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# Predicting $\text{Ca}(\text{OH})_2$ content and chemical shrinkage of hydrating cement pastes using analytical approach

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A semiempirical model is proposed to predict the evolution of chemical shrinkage and  $\text{Ca}(\text{OH})_2$  content of cement paste at early age of hydration. The model is based on chemical equations and cement compound hydration rates. Chemical shrinkage and  $\text{Ca}(\text{OH})_2$  amount are computed using the stoichiometric results of the hydration reactions considered in the model and the density of hydration products and reactants. The model validation is conducted by comparison between computed and experimental results achieved on ordinary cement pastes with different water-to-cement (w/c) ratios (0.25, 0.30, 0.35 and 0.40) cured at 10, 20, 30, 40 and 50 °C, respectively. Hydration degree and  $\text{Ca}(\text{OH})_2$  content are determined using the thermogravimetric analysis (TGA) and chemical shrinkage evolution using a gravimetric method.

The comparison reveals a good consistency between modelled and experimental data at early age of hydration.

*Keywords:* Cement paste; Hydration;  $\text{Ca}(\text{OH})_2$ ; Chemical shrinkage; Modelling

## 1. Introduction

Concrete's early volumetric change is generally considered as the main driving mechanism leading to early age cracking and, consequently, to the loss of durability in concrete structures. Previous studies have shown that concrete with low water-to-cement (w/c) ratio (high performance concrete, for example) is sensitive to cracking at early age, from placing to a few hours after casting even when great care is taken to avoid evaporation [1,2]. For materials with a low water-to-binder ratio, autogenous shrinkage represents an important part of these early volumetric changes. A better understanding of the fundamental mechanisms leading to autogenous shrinkage in the perspective of limiting or preventing cement-based material cracking is then necessary.

The present paper comes within the scope of a larger study [3] conducted to examine the development of autogenous deformations of cement pastes in relation with the material chemical and microstructural evolutions. One of the

major achievements of this research is the demonstration of the importance of considering chemical deformation mechanisms at both microscopic (hydrates' scale) and macroscopic levels to propose a consistent and global understanding of the material behaviour.

The present paper focuses on the first 24 h of hydration, which correspond to a particularly difficult period to investigate, since the material undergoes important structural changes. It addresses the problem of chemical shrinkage evolutions, which are considered to be the driving mechanism of autogenous shrinkage. Cement paste  $\text{Ca}(\text{OH})_2$  content is also discussed.  $\text{Ca}(\text{OH})_2$  content is usually considered as a good indicator of the evolution of hydration reactions. It is interesting to observe and quantify how temperature and w/c ratio influence the correlation between  $\text{Ca}(\text{OH})_2$  and the hydration degree of cement. To improve our understanding of the microstructural and chemical developments of cement pastes at early age of hydration, a semiempirical predictive model based on both chemical equations and experimental data about cement compound hydration kinetics is proposed. Finally, a comparison between calculated values and experimental results achieved for chemical shrinkage (macroscale) evolution and  $\text{Ca}(\text{OH})_2$  content (microscale) is proposed.

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The modelling hypothesis and the calculation of the hydration degree, the chemical shrinkage and the  $\text{Ca}(\text{OH})_2$  content as a function of time are first presented. The hydration process is represented by a set of chemical equations describing the hydration of the main cement phases ( $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ ). The hydration kinetics of the phases, whose value has been fixed in a previous study [4], is applied to the cement tested here to determine a global hydration degree. The chemical shrinkage and the  $\text{Ca}(\text{OH})_2$  content are computed using chemical equations, modelled hydration reaction stoichiometry and product and reactant density.

Then, the experimental results on hydration degree, chemical shrinkage and  $\text{Ca}(\text{OH})_2$  content evolutions for different cement pastes cured at different temperatures are described. Both the hydration degree and the  $\text{Ca}(\text{OH})_2$  amount are investigated using thermogravimetric analysis (TGA). The hydration degree is calculated as the ratio between the nonevaporable water amount at time  $t$  and the water necessary to reach complete cement hydration. Chemical shrinkage measurements are carried out using a gravimetric method, which allows for the continuous and automatic follow up of the chemical deformations [5–8].

Finally, experimental and simulated results are compared and discussed.

## 2. Modelling approach

### 2.1. Modelling principle

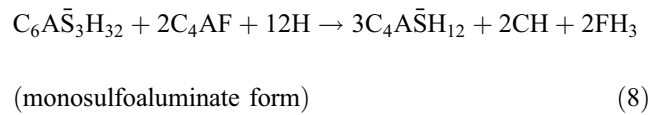
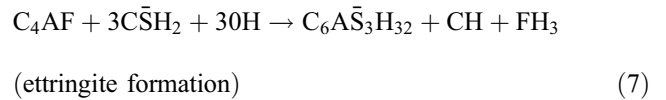
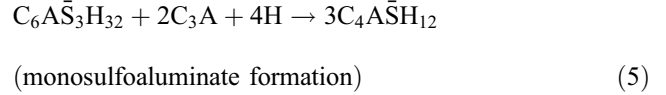
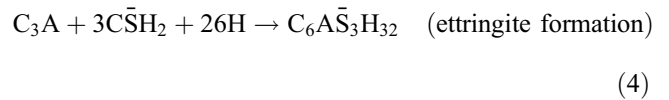
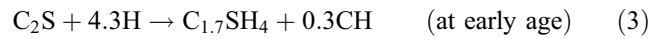
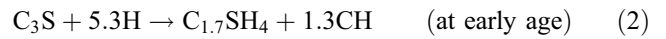
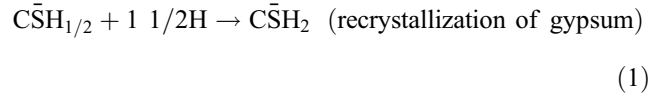
Several researchers were interested in modelling analytically the evolution of cement hydration. In 1979, Pommerheim and Clifton [9] reviewed some of these models. Studies by Powers and Brownyard [10], Knudsen [11] and, more recently, Tennis and Jennings [12] can be mentioned. The modelling presented here is of the semiempirical type. It consists in symbolizing cement hydration processes using a chemical equations set. From the equation stoichiometry and knowing the density of each reactant and product, computing the chemical shrinkage ( $\Delta V$ ) and the  $\text{Ca}(\text{OH})_2$  amount (CH) produced by the hydration reactions is possible.

