); but, however, they experiment a refineness in their capillary porosity structure (3,4), giving place to more tortuous pore nets (5) impeding or delaying the access of aggressive media that will produce, a decay of conglomerate materials through different mechanisms.

Porosity of hardened mortars containing fly ash (6) may present a different behaviour with respect to other pozzolanic materials.

In a former work (7), the direct influence of stirring and sonication on fly ashes granulometry was shown. It was observed how, as fly ashes had greater size, granulometry variations were more acute and very different to the values obtained through sieving method.

Stirring and sonication phenomena to which cementitious mass is subjected before it is moulded, may influence the fineness of fly ash particles and thus, their posterior behaviour, mainly from the viewpoint of porosity and strength of materials with this industrial by-product.

In this way, the investigation carried out is centred in a laboratory study in which these effects are simulated. For this purpose, techniques as laser diffraction for granulometry analysis, and scanning electron microscopy were used.

TABLE 1

Chemical Composition of Fly Ash

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Cl^-	CaO (Free)	LOI
48.64	22.94	8.89	5.30	0.35	0.0	0.75	5.1

Experimental

Materials. *Cement based: According to the Spanish UNE 80 301 standards (8), the base cement is a Type I/45 cement with a clinker content equal to or above 95% that may have up to 5% additional component.

*Fly ash: This is generated in a power plant that uses bituminous and anthracite coal as power source. The chemical composition of fly ash is shown in Table 1.

This fly ash presents low crystallinity, as can be observed in the diffractogram of Figure 1; the main mineralogical components are: Quartz (Q), mullite (Mu) and hematite (H).

In Table 2, other characteristics of this material are presented as its fineness, expressed as the cumulative percentage retained on the 45 μm sieve. Other data relating to mixes with cement like: water requirement (WR), Le Chatelier expansion and pozzolanic activity index (PAI)at 28 and 90 days, according to European Standards (9) are also shown.

These values indicate that fly ash is relatively fine, it does not increase the water requirement, it does not provoke expansion and presents pozzolanic activity, especially at 90 days.

*Sand: In mortars elaboration, a quartz sand is used, with 98% pureness and maximum particle size of 2mm.

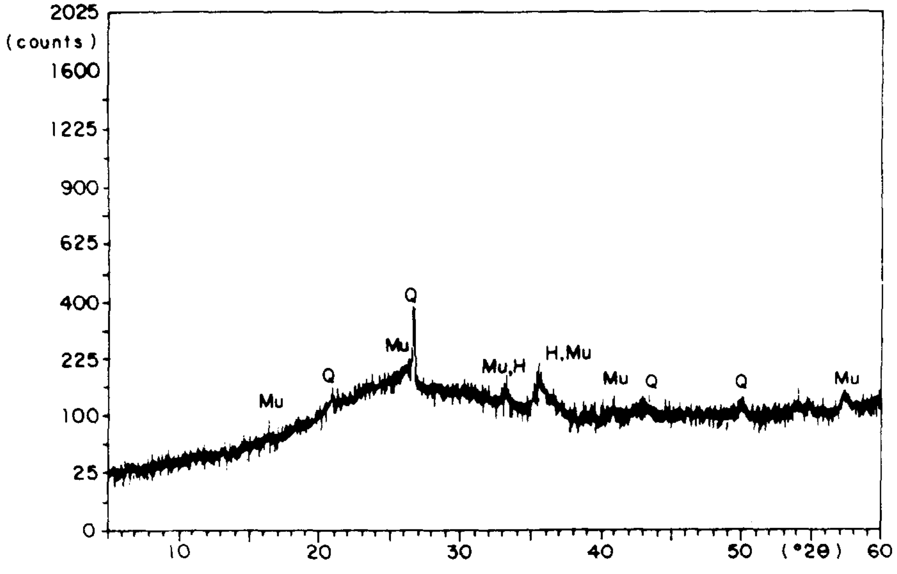


FIG. 1.
X-Ray diffraction of fly ash.

