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# From Chemical and Microstructural Evolution of Cement Pastes to the Development of Autogenous Deformations

by V. Baroghel-Bouny, P. Mounanga, A. Loukili, and A. Khelidj

**Synopsis:** A micro-macro experimental study has been performed, from the end of mixing up to several months, on a set of plain cement pastes prepared with the same type I ordinary Portland cement (OPC) and various water-to-cement ratios (W/C), and cured at various constant temperatures. Chemical shrinkage, volumetric and one-dimensional autogenous deformations have been measured and analyzed in relation to the hydration process (degree of hydration of the cement  $\alpha$ ,  $\text{Ca(OH)}_2$  content, ...) and to the microstructural characteristics of the material. The effects of the curing temperature at early age (< 24 hours) in the range 10-50°C, and of W/C in the range 0.25-0.60, have been investigated. The temperature-induced changes recorded on both the magnitude and the kinetics of volumetric autogenous shrinkage clearly show the irrelevance of using the usual maturity concept to describe such phenomena within the whole early-age period. In addition, a threshold is pointed out at about  $\alpha = 7\%$ , both defining the range where autogenous shrinkage is linearly related to  $\alpha$  and corresponding to the precipitation of  $\text{Ca(OH)}_2$ . Moreover, a W/C threshold is pointed out both at the macro-level (autogenous deformations, ...) and at the micro-level (characteristics of the hydration products, MIP porosity and pore size distribution, ...). The chemical and (micro)structural basic effects of calcium hydroxide are in particular distinguished.

**Keywords:** autogenous deformations; calcium hydroxide; cement paste; chemical shrinkage; degree of hydration; early age; microstructure; temperature; water-to-cement ratio

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## INTRODUCTION

Nowadays, engineers have to take into account the required service lifetime, when selecting a concrete mixture and designing a structure. Hence, in recent years, the durability of reinforced or prestressed concrete structures has becoming a main concern. However, the most reliable, scientific-based, and accurate methodology used in the design stage to insure the required service lifetime for the structure will remain quite inefficient, if the early hours of the constitutive material's (concrete) life are not treated with the same accuracy in terms of execution quality and curing. The long-term properties of the material and even the whole life of the structure itself will indeed be determined by the early age behavior of concrete. For example, autogenous shrinkage as well as thermal dilation, which occur at early age, may yield, if restrained, the development of prejudicial cracking, particularly in high-performance concrete. In addition to mechanical problems, agents aggressive to concrete or reinforcement can more easily be carried from the surface through these (micro)cracks and thus reduce the durability of the structure.

Physical and chemical mechanisms are at the origin of the autogenous volume changes and cracking of cementitious materials, which determine the macroscopic behavior of concrete structures. But the precise mechanisms are not very well understood, in particular because complex moisture and temperature combined effects take place. This makes a reliable predictive approach to the behavior of concrete structures impossible.

The purpose of this paper is to improve the knowledge of cementitious materials and to contribute to the understanding of these mechanisms. This step is of primary importance in order to predict both early age (autogenous) and delayed (drying, carbonation, ...) deformations. In addition to the fact that a lot of research work has already been made

regarding the long-term period, it seems particularly relevant from both the scientific and practical points of view, as previously mentioned, to focus on the early age, in particular the first 24 hours. Within this framework, monitoring the hydration process and characterizing the microstructure of cement pastes have been used here as tools to help understand and interpret volume change results.

Studies dealing with the influence of temperature on the development of chemical shrinkage are scarce. Knudsen and Geiker have shown a two-fold effect: on the one hand, the rate of chemical shrinkage increases with the temperature, and on the other hand, the ultimate value of chemical shrinkage decreases when the temperature increases (1). Besides, some studies have shown that the rate and the magnitude of autogenous shrinkage of concrete, for a given degree of hydration, were influenced by the temperature history (2,3). The maturity concept is based on the assumption that the influence of temperature on the hydration rate (and associated properties) is independent of the degree of hydration. Therefore, the previously mentioned results question the relevance of this usual concept to account for temperature effects on autogenous deformations. In order to further investigate this aspect, the effects of temperature (isothermal curing process) on various properties (chemical shrinkage, autogenous shrinkage, ...) of cement pastes at early age (< 24 hours) have been studied in this paper.

Along with the parameters related to the hydration process, it is well known that mix-parameters influence autogenous deformations (see for example (4,5)). Given the great influence of the water-to-cement ratio (W/C) on various properties of concrete, the effect of this parameter on autogenous deformations has been investigated here. As far as chemical shrinkage is concerned, Justnes *et al.* did not find any significant effect of W/C on the final value of chemical shrinkage of cement pastes, in the W/C range 0.30-0.50 and from 0 to 48 hours after mixing (6). Boivin *et al.* confirmed these results and pointed out a purely kinetic influence of W/C on chemical shrinkage (7). The effect of W/C on chemical shrinkage has also been investigated in this paper.

## EXPERIMENTAL PROGRAM, MATERIALS AND TEST METHODS

### Experimental Program and Materials

An experimental study has been performed from the end of mixing up to several months on a set of plain cement pastes prepared with the same type I OPC (CEM I - 52.5) and distilled water. W/C ranged from 0.25 up to 0.60 and the mixtures were submitted to different isothermal curing processes at 10, 20, 30, 40, or 50°C. Chemical shrinkage, volumetric and one-dimensional autogenous deformations have been measured and analyzed in relation to the hydration process (degree of hydration of the cement, Ca(OH)<sub>2</sub> content, ...) and to the microstructural characteristics of the material.

The cement contained 70.2% C<sub>3</sub>S, 7.8% C<sub>2</sub>S, 3.8% C<sub>3</sub>A, and 6.0% C<sub>4</sub>AF (Bogue calculation). Its loss on ignition was 2.3% and its Blaine specific surface area was 3320 cm<sup>2</sup>.g<sup>-1</sup>. The gypsum content was 5.2%. The cement was mixed in a 5-L laboratory mixer for 1 minute, before addition of distilled water and a further mixing period of 3 minutes to ensure good homogeneity. A specific procedure has been carried out for the preparation of the samples intended for length change measurements (5). As far as the

curing temperature is concerned, the mixing water was heated or cooled on a case-by-case basis. This ensured a rapid equilibrium of the mixture to the required temperature.

### Measurement of Non-evaporable Water and Calcium Hydroxide Contents by TGA, and Determination of the Degree of Hydration

The evolution of both the non-evaporable water and the calcium hydroxide contents of the cement pastes has been monitored as a function of time (age) by means of thermogravimetric analysis (TGA) conducted between 20 and 1100°C, in a N<sub>2</sub> atmosphere (1 bar). The tests were performed at 3, 6, 9, 12, 15, 18, 21, and 24 hours after mixing (curing temperatures from 10 to 50°C), and also at the ages of 28 days, 6 months, and 2 years (at T = 20°C). The testing and calculation procedures applied are described in (8). No treatment (crushing or drying) was applied to the specimens before TGA measurement. The non-evaporable water amount is defined here as the mass loss recorded between 145 and 1050°C, minus the mass loss due to CO<sub>2</sub> release caused by calcite decomposition between 600 and 800°C (9,10). This non-evaporable water amount was used to calculate the degree of hydration of the cement ( $\alpha$ ). The Ca(OH)<sub>2</sub> content of the cement pastes has been determined by considering that dehydroxylation took place between 400 and 600°C (11).

