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Materials in Concrete). His work from sponsored and other research has resulted i 1 n over 280 technical papers and reports.

SYNOPSIS

A powder obtained as a by-product of marble sawing and shaping was characterized from a chemical and physical point of view in order to use it as mineral addition for mortars and concretes, especially for self-compacting concrete. This marble powder showed a very high Blaine fineness value of about 1500 m^2/kg, with 90% of particles finer than 50 μm (0.0020 in.) and 50% under 7 μm (0.00028 in.). For rheological studies, several cement pastes were prepared using marble powder, with and without the addition of an acrylic-based superplasticizer. Water to cementitious materials ratio was also varied. In order to evaluate the effects of the marble powder on mechanical behavior, many different mortar mixtures were tested, all prepared with sand to cement ratio of 3:1 at about the same workability. Mixtures were evaluated based upon cement or sand substitution by the marble powder. Results obtained show that 10% substitution of sand by the marble powder provided maximum compressive strength at about the same workability.

Keywords: marble, mortar, paste, rheology, recycling, self-consolidating concrete, thixotropy, viscosity, yield stress.

INTRODUCTION

A marble powder, obtained as a by-product of marble sawing and shaping, was characterized from a physical and chemical point of view for evaluating the possibility of using it in mortar and concrete production.

Mineral additions in general influence the performance of fresh concrete and mortar. Therefore, a rheological study was carried out on various cement pastes prepared with marble powder in combination with cement, and eventually, also, with a superplasticizing admixture. In particular, the goal was to investigate the influence of marble powder on rheological properties of cement pastes for predicting the effect of its addition on self-compacting concrete mixtures[1-6].

RESEARCH SIGNIFICANCE

In this study very fine marble powder was used. It was obtained as a by-product of marble sawing and shaping. It was characterized from a physical and chemical point of view for evaluating the possibility of using it in mortar and concrete production. The test results indicate that due to high fineness of the marble powder, it was very effective in assuring very good cohesiveness of mortar and concrete. This research should lead to proper use of such materials for sustainable use of otherwise discarded materials.

MATERIALS

Portland cement

A commercial portland-limestone blended cement type CEM II/A-L 42.5R, according to the European Standards EN-197/1, was used. The Blaine fineness of cement was 410 m^2/kg and its relative density (specific gravity) was 3.05.

Aggregate

Natural sand (5 mm (0.20 in.)) maximum size, with 0.9% passing the 75 μm (0.003 in.) (No. 200) sieve was used. Its relative density (at SSD condition) was 2.62, and its SSD condition water absorption of 3.0%.

Chemical admixture

In some cases, a water-reducing admixture was added to the mixtures. It was constituted of a carboxylic acrylic ester polymer in the form of 30% aqueous solution.

Mineral addition

A marble powder was used, which was obtained as a by-product of marble sawing and shaping. Its relative density was 2.55 and the value of Blaine fineness was 1500 m^2/kg. It can be observed that the marble powder had a high specific surface area; this could mean that its addition should confer more cohesiveness to mortars and concretes[4-5].

For better physical characterization of the marble powder, its grain size distribution was performed using laser diffraction. From the graph shown in **Fig. 1**, it can be observed that 50% of particles had a diameter of 7 μm (0.00028 in.) (d_{50} = 7 μm (0.00028 in.)) and 90% of particles had a diameter lower than 50 μm (0.0020 in.) (d_{90} = 50 μm (0.0020 in.)).

The marble powder is produced as “slurry”, a mud made of powder and water. Therefore, for its use in concrete it is important to know how much water is contained in the slurry, by drying it and registering the weight loss related to water evaporation. A known weight of slurry was put in an oven to dry at a temperature of 110 ± 5°C (230 ± 9°F). At fixed intervals (1 hour, 4 hours, 24 hours, 48 hours, and 72 hours) the weight loss was registered with the aim to reach a constant weight. The results obtained are reported in **Fig. 2**. It is evident from the graph that the sample loses water quickly and reaches the constant weight after about 24 hours.

In order to characterize the marble powder from a chemical point of view, thermal analysis and X-ray diffraction were carried out. Thermal analysis carried out show that the examined material contains about 66% of calcium carbonate, $CaCO_3$. As a matter of fact, as it can be observed in **Fig. 3**, a sharp weight loss (corresponding to the flex of the DTA curve) occurs from about 730°C (1350°F) to 900°C (1650°F) while strong heat absorption was detected. This was due to the decomposition reaction of calcite, which is endothermic. X-ray diffraction analysis, **Fig. 4**, show the presence of quartz, which could be estimated at about 3%, and ankerite (ferroan dolomite) at about 2%. The remaining part of the marble powder consist of amorphous silica or silicates, coming from natural stones other than marble, whose low crystallinity (making them mostly undetectable by X-ray diffraction) may be due to mechanical processing (sawing and shaping).

RHEOLOGICAL BEHAVIOR OF CEMENT PASTES

The study of the rheological behavior of cement pastes is an essential step for the evaluation of fresh concrete behavior and for the optimization of self-compacting concretes[7]. For this purpose, eight cement pastes were prepared by varying the water to cement ratio (0.4 - 0.5), the amount of marble powder addition (10% and 20% by weight of cement), the basis for adding marble powder (as either cement or sand replacement), and by eventually adding a superplasticizing admixture (at a dosage of 0.5% by weight of very fine materials, i.e., cement plus marble powder). The proportions of these paste mixtures are shown in **Table 1**.

The rheological behavior of these cement pastes was determined at 15 minutes after ingredients mixing, and then every 20 minutes up to 1 hour.

The apparatus was a rotating rheometer based on coaxial rotary cylinders with a slowly increasing shear rate (D), ranging from 1 to 100 s^{-1}. Bui et al.[7] found that the rate of 1 to 100 s^{-1} was the most suitable for rheological model of concretes, while higher rotation rates were considered too fast and rates limited to 50 s^{-1} did not produce consistent results.

The walls of the concentric cylinders were not smooth but roughened in order to reduce (if not completely eliminate) the “slip” phenomenon; i.e., the development of a water-rich layer close to the inner surface of the rotating cylinder, which produces a lubricating effect, making flow easier, and not representative of the bulk material[8].

