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EFFECT OF CURING TEMPERATURE IN SOME HYDRATION CHARACTERISTICS OF CALCIUM ALUMINATE CEMENT COMPARED WITH THOSE OF PORTLAND CEMENT

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ABSTRACT

In the present paper the hydration of 1:3 Calcium Aluminate Cement (CAC) and Portland Cement (PC) mortars at temperatures of 5°C, 20°C, and 60°C have been studied. An evaluation of the compressive and flexural strengths obtained from different curing conditions is made. The evolution of phases presented was also studied from XRD spectra. The relationship between the values of ultrasonic propagation velocity, UPV, (Y1-axis) and compressive strengths (Y2-axis) versus w/c ratios for CAC mortars, cured at 5°C, 20°C and 60°C respectively, have also been obtained, at a curing age of 28 days. The great similarity of curves enables us to establish the hypothesis that it is possible to use a non destructive test as an empirical determination of compressive strength for CAC mortars with the same proportions of aggregates/cements/water as those used in the test. Abrams rule was applied in order to check the reality of this model in the CAC mortars studied. The percentage of variability of the variable response (Rc), obtained in our regression models is highly satisfactory. © *1997 Elsevier Science Ltd*

Introduction

Although the cost of Calcium Aluminate Cement (CAC) is higher than that of Portland Cements (PC) its use could be recommended in situations where resistance to sulphate or high temperature is required (1). It has been known for some time that CAC concrete may lose strength over a period of time due to the process of "conversion" (2–5) among others. The relationship between strength of concrete and conversion is complex and is dependent on the temperature and moisture of the concrete and the initial water content of the mix (1).

Compressive strength is the most important property of concrete for designing concrete structures. Usually, this strength is also responsible for the development of other engineering properties such as modules of rupture, splitting tensile strength and elastic modules. Nevertheless, not all cements have the same behaviour in certain climatic-temperature conditions (6). In order to compare the behaviour of CAC and PC, we have studied the hydration of 1:3 CAC and PC mortars at temperatures of 5°C, 20°C, and 60°C. In the present paper, an

TABLE 1
Summary of the Experimental Programme

Test	Type of Specimens	Temperature Condition	Testing Age (days)	No. of specimens
Flexural Strength	40 × 40 × 160 mm prisms	5°C, 20°C, 60°C	2, 28, 60, 120	252
Compres. Strength	40 × 40 × 80 mm prisms	5°C, 20°C, 60°C	2, 28, 60, 120	504
Porosity	40 × 40 × 20 mm prisms	5°C, 20°C, 60°C	2, 28, 60, 120	89
X-Ray Diffraction	powder samples	5°C, 20°C, 60°C	2, 28, 60, 120	89
UPV	40 × 40 × 160 mm prisms	5°C, 20°C, 60°C	2, 28, 60, 120	252

evaluation of the compressive and flexural strengths obtained from different curing conditions is described. The evolution of phases present is also studied from XRD spectra. With this paper we aim to build on knowledge of developed intrinsic strengths. We establish the hypothesis that it is possible to use a non destructive test as an empirical determination of compressive strength for CAC mortars with the same proportions of aggregates/cements/water as those used in the test. Abrams' rule is applied to check the reality of this model in the CAC mortars studied. The results are then discussed.

Experimental Programme

Materials and Specimen Preparation. VI/55 electroland CAC, was used. I/55PC, produced locally, was also used. In both cases the Spanish standard (7) requirements were met. Silica sand was always employed as the aggregate, and distilled water was always used. Different types of mortar were prepared. The w/c ratio range used was from 0.3 to 0.9. The main variables for the curing process were the temperature and the time. 40 × 40 × 160 mm prisms of a c/s: 1:3 mortars were prepared using CAC and PC. The mortar specimens were prepared in the laboratory at 5°C, 20°C and 60°C and 90% R.H. with mechanical compaction in two layers. Immediately after casting and surface finishing, the test specimens, once in the mould, were covered with a polyethylene film 0.2 mm thick in prevailing weather, and keep also at 5°C, 20°C and 60°C. After demoulding 24 hours later, the test specimens were introduced for curing into water, at the same different temperatures as those mentioned above.

Testing. The types of specimens and test for the determination of various properties are described below and summarized in Table 1. XRD spectra were obtained in order to identify the phases present in each case.

Flexural Strength. All control specimens were tested under laboratory conditions, taken directly from the storage container. Three specimens at each specified age, temperature and w/c ratio were broken in flexion with two loading points. The maximum breaking load was determined using a 63 kN capacity miniflexural machine.