### Chemical Shrinkage Measurement

(Total) chemical shrinkage measurement has been performed by using a weighing method (12,7). The testing and calculation procedures applied here are described in (8). The whole system, including the cement paste sample in its flask, is hung from a balance and immersed at the required temperature 20, 30, 40, or 50°C ( $\pm 0.1^\circ\text{C}$ ). The measurement starts 10 minutes after water-cement contact and lasts for 24 hours. Distilled water was used, since same results were expected as in the case of lime saturated water, according to (13). No significant leaching effect during such a test was indeed reported in the literature.

### Autogenous Deformation Measurements

A review of the literature shows that autogenous deformations of cement pastes can be measured in two different ways: measurement of volumetric deformations (see for example (12,14,6)), and measurement of one-dimensional deformations (4,15,5). The first type of measurement is particularly suitable to obtain shrinkage data at very early age, whereas the other is more often performed for long-term investigations.

Volume Change Measurement at Early Age--The test method used here for volume change (external chemical shrinkage) measurement at early age is based on Archimedes' principle. It consists of measuring, by hydrostatic weighing, the buoyancy variations of a sample constituted by an elastic rubber (latex) membrane filled with cement paste (about 100-150 g) and immersed in a thermo-regulated bath. The test method is described in (16). The sample is placed on a nacelle hung from a balance, and immersed in the water bath at the required temperature 20, 30, 40, or 50°C ( $\pm 0.1^\circ\text{C}$ ). The sample is not rotated. Both the bath temperature and the mass are continuously recorded

from 30 minutes after water-cement contact up to 24 hours. The greatest care is exercised to evacuate air. As bleeding (which may occur in the case of medium or high W/C) makes the measurement of "true" shrinkage difficult to carry out (14,6), volume change measurements were performed here only on the cement paste with W/C = 0.25.

Length Change Measurement--Free one-dimensional autogenous deformations have been measured on Ø20x160 mm cement paste samples (W/C ranging from 0.25 to 0.60) with a simple technique, allowing length change measurement by means of dial gauge (with an accuracy of 10 µm per meter), from initial setting time up to 1 year, at T = 20°C (± 1°C). The samples are cast in polyethylene moulds ensuring tightness and low restraint (unimpeded deformations), and also avoiding trapping air bubbles during the pouring of the fresh paste. The moulds have a longitudinal opening system allowing an initial (reference) length measurement inside the mould, and also an easy demoulding of the paste samples at the age of 24 hours in order to carry out the further measurements on demoulded and sealed samples. The set-up and the test procedure are detailed in (5). From casting, the samples in their moulds are kept in rotation at least up to the initial setting time, in order to minimize segregation and bleeding expected in particular with medium and high W/C. Just after demoulding, the samples are sealed by wrapping them in three adhesive aluminum foil sheets, in order to avoid moisture exchange with the surroundings. The specimens are weighed at each time of length measurement, in order to verify if the water losses are negligible during this long-term experiment.

### Complementary Investigations

The initial and final setting times of the cement pastes were determined by means of the Vicat (needle) test. The microstructure of the hardened cement pastes (hcp) was investigated at various ages by means of secondary or backscatter mode scanning electron microscopy (SEM) after vacuum-drying, along with energy dispersive X-ray (EDX) semi-quantitative analysis. In particular, the size of the calcium hydroxide crystals was estimated by secondary mode SEM on fractures, whereas the C/S ratio and the thickness of the C-S-H rims were quantified by backscattered electron microscopy on polished sections in the neighborhood of the unreacted cement cores (17). Moreover, porosity and pore size distribution were determined by mercury intrusion porosimetry (MIP), after freeze-drying of the specimens.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Calcium Hydroxide Content vs. Degree of Hydration

At a given age, both the degree of hydration of the cement and the Ca(OH)<sub>2</sub> content increase when the temperature increases. The calcium hydroxide content of the cement pastes with W/C ≤ 0.40 and cured at various temperatures is plotted in Fig. 1a vs. α (ages below 24 hours). The results show that temperature does not influence the correlation existing between Ca(OH)<sub>2</sub> content and degree of hydration. Focusing on the very early age (α < 15%), Fig. 1b reveals a threshold at about α = 7% for the cement pastes investigated (W/C ranging from 0.25 to 0.40 and temperature ranging from 10 to 50°C). This threshold corresponds to the appearance (precipitation) of Ca(OH)<sub>2</sub> in the material,

as detected by TGA. Moreover, from this threshold, the  $\text{Ca(OH)}_2$  content is linearly related to the degree of hydration. These purely experimental findings were confirmed through a semi-empirical model based on an analytical description of the hydration process (8). If the investigation range is now extended up to  $\alpha = 100\%$  (W/C ranging from 0.25 to 0.60, and ages up to 2 years), it can be seen that the same linear relationship still seems valid within the whole range of degrees of hydration (from  $\alpha = 7\%$ ), when  $W/C \leq 0.40$ . This is illustrated in Fig. 2a for  $T = 20^\circ\text{C}$ . Conversely, when  $W/C \geq 0.40$ , the  $\text{Ca(OH)}_2$  content seems to increase as a function of W/C, for the same degree of hydration (see Fig. 2a). The latter observation has been confirmed by the results obtained for the C/S ratio of the C-S-H, which is the major other solid phase including calcium. The investigations pointed out that for the same degree of hydration, the C/S ratio decreases when W/C increases (see Fig. 2b).

It seems relevant to confirm here the link between the *chemical* evolution of the material, characterized at the microscopic scale in particular by an increase in the TGA calcium hydroxide amount, and the development at the macroscopic scale of its *mechanical* properties (increase in stiffness). With this purpose, the ages corresponding to the respective chemical and mechanical thresholds were plotted on the same graph, as illustrated in Fig. 3 for  $W/C = 0.25$  and  $W/C = 0.30$ . As regards the chemical threshold ( $\alpha = 7\%$ ), the ages were obtained by linear interpolation between two experimental plots. The mechanical threshold is characterized here by the initial and final setting times obtained from the mean values of three Vicat tests. Given the Vicat test accuracy, it can be deduced from Fig. 3 that, in most of cases, the initial detection of  $\text{Ca(OH)}_2$  crystals by TGA coincides rather well with the setting times given by the Vicat needle. Note that at this stage, initial formation of C-S-H and AFt has already taken place (18). The consistency is particularly good at  $T = 50^\circ\text{C}$ , since increasing the curing temperature yields a decrease in the initial and final Vicat setting times and in the respective setting period (see Fig. 3). This last result was expected given the temperature-activated nature of the hydration process, usually described by an Arrhenius law: when the temperature increases, the hydrate production rate increases and the solid network required to resist the penetration of the falling Vicat needle is obtained more rapidly. These results show the strong link existing between the chemical development of the material (as described here by TGA calcium hydroxide content) and its gain in mechanical stiffness. More precisely,  $\text{Ca(OH)}_2$  precipitation could be considered as a relevant chemical indicator of the setting of cement pastes (for low W/C). This was expected, as the lime concentration of the solution is the parameter controlling both the hydration and the setting process, and since the increase in this concentration ends with the start of precipitation of  $\text{Ca(OH)}_2$  (18). In addition, these results enhance the notion of threshold in the material structure evolution, which separates the "fluid" state from the "solid" state.