To determine the evolution of both parameters as a function of time and cement hydration degree, it is necessary to know the hydration kinetics of all cement compounds. This information, however, appears in previous experimental studies [4,13]. Lea's experimental data are chosen here because of two reasons. First, they are based on the study of Portland cement hydration, and not on individual clinker phases, whose hydration is known for its different evolution depending on whether it is present in cement or in pure phase. The second advantage of Lea's results is that they apply to a relatively long period, which extends from the very early age of hydration (0.1 h) to 1 month of hydration. The hydration rate of cement is signif-

icantly influenced by its particle-size distribution (PSD) [11,14]. As individual hydration rate is considered for each clinker phases, it remains difficult to take account of cement PSD in the modelling. The next improvement of the present model should include the effects of this parameter.

### 2.2. Reaction equation set

The hydration of Portland cement is represented by a set of chemical equations, each of them defining the basic reactions of the different clinker phases. In presence of gypsum in the mixture, the following set of equations is generally proposed [15–19]:



Eq. (1) corresponds to the recrystallization of hemihydrate into gypsum. Beltzung and Wittmann [20] show that this reaction takes place within the first minutes following the cement/water contact.

The hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  produces a nanoporous, amorphous calcium silicate hydrate (C-S-H) gel (Eqs. (2) and (3)), which develops on the surfaces of the original  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  and on previously produced C-S-H. At early age of hydration and according to previous research works, the composition of this gel is considered as  $\text{C}_{1.7}\text{SH}_4$  [21]. The calcium hydroxide (CH) crystals nucleate and grow in the

available capillary pore space. As time passes, silicate chains polymerize [22], but since the present work is limited to early age processes, the C-S-H polymerization is beyond the scope of the study.

The primary initial reaction of C<sub>3</sub>A follows Eq. (4). If the sulfate (provided by the gypsum) is fully consumed before the C<sub>3</sub>A has completely hydrated, ettringite changes to monosulfoaluminate, as shown in Eq. (5). When all the ettringite has been transformed, the remaining C<sub>3</sub>A reacts as shown in Eq. (6). The reactions for C<sub>4</sub>AF are similar (Eqs. (7)–(9)), save for CH, which is formed because of the higher Ca/Al molar ratio of the initial C<sub>4</sub>AF. Moreover, among Portland cements, C<sub>4</sub>AF usually reacts at a slower rate than C<sub>3</sub>A.

All these reactions are characterized by a difference between the product and reactant volumes. The values of this chemical deformation are calculated using the density of each element (Table 1) and hydration reaction stoichiometry and presented in Table 2. The Ca(OH)<sub>2</sub> amounts produced by all the chemical reactions involved are also displayed in this table.

### 2.3. Computation of cement hydration degree, chemical shrinkage and Ca(OH)<sub>2</sub> content of cement paste

The computation of the evolution in time of both chemical shrinkage and Ca(OH)<sub>2</sub> content in cement paste requires to know the cement component hydration rate. The hydration rates of each compound, obtained from Lea's results, are shown in Table 3. It should be noticed that the author does not give the initial water-to-binder ratio of the cement paste he investigated.

From these data, the evolution of the chemical shrinkage  $\Delta V(t)$  (in mm<sup>3</sup>/g of cement) can be expressed as:

$$\begin{aligned} \Delta V(t) = & \Delta V_{Gy} \cdot M_{Gy} + \Delta V_{C_3S} \cdot M_{C_3S}(t) + \Delta V_{C_2S} \cdot M_{C_2S}(t) \\ & + \Delta V_{C_3A} \cdot M_{C_3A}(t) + \Delta V_{C_4AF} \cdot M_{C_4AF}(t) + \Delta V_{Et} \cdot M_{Et}(t) \end{aligned} \quad (10)$$

where  $\Delta V_{Gy}$ ,  $\Delta V_{C_3S}$ ,  $\Delta V_{C_2S}$ ,  $\Delta V_{C_3A}$ ,  $\Delta V_{C_4AF}$ ,  $\Delta V_{Et}$  are the chemical shrinkage (in mm<sup>3</sup>/g) produced by the hydration

Table 1  
Densities of cement compounds and hydration products used for chemical shrinkage computations

Initial cement compounds			Hydration products		
Compound	Density (g/cm <sup>3</sup> )	Reference	Compound	Density (g/cm <sup>3</sup> )	Reference
C <sub>3</sub> S	3.15	[15]	C <sub>1.7</sub> SH <sub>4</sub>	2.01	[21]
C <sub>2</sub> S	3.28	[15]	CH	2.24	[15]
C <sub>3</sub> A	3.03	[15]	C <sub>6</sub> A $\bar{S}$ <sub>3</sub> H <sub>32</sub>	1.78	[15]
zC <sub>4</sub> AF	3.73	[15]	C <sub>4</sub> A $\bar{S}$ H <sub>12</sub>	2.02	[15]
C $\bar{S}$ H <sub>2</sub>	2.32	[15]	C <sub>3</sub> AH <sub>6</sub>	2.52	[15]
C $\bar{S}$ H <sub>1/2</sub>	2.74	[15]	FH <sub>3</sub>	2.20	[19]

Table 2  
Chemical shrinkage and Ca(OH)<sub>2</sub> amount produced by the modelling hydration reactions