TABLE 2

Physical Characteristics of Fly Ash

Residue on 45μm sieve (%)	W.R. (%)	Expansion (mm)	P.A.I. 28 d (%)	P.A.I. 90 d (%)
18.8	90	0.1	76	96

Mixed Cements. The mixed cements were prepared in a high speed powder mixer to guarantee their perfect homogeneity and safeguard their granulometry. Cement/fly ashes mixtures were made up by weight in the following base cement to addition ratios: 100/0, 90/10, 80/20, 70/30 and 60/40.

These mixed cements are used to prepared mortars, whose sand/cement ratio is 3/1 and W/C is 0.5.

Testing Methodology. *Granulometric determination of fly ash is carried out by means of a laser diffraction equipment, that provides particle size distribution curve between 0,1 μm and 2mm.

With this technique, the evolution of particle size with time can be followed, considered under the influence of mechanical stirring and/or sonication. A suspension of fly ash in isopropilic alcohol is prepared and the granulometric determination is carried out:

- Stirring (control test)
- Simultaneous stirring and sonication at different times (15 seconds, 30 seconds, 60 seconds and 180 seconds). Once the sample is subjected to maximum stirring and sonication times (180 seconds), it is filtered and dried at 105°C, and observed by SEM.

*In mortars prepared with different proportions of fly ash (con su granulometria original), mechanical strengths at 28, 90 and 360 days are tested; at the same age, porosity and pore size distribution curve are determined through mercury porosimetry. In the elaboration of these mortars fly ash particles are subjected to the real processes of stirring and vibration whose effects have been simulated.

Results and Discussion

1. Granulometric Variations in Fly Ash. Granulometric results of fly ash are collected in Figure 2. They show how particle size distribution curve evolves towards smaller sizes when mechanical stirring and sonication is applied and it is smaller as test time increases. A more detailed study about granulometric variations experimented by the different fly ashes is in a former work where the most suitable form of determining the fineness of these by-product through laser granulometry is recommended.

These granulometry changes are produced in particles with size inferior to 40-50 μm, becoming notably between 2 and 10 m. Then, for control test only 15% of the particles are inferior to 6 μm, while when the same sample is subjected to stirring or sonication phenomena (180 seconds), particles percentage is more than 30%.

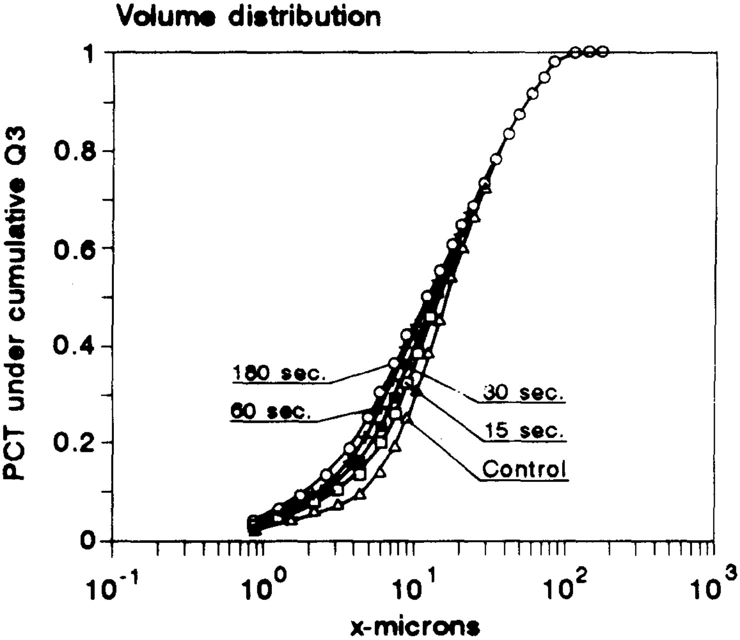


FIG. 2.
Particle size evolution as a function of tests conditions.