Compressive Strength. Six specimens, from each flexural test, were tested (at their respective moisture conditions) under the same laboratory conditions as those applied in the former strength test. The method used to determine the flexural and compressive strengths of mortar prisms was carried out according to Spanish standards (8). The crushing load was determined using a 10000 kN capacity automatic compression machine.

X-Ray Diffraction Spectra. The XRD experiments were carried out in a Scheifer powder diffractometer with a graphite monochromator and an NaI (Tl) scintillation detector using Cu Kα radiation. The aperture slit of 3° and the detector slit of 0.15° were used. After being crushed in an agate mortar to 40μ size, the samples were preserved in acetone at 5°C. The XRD spectra were taken at a speed of 1° min^{-1} and the intensities were calculated from the maxima of diffraction after discounting the background.

Ultrasonic Propagation Velocity (UPV). A concrete tester CCT-4 (from C.S.I.) was used for measuring the propagation time of a sonic wave through cement mortar specimens. Two standard cylindrical heads are best suited for such measurements. The measuring surface on the measuring heads must be pressed against the mortar specimens at two exactly opposite points. The surface of the concrete must be reasonably flat and duly cleaned, using vaseline to guarantee good contact. The speed of the ultrasonic sound wave (V in m/s) can be found by the following formula: $V = s/t \times 10^6$ (V: sonic velocity in m/s; s: distance in meters; time in microseconds).

Scanning Electron Microscope (SEM). The scanning electron microphotographs were taken with a JEOL JSM-840 SEM equipped with an energy dispersive X-ray (EDX) and with 20 kV accelerating voltage. High vacuum evaporation (SCD 004 from BALZERS UNION) was the method used for producing a thin gold film to make the specimens' surface electrically conductive.

Porosity (%). The percentage taken up by the pores in the specimens volume can be found by the following formula: Porosity (%) = (Wsat − Wdry)/(Wsat − Wsubm) with Wsat = weight of the specimens drenched in water (with a vacuum pump); Wdry = weight of the specimens dried by heating to 110°C and later cooled into a chemical desiccator; and Wsubm = weight of the sample in a hydrostatic scale (drenched and submerged).

Results and Discussion

Figure 1 shows the relationship between compressive strength (axis Y1)- porosity (axis Y2) versus w/c ratio (axis X), for CAC mortars cured under water at several temperatures: 5°C, 20°C and 60°C, at a curing age of 28 days.

Firstly, it is observed that for any temperature and curing age, specimens manufactured with ratio w/c = 0.3, develop very low strengths and high levels of porosity. For the same w/c ratio, the deficit of water implies that the formation and interlacing of microcrystals and the agglutinative "gel of alumina" remain incomplete (9).

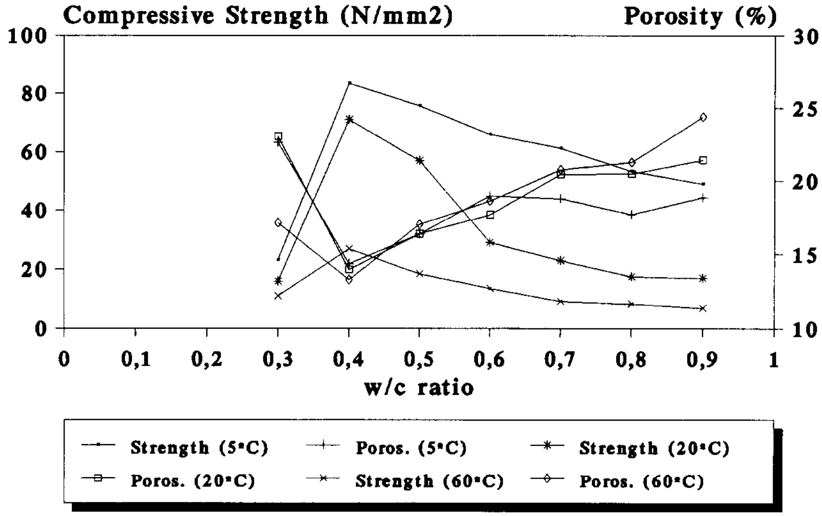

FIG. 1.
Relationship between compressive strength (Y1-axis) -porosity (Y2-axis) for CAC mortars (28 days: age of curing at 5°C, 20°C and 60°C).

It is also observed that, in general the high levels of strength and low levels of porosity are developed in specimens manufactured with ratios w/c = 0.4. Some very notable differences are observed at this w/c, in the strength characteristics of the specimens cured at 5°C and at 60°C, i.e at 5°C the strength characteristics are much higher. For greater water-cement ratios, the differences continue to decrease progressively.