Equations	Chemical shrinkage ( $\Delta V$ )	Ca(OH) <sub>2</sub> content (CH)
	Per g of hydrating compound	Per g of hydrating compound
(1)	40.2 mm <sup>3</sup> /g of gypsum	–
(2)	54.5 mm <sup>3</sup> /g of C <sub>3</sub> S	0.4219 g/g of C <sub>3</sub> S
(3)	195.8 mm <sup>3</sup> /g of C <sub>2</sub> S	0.1291 g/g of C <sub>2</sub> S
(4)	284.6 mm <sup>3</sup> /g of C <sub>3</sub> A	–
(5)	26.2 mm <sup>3</sup> /g of ettringite	–
(6)	178.5 mm <sup>3</sup> /g of remaining C <sub>3</sub> A	–
(7)	105.4 mm <sup>3</sup> /g of C <sub>4</sub> AF	0.1525 g/g of C <sub>4</sub> AF
(8)	–19.0 mm <sup>3</sup> /g of ettringite	0.1181 g/g of ettringite
(9)	46.5 mm <sup>3</sup> /g of remaining C <sub>4</sub> AF	0.1525 g/g of C <sub>4</sub> AF

of 1 g of C $\bar{S}$ H<sub>2</sub>, C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF and C<sub>6</sub>A $\bar{S}$ <sub>3</sub>H<sub>32</sub>, respectively, and  $M_{Gy}$ ,  $M_{C_3S}$ ,  $M_{C_2S}$ ,  $M_{C_3A}$ ,  $M_{C_4AF}$ ,  $M_{Et}$  are the proportions (in g/g of cement) of C $\bar{S}$ H<sub>2</sub>, C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF and C<sub>6</sub>A $\bar{S}$ <sub>3</sub>H<sub>32</sub> hydrated at time  $t$ , respectively. These proportions are calculated by multiplying the hydration degree of each phase at time  $t$  by its initial proportion in anhydrous cement. For example:

$$M_{C_3S}(t) = \alpha_{C_3S}(t) \cdot [\% \text{ of } C_3S] \quad (11)$$

where  $\alpha_{C_3S}(t)$  is the hydration degree of C<sub>3</sub>S at time  $t$  and [% of C<sub>3</sub>S] is the initial mass proportion of C<sub>3</sub>S in anhydrous cement calculated from Bogue's formulae [23].

Table 3  
Hydration rate of ordinary Portland cement paste initial compounds at ambient temperature (after Lea [4])

Age (h)	Cement compounds			
	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
	Hydration degree (%)	Hydration degree (%)	Hydration degree (%)	Hydration degree (%)
0.01	0.0	0.0	0.0	0.0
0.1	0.0	0.0	11.3	9.0
0.5	0.0	0.0	11.3	9.0
1	0.0	0.0	11.3	9.0
2	1.4	0.0	11.3	9.0
3	3.3	0.0	11.3	9.0
4	5.7	0.0	12.4	9.0
6	14.2	0.0	13.1	9.0
8	15.8	0.0	13.6	9.5
16	25.0	0.0	15.8	9.5
20	32.8	0.0	24.8	9.5
24	33.7	0.0	26.3	10.4
27	40.0	3.8	28.5	11.3
48	43.0	8.6	35.4	13.6
64	44.5	10.4	38.0	19.8
158	47.0	14.0	42.0	19.8
311	48.4	21.1	47.7	19.8
615	50.2	26.3	57.4	19.8
1000	50.8	29.4	60	19.8

Similarly, the evolution of the  $\text{Ca}(\text{OH})_2$  content as a function of time can be calculated:

$$\begin{aligned} \text{CH}(t) = & \text{CH}_{\text{Gy}} \cdot M_{\text{Gy}} + \text{CH}_{\text{C}_3\text{S}} \cdot M_{\text{C}_3\text{S}}(t) + \text{CH}_{\text{C}_2\text{S}} \cdot M_{\text{C}_2\text{S}}(t) \\ & + \text{CH}_{\text{C}_4\text{AF}} \cdot M_{\text{C}_4\text{AF}}(t) + \text{CH}_{\text{Et}} \cdot M_{\text{Et}}(t) \end{aligned} \quad (12)$$

where  $\text{CH}_{\text{Gy}}$ ,  $\text{CH}_{\text{C}_3\text{S}}$ ,  $\text{CH}_{\text{C}_2\text{S}}$ ,  $\text{CH}_{\text{C}_3\text{A}}$ ,  $\text{CH}_{\text{C}_4\text{AF}}$ ,  $\text{CH}_{\text{Et}}$  are the  $\text{Ca}(\text{OH})_2$  amount (in g/g of compound) produced by the hydration of 1 g of  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$  and  $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ , respectively.

To express the evolution of both chemical shrinkage and  $\text{Ca}(\text{OH})_2$  as a function of the hydration degree, the hydration degree  $\alpha(t)$  of cement has been calculated from the hydration degree of its compounds, using the following equation:

$$\begin{aligned} \alpha(t) = & \alpha_{\text{C}_3\text{S}}(t) \cdot [\% \text{ of } \text{C}_3\text{S}] + \alpha_{\text{C}_2\text{S}}(t) \cdot [\% \text{ of } \text{C}_2\text{S}] \\ & + \alpha_{\text{C}_3\text{A}}(t) \cdot [\% \text{ of } \text{C}_3\text{A}] + \alpha_{\text{C}_4\text{AF}}(t) \cdot [\% \text{ of } \text{C}_4\text{AF}] \end{aligned} \quad (13)$$

where  $\alpha_{\text{C}_3\text{S}}(t)$ ,  $\alpha_{\text{C}_2\text{S}}(t)$ ,  $\alpha_{\text{C}_3\text{A}}(t)$  and  $\alpha_{\text{C}_4\text{AF}}(t)$  are the hydration degree of  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  at time  $t$ , respectively, and  $[\% \text{ of } \text{C}_3\text{S}]$ ,  $[\% \text{ of } \text{C}_2\text{S}]$ ,  $[\% \text{ of } \text{C}_3\text{A}]$  and  $[\% \text{ of } \text{C}_4\text{AF}]$  are the initial mass proportion of  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  in anhydrous cement (determined using Bogue's formulae [23]), respectively.

