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Autogenous deformations of cement pastes
Part II. W/C effects, micro–macro correlations, and threshold values

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Abstract

A broad experimental study has been performed, from the end of mixing up to 2 years, 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. Several parameters have been measured on the hydrating materials, such as chemical shrinkage, volumetric and one-dimensional autogenous deformations, degree of hydration of the cement, $Ca(OH)_2$ content and Vicat setting times. Drying shrinkage has also been measured on the mature materials. In this part II of the paper, the effects of W/C within the range 0.25–0.60 have in particular been analysed in relation to the microstructural characteristics of the materials. This micro–macro analysis has highlighted a W/C threshold value (located around 0.40) both at the macro-level (on autogenous, but also on drying deformations and durability-related properties) and at the micro-level (characteristics of the hydration products, MIP porosity and pore size distribution, etc.).

In addition, volumetric and one-dimensional autogenous shrinkage deformations have been compared in the case of W/C=0.25 and T=20 °C. Finally, a critical twofold (chemical and structural) effect of calcium hydroxide has been found. When significant structural effects, generated by the formation and the growth of large-size $Ca(OH)_2$ crystals, take place, swelling can become prominent, as observed for one-dimensional autogenous deformations in the case of medium and high W/C, and deviations are recorded on linear relationships.

Keywords: Cement paste; Shrinkage; Hydration; $Ca(OH)_2$; Microstructure

1. 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 material 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 behaviour 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 structures. In addition to mechanical problems, species aggressive to concrete or to reinforcement can more easily be carried from the surface through these (micro)cracks and then reduce the durability of the structure.

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Various physical and chemical mechanisms are at the origin of autogenous volume changes and cracking of cementitious materials. 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 behaviour of concrete structures impossible.

As regards the test methods, autogenous deformations of cement pastes can be measured in two different ways: measurement of volumetric deformations (see for example Refs. [1–5]), and measurement of one-dimensional deformations (e.g. Refs. [6–8]). 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.

Within the framework of the study of cementitious materials shrinkage, in addition to the fact that a lot of research work has already been done 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 h. The question of the selection of a relevant initial (reference) time t_0 (<24 h) for the deformation measurements has, for example, not been solved at the present time. Besides, along with the parameters related to the hydration process, it is well known that mix parameters, and in particular the water-to-cement ratio (W/C), influence autogenous deformations (see for example [6,8–11]). As far as chemical shrinkage is concerned, Justnes et al. [3] did not find any significant effect of W/C (ranging from 0.30 to 0.50) on the final chemical shrinkage value of cement pastes at 20 °C, from 0 to 48 h after mixing. Boivin et al. [12] confirmed these results and pointed out a purely kinetic influence of W/C on chemical shrinkage. Nevertheless, a broader range of investigations is still required, in order to accurately characterize the influence of W/C.

The purpose of this paper is to improve the knowledge of cementitious materials and to contribute to the understanding of the mechanisms related to autogenous deformations. This step is of primary importance in order to enable the prediction of both early-age (autogenous) and delayed (drying, carbonation, etc.) deformations. Within this framework, the monitoring of the hydration process (through degree of hydration of the cement, $Ca(OH)_2$ content, Vicat setting times, etc.) and the characterisation of the cement paste microstructure have been carried out here as tools to help understand and interpret deformation results. The paper is separated in two parts. Part I was devoted to the analysis of curing temperature effects on early-age (≤24 h) volume changes and to the investigation of the relevance of the maturity concept. In addition, micro–macro relationships have been pointed out in part I between volume changes and chemical and physical parameters. In this part II, the effects of W/C within the range 0.25–0.60 will be investigated on various properties (chemical shrinkage, autogenous deformations, drying shrinkage, etc.), in relation to the microstructural characteristics of the materials. Moreover, a comparison between volumetric and one-dimensional autogenous shrinkage will be carried out in the case of W/C=0.25 and T=20 °C.

2. Experimental program, materials and test methods

2.1. Experimental program and materials

A broad experimental study has been performed from the end of mixing up to 2 years on a set of plain cement pastes prepared with the same type I ordinary portland cement (OPC) (CEM I—52.5, according to the EN 197-1 European standard). W/C ranged from 0.25 up to 0.60 and the mixtures were submitted to an isothermal curing process at 10, 20, 30, 40, or 50 °C (±0.1 °C). The cement contained 70.2% C_3S, 7.8% C_2S, 3.8% C_3A, and 6.0% C_4AF (Bogue calculation). Its loss on ignition was 2.3% and its Blaine specific surface area was 3320 cm^2 g^{-1}. The gypsum content was 5.2%. The chemical composition and the particle size distribution of the cement are given in Ref. [13]. The cement was mixed in a 5-L laboratory mixer for 1 min, before addition of distilled water and a further mixing period of 3 min, in order to ensure a good homogeneity. A specific procedure has been carried out for the preparation of the samples intended for length change measurements. This procedure will be detailed further in the paper. 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 at the required temperature.

In this study, chemical shrinkage, volumetric and one-dimensional autogenous deformations, and drying shrinkage have been measured, as well as other parameters characterizing the hydration process or the microstructure of the material (degree of hydration of the cement, $Ca(OH)_2$ content, size of $Ca(OH)_2$ crystals, C/S ratio and thickness of the C–S–H rims, MIP porosity and pore size distribution, etc.).

2.2. Determination of degree of hydration and $Ca(OH)_2$ content

The evolution of both the non-evaporable water content and the calcium hydroxide content 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 an inert N_2 atmosphere (1 bar). The tests have been performed at 3, 6, 9, 12, 15, 18, 21, and 24 h after mixing (curing temperatures from 10 to 50 °C), and also at the ages of 28 days, 6 months, and 2 years (curing at T=20 °C). The specimens were not submitted to crushing or drying prior to TGA measurement, in order to reduce their perturbation. The testing and calculation procedures applied are described in Ref. [13].

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_2 release caused by calcite decomposition between 600 and 800 °C [14,15]. This non-evaporable water amount has been used to calculate the degree of hydration of the cement (α). The $Ca(OH)_2$ content of the cement pastes has been determined by considering that dehydroxylation took place between 400 and 600 °C [16].

2.3. Chemical shrinkage measurement

(Total) chemical shrinkage has been measured on the various cement pastes by using a weighing method [1,12]. The testing and calculation procedures applied are detailed in Ref. [13]. The contact surface with the water bath is 20 cm^2 and the specimens are thin enough (7 mm), in order to permit absorption of water from the bath at the rate that the water is being consumed by the chemical reactions. The whole system, including the cement paste sample in its flask, is hung from a balance and is immersed in distilled water at the required temperature, 10, 20, 30, 40, or 50 °C (±0.1 °C). The measurement started 10 min after water–cement contact and last for 24 h.

2.4. Autogenous deformation measurements

2.4.1. Early-age volume change measurement

The test method used here for early-age volume change (also called external chemical shrinkage) measurement consists of measuring, by hydrostatic weighing, the buoyancy variations of a sample constituted by a latex membrane filled with cement paste and immersed in a thermo-regulated bath. The test method is described in part I of the paper. The sample is placed on a nacelle hung from a balance, and immersed in the bath at the required temperature, 10, 20, 30, 40, or 50 °C (±0.1 °C). The accuracy of the balance is 0.0001 g. Both the bath temperature and the mass of the system are continuously recorded from 30 min after water–cement contact up to 24 h. In order to guarantee the absence of bleeding (see part I), volume changes have been measured here only on the cement pastes with W/C=0.25.