Figures 2: a, b, and c, show the effect of storage temperature on the evolution of compressive strengths over time in CAC specimens of mortars manufactured at different w/c ratios. The specimens cured at 20°C reach, in 2 days, levels of strength which are even higher to those reached by the specimens cured at 60°C. By increasing the age of curing, the strengths of the specimens cured at 5°C go on increasing progressively. Conversely, the strengths of specimens cured at 20°C, go on decreasing progressively until they reach (approximately) the levels of strength presented by specimens cured at 60°C. The strength reached at 20°C is 75.23 Nw/mm^2 for specimens manufactured with ratio w/c = 0.4 and 29.88 Nw/mm^2 for specimens with ratio w/c = 0.9. The strength reached at 60°C is 29.63 Nw/mm^2 for specimens manufactured with ratio w/c = 0.4 and 8.57 Nw/mm^2 for specimens with ratio w/c = 0.9. These results are coherent bearing in mind the phenomenon of the conversion of hexagonal phases (phases that remain stable indefinitely at 5°C) to the cubic stable phase (which is the greatest phase from the first ages, 2 days, cured at 60°C).

A curing process at 20°C implies a kinetics of conversion slower than the one at 60°C. Nevertheless, after 120 days the transformation is total and the curves of strengths for both temperatures practically coincide with each other. It should be pointed out that the strength of the concrete is determined by the physical form of the constituent phases, whereas conversion is related purely to a chemical reaction which initiates these physical changes. In particular, small crystals formed immediately after the conversion reaction are less likely to initiate crack propagation than larger crystals which may be formed later due to recrystallization. The actual size of the crystals at a given moment in time is obviously directly related

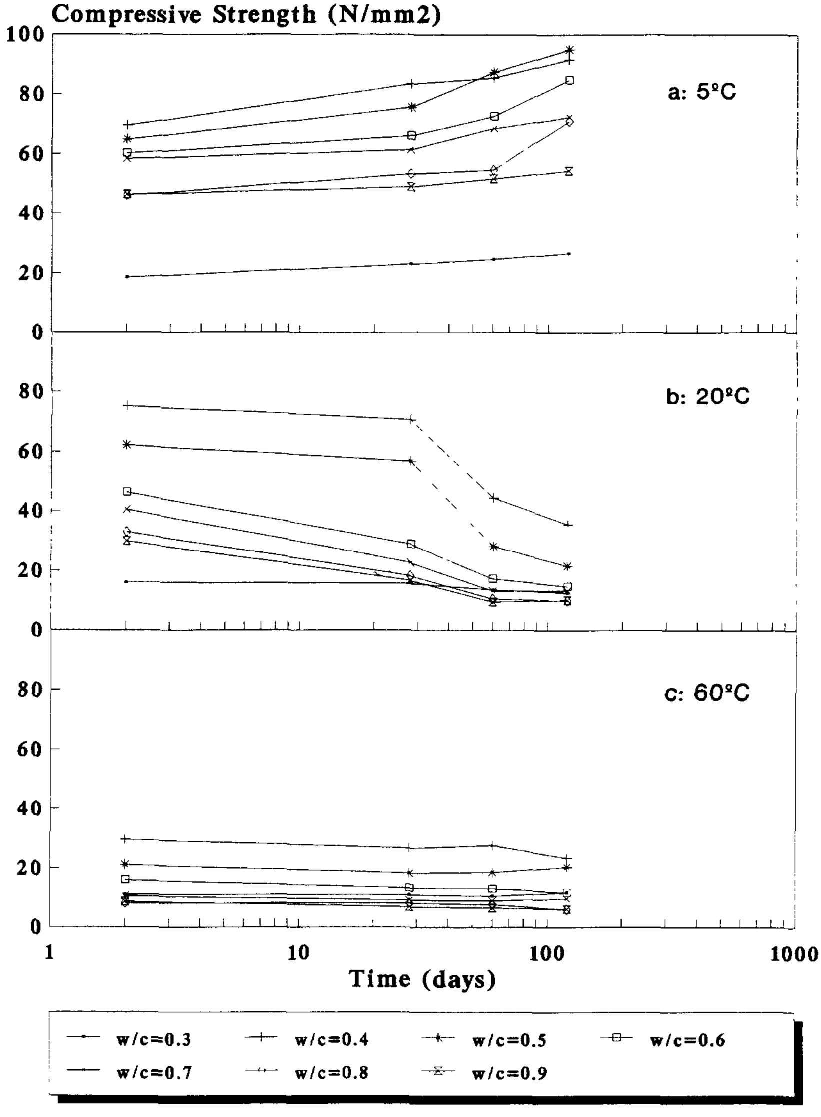

FIG. 2.