### Chemical Shrinkage

Effect of W/C--The chemical shrinkage of the cement pastes with various W/C is plotted vs. the age in Fig. 4, from about 10 minutes after water-cement contact up to 24 hours, for each temperature (20, 30, 40, or  $50^\circ\text{C}$ ). Each plot is obtained from the mean value of two measurements. These experimental results are in agreement with previous research works (6,7,19): the chemical shrinkage value at 24 hours shows little and

unsystematic variation with W/C. Besides, at each temperature, the initial slope value corresponding to W/C = 0.25 is slightly detached, demonstrating an acceleration effect induced by low W/C (see Fig. 5, where the initial slope values are plotted vs. the temperature, for the various W/C). This acceleration phenomenon is indeed significant between W/C = 0.25 and W/C = 0.30, but is no more noticeable within the W/C range 0.30-0.60. The possible explanation combines chemical and physical processes:

- in low W/C cement pastes, the greater ionic concentration of the interstitial liquid phase leads to a rapid supersaturation and therefore to a faster precipitation of hydrates,
- by decreasing W/C, the number of contacts between particles is increased. As contact zones are preferential sites for nucleation of C-S-H (or even act as nuclei), the precipitation starts earlier and the reactions are accelerated (18).

Temperature Effects--The chemical shrinkage of the cement pastes cured at 20, 30, 40, or 50°C is plotted vs. the age for W/C = 0.25 (respectively W/C = 0.30) in Fig. 6a (respectively Fig. 6b). In order to select the same hydration state as the time reference for each cement paste, the initial setting time (Vicat) was taken as the zero point on the time scale of the curves. The experimental results clearly show a two-fold temperature effect. The effect on the ultimate value is particularly significant between T = 20°C and the other temperatures (see Fig. 6). Fig. 5 shows that the kinetic effect of temperature is expressed by a multiplying factor of 4 regarding the initial slope value (rate). This kinetic effect can be explained by the temperature-induced acceleration of hydration reactions.

The chemical shrinkage is plotted vs. the degree of hydration (assessed from non-evaporable water content) in reference (8), where the influence of both W/C and temperature is further discussed.

### Volumetric Autogenous Shrinkage - Temperature Effects at Early Age

The volumetric autogenous shrinkage of the cement pastes with W/C = 0.25 and cured at various temperatures (20, 30, 40, or 50°C) is plotted vs. the age in Fig. 7a, from initial setting time (Vicat) up to 24 hours. Each plot is obtained from the mean value of three samples. The initial slope of these curves (rate) increases with increasing temperature. Moreover, each plot displays a first stage that ends by a knee-point. From this knee-point, the curves start to flatten. This knee-point and the subsequent drastic reduction of autogenous shrinkage are usually attributed to the formation of a semi-rigid (self-supporting) skeleton of interconnected hydration products, *i.e.* a load-bearing microstructure strong enough to resist the contracting forces created by chemical shrinkage (14). In addition, this time may also correspond to a significant build-up of self-desiccation. But it is not elucidated yet whether self-desiccation begins at this moment, or as early as just a few minutes after casting, in very low W/C cement pastes. The latter case means that self-desiccation would start far before setting (e.g. at the mineral suspension-solid transition (20)), even if its consequences on apparent deformations are only visible later.

Fig. 7a shows that, at T = 50°C, the knee-point is reached more rapidly but the ultimate value of autogenous shrinkage is lower than the value reached at T = 40°C. This decrease in the magnitude, when the temperature increases in the range considered, is probably the result of various chemical, physical and microstructural changes. First, changes in the

distribution of hydrate clusters and consequently of inter-cluster voids are expected. The pore structure of cement pastes hydrated at relatively high temperature is indeed modified as illustrated in Fig. 8 (see also (21)). Slight changes in the chemical composition, stability, and structure of the hydration products (in particular the C-S-H) can also be expected from an exposure to relatively high temperatures during their formation, according to the literature. In particular, an increase in the polymerization of the silicate network of the C-S-H (increase in the length of the chains) has been recorded by Jennings (22,23). In addition, a link between changes in the C-S-H gel structure and the deformations of cement pastes has also been pointed out by the author: a temperature rise reduces shrinkage in particular because high temperature pre-shrinks the low-density C-S-H (see (22,23)). Another thermodynamic (physical) effect can be added: in materials with low W/C, self-desiccation occurs early and may contribute hence to a great extent to the recorded shrinkage (see further). As the liquid-vapor equilibrium governed by the Kelvin(-Laplace) law, at the origin of this process, is temperature-dependent, the measured shrinkage value will consequently be temperature-dependent.

The experimental results clearly show the irrelevance of the usual maturity concept (based on a single apparent activation energy) to describe and predict the evolution of autogenous deformations of cement pastes for realistic temperature histories (in particular above 40°C) within the whole early age period. This finding is in agreement with Turcry *et al.* (16) (see also (24)).

Plotting the volumetric autogenous shrinkage vs. the degree of hydration reveals the existence of a knee-point at 20 and 30°C (see Fig. 7b) at about  $\alpha = 7\%$ , which matches the chemical threshold (calcium hydroxide precipitation detected by TGA) previously pointed out in this paper (see Fig. 1). This knee-point could not be observed here at 40 and 50°C, probably as a result of a late first measurement of  $\alpha$  at these temperatures. Above the knee-point, the curves exhibit an almost parallel evolution. This means that the same degree of hydration increment leads to the same volumetric autogenous shrinkage increment for the various temperatures investigated. It is therefore possible to define a threshold for the degree of hydration, beyond which the autogenous shrinkage of cement pastes is directly linked to their chemical evolution. In order to enhance this finding, the volumetric autogenous shrinkage has been plotted in Fig. 9 vs. the degree of hydration, when taking  $\alpha = 7\%$  as the reference. These plots have been obtained as follows: for each temperature, the measured shrinkage values have been lowered by the shrinkage values recorded at  $\alpha = 7\%$  by extrapolation of the trend lines of Fig. 7b.