Therefore, by making use of Eqs. (10), (12) and (13), it is possible to represent graphically the evolution of both chemical shrinkage and  $\text{Ca}(\text{OH})_2$  content as a function of cement hydration degree (see Figs. 7–9).

### 3. Experimental study

In the experimental part of the present research, chemical shrinkage, nonevaporable water content and  $\text{Ca}(\text{OH})_2$  amount have been measured on different cement pastes.

The cement used is type I (CPA CEM I 52.5 HTS PM ES CP 2), its chemical composition is detailed in Table 4. Fig. 1 presents its particle-size distribution obtained by means of laser granulometry (the dispersion liquid used during the test is ethanol).

Cement pastes are prepared by mixing cement and distilled water together in a 5-l laboratory mixer during 3 min to ensure good homogeneity.

Four w/c ratios are investigated (0.25, 0.30, 0.35, 0.40). The influence of curing temperature is also examined through five different imposed curing temperatures (10, 20, 30, 40 and 50 °C). To reach the equilibrium of the cement pastes at the required curing temperature rapidly, the mixing water is heated or cooled depending on the case.

#### 3.1. Chemical shrinkage measurements

Justnes et al. [24] distinguish three main methods to measure chemical shrinkage (gravimetry, dilatometry and

Table 4  
Chemical composition of the cement used

CPA CEM I 52.5 HTS PM ES CP2 Blaine specific surface: 3320 cm <sup>2</sup> /g	
Composition	% (mass)
CaO	66.39
SiO <sub>2</sub>	21.17
Al <sub>2</sub> O <sub>3</sub>	2.69
Fe <sub>2</sub> O <sub>3</sub>	1.96
MgO	0.65
SO <sub>3</sub>	2.43
NaO <sub>2</sub>	0.30
K <sub>2</sub> O	0.22
Loss on ignition	2.26
Insoluble residue	0.96
Equivalent alkali content	0.44
Free lime	0.84
Bogue's cement composition	
Cement phases	% (mass)
C <sub>3</sub> S	70.15
C <sub>2</sub> S	7.77
C <sub>3</sub> A	3.81
C <sub>4</sub> AF	5.95
Gypsum	5.22

pycnometry). In this study, chemical shrinkage measurements are carried out using a gravimetric method, which is quite similar to the one developed and used by Geiker and Knudsen [5–7] and Boivin et al. [8]. Immediately after mixing, a 30-g cement paste sample is introduced into a 50-ml flask. This sample mass has been calculated to obtain a sample thickness of about 7.0 mm. Indeed, the sample thickness is an important experimental parameter since if it is too high, the exterior water may not fully permeate into internal voids when they are being formed [16]. Boivin et al. [8] have shown that, for cement paste with a low w/c ratio, this scale effect was not significant for sample thickness inferior to 10 mm during the first 24 h of hydration. Entrapped air bubbles are flushed out with a 1-min vibration sequence. The remaining empty volume of the flask is filled with distilled and desaturated water, poured gently enough to avoid sample perturbation. The contact area between the top of the sample and the exterior water is about 20 cm<sup>2</sup>. The flask is then closed. A small orifice in the flask cap allows for a continuous water supply. The flask is hung on a balance (accuracy ±0.0001 g) by a nylon thread and immersed in distilled water at the required curing temperature (±0.1 °C) (see Fig. 2). The measurement series starts 10 min after initial water–cement contact and lasts 24 h.

From the recordings of the apparent mass of the flask, the amount of water penetrating into the paste and filling the porosities, generated by Le Chatelier's contraction, can be determined. Therefore, we obtain:

$$\Delta V_{\text{exp}}(t, T) = \frac{[M_s(t) - M_s(t_i)]}{M_c \cdot \rho_w(T)} \quad (14)$$

where  $\Delta V_{\text{exp}}(t, T)$  is the chemical shrinkage of the cement paste (mm<sup>3</sup>/g of initial anhydrous cement),  $M_s(t)$  is the

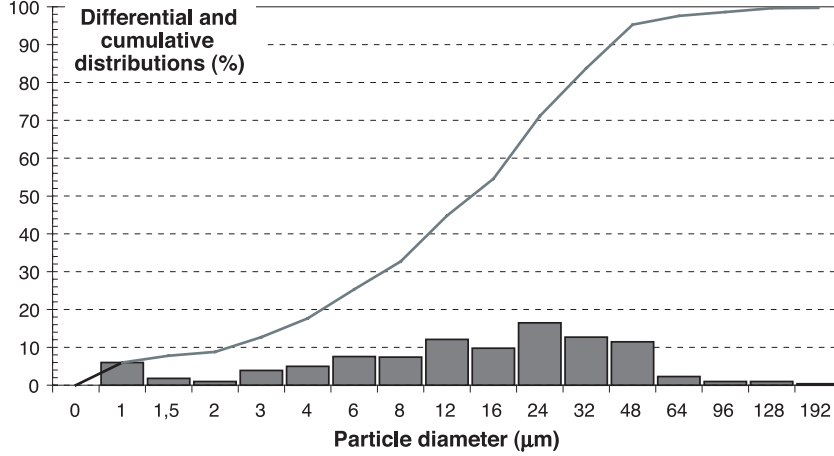


Fig. 1. Particle-size distribution of the cement used.

apparent mass of both flask and sample recorded by the balance at time  $t$  (g),  $M_s(t_i)$  is the apparent mass of both flask and sample at initial time  $t_i$  (g),  $\rho_w(T)$  is the water density ( $\text{g}/\text{mm}^3$ ),  $T$  is the water bath temperature ( $^\circ\text{C}$ ) and  $M_c$  is the initial anhydrous cement mass of the sample (g).