Effect of storage temperature on compressive strength development in CAC mortars (a: 5°C; b: 20°C; c: 60°C).

to the degree of porosity. It would thus be useful to study the size of the converted crystals to see whether there exists any difference between cubes stored at 20 and 60°C. A short study (10) using scanning electron microscopy showed slight evidence of smaller crystals and crack patterns in the more recently converted CAC concretes, but this was insufficient to prove the hypothesis.

The results obtained could be used to attempt to arrive at a conclusion about the intrinsic strength offered by the present hydrates at higher temperatures: C_3AH_6 and AH_3, and at

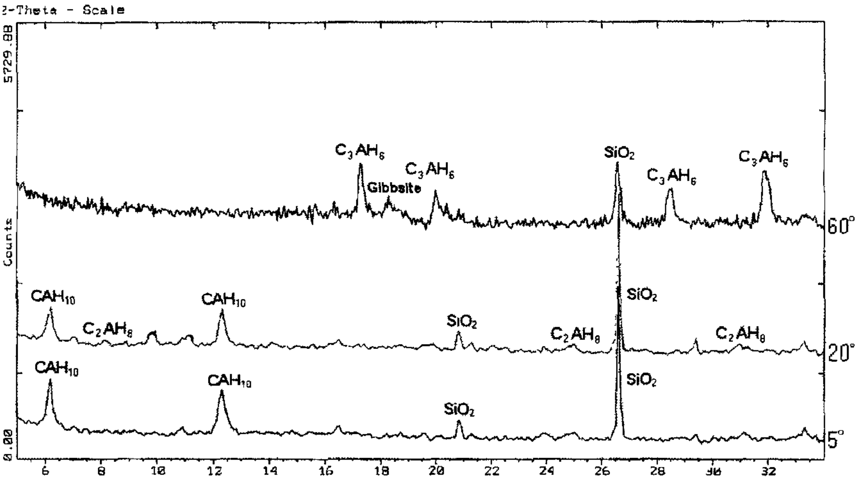

FIG. 3.
XRD spectra of the CAC mortars (w/c = 0.7; 28 days: age of curing). a) 5°C; b) 20°C; c) 60°C.

lower temperatures: CAH_{10} and C_2AH_8. Different w/c ratios can be found (see Figure 1) where the porosity of the specimens cured at 5°C and 60°C coincide, and yet they develop very different strengths. These differences must therefore be attributable either to several values of density or to the fact that the hexagonal phases develop some intrinsic strengths superior to those developed by the cubic phases on their own, because the hydrated components of the paste have different strength bonds. These results are different from those described by other authors (11).

Figures 3 and 4 show the XRD spectra of specimens manufactured with a ratio w/c = 0,7,

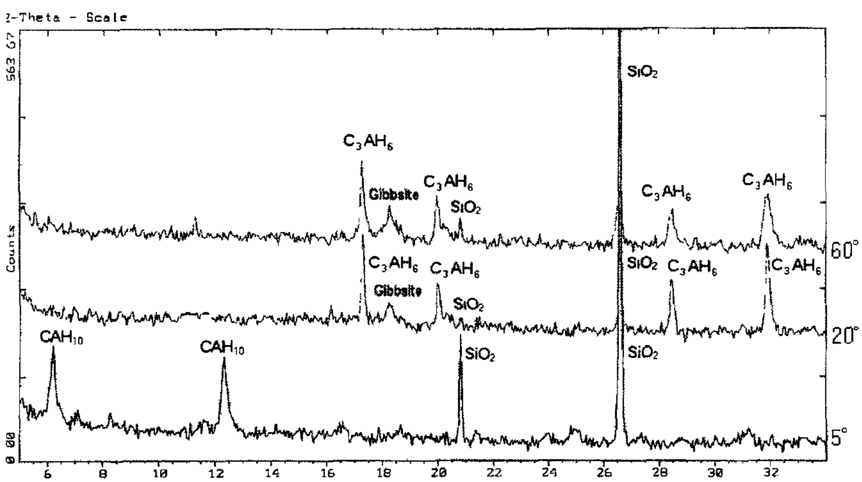

FIG. 4.
XRD spectra of the CAC mortars (w/c = 0.7; 120 days: age of curing). a) 5°C; b) 20°C; c) 60°C.