The linear fit displayed in Fig. 9 between autogenous shrinkage and degree of hydration, from  $\alpha = 7\%$  up to  $\alpha = 50\%$ , and from 20 up to 50°C, could appear inconsistent with the results shown in Fig. 7a. On the one hand, the ranking (20°C < 30°C < 50°C < 40°C) of the plots "*autogenous shrinkage vs. age*" from initial setting time up to 24 hours prevents applying the usual maturity concept. On the other hand, the plot "*autogenous shrinkage vs.  $\alpha$* " from  $\alpha = 7\%$  up to  $\alpha = 50\%$  can be fitted by a unique linear function within the whole temperature range investigated, allowing the use of the maturity concept within this range of  $\alpha$ . The contradiction is only apparent. It lies in the fact that the maturity concept is not suitable to describe the temperature effect on autogenous deformations within the whole early-age period (0-24 hours), but it is yet possible to separate this period into two stages, in order to assign to each of these stages a different value of

apparent activation energy. Such an approach has already been applied by Turcry *et al.* (16). Here, on the basis of the experimental data, the following partition can be proposed: the first stage will take place before initial setting (very early age) and the second stage will correspond to the range between final Vicat setting time and 24 hours. In this scheme, the setting period is not covered, because it is difficult to apply rigorously the maturity concept and to calculate a single value of apparent activation energy within the setting period. However, as seen in Fig. 3, at  $T = 50^{\circ}\text{C}$  the setting period is particularly short and a very good consistence is observed between the Vicat setting times and the  $\text{Ca}(\text{OH})_2$  threshold. Therefore, from a practical point of view, as the maturity concept is intended to be applied within such a temperature range, the proposed scheme will be particularly relevant in this case, where nearly the whole early-age period will be covered.

Moreover, it can be deduced from the linear fits pointed out at the micro-scale in Fig. 1 (calcium hydroxide content vs. degree of hydration) and at the macro-scale in Fig. 9 (volumetric autogenous shrinkage vs. degree of hydration), and from the threshold located at about  $\alpha = 7\%$  for both deformations and calcium hydroxide content, that  $\text{Ca}(\text{OH})_2$  is a key-parameter in the development of autogenous deformations of cement pastes and that volumetric autogenous shrinkage at early age for  $W/C = 0.25$  is linearly related to the  $\text{Ca}(\text{OH})_2$  content.

From tests performed on cement pastes cured at  $20^{\circ}\text{C}$  and with  $W/C$  within the range 0.30-0.40, Garcia Boivin was able to situate the knee-point of the volumetric autogenous shrinkage vs. age plot between initial and final Vicat setting times (13). On the other hand, Justnes *et al.* found that this knee-point corresponded well to the final Vicat setting time for  $W/C=0.40$ , but occurred later for  $W/C=0.30$  and earlier for  $W/C=0.50$ , at  $T = 23^{\circ}\text{C}$  (19). Given the very similar composition and fineness of the cements used in both reported studies, these different results could be explained by the different systems used to avoid bleeding. Bleeding may indeed influence autogenous shrinkage results to a great extent, particularly the knee-point. Here, for  $W/C = 0.25$  and for any temperature within the range investigated, and in accordance with the results reported by Justnes *et al.* (19), the knee-point is observed much later than the final setting time (see Fig. 3a). It can be deduced from the whole of these studies that, at early age, a (percolation) threshold takes place at about  $W/C = 0.40$  for the cements used. In addition, this threshold seems linked to the degree of connectivity of the pore network. Moreover, as the best coincidence between the Vicat setting times and the knee-point of the autogenous shrinkage vs. age plot seems obtained around  $W/C = 0.40$ , the scheme previously proposed for applying the maturity concept will hence be more relevant within this  $W/C$  range.

#### Comparison between Chemical and Volumetric Autogenous Shrinkages - Temperature Effects at Early Age

According to the literature, the evolutions vs. the age of chemical shrinkage and volumetric autogenous shrinkage are merged at very early age (before setting), but after a couple of hours a deviation appears at the same time as the autogenous shrinkage knee-point previously discussed (14,19,13).

For low W/C, cement particles are very close to each other. In this case, little hydration is necessary to bridge up the distance between the hydrating particles and then give strength and stiffness to the developing microstructure, and consequently, start self-desiccation that can more rapidly become the driving force of deformations. In addition, if the temperature is relatively high, the microstructure will be stabilized even earlier as a result of the temperature-induced acceleration of the chemical reactions. Therefore, in the case of W/C = 0.25 and T = 50°C, self-desiccation will occur very early and the period where chemical and autogenous shrinkages are merged will be very short. This is illustrated in Fig. 10, where the experimental results of chemical shrinkage, volumetric autogenous shrinkage, and initial and final Vicat setting times, obtained for the cement paste with W/C=0.25 and cured at T = 50°C, are plotted vs. the age.

### One-dimensional Autogenous Deformations

Free one-dimensional autogenous deformations (length changes) at T = 20°C ( $\pm 1^\circ\text{C}$ ) are plotted vs. the age in Fig. 11, from initial Vicat setting time (this moment is taken as the zero point on the time scale of the curves) up to 1 year. The results are the mean values obtained from six samples.

Effect of W/C--The experimental results point out that, at a given age, the magnitude of autogenous shrinkage increases linearly as W/C decreases from 0.60 down to 0.25 (see Fig. 12). In the case of mixtures with low W/C, a great proportion of the long-term autogenous shrinkage value occurs before 1 day. In the case of mixtures with medium or high W/C, swelling is exhibited from a few hours up to several days (see Fig. 11). Self-desiccation shrinkage becomes after a given time (which depends on the composition) the main component of autogenous deformations, the other components (chemical shrinkage and swelling) being negligible (25). The correlation between W/C and autogenous deformations can be mainly explained by this self-desiccation process. Assuming that self-desiccation shrinkage is based on the capillary tension mechanism, a finer initial pore structure will generate lower equilibrium internal RH according to the Kelvin-Laplace law and will create higher tension in the pore water. Therefore, the lower the initial pore volume and the finer the pore network, the higher the self-desiccation shrinkage. As a matter of fact, when W/C decreases, the porosity and mean pore radius, measured by MIP on the hcp at a given age, also decrease (see Fig. 13), which is consistent with the increasing shrinkage value measured at the same age (see Fig. 12).

Interpretation of the Swelling observed at Medium and High W/C--Autogenous swelling of cementitious materials with medium or high W/C, within the first days, has already been reported in the literature (e.g. (4)), but no deep insight into its associated mechanism was really performed.

The swelling observed on the experimental results presented here cannot be attributed to thermal effects due to the exothermic nature of chemical reactions. These effects disappeared indeed quickly as a result of the small size of the test samples, unlike the swelling increase, which lasts several days (about 2 weeks, in the case of W/C = 0.60).