### 3.2. Nonevaporable water and $\text{Ca}(\text{OH})_2$ contents

TGA is used to determine the evolution of the non-evaporable water content  $W_n(t)$  and the  $\text{Ca}(\text{OH})_2$  content in cement pastes during hydration. This indirect method is commonly used to quantify the hydration degree of cement. Parrott et al. [25] have studied the applicability of non-evaporable water amount as a measure for degree of hydration on cement paste samples ( $w/c=0.71$ ) cured at  $20^\circ\text{C}$ . They found a closely but not completely linear correlation between direct measurements (achieved by means of quantitative X-ray diffraction analysis) and nonevaporable water measurement. Moreover, they observed that this correlation depended on the cement chemical composition. In spite of this limitation and considering only one cement composition in the present work, we assume, in agreement with previous studies [26–30], for example, a linear correlation between the amount of nonevaporable water and the hydration degree of cement pastes.

TGA tests are conducted on 30- to 60-mg cement paste samples sealed and kept in a thermostatic bath until measurements start. No special treatment (crushing or drying) is applied to the specimens before testing since the measurement is carried out immediately after the sampling. Moreover, Baroghel-Bouny [27] has shown that the drying stage temperature had a significant effect on the dehydration temperature of C-S-H. The thermal analysis is performed between 20 and  $1100^\circ\text{C}$ , in an  $\text{N}_2$  atmosphere (1 bar). The heating rate is  $10^\circ\text{C}/\text{min}$  and a platinum crucible is used to keep the specimens. All differential thermal (DT) curves, TG curves, mass losses and temperature peaks are calculated using the thermal analysis apparatus software. “Blank tests” (without specimens) show that a fictitious mass gain ( $0.001 \text{ mg}/^\circ\text{C}$ ) is recorded by the apparatus during heating. The final results presented below take the correction of this artificial datum into account.

From the knowledge of the nonevaporable water content, it is possible to compute the hydration degree of the sample  $\alpha_{\text{TGA}}(t)$ , using the following equation:

$$\alpha_{\text{TGA}}(t) = \frac{W_n(t)}{[M_c \cdot W_n(\infty)]} \quad (15)$$

$W_n(\infty)$ , the nonevaporable water mass (g/g of cement) at  $t \rightarrow \infty$  corresponding to full hydration of 1 g of cement, is

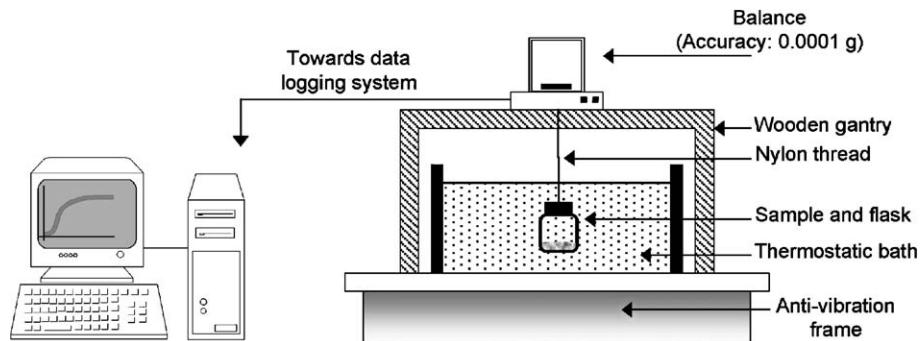
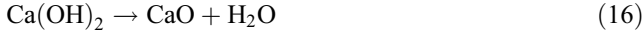


Fig. 2. Schematic diagram of the test device used for chemical shrinkage measurements.

estimated from the mineralogical composition of cement (Bogue's formulae and Czernin's [31] results):  $W_n(\infty)=0.2293$  g.  $W_n(t)$ , the nonevaporable water mass (g) at time  $t$ , is defined here as the mass loss recorded between 145 and 1050 °C in agreement with Ref. [32], minus the mass loss due to CO<sub>2</sub> releases produced by the calcite decomposition between 600 and 800 °C.  $M_c$  is the initial anhydrous cement mass of the sample (g).

According to El-Jazairi and Illston [33], the deshydroxylation of Ca(OH)<sub>2</sub> takes place between 400 and 600 °C such as:



Then, the following equation is used to determine the calcium hydroxide content  $\text{CH}_{\text{exp}}(t)$  (g/g of anhydrous cement) of the hydrating cement pastes:

$$\text{CH}_{\text{exp}}(t) = \frac{74.09}{18.01} \cdot \frac{M_s^{400\text{ }^\circ\text{C}}(t) - M_s^{600\text{ }^\circ\text{C}}(t)}{M_c} \quad (17)$$

where  $M_s^{400\text{ }^\circ\text{C}}(t)$  and  $M_s^{600\text{ }^\circ\text{C}}(t)$  are the sample masses (g) recorded during the TGA tests at  $T=400\text{ }^\circ\text{C}$  and  $T=600\text{ }^\circ\text{C}$  at hydration time  $t$ , respectively and  $M_c$  the initial anhydrous cement mass of the sample (g). The ratio (74.09/18.01) corresponds to the molar mass ratio of Ca(OH)<sub>2</sub> and H<sub>2</sub>O.

## 4. Results and discussion

### 4.1. Experimental results

#### 4.1.1. Influence of temperature and w/c ratio on hydration degree evolution

Hydration kinetics is known to increase with increasing w/c [34,35] and increasing temperature (e.g., Refs. [26,36]).

The cement paste hydration degree values (achieved with TGA tests) vs. age (from 0 to 24 h) are plotted in Fig. 3.