2.4.2. Length change measurement

Unrestrained one-dimensional autogenous deformations have been measured on ∅20×160-mm cement paste samples (W/C ranging from 0.25 up to 0.60) by using a simple technique, allowing length change measurement by means of dial gauge (with an accuracy of 10 μm/m), from initial Vicat setting time up to 1 year, at T=20 °C (±1 °C).

The samples were cast in polyethylene moulds ensuring tightness and low restraint, 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 h in order to carry out the further measurements on demoulded and sealed samples. The set-up and the test procedure are detailed in Ref. [8].

The fresh paste was poured from the bottom of the mixing bowl into the moulds without stopping the mixer. This ensured a good homogeneity of the paste [17,18]. Two stainless steel plugs remained gripped to the paste by means of embedded screw rods (see Fig. 1) and constituted the ends of the mould as well as of the sample. Each end had a recessed stud placed at the centre for length change measurement. From casting, the samples in their moulds were kept in rotation until at least the initial Vicat setting time, in order to minimize segregation and bleeding expected in particular with medium and high W/C. Just after demoulding, the samples were sealed by wrapping them in three self-adhesive aluminium foil sheets, in order to avoid moisture exchange with the surroundings (see Fig. 1).

The specimens were weighed at each length change measurement time. A 0.005% relative weight loss was measured for the mix with W/C=0.25 (vs. 0.018% with W/C=0.60) within 1 year, thereby confirming weak water losses during this long-term experiment. The observed deformation values were not corrected by the thermal dilation coefficient of the materials, as the temperature rise was low inside the small samples tested here and disappeared very early compared to the ages of length change measurements.

2.5. Drying shrinkage measurement on mature materials

After 1-year length-change measurements in autogenous conditions, the self-adhesive aluminium foil sheets of some of the ∅20×160-mm sealed samples were removed and the hardened cement pastes (hcp) were exposed in sealed chambers to various relative humidities (controlled by saturated salt solutions), in order to measure "pure" drying shrinkage at T=20 °C (±1 °C). The same measurement device (dial gauge) as in autogenous conditions was used.

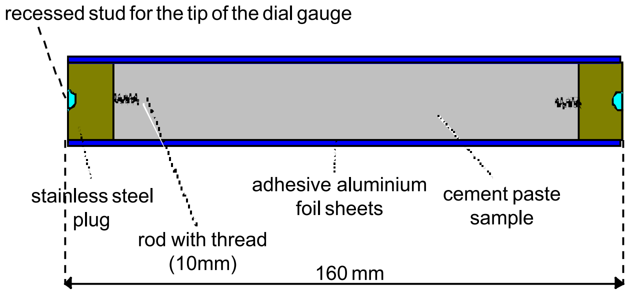


Fig. 1. Scheme of the sealed cement paste sample, wrapped in self-adhesive aluminium foil sheets, used for length change measurements in autogenous conditions.

2.6. Other chemical, physical and microstructural investigations

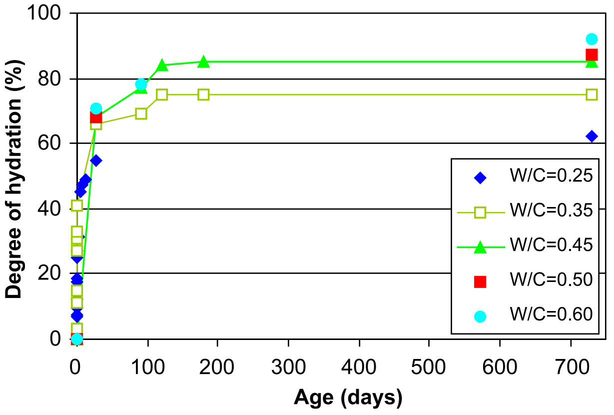
The initial and final setting times of the cement pastes have been assessed by means of the Vicat (needle) test. The microstructure of the hcp has been investigated at various ages by means of secondary or backscatter mode scanning electron microscopy (SEM) after vacuum-drying, along with energy dispersive X-ray (EDX) semi-quantitative analysis. In particular, the size of the $Ca(OH)_2$ crystals has been estimated by secondary mode SEM on newly broken surfaces, whereas the C/S ratio and the thickness of the C–S–H rims have been quantified by BSE-SEM on polished sections in the neighbourhood of the unreacted cement cores [19]. Moreover, porosity and pore size distribution have been determined by mercury intrusion porosimetry (MIP), after freeze-drying of the specimens, with an apparatus (P_{max}=200 MPa) allowing the investigation of pore radii ranging from 3.7 nm up to 60 µm.

3. W/C effects: experimental results and discussion

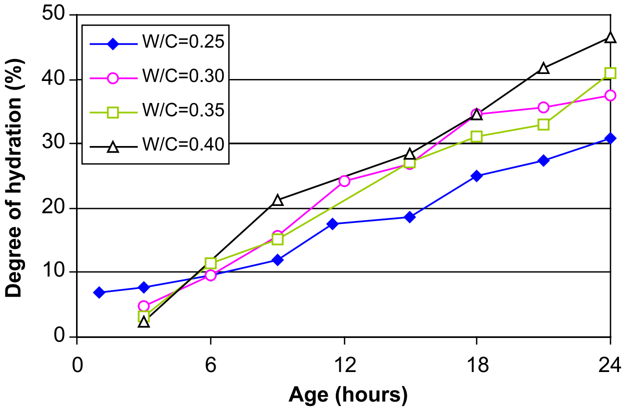
3.1. Calcium hydroxide content

The calcium hydroxide content of the cement pastes with W/C ranging from 0.25 up to 0.60 and cured at T=20 °C is plotted in Fig. 2a vs. the degree of hydration of the cement (from 3 h up to 2 years). The degree of hydration of the cement vs. the age is displayed in Fig. 3 (see Ref. [13] for results obtained at other temperatures).

The results show that for 0.25≤W/C≤0.40, both at early age and in the long term, the amount of $Ca(OH)_2$ produced at a given α is not influenced by W/C (note that a given α is obtained at different ages for different W/C). A linear relationship is exhibited between $Ca(OH)_2$ content and degree of hydration within the whole range of degrees of hydration, from α=7% (threshold corresponding to the precipitation of $Ca(OH)_2$, as detected by TGA, see part I) up to α ≈ 80%.



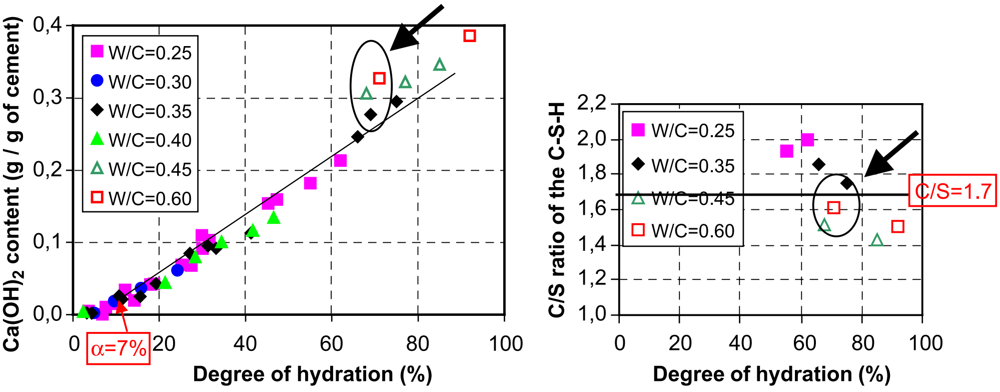
a) 0 - 2 years



b) Zoom at early age: 0 - 24 hours

Fig. 3. Degree of hydration of the cement vs. age for cement pastes with various W/C and cured at 20 °C.