This swelling may rather be attributed to the formation and the growth, through the hydration reactions of the cement, of large-sized crystals of calcium hydroxide and

maybe needles of ettringite (AFt). The growth of these crystals generates a crystallization pressure on the pore walls, related to the supersaturation rate according to Riecke's law. The pressure can induce expansion of the microstructure (26,27), by direct solid-crystal contact or through the water phase. In mixtures with high W/C, large-sized  $\text{Ca(OH)}_2$  crystals and AFt needles do have enough time, water amount and space for growing up, before the strength of the solid matrix and the self-desiccation process become strong enough to balance the crystallization pressure, and before self-desiccation shrinkage becomes prominent. In porous areas, calcium hydroxide crystals can indeed even become bigger than the initial clinker particles. Microstructural investigations of the hcp tested here provide arguments to support this explanation. The magnitude of the swelling deformation is correlated with the amount and the mean size of  $\text{Ca(OH)}_2$  crystals, measured by TGA and SEM-EDX analysis, respectively. The values of these parameters, and therefore the volume occupied by the calcium hydroxide crystals, increase both with hydration time (even after 28 days) and W/C (e.g. at 28 days, the  $\text{Ca(OH)}_2$  content is 18.2, 24.6, 30.6, and 32.7%, and the mean size of the crystals is 4-10, 10-20, 10-30, and 80-100  $\mu\text{m}$ , when W/C is respectively 0.25, 0.35, 0.45, and 0.60). With low W/C, SEM observations show that calcium hydroxide appears mainly as small crystals spread out among the C-S-H phase. Likewise, AFt cannot be easily detected in the microstructure of hcp with W/C = 0.25, whereas it appears as well crystallized needles in the case of W/C = 0.45 and W/C = 0.60. This indicates that the contribution of AFt to early-age swelling, before its dissolution, is probably more important in high W/C mixtures. The fact that expansion, mainly attributed here to the growth of "large"  $\text{Ca(OH)}_2$  crystals, proceeds for several days is also in agreement with the results of Bentz and Stutzman on  $\text{Ca(OH)}_2$ , obtained by means of quantitative image analysis (28). The authors showed that the area occupied by "large" crystals of calcium hydroxide (area > 16  $\mu\text{m}^2$ ) increased with the age in a material with W/solid = 0.45 for at least 7 days, as the hydration process goes on and "large" crystals continue to grow up at the expense of smaller ones. The basic role of  $\text{Ca(OH)}_2$  with respect to autogenous deformations is pointed out again, but here as a (micro)structural effect.

Another mechanism (29,20) could also be suggested to explain the swelling observed at medium and high W/C. It is based on the inner C-S-H, whose volume is higher than that of the portions of the anhydrous grains they replace, and which require water from outside the borderline of the cement grains for their formation (by topochemical reaction of  $\text{C}_3\text{S}$ ). These products are thus developing with an increase in solid volume (contrary to outer C-S-H). As a matter of fact, for the hcp tested here, when W/C increases from 0.25 up to 0.60, the thickness of the C-S-H rims (surrounding residual unreacted cement cores) at the age of 28 days increases from 1 to 10  $\mu\text{m}$ . The volume of pseudomorphic (inner) C-S-H will therefore be greater in higher W/C cement paste, similarly as swelling. Nevertheless, still according to the literature, a significant contribution based on this mechanism to the expansion of the microstructure could be expected, only in the case of solid contacts between the C-S-H rims (in order to raise stresses). This occurs yet when the pore space is restricted, which means in the case of low W/C. These opposite deductions stress that further investigations are needed, in order to determine the actual contribution of this mechanism to the observed swelling.

## SUMMARY AND CONCLUSIONS

Experimental tools for measuring key-parameters have been presented in this paper. These tools can be used in view of optimizing mixtures, within the framework of the prediction of early-age deformations and the prevention of early-age cracking. The experimental results obtained by means of these tools on a set of plain cement pastes prepared with the same type I OPC, with W/C ranging from 0.25 to 0.60, and isothermally cured at various temperatures ranging from 10 to 50°C, are summarized in the following sections. These results appear as useful data for developing engineering models, capable of predicting both early age and delayed deformations of concrete, from the mix-parameters and/or from the microstructural characteristics of the material.

### Temperature Effects at Early Age (< 24 hours)

- An increase in (isothermal) curing temperature within the range 20-50°C yields a decrease in initial and final Vicat setting times and in the respective setting period.
- The amount of  $\text{Ca(OH)}_2$  produced at a given degree of hydration is not influenced by the curing temperature within the range 10-50°C.
- A two-fold temperature effect is observed on the evolution of chemical shrinkage and volumetric autogenous shrinkage at early age vs. the age, within the range 20-50°C: the initial slope increases with temperature and the magnitude is changed.
- At  $T = 50^\circ\text{C}$ , the period where chemical and volumetric autogenous shrinkages are merged is very short for  $W/C = 0.25$ .

### Effect of W/C

- Both at early age and in the long term, the amount of  $\text{Ca(OH)}_2$  produced at a given degree of hydration is not influenced by W/C in the range 0.25-0.40. Conversely, in the range 0.45-0.60, at a given degree of hydration, the  $\text{Ca(OH)}_2$  amount increases as a function of W/C.
- W/C does not influence the chemical shrinkage in a significant manner within the W/C range 0.30-0.60 and for curing temperature ranging from 20 to 50°C. However, W/C has a significant kinetic effect within the range 0.25-0.30.
- At  $W/C = 0.25$ , and for temperatures ranging from 20 to 50°C, the final Vicat setting time is sooner than the knee-point of the volumetric autogenous shrinkage plot.
- At a given age, the magnitude of one-dimensional autogenous shrinkage increases linearly as W/C decreases from 0.60 down to 0.25, as a result of the self-desiccation process and in agreement with the pore structure of the material.

### Threshold Values and Micro-Macro Correlations

- At the micro-scale, a threshold corresponding to the precipitation of  $\text{Ca(OH)}_2$  has been detected by TGA at about  $\alpha = 7\%$ . The comparison with the setting times measured at the macro-scale by the Vicat needle exhibits a good correlation between these two types of parameters, particularly at  $T = 50^\circ\text{C}$ . Moreover, the same threshold ( $\alpha \approx 7\%$ ) has been found at the macro-scale with respect to deformations:

beyond this threshold, early age volumetric autogenous shrinkage is a linear function of  $\alpha$ , for  $W/C = 0.25$ .

- A  $W/C$  threshold has been pointed out (at about 0.40, for the type of cement tested here) at early age and in the long term, at the macro-level, with respect to volumetric and one-dimensional autogenous deformations. The same threshold value was already pointed out with respect to drying shrinkage: a change in the slope of the plot giving equilibrium drying shrinkage at  $T = 20^\circ\text{C}$  (between  $RH = 71.5\%$  and  $RH = 63\%$ ) vs.  $W/C$  was registered at  $W/C = 0.40$  (30). Furthermore, the same threshold has been found at the micro-level, with respect to the amount and characteristics of the hydration products assessed by means of SEM-EDX or TGA (see also (30), where it was found for the C-S-H:  $C/S \leq 1.7$  for  $W/C = 0.45$  and  $0.60$ , and  $C/S \geq 1.7$  for  $W/C = 0.35$  and  $0.25$ ), as well as with respect to the MIP porosity and pore size distribution (see Fig. 13b and (5,30)).

### Chemical and (Micro)structural Effects of $\text{Ca}(\text{OH})_2$

All the findings presented in this paper show the critical two-fold effect of calcium hydroxide:

- chemical effect: the  $\text{Ca}(\text{OH})_2$  content of the cement paste plays the role of a chemical indicator of the hydration process, similar to that of the degree of hydration of the cement,

- (micro)structural effect, generated by large-sized  $\text{Ca}(\text{OH})_2$  crystals.

When only the chemical effect (amount) is prominent, autogenous shrinkage is linearly linked to this amount, as seen here on volumetric autogenous shrinkage measured at early age for  $W/C = 0.25$ . When significant structural effects take place, swelling can become prominent, as measured here for one-dimensional autogenous deformations in the case of high  $W/C$ , and deviations are registered from linear correlations.