The rheological behavior was described by means of the Bingham flow model (**Fig. 5**):

$$\tau = \tau_y + \eta \cdot D \qquad (1)$$

where τ is the shear stress [Pa, or psi], τ_y is the yield stress [Pa, or psi], η is the plastic viscosity [Pa·s, or psi·s], and D is the shear rate [s^{-1}].

The slope of the down-curve (decreasing shear rate) was used to calculate the plastic viscosity, while the intercept at zero shear rate was used to calculate the yield stress (see **Fig. 6**).

In **Fig. 7**, the measured yield stress values are plotted as a function of time. It is evident that the pastes prepared with marble powder, superplasticizing admixture, and water/cement of 0.4 showed the highest values of the yield stress, more than 40 Pa (0.0058 psi). Quite high values also were obtained for the cement pastes prepared with marble powder and water/cement of 0.5 but in absence of superplasticizer. On the other hand, when the water to cement ratio was 0.5 and the superplasticizing admixture was added, even at the low dosage (0.5% by weight of cement), the yield stress was very low, less than zero, thus implying low cohesiveness of the related mortars and concretes, particularly for self-compacting concretes.

In **Fig. 8** the measured plastic viscosity values are plotted as a function of time. Also in this case, the same hierarchy of yield stress values was maintained among the various cement pastes.

For maximum segregation resistance, the yield stress of the paste should be high[1-3, 7] and the difference in density between the aggregate and the paste should be low. If the density of the aggregate particle is greater than the density of the cement paste, segregation will occur to some extent. However, if the plastic viscosity of the matrix were high enough the velocity of the falling aggregate particle would be so slow that segregation would be avoided[7]. On the basis of the results reported in **Fig. 7** and **Fig. 8**, it can be seen that in the presence of a superplasticizing admixture (e.g., for preparing self-compacting concrete), the addition of marble powder is very effective in improving segregation resistance provided that water/cement is lower than 0.5. Otherwise, a viscosity-modifying agent should be added to the mixture for adjusting its rheological behavior[10-11].

Thixotropy is the property of certain gels, such as cement paste, which are rigid when left standing but increase their fluidity when put into movement. **Fig. 9** shows the measured thixotropy values, plotted as a function of time, where thixotropy was calculated as the area included between the up-curve and the down-curve (**Fig. 5**). This measure can give an estimate of the energy necessary to move mortars and/or concretes and even an estimate of the lateral formwork pressure that concrete, especially self-compacting concrete, will exert after placing, the lower the formwork pressure the higher the thixotropy value[12]. In this case, particularly with increasing time, the difference among the various cement pastes is slight and the value of the energy loss is generally quite low. As a consequence, an excellent ability to flow through narrow sections can be predicted for SCCs containing marble powder. The reason for this excellent rheological behaviour conferred to concrete mixtures by marble powder (high cohesiveness when already placed and low energy loss when put into movement) can be ascribed to the particular grain size distribution of the powder (and to the corresponding fineness). In fact, the fineness of the marble powder is higher than cement and other traditional mineral additions (i.e. limestone powder, fly ash), characterized by Blaine fineness in the range 200-600 m^2/kg, but not very high like silica fume (15000-20000 m^2/kg), which is well-known for its strong thixotropic behaviour.

MORTAR MIXTURES PROPORTIONS

The mortar mixtures proportions are reported in **Table 2**. All mortars were prepared with the same ratio of sand to cement (ratio of 3:1). For practical reasons, marble powder was added to the mixture as slurry. The water content of which was taken into account for calculating the actual total water amount to be added to the mixture.

Consistency of fresh mortars was evaluated through the use of a shaking table by measuring the mortar flow. The test was carried out according to the procedure reported in the Italian Norm UNI 7044-72. In this study the flow measure was the same for each mortar and its value was equal to 13. On the other hand, the water content and, consequently, the water to cement ratio are different for the various mortars, keeping constant the fresh mortar fluidity.

Marble powder was used as a 10% replacement of either cement or 2 sand, with or without an acrylic based superplasticizing admixture, which was added at a dosage of 0.5% by weight of cement.

PREPARATION AND CURING OF SPECIMENS

Prismatic specimens, 40 × 40 × 160 mm (1.575 × 1.575 × 6.300 in.) in size, were manufactured for mechanical tests. These specimens were cast in stainless steel molds and wet cured at 20°C (68°F) until the time of test.

COMPRESSION TESTS: RESULTS AND DISCUSSION

Mechanical behavior of mortars prepared without chemical admixture was studied by compression tests at curing times of 3, 7, 28, and 56 days. Results obtained are reported in **Fig. 10**. It can be noticed that 10% replacement of either cement or sand with marble powder caused about 10 to 20% compressive strength decrease in late age. However, marble powder used as the replacement of sand performed better (10% decrease) than the case for the marble powder used as the replacement of cement (20% decrease). As a matter of fact, marble powder showed a filler effect (particularly important at early ages) and did not play any noticeable role in the hydration process. A mixture made of water, marble powder, and hydrated lime ($Ca(OH)_2$), and cured in sealed air-free environment, was not able to harden after 28 days of observation.

Compression tests of mortars prepared with superplasticizing admixture were carried out at curing times of 3, 7, and 28 days. The results obtained are reported in **Fig. 11**. In this case 10% replacement of either cement or sand with marble powder caused a small loss (about 10%) of strength. In fact, the use of marble powder in combination with superplasticizing admixture allowed for compensating the high water demand of marble powder itself. Consequently, the water to cement ratio could be maintained in order not to compromise the mortar mechanical strength. Again, marble powder used as the replacement of sand performed equal to or better than the case of the marble powder used as the replacement of cement. **Figure 11** shows that for early ages compressive strength of reference mortars is lower with respect to other mortars. In fact, the filler effect was enhanced when marble powder was used together with a superplasticizing admixture. Such a synergic effect is quite similar to that found by Bache[13] for water-reducing admixtures and silica fume.

CONCLUSIONS

Due to its quite high fineness, marble powder proved to be very effective in assuring very good cohesiveness of mortar and concrete, even in the presence of a superplasticizing admixture, provided that water to cement ratio was adequately low. This was not accompanied by an evident tendency to energy loss during concrete placing, as usual for other ultra-fine mineral additions (such as silica fume) that are able to confer high cohesiveness to the concrete mixture.