Conversely, when W/C>0.40, the $Ca(OH)_2$ content seems to increase as a function of W/C, for the same degree of hydration (ranging up nearly 100%) (see Fig. 2a). The latter observation is confirmed by the results obtained as



a) b)

Fig. 2. Correlation between $Ca(OH)_2$ 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 up to 0.60 and cured at T=20 °C, from 3 h up to 2 years.

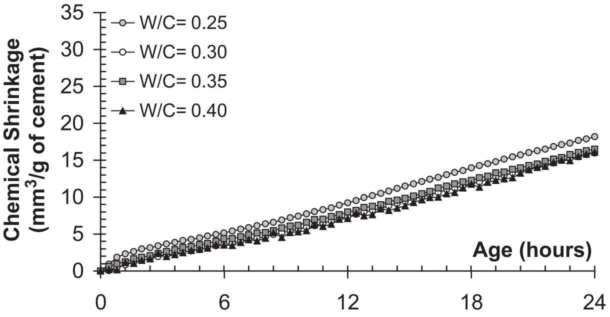
regards the C/S ratio of the C–S–H, which is the major other solid phase including calcium. The investigations do point out that for the same degree of hydration, the C/S ratio decreases when W/C increases (see Fig. 2b).

3.2. Chemical shrinkage

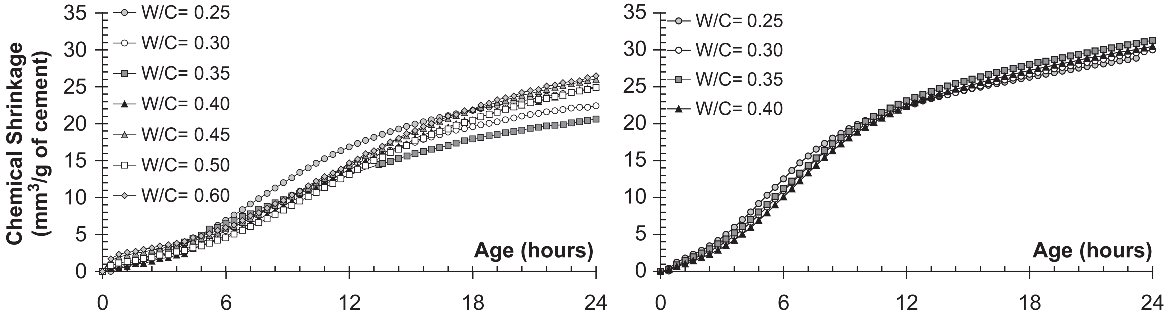
The chemical shrinkage of the cement pastes with various W/C is plotted vs. the age in Fig. 4, from about 10 min after water–cement contact up to 24 h, for each temperature investigated (10, 20, 30, 40, or 50 °C). Each plot is obtained from the mean value of two measurements. As seen on Figs. 3 and 4, for a given temperature, very slight and unsystematic variations are recorded as a function of W/C on the "ultimate" (at 24 h) chemical shrinkage value. These results are in agreement with previously published works [3,12,20]. Furthermore, they extend the range of validity of such a statement within the W/C range 0.25–0.60 (as displayed in Fig. 4b in the case of T=20 °C) and within the temperature range 10–50 °C. In addition, Fig. 5a shows that, whatever the water-to-cement ratio, for $T \geq 30$ °C, the temperature has no more influence on the "ultimate" chemical shrinkage value (see also Ref. [13]).

Besides, for a given temperature, the initial slope value of the chemical shrinkage vs. age plot corresponding to W/C=0.25 seems slightly detached, whereas the values obtained with the other W/C are merged. This effect is depicted in Fig. 5b, where the initial slope values are plotted vs. the temperature, for the various W/C tested. This points out an acceleration effect on the rate of chemical shrinkage, induced by low W/C. This acceleration phenomenon is indeed significant between W/C=0.25 and W/C=0.30, but is no more noticeable when W/C ranges from 0.30 up to 0.60. The possible explanation of this finding combines chemical and physical processes:

- by decreasing W/C, the number of contacts between solid particles is increased. As contact zones are

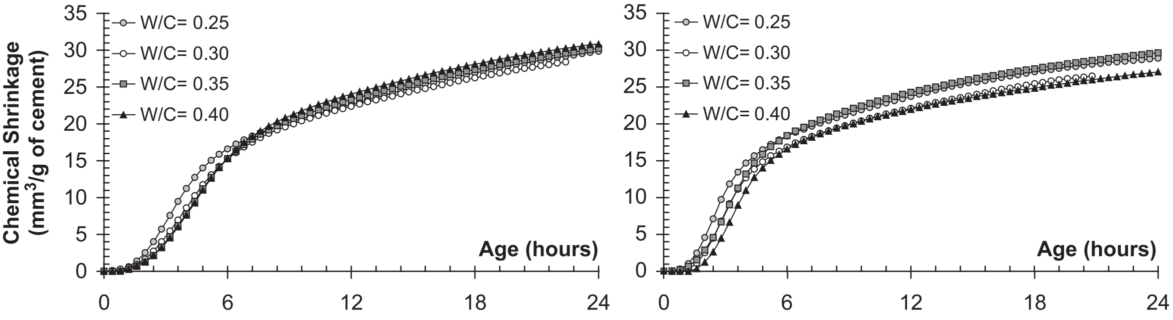


a) T = 10ºC



b) T = 20ºC

c) T = 30ºC



d) T = 40ºC

e) T = 50ºC

Fig. 4. Chemical shrinkage vs. age for cement pastes with various W/C and cured at 10 °C (a), 20 °C (b), 30 °C (c), 40 °C (d), or 50 °C (e).