### Maturity Concept

Practical conclusions can be drawn regarding the use of the maturity concept within the field of concrete technology. The temperature-induced changes, recorded on volumetric autogenous shrinkage, clearly show the irrelevance of the usual maturity concept (based on a single apparent activation energy) for the prediction of shrinkage within the whole early-age period (0-24 hours). Hence, on the one hand, if the degree of hydration (or the  $\text{Ca}(\text{OH})_2$  content) has experimentally been assessed within a given temperature range, the complex determination of the apparent activation energy can be avoided. Early-age autogenous shrinkage at required temperatures can indeed be derived from the linear relationship existing between shrinkage and the degree of hydration (or the  $\text{Ca}(\text{OH})_2$  content) within the ad-hoc range, whatever the temperature. On the other hand, if these parameters are not available, the maturity concept can be used after separating the early-age period (0-24 hours) into two stages (before and after setting) and calculating the respective values of apparent activation energy.

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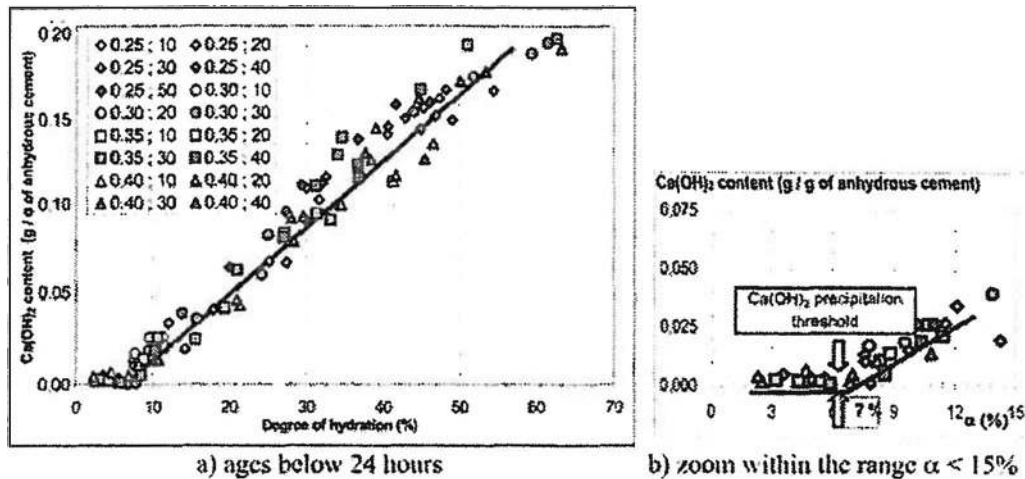


Figure 1 - Evolution of the  $\text{Ca}(\text{OH})_2$  content of the cement pastes with  $W/C \leq 0.40$  cured at various temperatures, as a function of the degree of hydration of the cement, at early age.

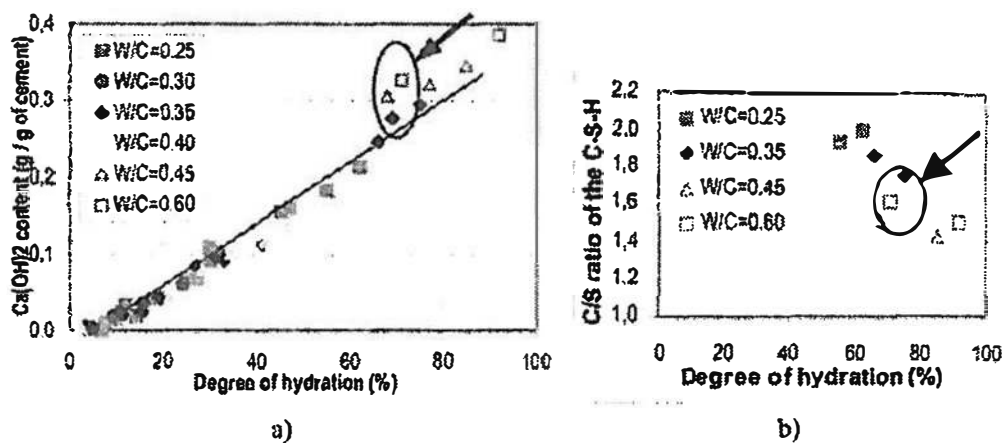


Figure 2 - Correlation between  $\text{Ca}(\text{OH})_2$  content (a) or C/S ratio of the C-S-H (b) and degree of hydration, for cement pastes with  $W/C$  ranging from 0.25 to 0.60 and cured at  $T = 20^\circ\text{C}$ , from 3 hours up to 2 years.

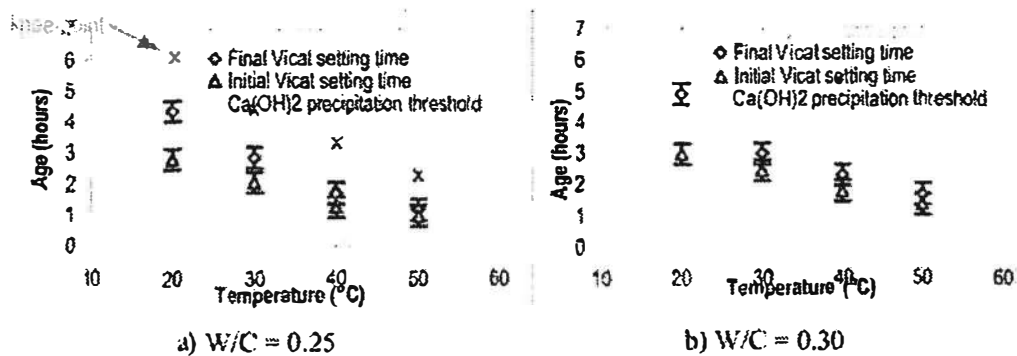


Figure 3 - Comparison between initial and final setting times obtained from Vicat needle, chemical threshold (precipitation of  $\text{Ca}(\text{OH})_2$  detected by TGA), and autogenous shrinkage knee-point, for cement pastes cured at various temperatures.

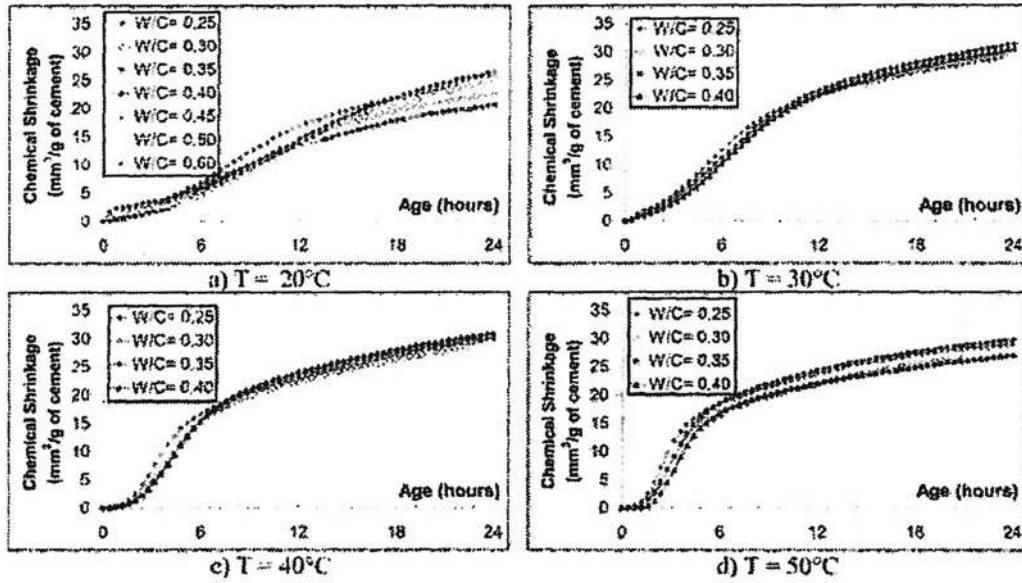


Figure 4 - Evolution of chemical shrinkage of cement pastes with various W/C.