Considering Fig. 3, as far as w/c ratio is concerned and within the w/c ratio range investigated here, the influence of this parameter on the hydration rate is limited during the first 24 h of hydration: at a 10-°C curing temperature, the hydration level reached at 24 h of hydration is the same for all the w/c ratios investigated. With the highest curing temperatures, the hydration kinetics followed by the cement pastes with w/c=0.30, 0.35 and 0.40, respectively, are also very close.

The hydration kinetics of the cement paste with a w/c of 0.25 is remarkable. During the first hydration hours, the curve follows the same rise than the other cement pastes. But after approximately 10 h of hydration, it clearly slows down to finally plateaus at a lower hydration level than the other cement pastes at 24 h. This slowing down of the hydration reactions can be explained by a twofold effect of w/c ratio at early and very early ages of cement paste: during the first period of hydration (between mixing and induction period), the lower is the w/c ratio, the faster is reached the saturation degree of hydrates; therefore, in the first moment of hydration, the cement hydration degree in cement paste with w/c ratio=0.25 is superior to the cement hydration degree in cement paste with w/c ratio  $\geq 0.30$ . As hydration process goes on, water is progressively chemically and physically bound to hydrate and the hydration rate is enhanced in the cement pastes with (relatively) higher w/c ratio.

This hydration rate decrease related to a low w/c ratio is not observed at 10 °C. This can be explained by the low cement hydration level reached at this curing temperature at 24 h of hydration. Indeed, considering Fig. 4, the 20-°C hydration curve of the cement paste with a w/c ratio of 0.25 begins to curve at about 20% of hydration, a value, which is

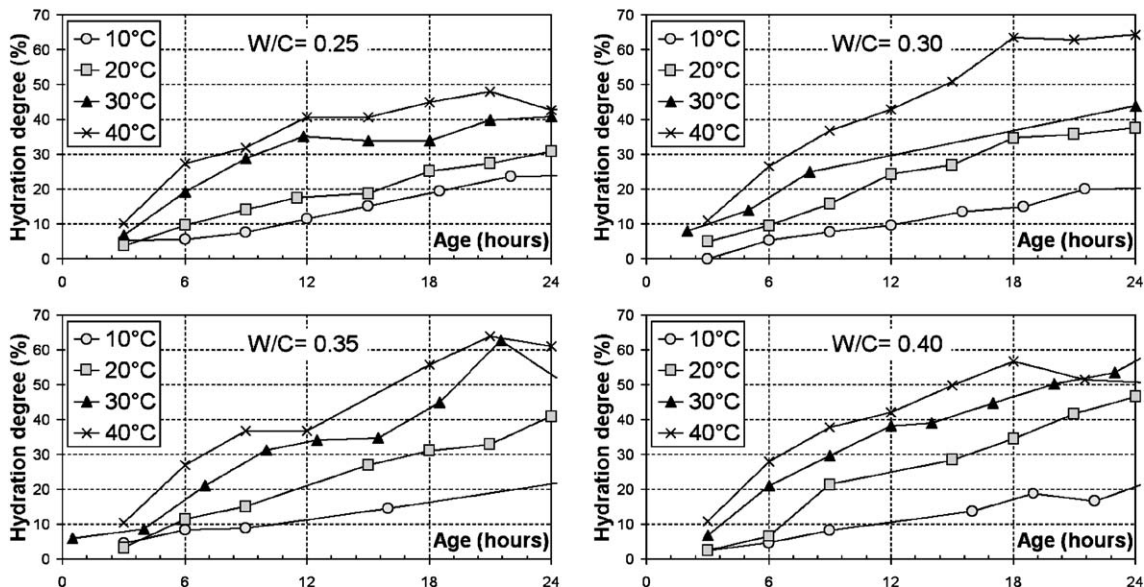


Fig. 3. Evolution of hydration degree vs. the age of different w/c ratio-cement pastes (w/c=0.25, 0.30, 0.35, 0.40) cured at 10, 20, 30 and 40 °C.

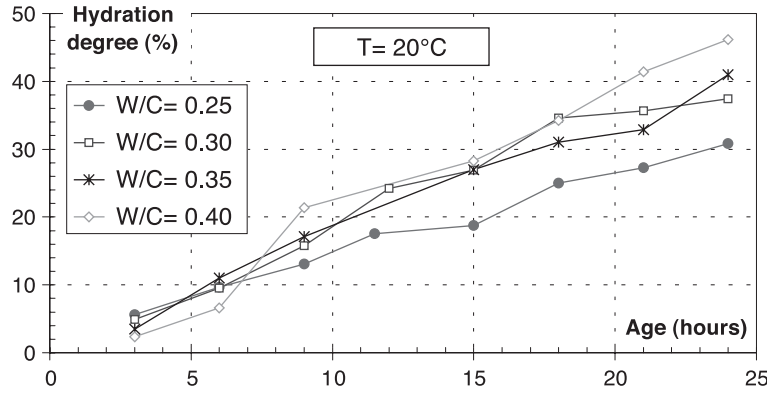


Fig. 4. Comparison of the hydration degree evolutions of different cement pastes cured at 20 °C as a function of hydration time achieved with TGA tests.

close to the cement hydration level reached at 10 °C at the end of the investigation period.

According to Fig. 3, the cement hydration rate increases with increasing temperature. For all the cement pastes studied here, the influence of the temperature on the hydration rate is significant from the first hours of hydration, which is in good agreement with the results of previous research works [36] and can be attributed to the thermoactivated characteristics of the cement hydration process.

The increase in the hydration rate is relatively significant (for example, with  $w/c=0.35$ , the hydration degree reached at 24 h of hydration is multiplied by a factor 1.5 between 20 and 40 °C and by a factor 3 between 10 and 40 °C) particularly within the first hours of cement hydration: the hydration degree reached at 5 h of hydration, indeed, is multiplied by a factor of about 4 between 10 and 40 °C for all the cement pastes studied.