In terms of mechanical performance, 10% substitution of sand by the marble powder in the presence of a superplasticizing admixture provided maximum compressive strength at the same workability level, comparable to that of the reference mixture after 28 days of curing. Moreover, an even more positive effect of marble powder is evident at early ages, due to its filler ability.

Next step of this continuing experimental work is preparation of concretes, fluid and self-compacting, by using the marble powder.

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APPENDIX

The following symbols are used in the paper:

d_{50} = particle diameter for which the cumulative volume is 50% [μm, or in.]

d_{90} = particle diameter for which the cumulative volume is 90% [μm, or in.]

τ = shear stress [Pa, or psi]

τ_y = yield stress [Pa, or psi]

η = plastic viscosity [Pa·s, or psi·s]

D = shear rate [s^{-1}]

TABLES AND FIGURES

List of Tables:

List of Figures:

Table 1–Paste mixture proportions

CEMENT PASTE	W/C	Cement, g (lb)	Water, g (lb)	Marble Powder, MP, g (lb)	Admixture, ADM, g (lb)
CEM (0.5)	0.5	100 (0.220)	50 (0.110)	-	-
CEM+MP10 (0.5)	0.5	90 (0.198)	50 (0.110)	10 (0.022)	-
CEM+MP20 (0.5)	0.5	80 (0.176)	50 (0.110)	20 (0.044)	-
CEM+ADM (0.5)	0.5	100 (0.220)	50 (0.110)	-	0.5 (0.001)
CEM+ADM (0.4)	0.4	100 (0.220)	40 (0.088)	-	0.5 (0.001)
CEM+ADM+MP20 (0.5)	0.5	80	50 (0.110)	20 (0.044)	0.5 (0.001)
CEM+ADM+MP20 (0.4)	0.4	80 (0.176)	40 (0.088)	20 (0.044)	0.5 (0.001)
CEM+ADM+MP10 (0.4)	0.4	90 (0.198)	40 (0.088)	10 (0.022)	0.5 (0.001)

Table 2–Mortar mixture proportions

Mixture	REF	10% CEM	10% SAND	REF+A	10% CEM+A	10% SAND+A
W/C	0.61	0.68	0.59	0.48	0.49	0.53
Water, kg/m^3 (lb/yd^3)	275 (464)	276 (465)	266 (448)	220 (371)	200 (337)	240 (405)
Cement, kg/m^3 (lb/yd^3)	450 (758)	405 (683)	450 (758)	450 (758)	405 (683)	450 (758)
Sand, kg/m^3 (lb/yd^3)	1350 (2275)	1350 (2275)	1215 (2048)	1350 (2275)	1350 (2275)	1215 (2048)
Marble Powder, kg/m^3 (lb/yd^3)	0	45 (76)	135 (228)	0	45 (76)	135 (228)
Chemical Admixture, kg/m^3 (lb/yd^3)	0	0	0	2.25 (3.79)	2.02 (3.40)	2.25 (3.79)

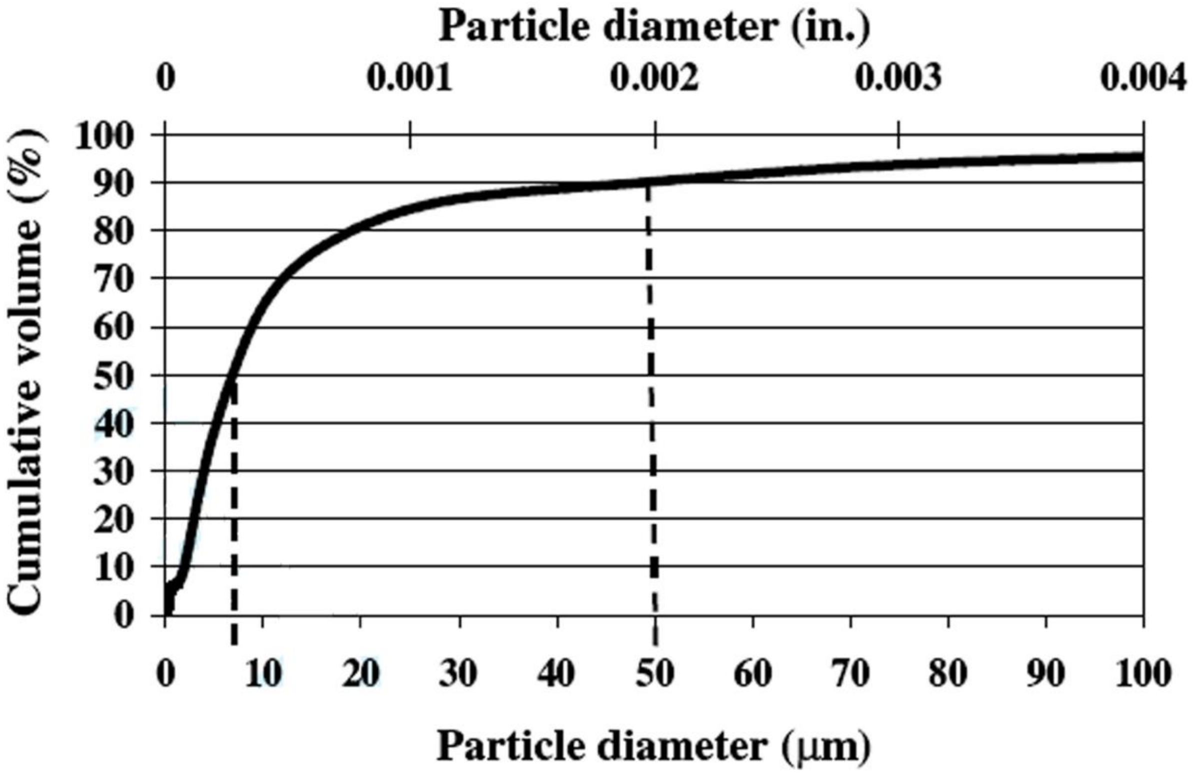

Fig. 1 – Grain size distribution of the marble powder by laser diffraction.