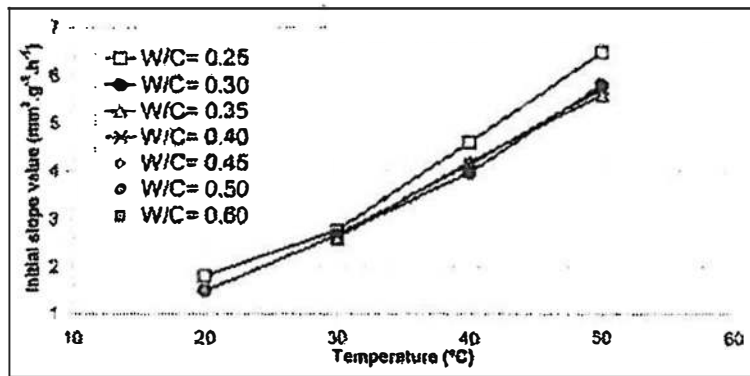


Figure 5 - Initial slope of the chemical shrinkage vs. age plot, as a function of temperature, for cement pastes with various W/C.

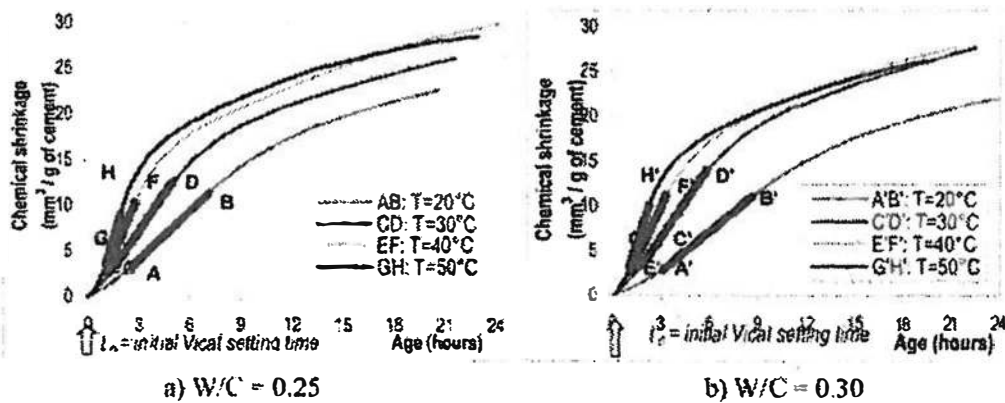


Figure 6 - Evolution of chemical shrinkage of cement pastes cured at various temperatures.

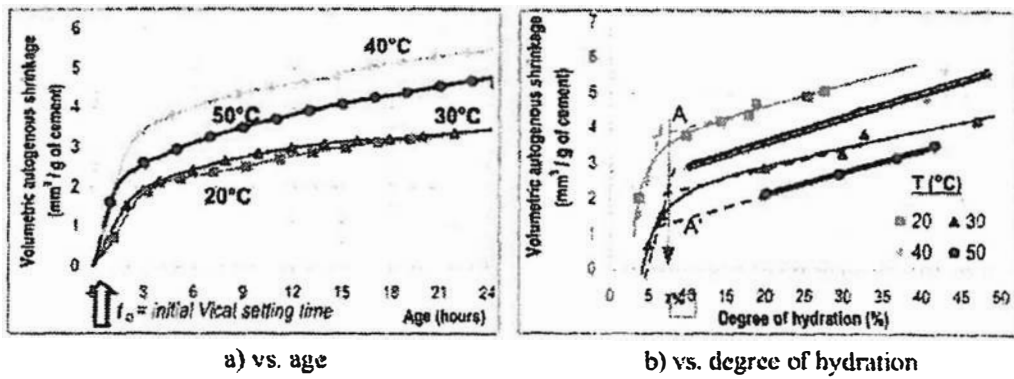


Figure 7 - Evolution of volumetric autogenous shrinkage of cement pastes with W/C = 0.25 and cured at various temperatures (ages below 24 hours).

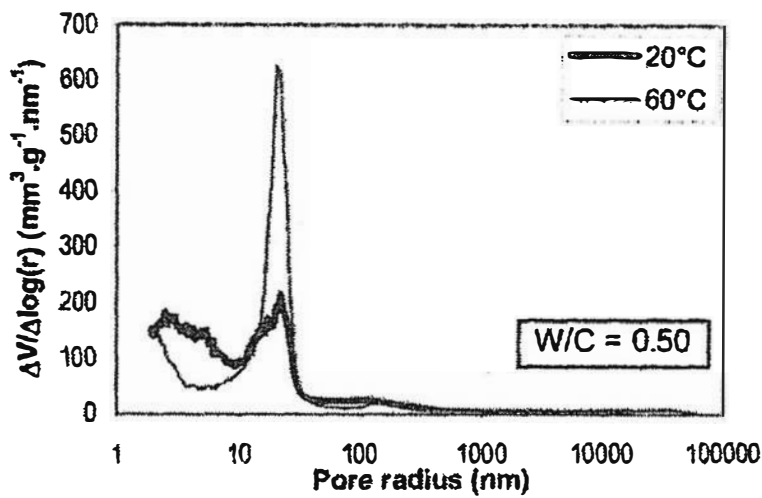


Figure 8 - Pore size distribution measured by MIP on hcp with W/C = 0.50, after 28-day curing at 20 or 60°C.

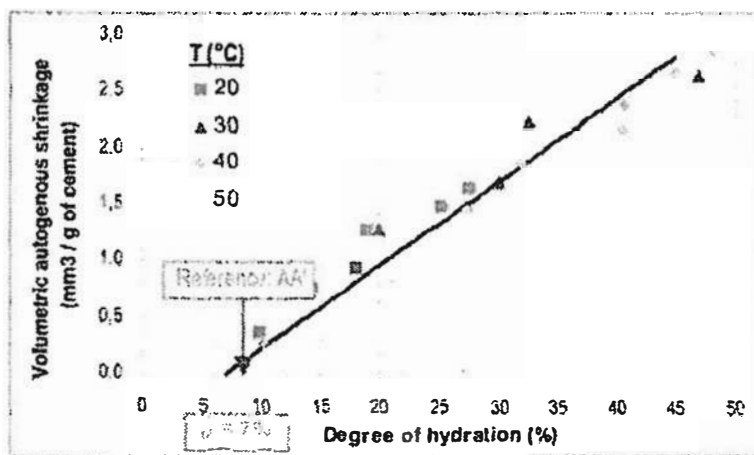


Figure 9 - Evolution of volumetric autogenous shrinkage between  $\alpha = 7\%$  and  $\alpha = 50\%$ , for cement pastes with W/C = 0.25 and cured at various temperatures (ages below 24 hours).