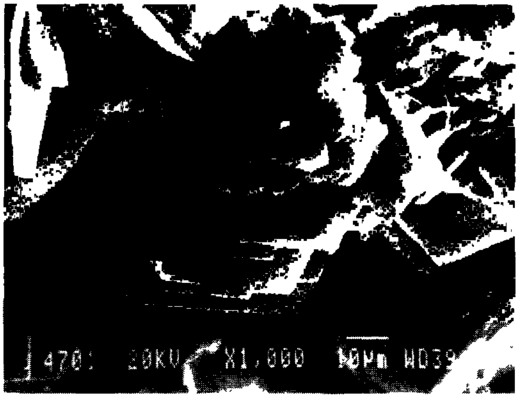

FIG. 5.
SEM photo of hexagonal phase.

cured at 5°C, 20°C and 60°C whose curing ages are 28 and 120 days respectively. In all figures, it can be seen that if the curing temperature is 5°C, the predominant phase is the hexagonal CAH_{10} (see Figure 5). If the temperature is 20°C the hexagonal phases, CAH_{10}, and C_2AH_8, are still present after 28 days. At superior ages, only the cubic phase, C_3AH_6, and gibbsite, AH_3, appear (see Figures 6 and 7). If the temperature is 60°C, and for all curing ages, only the cubic phase and the gibbsite appear.

On the other hand, in general for a same w/c ratio, the behaviour of the strengths of CAC hydrates in cold temperatures is superior to that of those hydrates in hot ones. This is explained by the fact that as well as developing some superior intrinsic strengths, the porosity is inferior under cold conditions to that produced under hot ones (see Fig. 1).

Figure 8 shows the evolution over time of the flexural strengths presented by specimens manufactured at different w/c ratio, at 20°C. For 28 days, the flexural strengths remain at an almost constant level, and from this time on they begin to decrease, reaching, at 120 days, the same levels of strengths as those presented after 2 days by specimens cured at 60°C.

On the other hand, at the same temperature, after 28 days, a maximum value of the flexural

FIG. 6.
SEM photo of cubic phase.

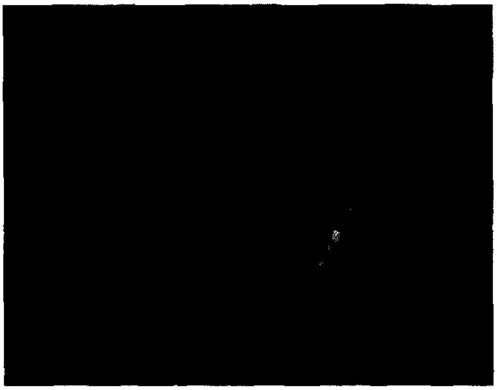

FIG. 7.
SEM photo of gibbisite.

strength is presented, except for w/c ratios from 0.7 to 0.9. These maximum values should be considered as a transitory stage, during which a provisional excess in the strength is produced. They are the final minimum values (from 5.27 Nw/mm^2 for specimens manufacturated with ratio w/c = 0.4 to 1.66 Nw/mm^2 for specimens with ratio = 0.9) drawn from the conversion of hexagonal phases to cubic ones, which along with other factors should be considered in civil engineering calculations.

Figure 9-a shows in comparison, the strengths presented at 120 days by specimens of CAC and PC cured at 5°C. For any w/c ratio, the difference of behavior is noticeable, with the greater strengths being those presented by the specimens of CAC. The extremely small strengths presented by the specimens of PC enhance this difference. As can be observed, and in spite of the differences in strengths, the levels of porosity are practically identical. This allows us to conclude that the hexagonal hydrates present at these early ages in the CAC

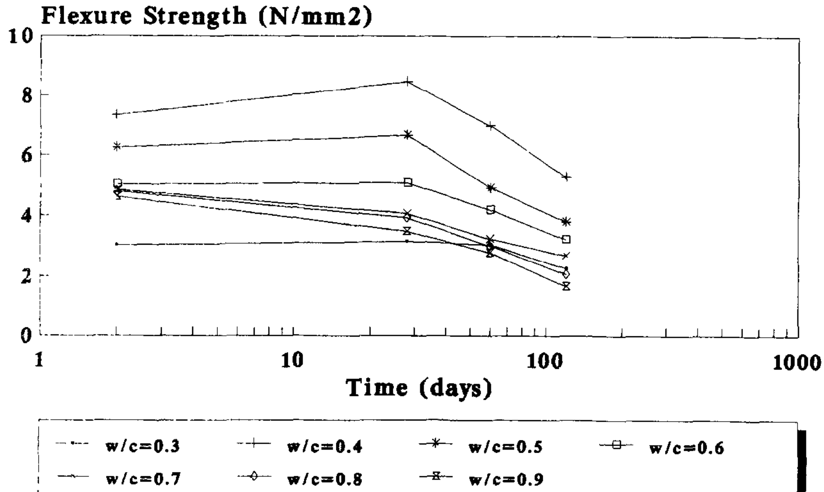

FIG. 8.
Effect of storage temperature (20°C) on flexure strength development in CAC mortars.