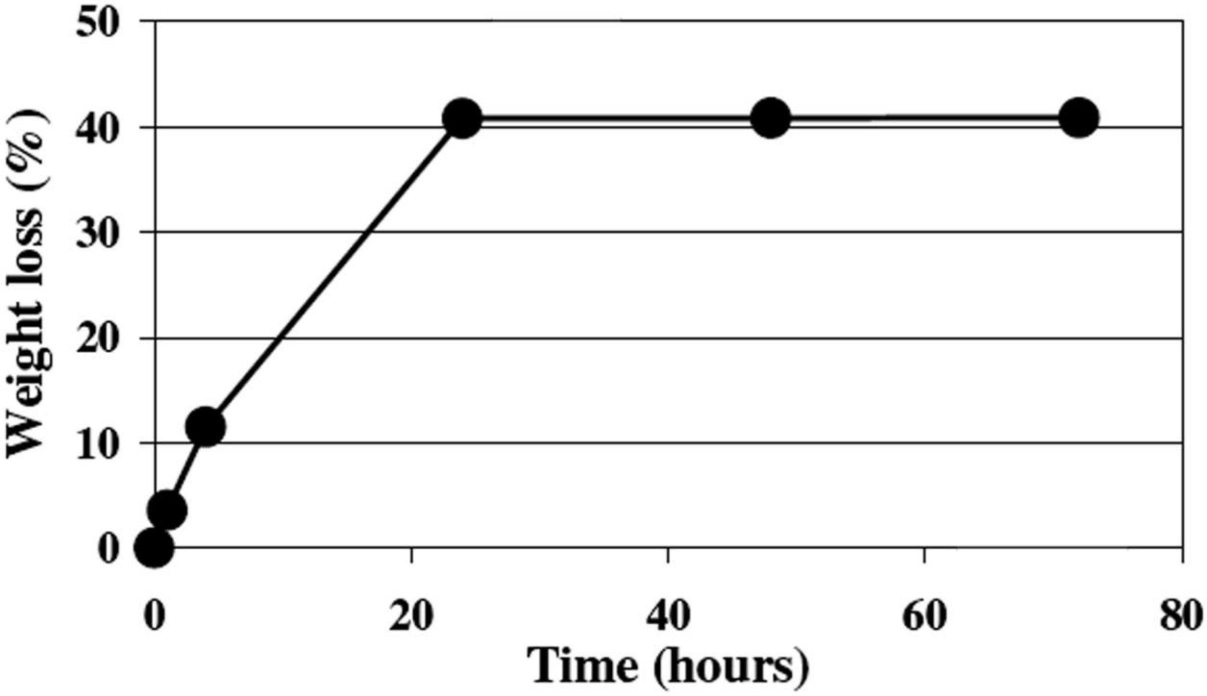

Fig. 2 – Weight loss of the marble powder slurry verses time.

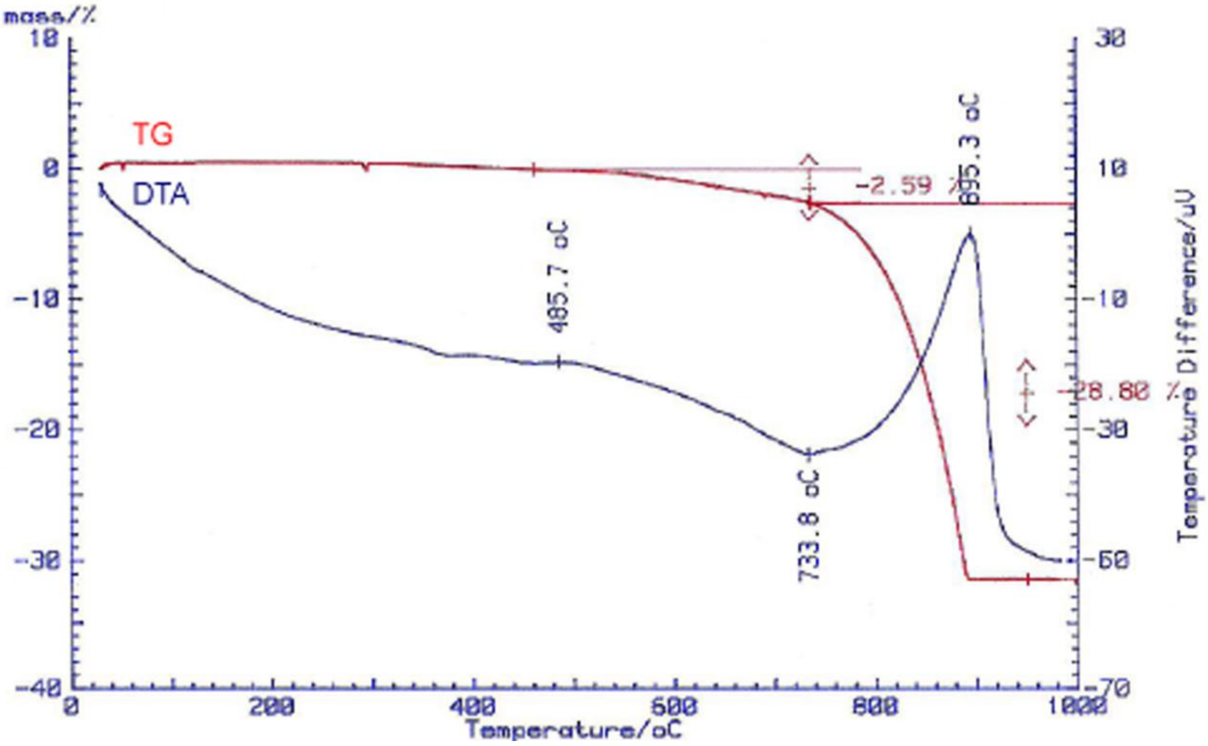

Fig. 3 – Results of the thermogravimetric (TG) and differential thermal analysis (DTA) of the marble powder.