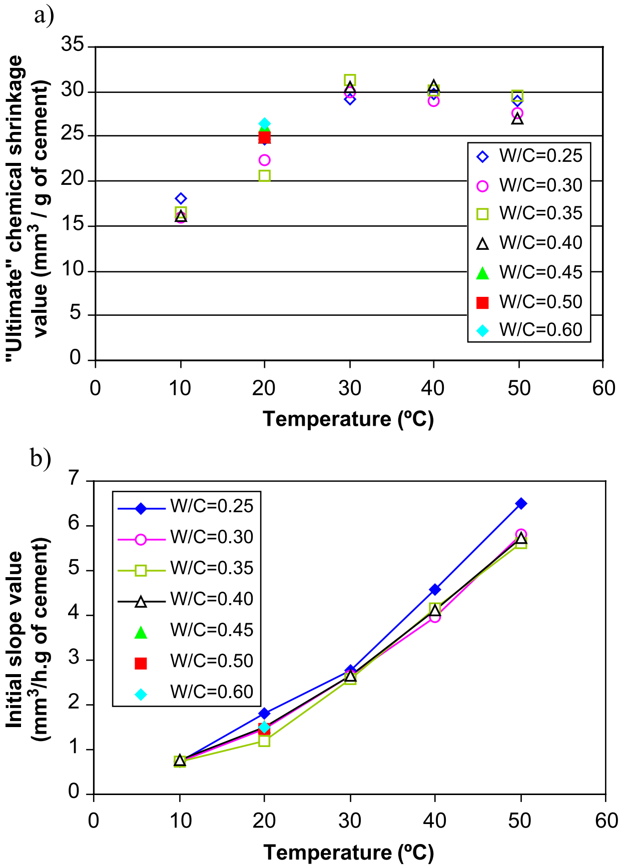


Fig. 5. "Ultimate" (at 24 h) chemical shrinkage value (a) and initial slope of the chemical shrinkage vs. age plots (b), as a function of temperature, for cement pastes with various W/C.

  preferential sites for heterogeneous nucleation of C–S–H (or even act as nuclei), the precipitation starts earlier and reactions are accelerated [21,22], and so the chemical shrinkage,
- in low W/C cement pastes, the dense packing of the cement particles, rapidly consolidated by C–S–H layers, hinders diffusional ion exchanges. This means that a greater ionic concentration and a rapid supersaturation take place in the interstitial liquid phase. This induces a faster precipitation of hydrates (e.g. $Ca(OH_2)$) and therefore an accelerated chemical shrinkage.

3.3. Volumetric autogenous shrinkage

The volumetric autogenous shrinkage of the cement pastes with W/C=0.25 and cured at various temperatures (10, 20, 30, 40, or 50 °C) is plotted vs. the age in Fig. 6, from initial Vicat setting time (this moment is taken as the zero point on the time scale of the curves) up to 24 h. Each plot is obtained from the mean value of three samples. The knee-point observed on each plot (see also part I) appears later than the final Vicat setting time, for any temperature within the range investigated and for W/C=0.25 (see Fig. 7). These results are in accordance with those reported by Justnes et al. [20] and complement them within the temperature range 10–50 °C. These authors found that the knee-point of the volumetric autogenous shrinkage vs. age plot matched 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 °C. Note that from tests carried out on cement pastes cured at 20 °C and with W/C ranging from 0.30 to 0.40, Garcia was able to rather situate the knee-point between initial and final Vicat setting times [4]. It can be deduced from the whole of these studies that, at early age, a threshold takes place at about W/C=0.40 (where a coincidence between autogenous shrinkage knee-point and setting time is observed) for the cements used. This "percolation" threshold seems linked to the degree of connectivity of the pore (and solid) network, as it will be detailed further in this paper.

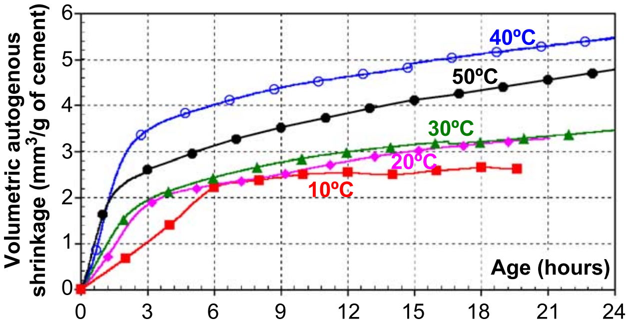


Fig. 6. Volumetric autogenous shrinkage vs. age for cement pastes with W/C=0.25 and cured at 10, 20, 30, 40, or 50 °C (zero point of the time scale: t_0=initial Vicat setting time).

3.4. One-dimensional autogenous deformations

The unrestrained one-dimensional autogenous deformations (length changes) measured on the cement pastes with various W/C at T=20 °C are plotted vs. the age in Fig. 8, 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 at least six samples. Note that a good "repeatability" was recorded, since the standard deviation was of the order of magnitude of the accuracy of the device.

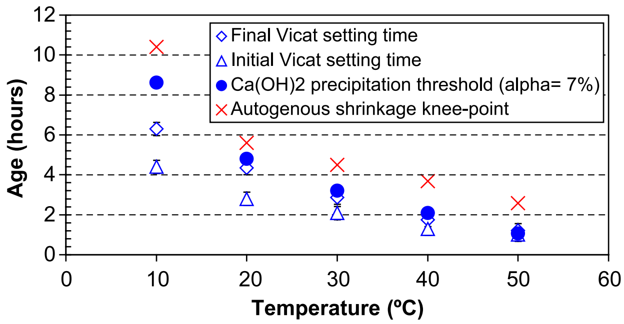
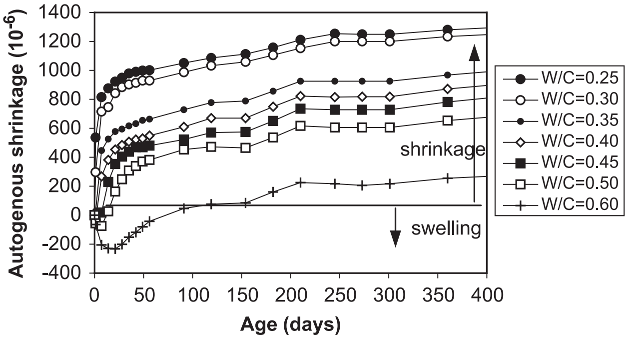
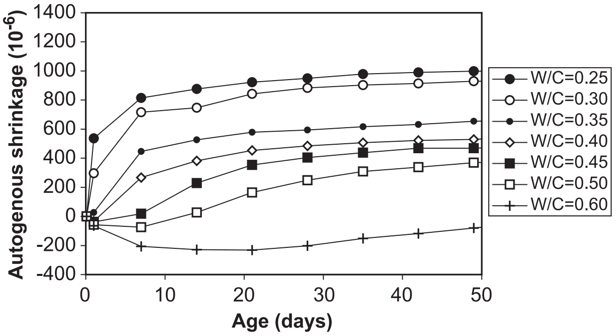


Fig. 7. Comparison between initial and final setting times obtained by means of Vicat needle, chemical threshold (precipitation of calcium hydroxide detected by TGA), and volumetric autogenous shrinkage knee-point, for cement pastes with W/C=0.25 and cured at various temperatures.



a) 0 - 400 days



b) Zoom: 0 - 50 days

Fig. 8. One-dimensional autogenous deformations vs. age, measured from initial Vicat setting time up to 1 year on ∅20×160-mm sealed samples of cement pastes with various W/C, at T=20 °C (zero point of the time scale: t_0=initial Vicat setting time).

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 (an increase of 1025 μm/m has been recorded on the "ultimate", i.e. 1-year, value, see Fig. 9). In the case of mixtures with low W/C, a great proportion of the long-term autogenous shrinkage value occurs before 24 h (e.g. 540 μm/m has been recorded at 24 h, from initial Vicat setting time, with W/C=0.25, which accounts for 42% of the "ultimate", i.e. 1-year, value), illustrating thereby the need of an initial measurement far earlier than 24 h for this type of materials. In the case of mixtures with medium or high W/C, swelling is exhibited from a few hours up to several days (−230 μm/m has been recorded at 21 days with W/C=0.60, see Fig. 8).

