"DETERMINATION OF PARTICLE SIZE DISTRIBUTION IN CEMENTS WITH ADMIXTURES BY OPTICAL METHODS".

Raúl H. Prado[1], Mariela L. Álvarez[2], Mercedes Rosell[3], Noemí Rivera[3]

(1) Universidad de Alicante, Departamento de Construcciones Arquitectónicas, Campus de Sant Vicent del Raspeig, Ap.99 E-03080 Alacant (Alicante), España.

(2) Universidad de Alicante, Departamento de Física, Ingeniería de Sistemas y Teoría de la Señal.

(3) Centro Técnico para el Desarrollo de los Materiales de Construcción, Habana, Cuba.

Email: raul.prado@ua.es

INTRODUCTION

In determining particle size in powders, a large number of methods are employed including sedimentation (e.g. sedimentation scale method, Andreason´s pipette method and others), chromatography, microscopy, electrozone testing, scatter methods and filtration methods among others, each one of these with their own particular characteristics and corresponding degrees of accuracy.

In the study of cements, the most used of these methods are the filtration (and/or sifting method), and sedimentation, this last one based on Stoke´s Law which compares the rate of particle separation in a liquid at rest in a way that:

$$V = \frac{2ga^2(d_1 - d_2)}{9\eta}$$

where:

d_1 y **d_2**, are the sphere densities

η, is the viscosity coefficient of the liquid

a, is the radius of the sphere

V, is velocity

g, is gravity.

Unfortunately Stoke´s Law cannot be applied with total accuracy in relation to tests on cements since the particles are considered to be spherical, a fact which is seldom the case in cements, and other tests based on the percentages of quantities retained by or which pass through standard filtration screens, offering relative percentages of the different components. In both cases a detailed study is required and particularly in the case of cements which are not only influenced by particle size distribution but also by their morphology in relation to reactivity. New techniques are starting to be employed such as microscopy (which deals with small sample size and as such is not representative ith respect to volume) and scatter or laser particle diffraction which as well as providing representative and statistical diameters of the sample, also produce particle size distribution values.

However, almost all cements currently produced are mixtures containing different types of additions, which provide benefits not only from an economic point of view (with the consequent reduction in production costs), but also in relation to their physical-mechanical properties among other reasons for the pozzolanic characteristics of the active additions.

Our study was based specifically on the granulometic properties of cements that had been mixed with natural zeolites from Cuba and fly ashes from Spain. The study employed laser particle diffraction, to compare the results of each one of these mixtures with the physical-mechanical properties and morphology in relation to these properties.

Keywords: cements, mixtures, particle size.

EXPERIMENTAL PROCEDURE

Materials and sample preparation: Two fresh pure cement samples (referred to as **CE** and **CC**) were taken from different sources, two fly ash samples from thermal sites in Puertollano (**CP**) and Meirama (**CM**) in Spain, and a natural zeolite sample (**Z**) from deposits in the south of Cuba (with a size determined by screen of less than 200 μm). Each one of these additions displayed different characteristics from a granulometric, mineralogical and morphological point of view.

A pure cement sample was kept as control, and several mixtures were made by adding a variety of percentages by weight equivalent to 5, 15, 30, and 50 % for the fly ash (samples **CE5P**, **CE15P**, **CE30P**, **CE50P**, **CE5M**, **CE15M**, **CE30M** and **CE50M** using ashes emanating from Puertollano as well as those from Meirama), and 5, 10, 15 and 20 % in the case of zeolite (samples **CC10Z**, **CC15Z** y **CC20Z**, respectively), reaching in this case up to only 20 % after being optimised by compressive strength values.

In all cases, the samples once mixed, were added to acetone and submitted to agitation in an ultrasonic bath for a period of 1 hour followed by a period of 48 hours drying at a temperature of 40 °C. In this way we were able to obtain maximum homogenisation without affecting the granulometric distribution of each of the constituents. The samples thus produced were measured to compare the behaviour of the mixtures. The process employed laser particle diffraction using the *Malvern Instruments 2600* (software version B.OD), taking into account that the granulometry as much in the cements as in the mixtures, vary according to size intervals ranging from 7 to 18 μm.

Each one of these proportions of mixed cements and the control sample without additions, were made into mortar prisms of 40x40x160 mm mortar size, normalised with a water/cement 0.5 according to the UNE 80-101.88 Standard (Cement analysis method, determination of mechanical resistance) and are then kept in a moisture chamber for a period of 90 days (this being the standard period for this quality of mortar intended for analysis of cement mixtures with active additions) in order to then conduct compressive strength trials.