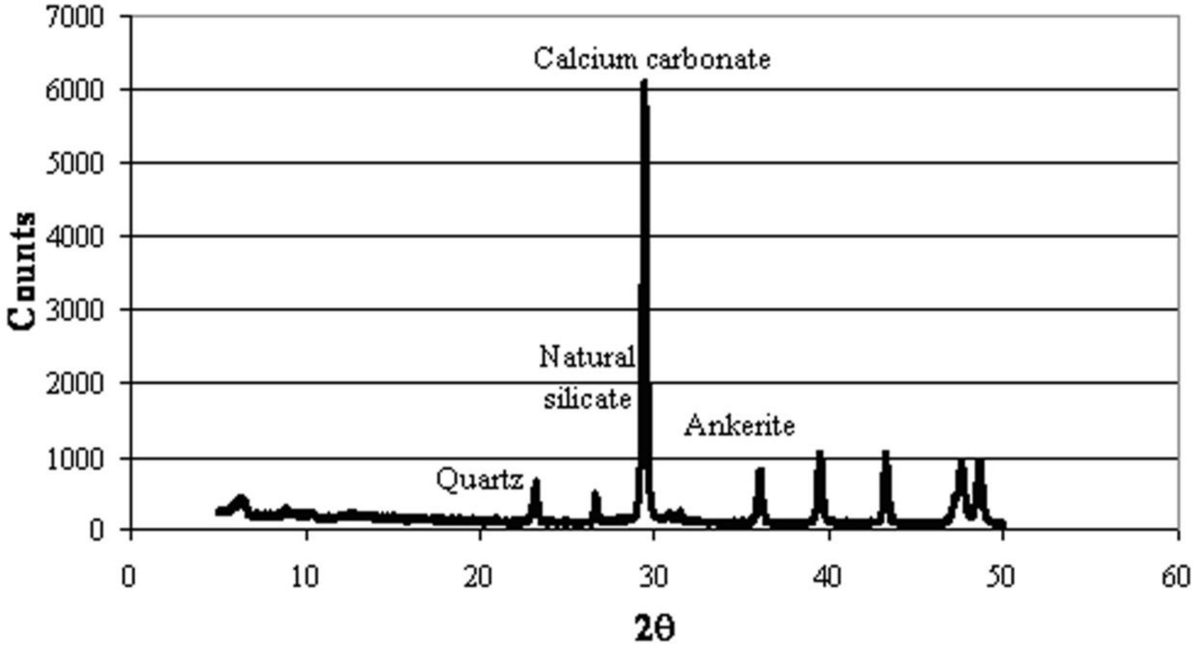

Fig. 4 – X-ray diffraction of the marble powder.

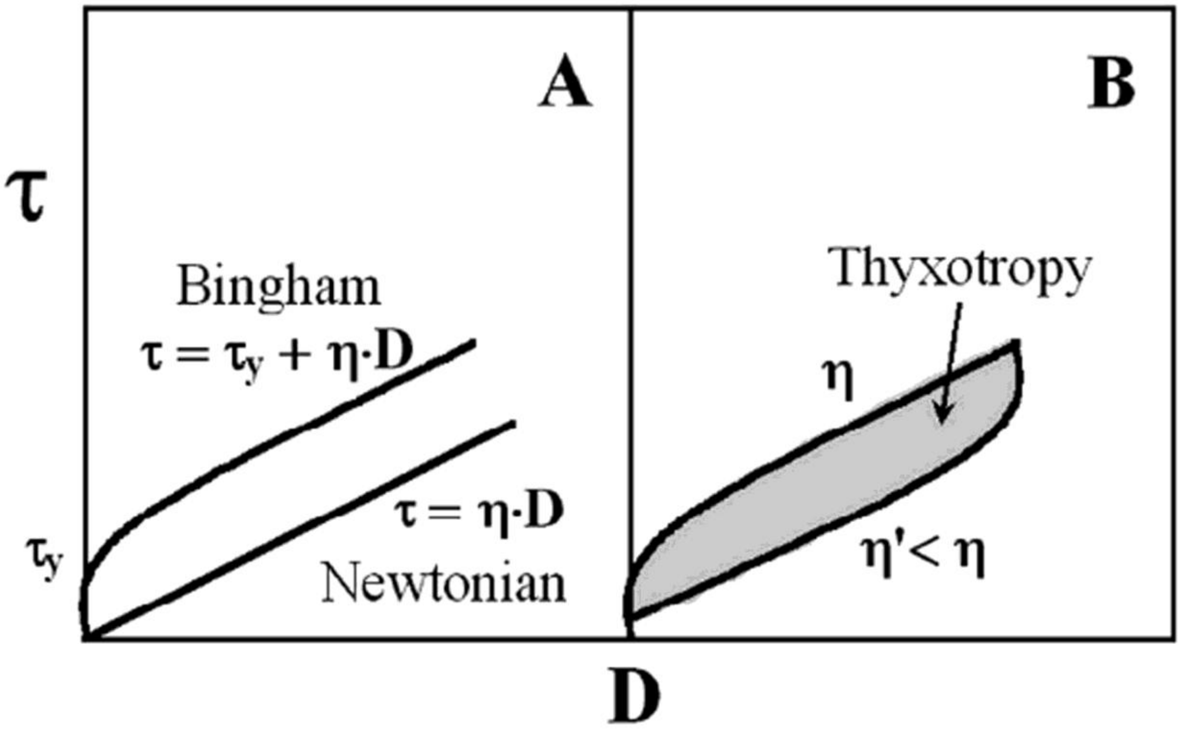

Fig. 5 – Typical shear stress (τ) verses shear rate (D) of Newtonian or Bingham fluid (A); thixotropy measured by the hysteresis area (B).