Various physical and chemical processes linked to cement hydration are involved in the unrestrained (isothermal) autogenous deformations measured on cement paste samples [2,9,8,11]. These deformations include in the general case three components: (total) chemical shrinkage, structural (chemical) swelling due to crystal growth, and self-desiccation shrinkage. The component which is prominent depends on the age at which the system is observed and on the mix-composition of the cement paste [8]. In the long term, another component may be added: the matrix creep under hygral stress [23]. The starting time of the period where self-desiccation shrinkage is prominent, the other components becoming negligible, can be assumed for each mixture to be the time when the relationship between autogenous shrinkage and internal relative humidity (RH) becomes linear, as experimentally exhibited for ordinary and high-performance cement pastes and concretes in Ref. [24]. Within this period, the correlation between W/C and autogenous deformations can thus be mainly explained by the 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 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. 10), which trend is consistent with the increasing shrinkage value measured at the same age (see Fig. 9). This interpretation is also in agreement with the work of Hua et al. [25], who modelled autogenous shrinkage, assumed as self-desiccation shrinkage, on the basis of MIP data.

The internal RH of the cement paste samples has been measured by RH-sensors on duplicates at the age of 1 year (360 days). Autogenous deformations are plotted vs. internal RH, at 360 days, in Fig. 11. The linear correlation observed confirms that the deformations recorded at this time are mainly the result of the self-desiccation process.

3.5. Drying shrinkage

It can also be deduced from Fig. 11 that the internal RH decreases as low as about 75% for the cement paste with W/C=0.25, after 1-year sealed curing. Therefore, the first RH step selected for the subsequent drying process at T=20 °C after 1-year curing in autogenous conditions was RH=71.5% (obtained by means of a saturated salt solution based on $SrCl_2$). Once the equilibrium state was reached at this RH, the hcp samples were submitted to RH=63% (NH_4NO_3 salt solution). The length changes registered when the hcp samples were submitted to RH=63%, from equilibrium state at RH=71.5%, are plotted vs. drying time

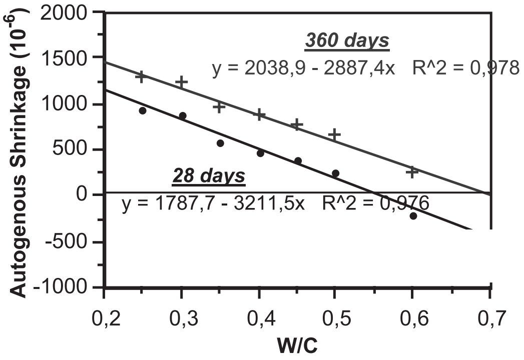
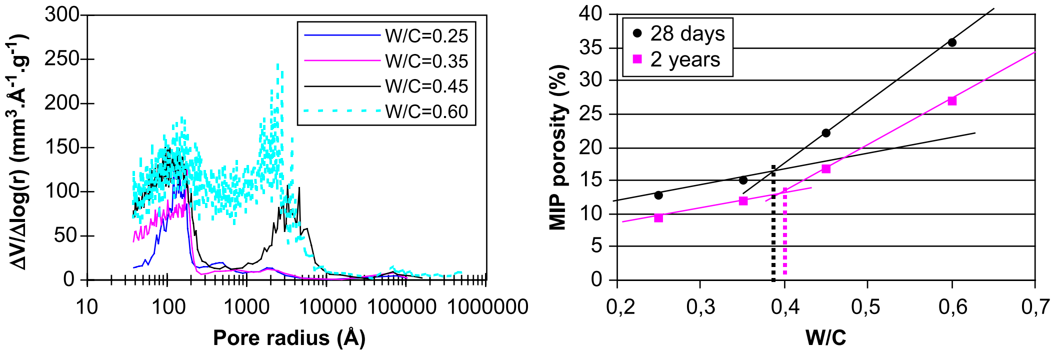


Fig. 9. Correlation between one-dimensional autogenous deformations measured at T=20 °C and W/C, at the ages of 28 and 360 days.



a) pore size distribution at 28 days

b) porosity vs. W/C

Fig. 10. Results obtained by MIP on hcp with various W/C, after curing at T=20 °C and freeze-drying.

in Fig. 12a. It can be seen that, contrary to autogenous deformations, the "ultimate" drying shrinkage value increases when W/C increases from 0.25 up to 0.60. More precisely, the relationship between the "ultimate" drying shrinkage values at RH=63% and W/C seems to be linear above and below a threshold value located at W/C=0.40 (see Fig. 12b).

4. Interpretation of the swelling observed on length changes with medium and high W/C

Autogenous swelling within the first days has also been reported in the literature by other authors, for cementitious materials with medium or high W/C (e.g. Refs. [6,10]). Nevertheless, until now any deep insight into its associated mechanism has not really been 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 specimens, unlike the swelling increase, which last several days (about 2 weeks, in the case of W/C=0.60).

Among the various components previously mentioned, the swelling, which appears here after setting may rather be attributed to the prominence of structural swelling, more precisely to the formation and the growth, through the hydration reactions of the cement, of large-size $Ca(OH)_2$ crystals (and also AFt needles, AFm crystals, etc.). During this period, swelling is prominent, although all the chemical reactions forming these products lead to a decrease in solid volume(s) and contribute to chemical shrinkage. Note that the manufacturing of expansive cements is based upon this principle (formation and growth of AFt needles). As the growth rate of platelet-like crystals is the slowest (compared to cubic or needle-like crystals), and according to the amount and the size of the products, the $Ca(OH)_2$ crystal growth is probably the main contributor to the "late" deformations registered here. Another argument supporting the major influence of $Ca(OH)_2$, as compared to that of AFt, is the low aluminate content of the cement tested here. The crystal growth 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 (with creation of porosity) [26,27], as long as a water film is present between the crystal and the pore wall (allowing an easy circulation of ions). Expansion is favoured at high W/C probably as a result of the greater compliance of those samples (lower stiffness), which allows them to expand more under a given crystallization pressure (see further). In mixtures with high W/C, large-size $Ca(OH)_2$ 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 (when a gas phase appears in the capillary pores). In porous areas, calcium hydroxide crystals can indeed become bigger than the initial clinker particles. Microstructural investigations of the hcp tested here provide arguments to support this explanation (see Fig. 13a). The amount and the mean size of $Ca(OH)_2$ crystals, measured by TGA and SEM-EDX analysis, respectively, and therefore the volume occupied by the calcium hydroxide crystals, increase both with hydration time (even after 28 days) and W/C. For example, at 28 days, the $Ca(OH)_2$ content was 18.2%, 24.6%, 30.6%,