RESULTS

Table 1 (below) illustrates the values obtained from particle size distribution and compressive strength tests:

Table I. Results

Sample	D[v,50 %](μm)	Span	R (N/mm²)
CE	6.94	1.93	52.62
CE5P	9.27	1.92	49.39
CE15P	10.03	2.01	54.98
CE30P	11.30	2.06	52.19
CE50P	12.82	2.03	52.19
CP	14.03	1.59	-
CE5M	11.50	1.82	54.72
CE15M	12.84	1.89	55.01
CE30M	14.18	2.02	53.32
CE50M	15.75	2.55	16.87
CM	17.46	2.62	-
CC	8.72	1.97	35.0
CC5Z	9.96	2.20	51.9
CC10Z	11.00	2.15	46.1
CC15Z	11.84	2.14	47.7
CC20Z	12.94	2.18	45.2
Z	14.21	2.00	-

Where, **D[v,50%]:** is the median distribution in volume, diameter of distribution below which is to be found 50 % of distribution by size.

Span: is the measurement of the range of distribution in volume, relative to diameter.

R: is the compression resistance of the cement mortars with and without additions after a period of 90 days.

From **Table 1**, it can be seen that for 20 and 30 % of additive, the relation between the granulometry of the mixtures and the pure additives are of 0.09, 0.19 and 0.24 for the zeolites and fly ashes (**CP** and **CM**) respectively. This shows that the mixture of zeolite and cement tends towards a granulometric behaviour much quicker than for any of the other additives. This is much more representative in relation to the Span, which in the case of the zeolite remains invariable, due to a greater homogeneity of the components of the mixture (varying between 1.97 and 2.00).

For a broader analysis of the results shown in **Table 1**, **Figure 1** shows graphically the relation between compressive strenght and the granulometry for the zeolites, and **Figure 2**, the granulometric distribution against the percentage of addition for the different samples

It can be appreciated that **Figure 1** shows a rising tendency towards compressive strength when zeolite is added to the cement. This behaviour stabilises with an increase in the percentage of zeolite addition from a 11 % of addition (for a compressive strength of 46 N/mm^2). In the case of additions of fly ash, values for compressive strength for pure cement remains approximately constant (52.62-52.19 N/mm^2), or falls (52.62-16.87 N/mm^2) in relation to the distribution of sample size.

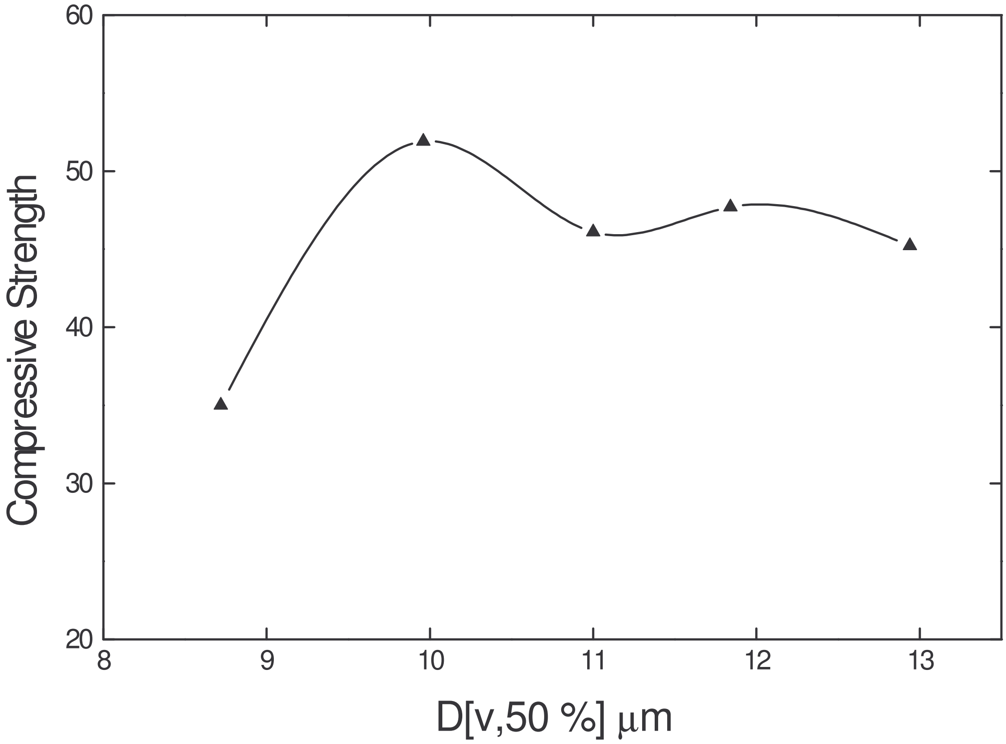

Figure 1. **Relation between the results of compressive strength in samples containing zeolite and the granulometry according to different percentages of additions.**

Figure 2 shows clearly that in the case of fly ash there is no appreciable linear correlation, and there is a marked change upon adding 5% of ash to pure cements. On the other hand, with the addition of zeolite, one can see a linear correlation between the median of distribution and the percentage of additive, from the size of pure cement up to 91 % of the size of the zeolite sample with a regression coefficient of 0.998. For higher percentages of zeolite addition, the curve follows the behaviour which can be seen in **Figure 2**, that the distribution median cannot exceed the size of pure zeolite.