#### 4.1.2. Influence of both temperature and w/c ratio on chemical shrinkage evolution

The chemical shrinkage of the cement pastes with  $w/c=0.25, 0.30, 0.35$  and  $0.40$ , respectively and cured at 10, 20, 30, 40 and 50 °C is plotted vs. the hydration time in Fig. 5 from 1 to 24 h of hydration. Each curve is obtained from two measurement mean values.

Regarding the role of w/c ratios in the chemical shrinkage evolution, this parameter does not seem to have a significant influence on the total chemical deformation rate during the first 24 h of hydration. These experimental results agree with previous works: the value of the chemical shrinkage at 24 h shows little and unsystematic variations with different w/c ratios [8,37].

As far as the curing temperature is concerned, the experimental results clearly show the dual action of the temperature on the chemical shrinkage rate [38]. The first effect is an increase in the initial curve slope with temper-

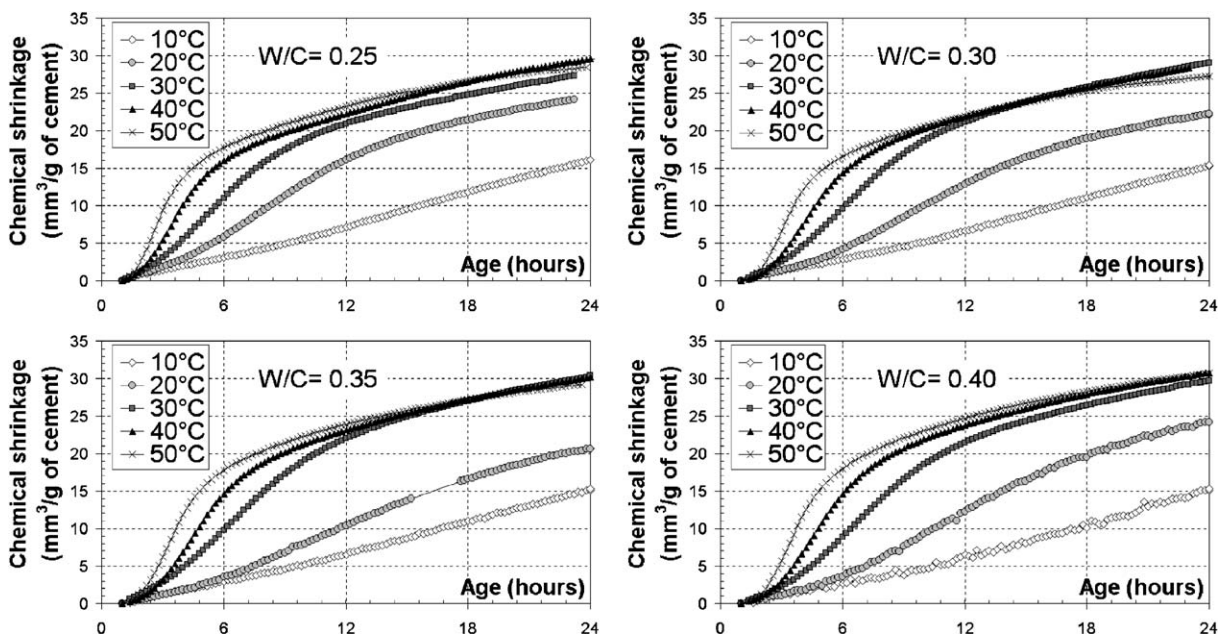


Fig. 5. Evolution of chemical shrinkage vs. the age of different w/c ratio-cement pastes ( $w/c=0.25, 0.30, 0.35, 0.40$ ) cured at 10, 20, 30, 40 and 50 °C.



ature, which can be explained by the acceleration of the hydration reactions (thermoactivated effect), previously observed on hydration degree evolution (see Fig. 3). The second effect affects the ultimate value. It is particularly significant at 40 °C for w/c=0.30, but only from T=50 °C for w/c=0.25, which means that the influence is felt at lower temperatures when w/c increases. The reason for this probably lies in the structural changes of hydration products and, therefore, in the microstructure of cement pastes cured at relatively high temperature [39].

#### 4.1.3. Influence of both temperature and w/c ratio on Ca(OH)<sub>2</sub> amount

Ca(OH)<sub>2</sub> is the crystallized phase of cement paste. In a completely hydrated cement paste, it usually represents 20–30% of the material, depending on the cement composition. The Ca(OH)<sub>2</sub> content of the cement pastes investigated is plotted in Fig. 6 as a function of hydration time. The results show that both curing temperature and w/c ratio affect the evolution of the Ca(OH)<sub>2</sub> amount. The observations previously made on the hydration rate also apply to Ca(OH)<sub>2</sub> formation rate. For a given w/c ratio, the temperature strongly accelerates the formation of Ca(OH)<sub>2</sub> whereas the w/c ratio causes small and unsystematic variations in the Ca(OH)<sub>2</sub> formation rate when  $\geq 0.30$ , which is not surprising since Ca(OH)<sub>2</sub> is a product of hydration.

#### 4.2. Comparison between experimental and simulated results of chemical shrinkage evolution and Ca(OH)<sub>2</sub> content

##### 4.2.1. Chemical shrinkage evolution

Fig. 7 shows both the evolution of the chemical shrinkage of the cement pastes and the evolution of

the chemical shrinkage calculated using Eq. (10) as a function of hydration degree. As regards the experimental results, the hydration degree is obtained using TGA tests whereas it is calculated using Eq. (13) in the case of the modelling. Additional TGA tests are performed on cement pastes with w/c=0.25, 0.30, 0.35 and 0.40 at 50 °C from 0 to 12 h of hydration to plot chemical shrinkage as a function of hydration at this relatively high temperature.