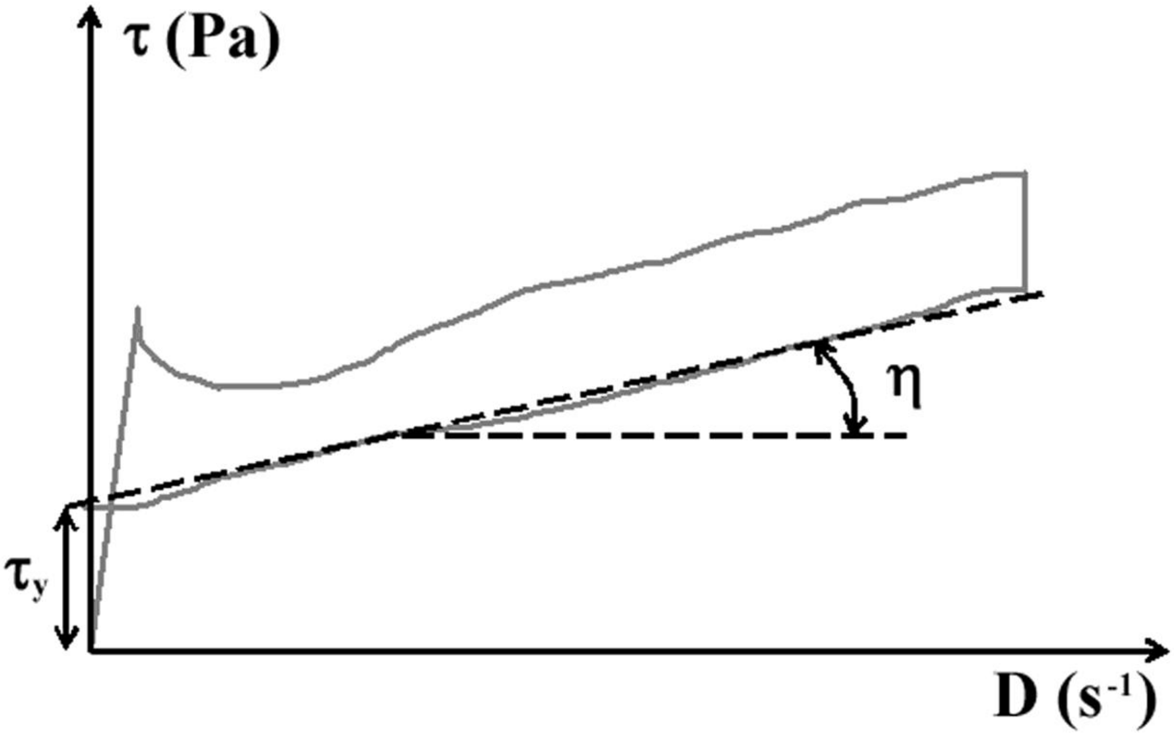

Fig. 6 – Indication of rheological parameters identified from a real curve.

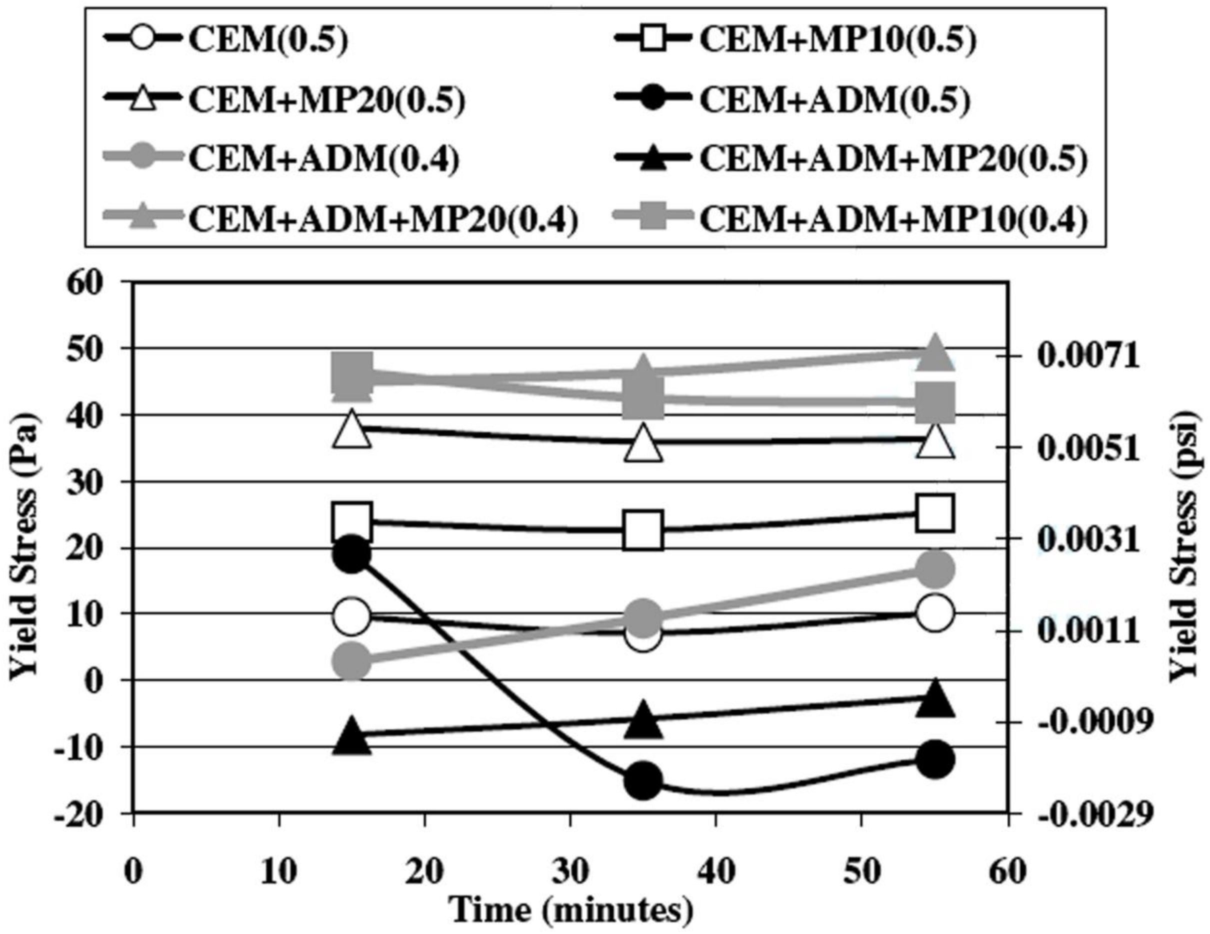

Fig. 7 - Yield Stress values verses time.