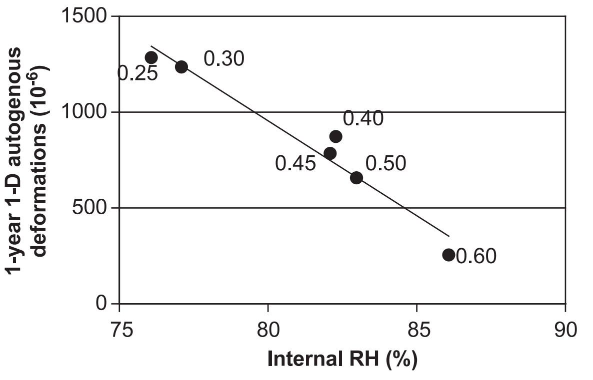
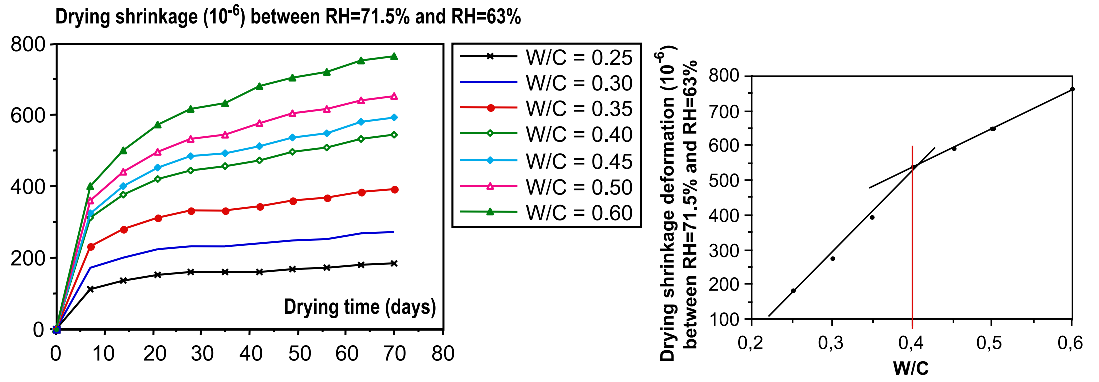


Fig. 11. Correlation between one-dimensional autogenous deformations and internal RH, for cement pastes with W/C ranging from 0.25 up to 0.60 and cured at T=20 °C, at the age of 360 days.



a) Kinetics b) "Ultimate" values at RH=63% vs. W/C

Fig. 12. Drying shrinkage (length changes) measured at T=20 °C on ∅20×160-mm hcp samples submitted to RH=63%, after 1-year curing in autogenous conditions and equilibrium at RH=71.5%.

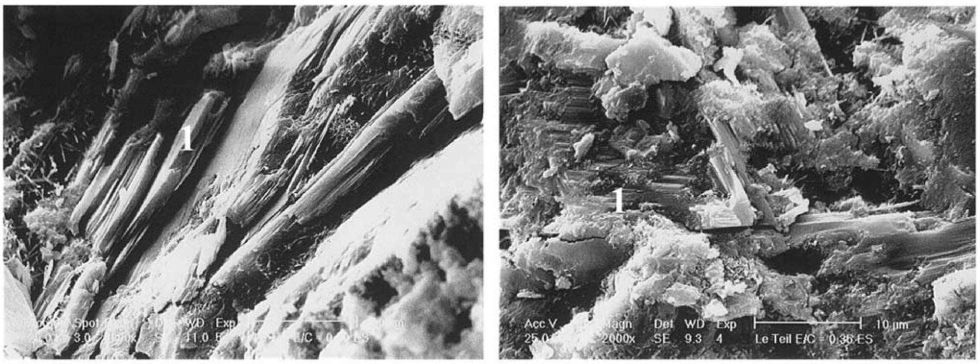
and 32.7%, and the mean size of the crystals was 4–10, 10–20, 10–30, and 80–100 μm, when W/C was respectively 0.25, 0.35, 0.45, and 0.60. Likewise, at 2 years, the $Ca(OH)_2$ content was 21.3%, 29.5%, 34.6%, and 38.6%, and the mean size of the crystals was 8–15, 10–30, 20–40, and 100–120 μm, when W/C was respectively 0.25, 0.35, 0.45, and 0.60. Therefore, even if on the one hand the increase in the $Ca(OH)_2$ amount is not very large when W/C increases from 0.45 up to 0.60, on the other hand the crystal size increases drastically. With low W/C, SEM observations showed that calcium hydroxide appeared mainly as small crystals spread out among the C–S–H phase (see Fig. 13b). Likewise, AFt could not be easily detected in the microstructure of hcp with W/C=0.25, whereas it appeared as well-crystallized needles in the case of W/C=0.45 and W/C=0.60. This last point 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, attributed here mainly to the growth of large-size $Ca(OH)_2$ crystals, proceeds for several days is also in agreement with the $Ca(OH)_2$ data reported by Bentz and Stutzman [28] and obtained by means of quantitative image analysis. The authors showed that the area occupied by "large" $Ca(OH)_2$ crystals (area>16 μm^2) increased with the age for at least 7 days, in a material with W/solid=0.45, as the hydration process goes on and as "large" crystals continue to grow up at the expense of smaller ones.

Furthermore, note that small $Ca(OH)_2$ crystals, invisible by SEM, could also be responsible for expansion.

Thus, the basic role of $Ca(OH)_2$, with respect to autogenous deformations, is pointed out again (see part I), but here as a (micro)structural effect.

Another mechanism [29,30] could also be suggested, in order to explain the swelling observed at medium and high W/C. This mechanism is based upon the formation of inner C–S–H rims (surrounding the residual unreacted cement cores), whose volume is higher than that of the portions of anhydrous grains they replace. These products do require water from outside the borderline of the cement grains for their formation (by topochemical reaction [31]). They are thus developing with a (local) increase in "solid" volume (contrary to outer C–S–H). Here, when W/C increases from 0.25 up to 0.60, the thickness of the C–S–H rims increases from 1 to 10 μm in the 28-day-old hcps. In particular, the thickness increases greatly above W/C=0.40. The volume of pseudomorphic (inner) C–S–H is therefore greater with high W/C cement pastes, and so would be the contribution of this



a) W/C = 0.60 b) W/C = 0.35

Fig. 13. SEM images (G=2000×) on newly broken surfaces of 28-day hardened cement pastes cured at T=20 °C. 1: $Ca(OH)_2$ crystals.

mechanism to swelling deformations. This is in accordance with the experimental deformation results, supporting thereby this mechanism along with the existence of a threshold located at W/C=0.40 with the cement used here.

For both mechanisms and according to the literature, significant stresses will be raised in the case of confinement, which occurs when the pore space is restricted (i.e. in small pores, in Hadley grains, or in the case of low W/C), if solid contacts are required (e.g. between the C–S–H rims). But that condition is not necessary if the stresses can be transmitted through the water phase, which always saturates the pore space of high W/C materials at least at early age. As regards the mechanism based on the crystal growth (crystallization pressure), significant stresses will be raised in the case of high supersaturation, which rather takes place in low W/C materials. Nevertheless, at early age, the low crystallization pressures that prevail in high W/C materials (as a result of low supersaturation) are able to generate a significant expansion of the microstructure and thus swelling deformations, owing to the low stiffness of the materials.

Finally, it can be concluded that the swelling observed is probably linked to the amount and the size of the various hydration products ($Ca(OH)_2$, inner C–S–H, AFt, etc.) likely to develop at early age in a concomitant way, in the complex cementitious system. Further investigations would be needed, in order to evaluate the actual contribution of each product. For example, tests performed on alite paste would allow to “eliminate” the contribution of aluminate phases (e.g. AFt). On the basis of the results obtained with the cement tested here, $Ca(OH)_2$ seems to be the main contributor.