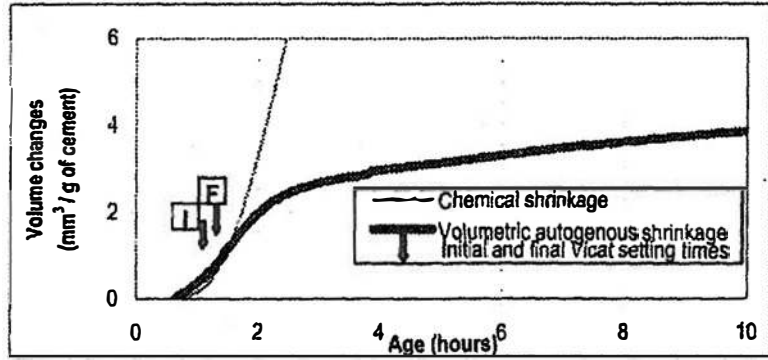


Figure 10 - Comparison between chemical shrinkage and volumetric autogenous shrinkage of cement pastes with W/C = 0.25 and cured at T = 50°C.

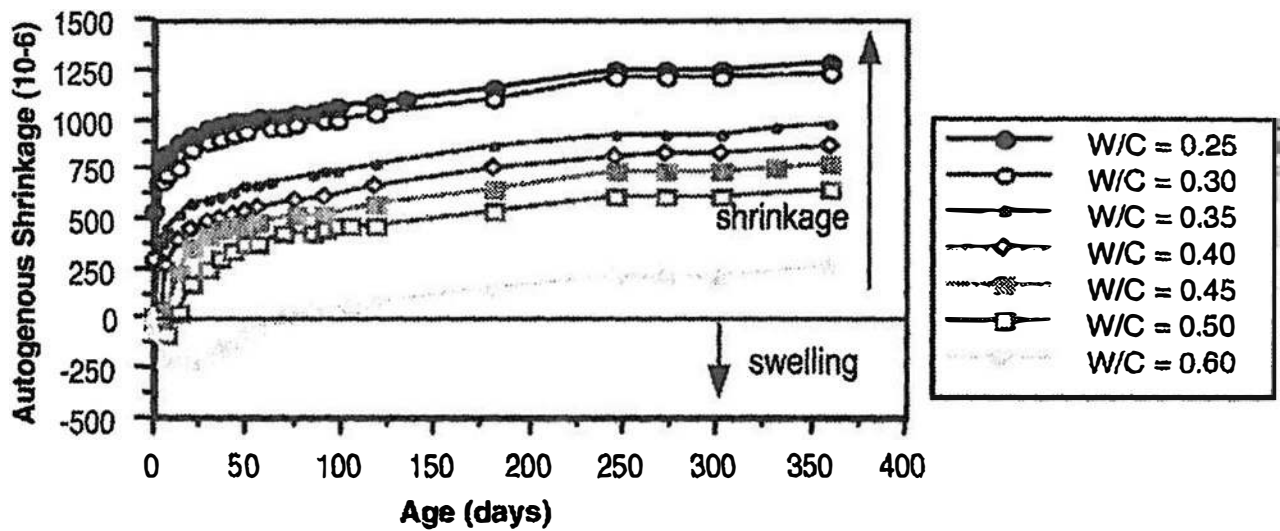


Figure 11 - One-dimensional autogenous deformation measured from initial Vicat setting time on Ø20x160-mm sealed samples of cement pastes with various W/C, at T = 20±1°C.

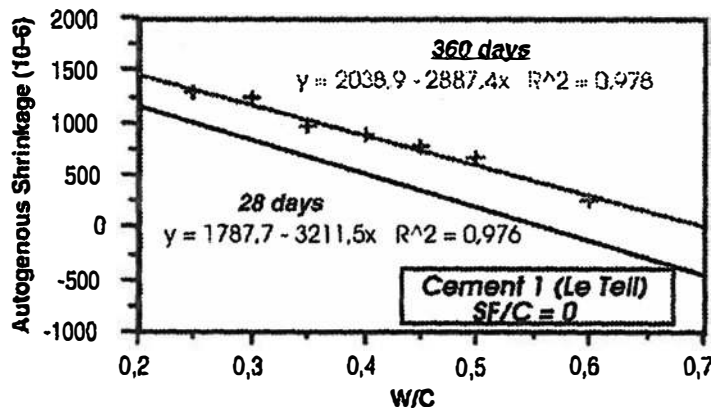
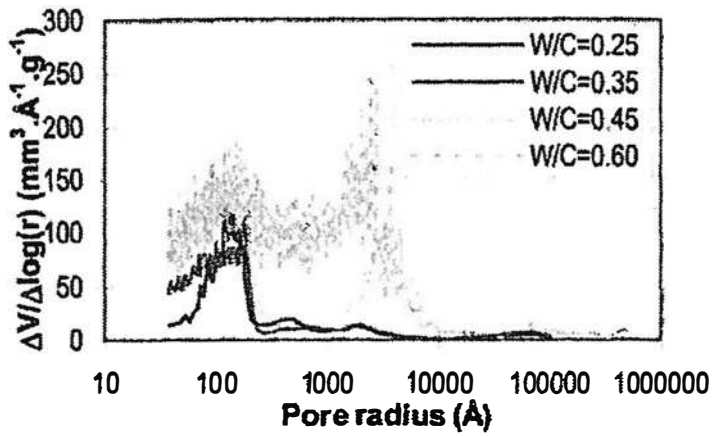
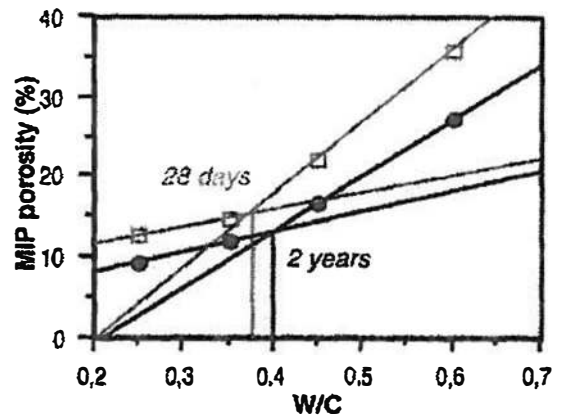


Figure 12 - Correlation between one-dimensional autogenous deformation (measured at T = 20±1°C) and W/C, at the ages of 28 and 360 days.



a) pore size distribution at 28 days



b) porosity vs. W/C

Figure 13 - Results obtained by MIP on hep with various W/C, after curing at  $T = 20 \pm 1^\circ\text{C}$ .