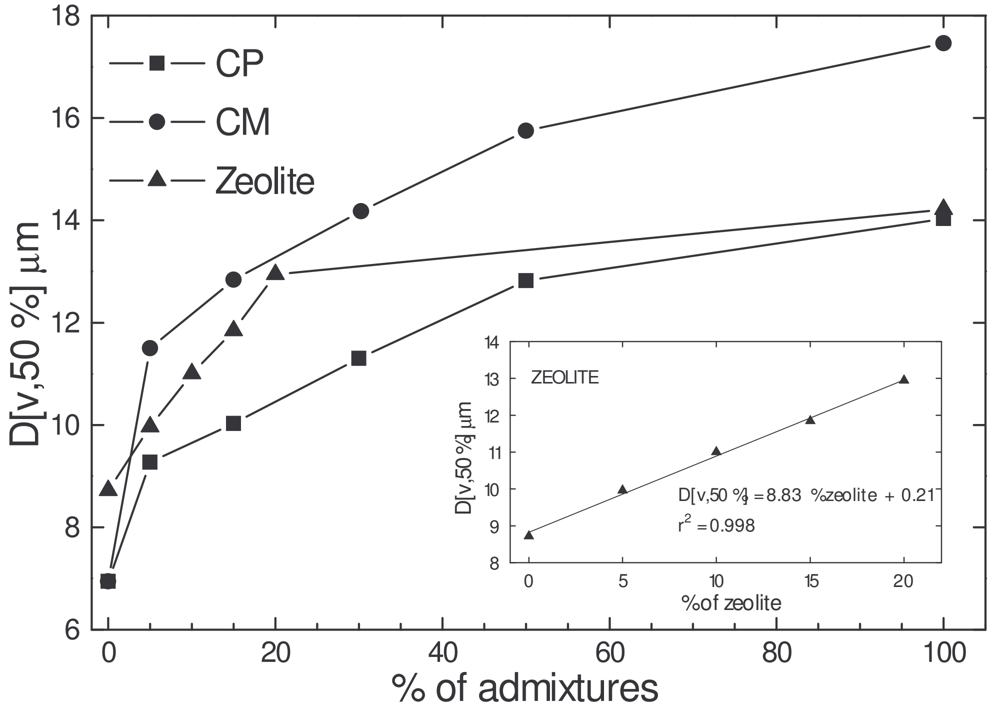

Figure 2. **Granulometric behaviour of additions in relation to the percentage of addition.**

CONCLUSIONS

The use of zeolite as an active additive to cement not only raises the compressive strength values to higher levels (as is already known), but also contributes to a linear behaviour of particle size distribution up to a figure of 20 % addition, from which it remains practically stable, without affecting the previously mentioned resistance values.

The use of laser diffraction technique has made it possible to conduct a detailed study of particle size distribution of cement samples with different additives and varying proportions of additives; what it demonstrates is the efficiency and reliability of this method in relation to other more commonly employed methods.

In the case of ash addition, despite its morphology, the results obtained did not follow the expected behaviour, neither in respect to compressive strength values (decreasing in one case) nor to particle size distribution.

REFERENCES

[1]. Bard, H. G., Sun, S. H., and Nickol, R. M., 1987: Particle Size Analysis. *Anal. Chem.*, **59**, 142R-162R.

[2]. Blackford, D. B., Simons G. R., 1986: Particle Size Analysis of Carbon Black. *Part. Charact.*, **4**, 112-117.

[3]. Klimesch, D. S., Ray, A. and Sloane, B., 1996: Autoclaved Cement-Quartz Pastes: The Effect on Chemical and Physical Properties when using Ground Quartz with Different Surface Areas. Part I. *Cement and Concrete Research.*, **26**, 1399-1408.

[4]. Kusters, K. A., Wijers, J. G. and Thoenes, D., 1991: Particle Sizing by Laser Diffraction Spectrometry in the Anomalous Regime. *Appl. Opt.*, **30**, 4839-4847.

[5]. Seville, J. K., Coury, J. R., Ghadiri, M. and Clift, R., 1984: Comparison of Techniques for Measuring the Size of Fine Non-Spherical Particles. *Part. Charact.*, **1**, 45-52.