This fact may be explained by means of the effect provoked by the stirring with sonication; fly ashes plenospheres release smaller cenospheres, in a way that sample fineness increases.

2. SEM. The phenomenon of plenospheres breaking in fly ash is observed with detail by SEM (Figure 3). Figure 3a, shows that in general, in sample subjected to 180 seconds of stirring and sonication, largest particles (plenospheres of 60 μm approximately), undergo a rupture process in different degrees, depending on walls width; because it is detected that fly ash particles are spheres, but irregular with respect to walls width.

Figure 3b shows a partially broken plenosphere, where this fact is shown. So, the widest wall is approximately 12 μm and the narrowest is 3-4 μm wide. Figures 3c and 3d show two different aspects of rupture. On one hand, the moment of the cenospheres release in a determined area (Figure 3c), broken by the joint action of stirring and sonication is collected; while other plenospheres break in halves, releasing the smaller particles and leaving particle rests with empty hollows, directly influencing mortars porosity (Figure 3d) as is described in the next point.

On the other hand, mortars porosity is also influenced by other factors as carbon particles present in fly ashes (Figure 3a) and the porosity in cenospheres walls, Figure 3e. The presence of pores with different diameters (2-5 μm) is detected; although higher values can be reached and the pores or hollows can be filled with smaller cenospheres (Figure 3f).

These phenomena have a direct incidence on porous structure of mortars with fly ashes. By this reason, a study of porosity and pore size distribution through mercury porosimetry is carried out.