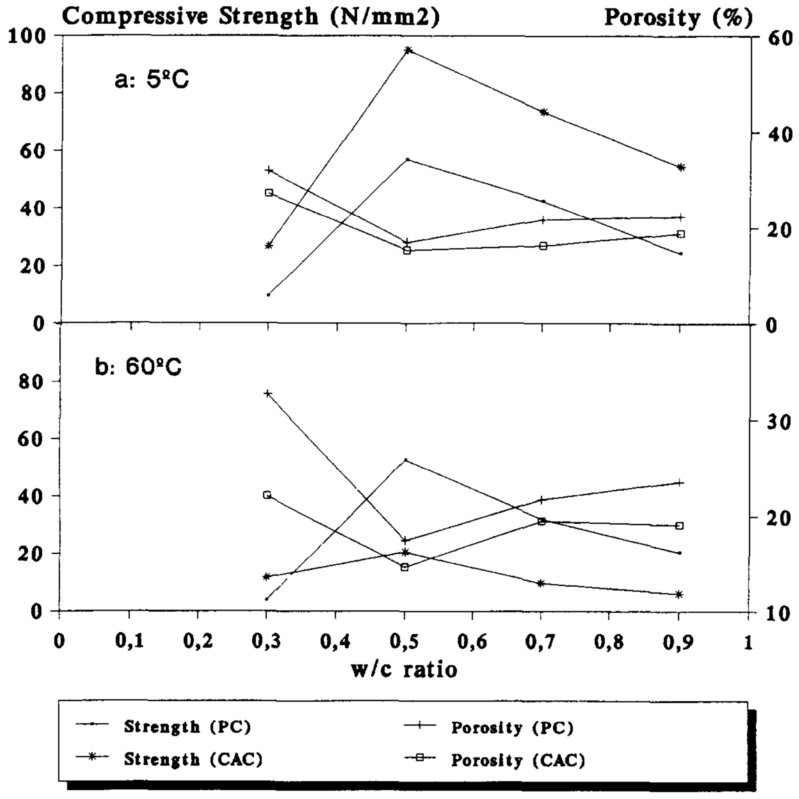

FIG. 9.
Comparative relationship between compressive strength (Y1-axis) versus w/c ratios, for CAC and PC mortars (120 days: age of curing) (a: 5°C, b: 60°C).

mortars, possess some intrinsic strengths superior to those presented by the PC-hydrates under the same conditions.

In Figure 9-b the strengths presented by specimens of CAC and PC, cured at 60°C, for 120 days, are shown and compared. Contrary to what occurs at lower temperatures, the strengths presented by the specimens of PC are superior to those of CAC right from the start. As happens at 5°C, w/c ratios where the porosities are practically identical are also presented. So, the intrinsic strengths presented by the hydrated phases of portland are superior at 60°C to the cubic hydrates, in the CAC.

Figures 10, 11 and 12 represent the relationship between the values of ultrasonic propagation velocity, UPV, (Y1-axis) and compressive strengths (Y2-axis) versus w/c ratios for CAC mortars, cured at 5°C, 20°C and 60°C respectively for 28 days. As established in the introduction of this paper the ultrasonic pulse method by direct transmission can be used to detect structural damage.

In general, when the waves spread through flowing air and water they suffer an attenuation in their velocity of pass.

The coherence between these general bases and the results presented in the figures, is

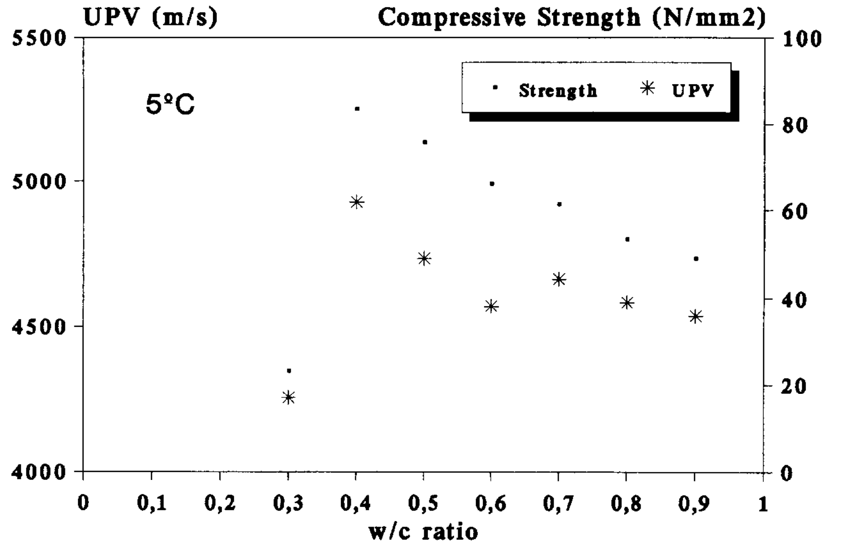

FIG. 10.
Relationship between Ultrasonic Propagation Velocity, UPV, (Y1-axis)- Compressive Strength (Y2-axis) versus w/c ratios (X-axis), for CAC mortars (28 days: age of curing at 5°C).