5. Micro–macro analysis: existence of a W/C threshold value

In part I of the paper, it has been pointed out that the early-age (≤24 h) volumetric autogenous shrinkage of cement pastes with W/C=0.25 was linearly related to the degree of hydration (α) of the cement or to the $Ca(OH)_2$ content, from α=7% and whatever the temperature. In the present part II, it is possible to analyse further the role of these two parameters, in particular in the long-term range, and as a function of W/C. Fig. 14a and b show that one-dimensional autogenous deformations at T=20 °C, at a given age, are linearly related to the degree of hydration or to the $Ca(OH)_2$ content, respectively, but below and above a threshold, whose value is found again around W/C=0.40 (a deviation is observed at this point on the linear relationships).

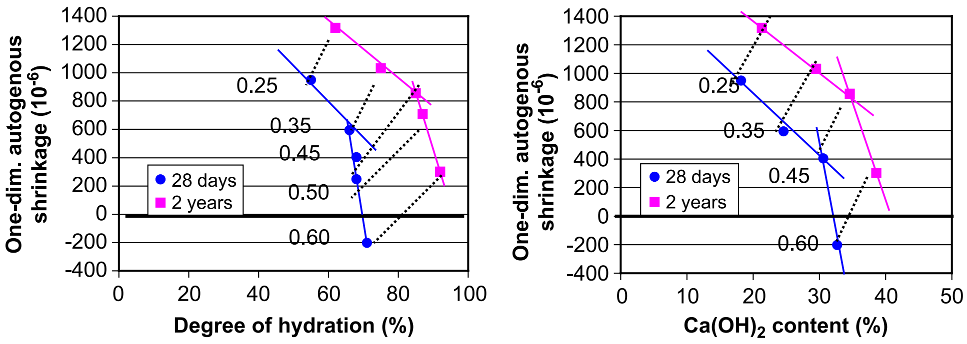
In addition, these results confirm the existence of a W/C threshold located at 0.40 for the cement tested here, at the macroscopic scale, with respect to one-dimensional autogenous deformations at T=20 °C. It has indeed previously seen that, when the reference of the length-change measurements was taken at initial Vicat setting time, for W/C≥0.40 swelling was exhibited at early age and continued for several days. Conversely, for W/C<0.40, shrinkage was recorded, whatever the age (see Fig. 8).

Likewise and as previously mentioned, the same threshold can be pointed out from the results presented in this paper and from those reported in the literature regarding the relative location of the knee-point of the volumetric autogenous shrinkage vs. age plot and the Vicat setting times [20].

Moreover, the same threshold is found (at W/C=0.40) with respect to drying shrinkage: a deviation is recorded on the linear relationship between “ultimate” drying shrinkage values (at RH=63%) at T=20 °C and W/C, as illustrated in Fig. 12b.

Furthermore, the same threshold has been reported as regards the various durability-related properties or processes (leaching, etc.). For example, a carbonation front has been observed after an accelerated carbonation test on the cement pastes tested here for W/C≥0.45, whereas no carbonation took place for W/C≤0.35 in the same experimental conditions [32]. Likewise, W/C=0.40 is widely recognized as a critical threshold, regarding the frost behaviour.

The same threshold value is obtained at the microscopic scale, confirming these findings and interpretation. For



a) b)

Fig. 14. Correlation between degree of hydration of the cement (a) or $Ca(OH)_2$ content (b) and one-dimensional autogenous deformations at a given age, for cement pastes with W/C ranging from 0.25 to 0.60 and cured at T=20 °C.

example, equivalent pore volumes are obtained by MIP, below and above 0.1 μm (two-mode pore size distribution), in the case of W/C=0.45 and W/C=0.60 at 28 days, whereas the major contribution to the MIP pore volume corresponds to pores with radius below 0.1 μm, in the case of W/C=0.25 and W/C=0.35 (single-mode distribution) (see Fig. 10a). Furthermore, the MIP porosity seems to increase to a greater extent from W/C=0.40 (see Fig. 10b).

Likewise, the amount, morphology, size, and distribution of the hydration products are very different above and below W/C=0.40, as described for $Ca(OH)_2$, AFt, and inner C–S–H in the previous section. In addition, the C/S mole ratio of the C–S–H rims, measured by BSE-SEM, becomes very low above W/C=0.40. As a matter of fact, when W/C is 0.25, 0.35, 0.45 and 0.60, the C/S mole ratio at 28 days is respectively 1.93, 1.86, 1.51 and 1.61, and the C/S mole ratio at 2 years is respectively 2.00, 1.75, 1.43 and 1.50 (see Fig. 2b). More precisely, the C/S mean value is 1.7 and C/S values are below 1.7 for W/C=0.45 and W/C=0.60, and above 1.7 for W/C=0.35 and W/C=0.25. According to the literature, this change in stoichiometry can be associated with a change in the silicate chain length [21,22,33,34]. A review of the literature shows that the 1.7 value found here is a quite usual mean value measured on C_3S pastes. Higher C/S values have been experimentally obtained here on pastes with low W/C. A low W/C means that hydration takes place in water-deficient conditions, that internal RH is lowered as a result of self-desiccation, and that dense C–S–H are produced. As a matter of fact, for W/C<0.40 and at the age of 2 years, the degree of hydration of the cement is below 80% (see Fig. 2a) and the internal RH is below 80% (see Fig. 11 and Ref. [24]). The higher C/S values measured in these conditions are in accordance with the literature. For example, somewhat higher C/S values than 1.7 have been measured on cement pastes [33,34]. More precisely, Richardson [34] reported that inner C–S–H generally had a higher mean C/S ratio than outer products. Likewise, Nonat found that high C/S (high lime concentration) corresponded to dense C–S–H (in very dilute solutions) [21,22]. Further, Jensen et al. [35] measured high C/S values (e.g. C/S=3, after 3 months at RH=83% and at T=40 °C) when studying hydration of C_3S and C_2S phases exposed to water vapour at RH<100%. Lower C/S values than 1.7 have been measured here in the case of high W/C, but such low values have seldom been reported until now in the literature. Nevertheless, these experimental results may be related to the observation made by Nonat (in very dilute solutions) [21,22]. The author showed that a discontinuity appears between the ranges [1.2−1.5] and [1.8−2], when the C/S of the C–S–H obtained by complete C_3S hydration is plotted vs. the lime concentration in solution. This discontinuity was attributed by the author to a change in the mode and kinetics of growth of the C–S–H, associated with a change in their structure and morphology. Similar changes may occur in cement pastes when W/C varies to a great extent.

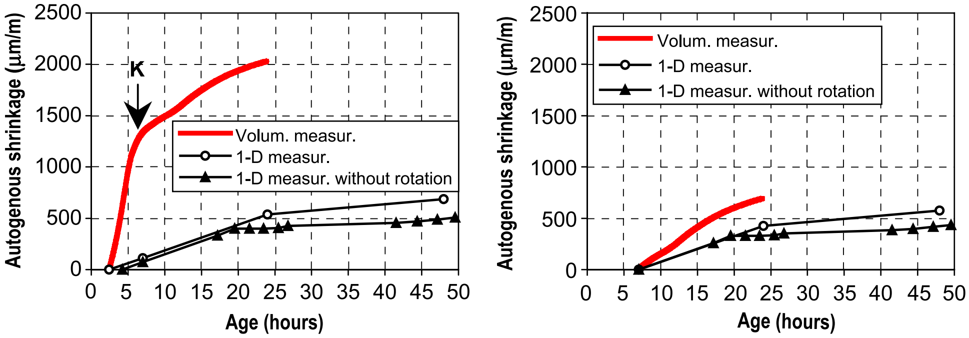
In addition, the threshold pointed out in this paper at about W/C=0.40 is quite consistent with the C–S–H model proposed by Jennings, where 50% of the products are low-density C–S–H and 50% are high-density C–S–H, for mature materials with W/C=0.40 [36].