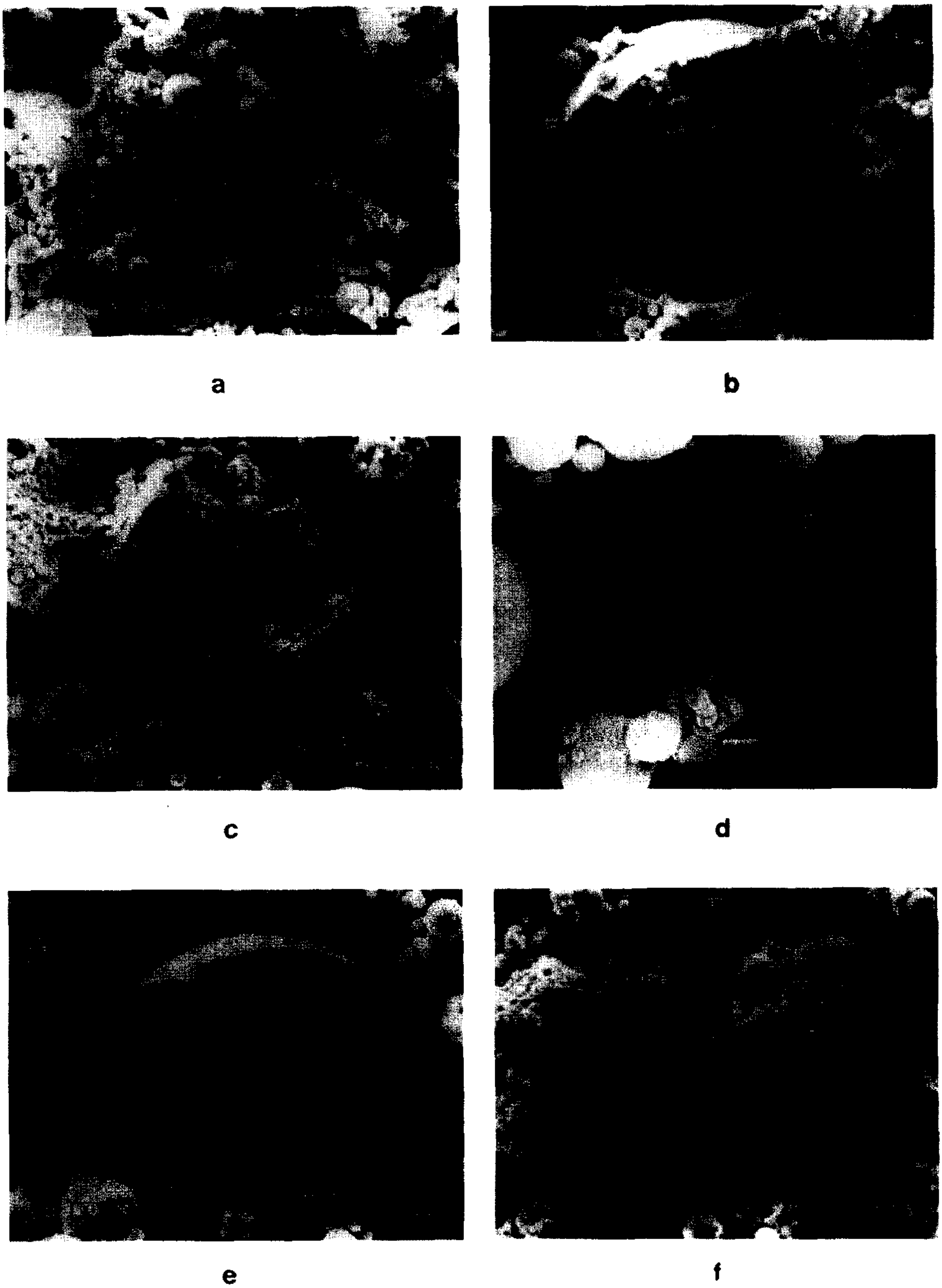


FIG. 3.
Fly ash particles aspect through SEM.

3. Pore Size Distribution of Blended Cement Mortar. Figure 4 shows the relative frequency of pore size as a function of time of the five mortars tested. In all the cases, the presence of pore sizes below 800-1000nm is observed.

In these blended mortars, the maximum shift may be due to the influence of the amount and the rupture of plenospheres that may provoke the increase of empty hollows with a negative influence on total porosity. The study of this influence is the objective of the present work.

At 90 days, a different behaviour is detected. Although pore size range is similar, maxima positions tends to unify; due to pozzolanic reaction, among the acid components of fly ashes and the portlandite from hydration reaction, giving place to a pore size refineness.

At this age, a defined porous structure is not observed because two simultaneous reactions are taken place, pozzolanic and hydration reactions and porous net is then constantly evoluting.

At long times (365 days), in all mortars studied a bimodal distribution is detected; there are two maxima, one at 10-12nm, like the one observed at early ages and the other with pore distribution superior to the former and less intense, placed at about 100-200nm. It is worth to remark that second maximum intensity is a function of fly ash amount added.

4. Capillary and Total Porosity. To know in detail the porous structure changes in the mortars studied, total porosity evolution as a function of time and partial porosity evolution as a function of different pore size fractions are shown in Figure 5. In general, fly ash mortars increase porosity with respect to control mortar (100/0), this fact has been observed by different authors (1,2).

Regarding total porosity, it is detected that after 28 days curing, samples porosity is slightly superior to that corresponding to 90 days. The compounds formed in pozzolanic reaction occupate the hollows existing (aggregate/matrix, fly ash/matrix interphases) giving place to a size refinement by reducing the amount of the largest pores (air pores > 5 μm and by increasing that of the smaller pores (<0,01 μm).

At 365 days curing the phenomenon is similar, although the trend of pore size is better defined. While pores with size greater than 5 micron, decrease with fly ash addition, capillary porosity (5-0.01 micron) increases.

These porosity variations due to fly ashes utilization directly influence mechanical strengths of blended mortars. When a study about mechanical strengths of mortars with fly ashes with respect to a control mortar is carried out, it is seen how fly ash mortars do not reach control mortar values, Figure 6(a). One of the reasons is, not only the slow fly ashes pozzolanic reaction, but mortars porosity effect as a consequence of the increase of hollows in their preparation (Fig. 3).

So, strengths decrease with respect to control mortar is a function of cement substitution by fly ash, in a direct relation (correlation coefficient: 0.99 at 365 days) between mortars total porosity and this compressive strength (Fig. 6b).