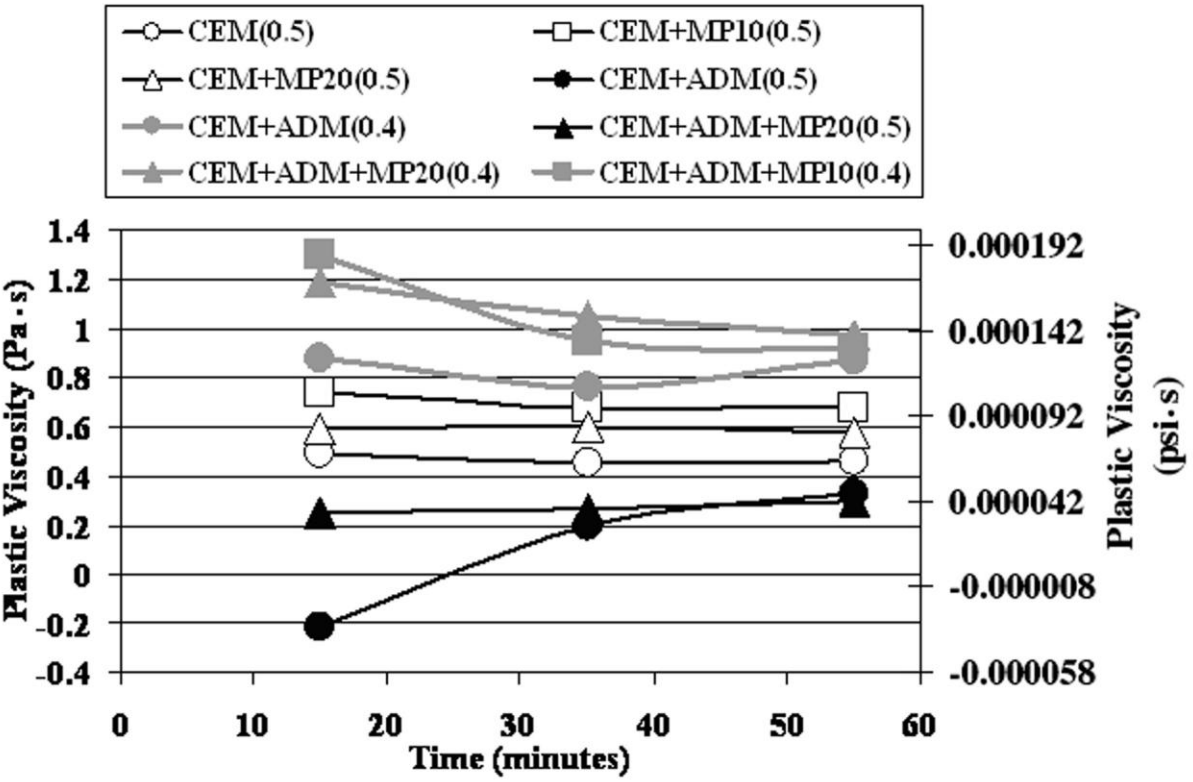

Fig. 8 - Plastic viscosity values verses time.

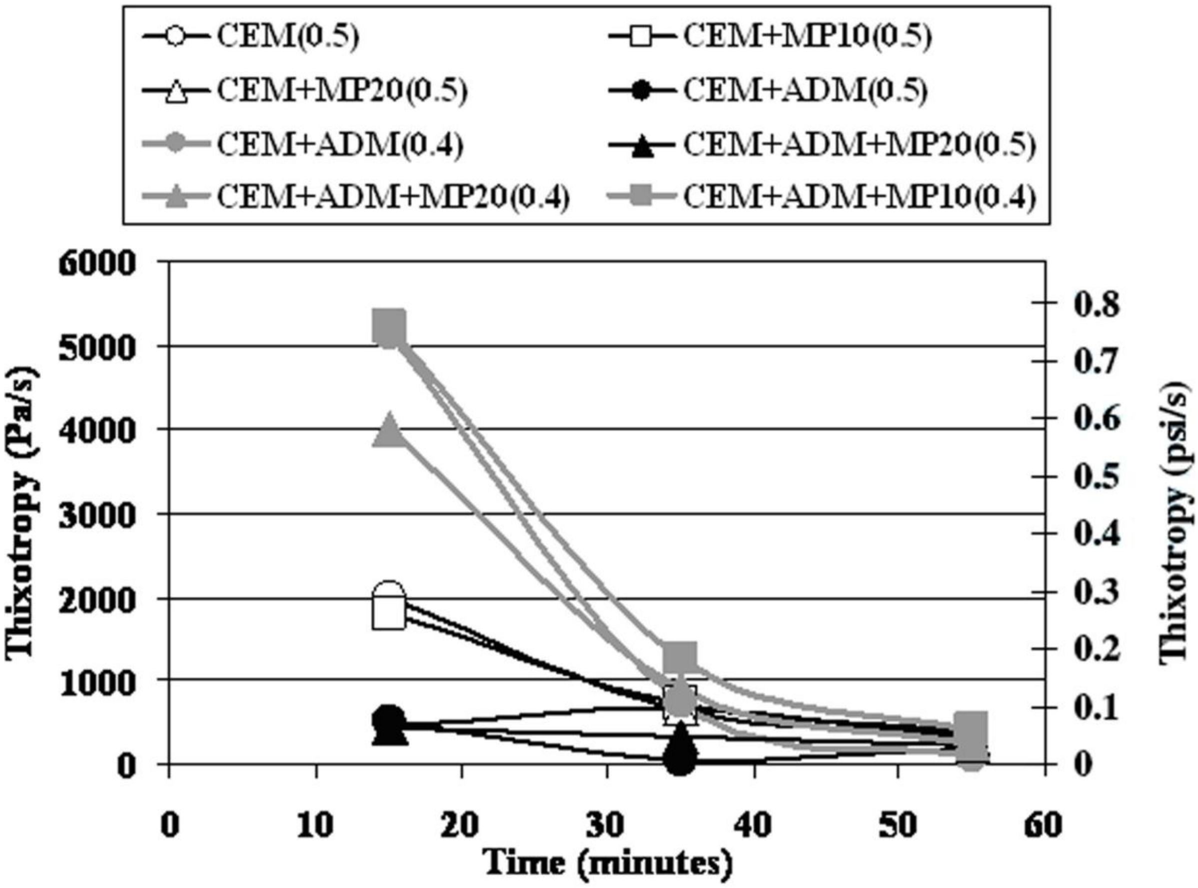

Fig. 9 - Thixotropy values verses time.