evident. Neville (12) did not consider the UPV to be of use in assessing the strength of CAC concrete in a structure, although he did feel that it helps in seeking out areas of weakness.

The great similarity in UPV vs. w/c curves and Compressive Strength vs. w/c curves at all temperatures (Figures 10, 11 and 12) allows us to establish the hypothesis that it is possible

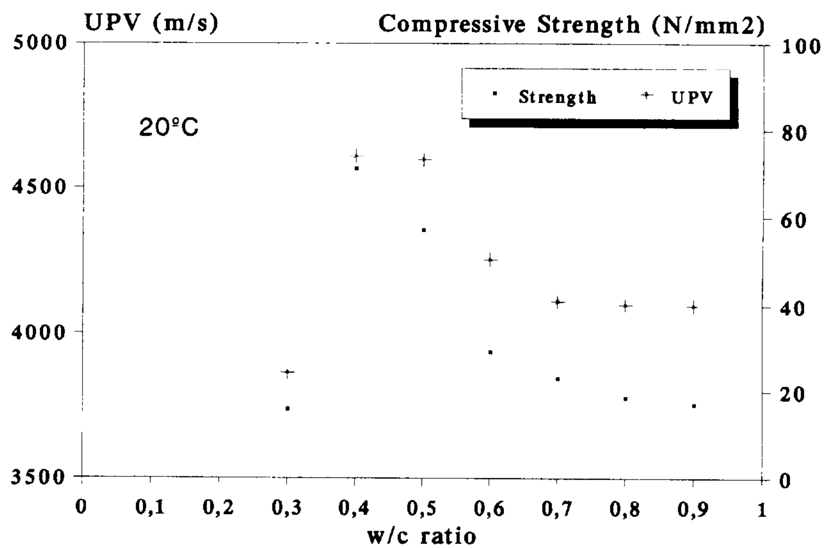

FIG. 11.
Relationship between Ultrasonic Propagation Velocity, UPV, (Y1-axis)- Compressive Strength (Y2-axis) versus w/c ratios (X-axis), for CAC mortars (28 days: age of curing at 20°C).

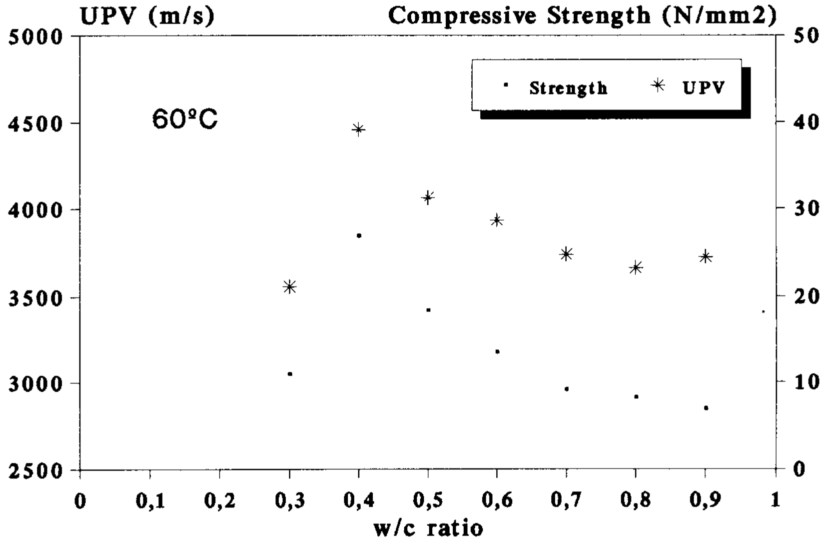

FIG. 12.
Relationship between Ultrasonic Propagation Velocity, UPV, (Y1-axis)- Compressive Strength (Y2-axis) versus w/c ratios (X-axis), for CAC mortars (28 days: age of curing at 60°C).

to use a non destructive test as an empirical determination of compressive strength for CAC mortars with the same proportions of aggregates/cements/water, as those used in the test.