Conclusions

* The fineness of fly ash increases with longer particle dispersion process duration.
* Some fly ash particles (plenospheres) are crushed during the dispersion process, releasing the leaving empty spaces.

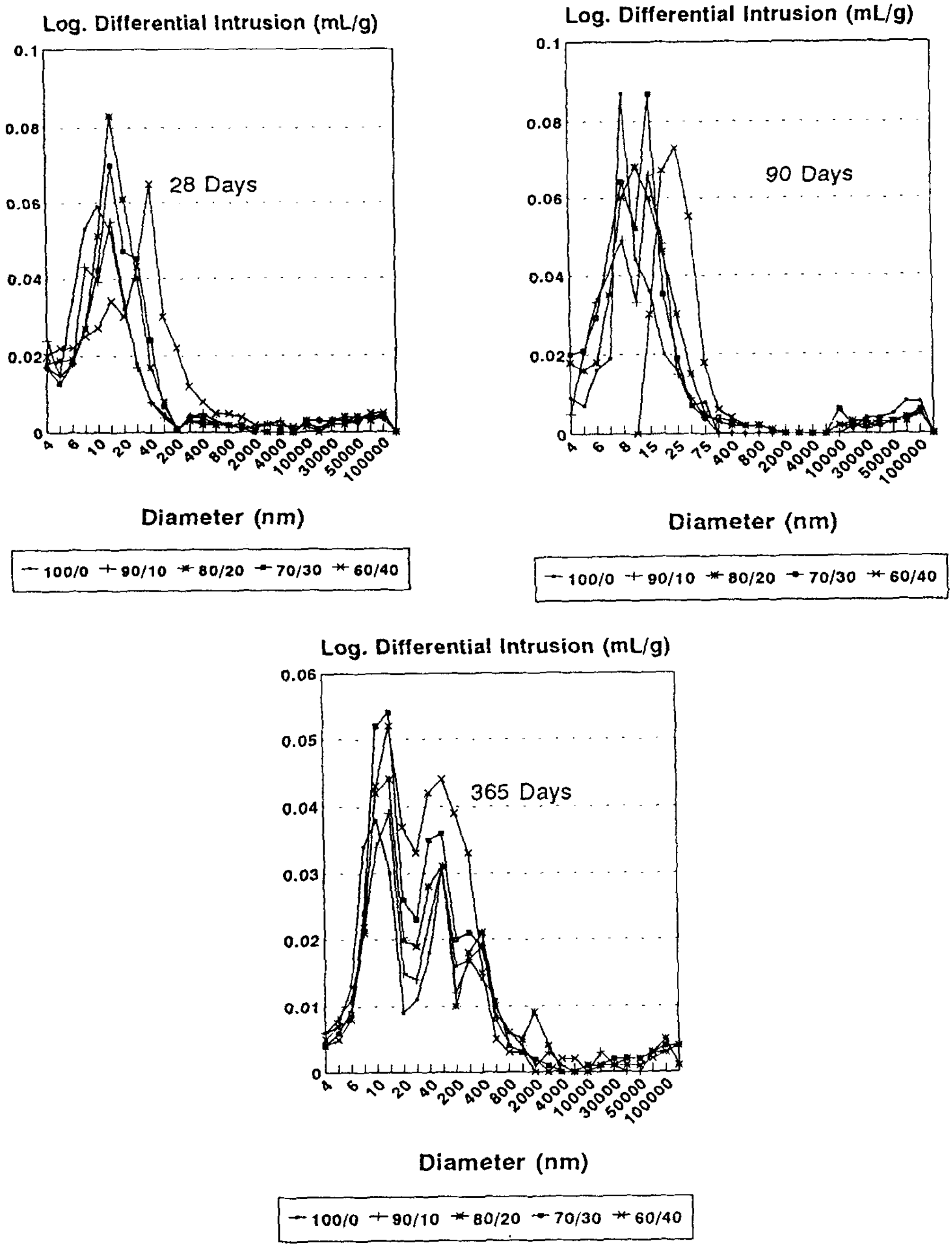


FIG. 4.