Finally, the threshold value found in this paper at W/C=0.40 can be attributed to chemical and physical phenomena linked to the hydration process, and can be related to the initial amount of capillary water. This W/C value probably corresponds to the borderline between well-connected and weakly connected pore networks (i.e. percolation threshold of the capillary phase, according to the definition given by Bentz and Garboczi [37]). Below this threshold, the capillary phase connectivity drops drastically and self-desiccation appears in moisture-insulated systems at the ages considered. In these conditions, the hydration process is hindered by the lack of water or space, and the reaction rate is drastically reduced by the slow diffusion of the reactants through the C–S–H layers. Therefore, hydration cannot completely be achieved, even over the long term. This is in agreement with the literature (see for example Ref. [33]) and with the previously mentioned experimental results with respect to degree of hydration and internal RH.

6. Comparison between volumetric and one-dimensional autogenous shrinkage for W/C=0.25

A comparison between volumetric and one-dimensional autogenous shrinkage measurements has been performed at T=20 °C for the cement paste with W/C=0.25, after converting the volumetric deformations into corresponding 1-D deformations (assumed as 1/3 of the volumetric ones) in μm/m. The results are plotted in Fig. 15a when the reference is taken at about 2.4 h, which approximately corresponds to the initial Vicat setting time. A factor of about 4 is found between the two types of measurement at 24 h. The discrepancy is further increased when the samples used for one-dimensional measurement are not kept in rotation until setting (see Fig. 15a). When the reference (of the deformations) is taken at the knee-point observed on the volumetric autogenous shrinkage vs. age plot, the difference is drastically reduced (see Fig. 15b), suggesting a better agreement between both types of measurement after the "knee-point period" (see part I) and a fortiori after the setting period (see Fig. 7). This illustrates once again that the choice of the reference (t_0) for expressing deformation data is critical for a relevant comparison of experimental results. Nevertheless, this does not provide sufficient explanations to the discrepancy observed.

Such discrepancies have already been reported, despite the very few comparisons available in the literature. For example, Barcelo et al. [38] observed a large difference between the results obtained from volumetric measurements on paste samples continuously rotated, from horizontal (enabling measurement from casting), and from vertical



a)   b)

Fig. 15. Comparison between volumetric and one-dimensional autogenous shrinkage for the cement paste with W/C=0.25 and cured at T=20 °C: (a) reference (t_0) taken at the initial Vicat setting time, (b) reference (t_0) taken at the knee-point (K) indicated in (a).

one-dimensional tests (see also Ref. [39], where mortars with W/C=0.35 and W/C=0.45 were tested). In addition to artefacts such as bleeding water re-absorption and internal underpressure inside the latex membrane (this effect is enhanced if air bubbles are present at the sample surface), the authors suggested the possibility of an anisotropic behaviour of the material at early age. Note that Beltzung and Wittmann [40] observed different vertical and horizontal shrinkage magnitudes before the age of 3 h and similar ones thereafter, on cubic HPC samples with W/C=0.32. Furthermore, on the one hand, an influence of the immersion depth of the sample or of a weak water penetration through the latex membrane in volumetric measurements, and on the other hand, possible artefacts occurring between initial and final Vicat setting times in one-dimensional measurements, could also be suggested, as well as a possible contribution of creep in the measured deformations.

All of these results illustrate that autogenous deformations are often difficult to measure and that the results appear to depend on the apparatus/procedure used. This is particularly true for (very) early volume changes occurring through the setting process.

Nevertheless, the results presented in this paper provide useful indications as regards the selection of a relevant initial time (t_0), valuable for both volume- and length-change measurements. Of course t_0<24 h, unlike the conventional measurements, in order to take into account the significant proportion of autogenous shrinkage (and the associate cracking risk), which occurs before 24 h with some materials (low W/C). In addition, t_0>$t(K)$, where K is the volumetric autogenous shrinkage knee-point, since before $t(K)$, volumetric and 1-D measurements seem to quantify different processes.

7. Summary and concluding remarks

Experimental tools for assessing key-parameters have been presented in this paper. These tools can be used in view of designing and optimising mixtures, within the framework of the prediction of early-age deformations and of the prevention of early-age cracking. Nevertheless, as illustrated for example by the comparison between volumetric and one-dimensional autogenous shrinkage measurements, further investigations are still required with respect to both the techniques and the test procedures, before the two methods could be efficiently used in a complementary way.

Numerous experimental results have been 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 up to 0.60, and isothermally cured at various temperatures ranging from 10 up to 50 °C. These results constitute a data base useful for further researches and 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. This database could be completed in the near future by results obtained at higher temperatures and on concrete mixtures with the one-dimensional system.

In the following sections are summarized, first, the effects of W/C, and secondly, the determining role of calcium hydroxide.

7.1. W/C effects

- Both at early age and in the long term, the amount of $Ca(OH)_2$ produced at a given degree of hydration is not influenced by W/C within the range 0.25–40. Conversely, within the range 0.45–0.60, at a given degree of hydration, the $Ca(OH)_2$ amount seems to slightly increase as a function of W/C. In addition, the crystal size, and therefore the contribution to the swelling observed, greatly increases when W/C increases.
- W/C does not influence the rate and the magnitude of chemical shrinkage in a significant manner within the W/C range 0.30–0.60 and for curing temperature ranging from 10 up to 50 °C. However, W/C has a kinetic effect within the range 0.25–0.30. Moreover, whatever the W/

C, for $T \geq 30$ °C, the temperature has no more influence on the magnitude.

- At W/C=0.25, and for temperatures ranging from 10 up to 50 °C, the final Vicat setting time is sooner than the knee-point of the volumetric autogenous shrinkage vs. age 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 of the structural swelling (and in agreement with the microstructural characteristics of the materials). Conversely, the magnitude of "pure" drying shrinkage decreases when W/C decreases from 0.60 down to 0.25,
- A W/C threshold has been pointed out (located around 0.40, for the type of cement tested here: CEM I 52.5) at early age and in the long term, at the macro-level with respect to volumetric and one-dimensional autogenous deformations, as well as to drying shrinkage and durability-related properties. 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 and TGA, as well as to the MIP porosity and pore size distribution.

7.2. Chemical and (micro)structural effects of $Ca(OH)_2$

All the findings presented in this paper show the critical twofold effect of calcium hydroxide:

- chemical effect: the $Ca(OH)_2$ content of the cement paste plays the role of a chemical indicator of the hydration (and of the setting) process, and hence of autogenous deformations, similar to that of the degree of hydration of the cement,
- (micro)structural effect: this effect is generated by the formation and the growth of large-size $Ca(OH)_2$ crystals.

When the chemical effect (amount) is prominent, it has been found that autogenous shrinkage was linearly linked to the $Ca(OH)_2$ amount, as seen in part I on early-age volumetric autogenous shrinkage of cement pastes with W/C=0.25. When significant structural effects take place, swelling can become prominent, as observed in this part II on one-dimensional autogenous deformations of cement pastes with medium and high W/C, and deviations are registered on the linear relationships.

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