The strength of CAC concrete has been expressed in Appendix A of reference [3] as a function of water/cement ratio, known as Abrams' rule, if the curing condition and test age are constant.

Abrams' formula is:

$$R = A/B^{w/c} \tag{1}$$

R = compressive strength
w and c = water and cement content
A and B = experimental parameters

Eq. (1) can be rewritten in the following form

$$\log R = \log A - w/c \log B \tag{2}$$

Abrams' rule implies that an increase in the w/c ratio decreases the concrete strength. Independently, this ratio is altered by changing the cement content, the water content or both. Although experimental data has demonstrated the practical acceptability of this rule within wide limits, a few deviations have also been reported. The best known of these deviations is the modifying one which consider the effect of maximum particle size. Such secondary effects have been studied by Popovics, firstly in qualitative terms, while subsequently he expressed some of them quantitatively in order to improve the accuracy of Abrams' formula (13). Collins, R.J. and col. (10) in their research on long-term properties of CAC concrete have also studied this relationship.

TABLE 2
Linear regression data

Curing Temperature	Log A	Log B	r^2	Probability level
5°C	4.85879	1.0854	0.994	0.00001
20°C	5.45318	3.1379	0.929	0.00193
60°C	4.2974	2.7585	0.966	0.00045

CAC mortars (28 days)

Experimental data from experiences previously described are used to check the reliability of this model and for comparative purposes, but curing time is lower than the last one (10). Linear regression analyses were carried out with slope: −log B and intercept log A. Table 2 gives estimates for logA, logB and r (the correlation coefficient for the linear regression and levels of probability) for CAC mortars' specimens test, with a curing time of 28 days and with curing temperatures of 5°C, 20°C and 60°C, (data corresponding to Fig. 10).

For the aforementioned group of experimental data with CAC (28 days testing age), the following is obtained from Table 2:

$$R_{5^\circ C} = 129/2.96^{w/c} \qquad R_{20^\circ C} = 233/23^{w/c} \qquad R_{60^\circ C} = 74/15{,}78^{w/c}$$

The percentage of variability (r^2) of the variable response (strength), that has been obtained by the model is quite satisfactory. Both the independent variable (w/c ratio) and the model itself are highly significant. The probability levels are much lower than 0.05. (A model is considered to be significant when the value of this parameter is lower than 0.05).

It is not advisable to research more complex models with this small set of data. Introducing new variables would render the model inadequate.

Conclusions

1. CAC mortars with identical w/c ratios, curing age and porosity, display different compressive strengths for different curing temperatures. This fact may be related to the nature of the mineralogical phase present in the mortars for each temperature stability range (Fig. 1).
2. In the X-ray diffraction spectra of CAC mortars, with a ratio w/c = 0.7 (Figures 4 and 5) it can be seen that if the curing temperature is 5°C, the predominant phase is the hexagonal CAH_{10}. If the temperature is 20°C, at 28 days, both the hexagonal phase, C_4AH_{13}, and cubic phase, C_3AH_6, are still present. At later ages, only the cubic phase, C_3AH_6, and gibbsite AH_3 appear. If the temperature is 60°C, for all curing ages, only the cubic phase and the gibbsite appear.
3. At 20°C, the maximum values of flexural strengths are obtained at 28 days. However, these values can be considered as a transitory stage in which a provisional excess in the strengths is produced. The final minimum values derived from the conversion of hexagonal phases to cubic ones, as well as other factors, are the ones that should be considered in the calculations of civil engineering.
4. The hexagonal hydrates present at 120 days (curing age) at 5°C, in the calcium aluminate

cements, possess some intrinsic strengths superior to those possessed by hydrates present in specimens of PC under the same conditions. Conversely, when the curing temperature is 60°C, the strengths presented by the specimens of PC are superior to those of CAC from the start, even at w/c ratios where the porosities are practically identical. So, the intrinsic strengths presented by the hydrates phases of portland are, at this temperature, superior to the cubic hydrates, in the CAC.

5. The great similarity of UPV vs. w/c curves with Compressive Strength vs. w/c curves at all temperatures (Figures 12, 13, 14) enables us to establish the hypothesis that it is possible to use a non destructive test as an empirical determination of compressive strength for CAC mortars with the same proportions of aggregates/cements/water as those used in the test.
6. If the strength of CAC mortars, with a curing age of up to 28 days, is expressed as a function of water/cement ratio, an exponential relationship is formed, Abrams' rule. The percentage of variability of the variable response (Rc), that has been applied by the model is quite satisfactory. The independent variable (w/c ratio) as well as the model itself are both highly significant.

Acknowledgments

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