Differential intrusion variation(ml/g) with pore diameter of the blended mortars.

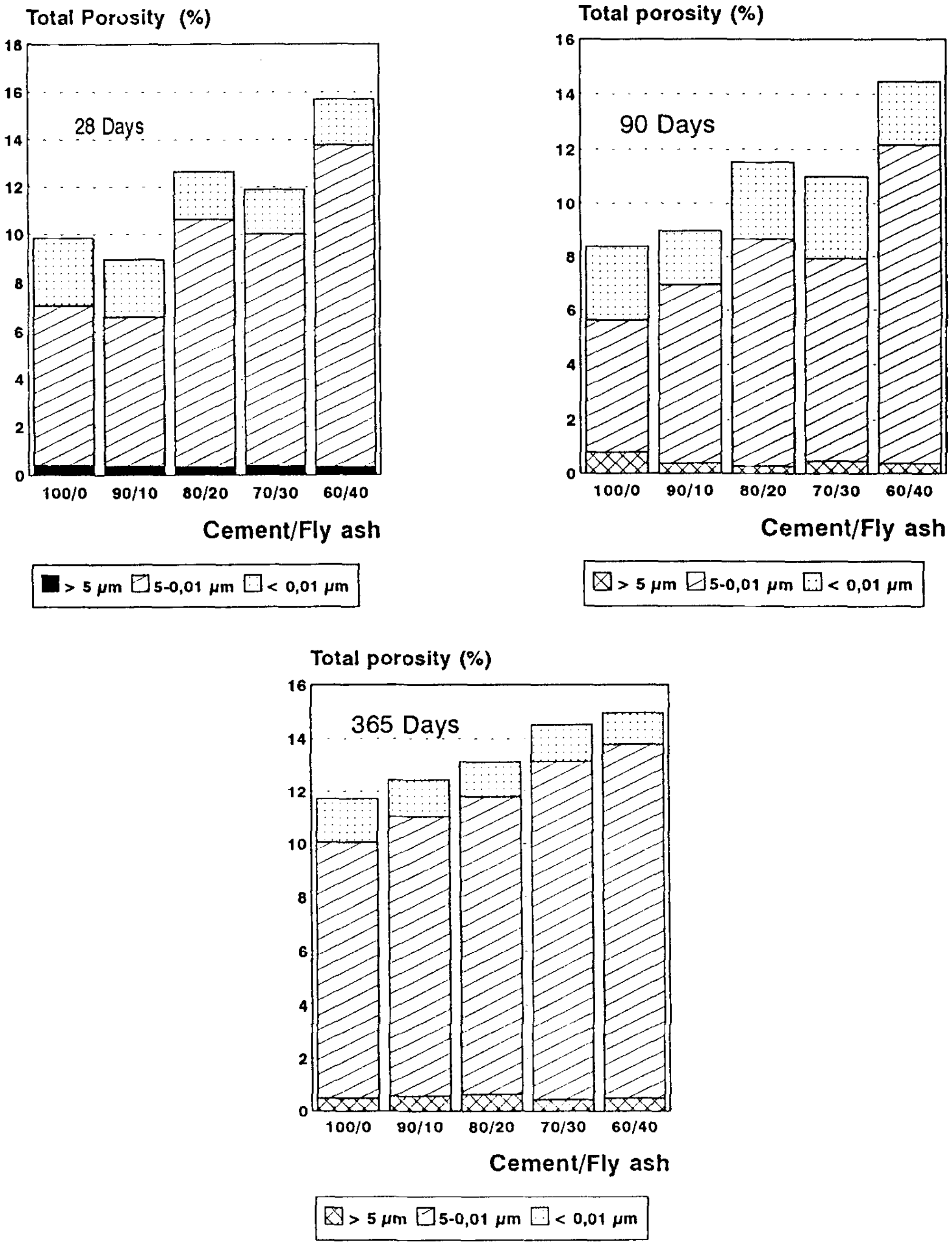
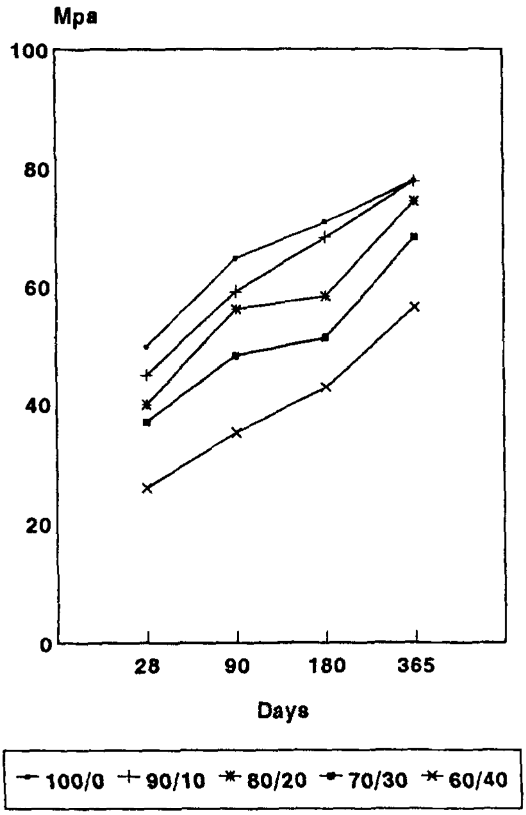