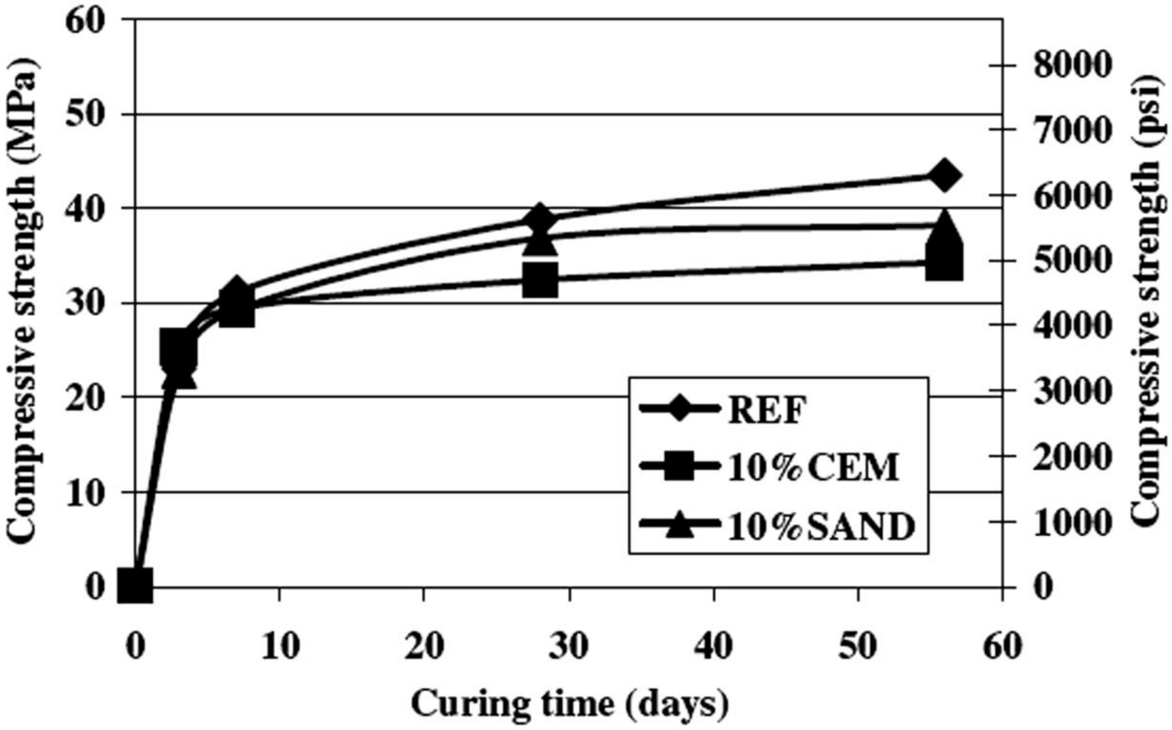

Fig. 10 - Compressive strengths vs. curing time for cement mortars without superplasticizer.

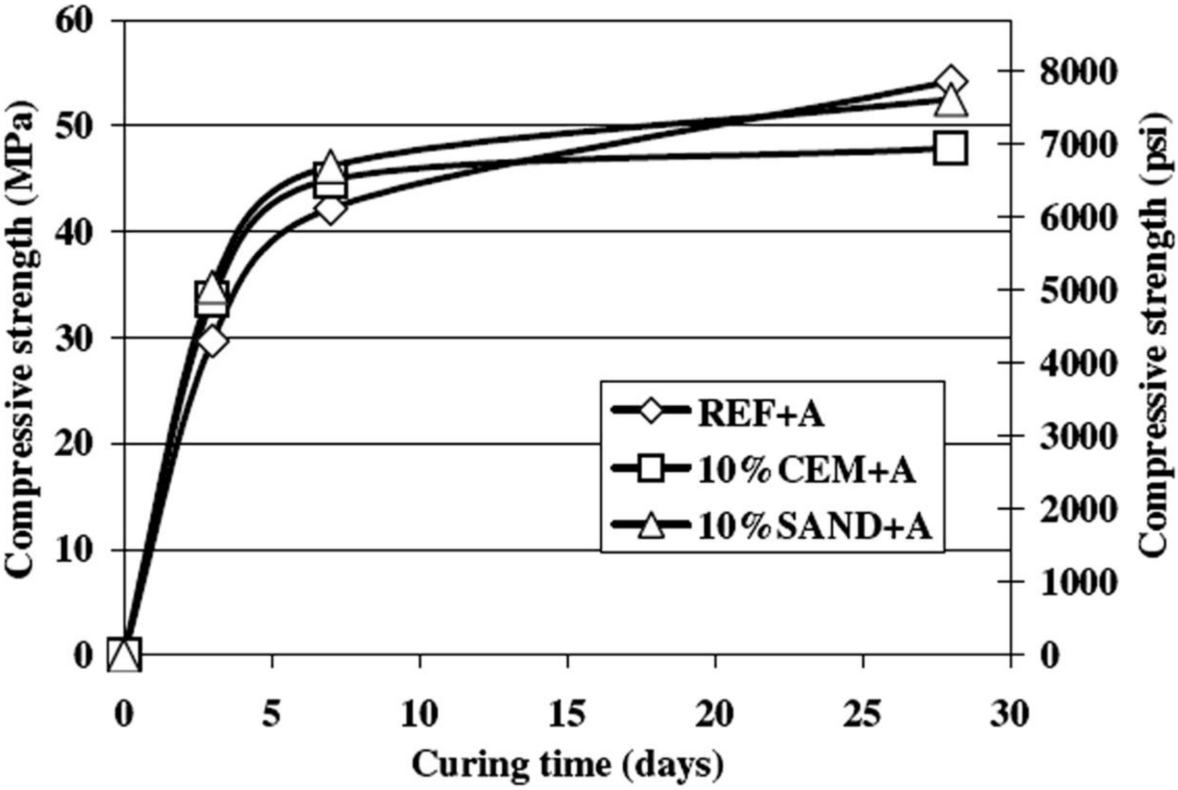

Fig. 11 - Compressive strengths vs. curing time for cement mortars with superplasticizer.