FIG. 5.
Different pore size fractions of mortar.



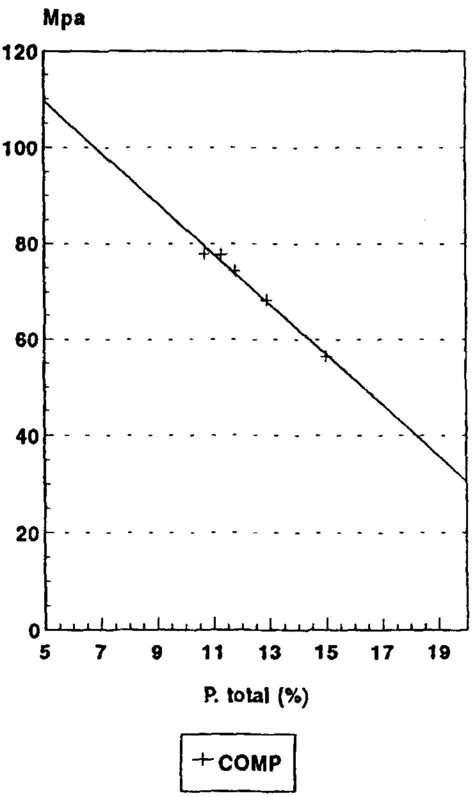


FIG. 6.
Compressive strength: a.- over time; b.- relationship with porosity.

* The destruction of spheric fly ash particles, caused by the stirring and vibration has a negative influence on the following properties:

1. Total porosity and pore size distribution of mortars with fly ash depend on the curing period and the fly ash/portland cement ratio as on external phenomena during elaboration process. This porosity may be assigned to three consecutive facts:
   a) The porosity increase at first ages (28 days) possibly due to the increase of broken plenospheres because of vibration and stirring during mortar elaboration process (Fig.3).
   b) At medium age (90 days), porosity decreases due to hydration reaction, principally.
   c) At long ages, porosity of mortars increase with age, conditioned by pozzolanic reaction, that appears as a progressive erosion in particle surface, giving place to particles disintegration (10) (11) and leaving empty hollows not completely filled by reaction products.
2. Mortar strength decreases with increasing fly ash/portland cement ratios.
3. Strength decreases linearly as the total porosity increases.

Acknowledgments

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