Until 30% of hydration, the calculated curve follows a slope similar to most of the experimental chemical shrinkage values. However, two major exceptions can be noticed. Firstly, the chemical shrinkage values of the cement paste with w/c=0.25 cured at T=20 °C are higher than the computed values. In other words, for the same degree of hydration, the cement paste with w/c=0.25 presents a greater chemical shrinkage than the cement pastes with ratio ranging between 0.30 and 0.40. We have seen previously that the hydration rate of the cement paste with the low w/c ratio (0.25) is significantly lower than that of cement pastes with w/c ratios ranging from 0.30 to 0.40. However, no significant difference in the evolutions of the chemical shrinkage of the cement pastes investigated has appeared. This phenomenon can be explained by the fact that, during chemical shrinkage measurements, the cement paste is constantly supplied with water, whereas TGA tests are carried out on cement pastes maintained in autogenous conditions. The difference in the curing conditions (constant water supply vs. autogenous conditions) leads to an overestimation of the “chemical shrinkage vs. hydration degree” curve, especially for a low w/c ratio (0.25).

Modelled and experimental values also diverge as regards the chemical shrinkage values measured at 40 and

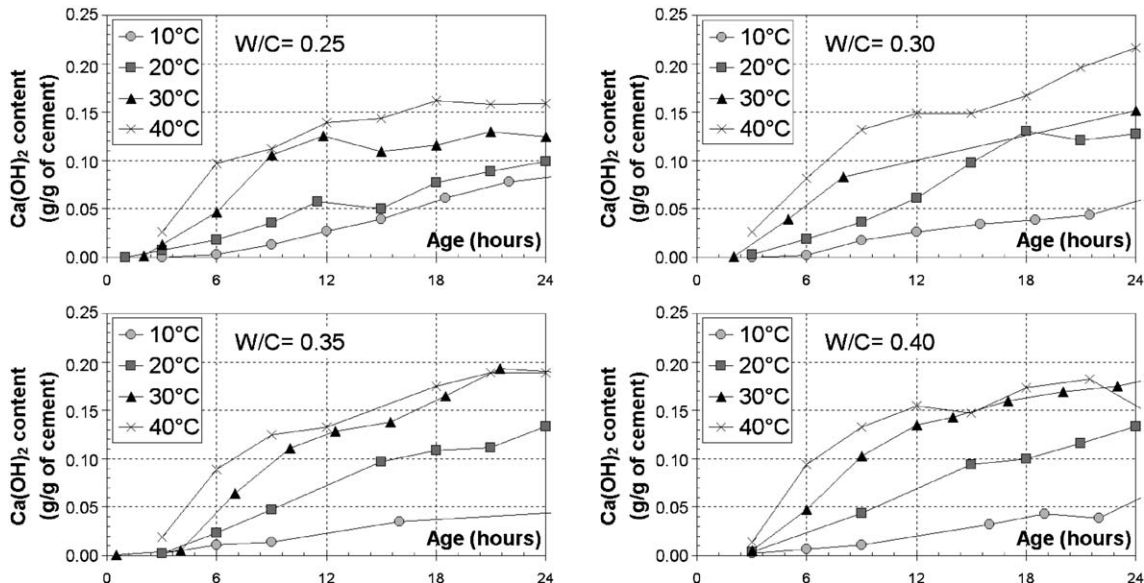


Fig. 6. Evolution of Ca(OH)<sub>2</sub> content vs. the age of different cement pastes (w/c=0.25, 0.30, 0.35, 0.40) cured at 10, 20, 30 and 40 °C, respectively.

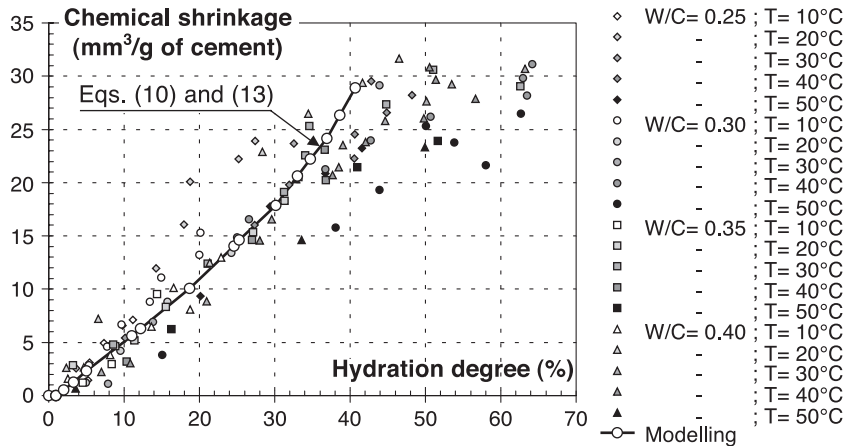


Fig. 7. Evolution of the chemical shrinkage of different cement pastes as a function of hydration degree—Comparison between experimental and simulated results.

50 °C. This observation is related to the dual action of the temperature already described in Section 4.1.2.

The best fitting between experimental results and computed chemical shrinkage values is obtained for the cement pastes with w/c=0.30, 0.35 and 0.40 cured at 20 °C, respectively. Fig. 8 shows that the assumptions made for the chemical reactions of cement hydration are suitable and give a good estimation of the chemical shrinkage within this w/c ratio range.

#### 4.2.2. Ca(OH)<sub>2</sub> content evolution

The amount of Ca(OH)<sub>2</sub> produced by the cement hydration is plotted in Fig. 9 for cement pastes with w/c=0.25, 0.30, 0.35, 0.40 cured at 10, 20, 30, 40 and 50 °C as a function of cement hydration degree determined with TGA tests. In the same figure the values of the Ca(OH)<sub>2</sub> content calculated from Eq. (12) as a function of the hydration degree computed from Eq. (13) are also presented.

The experimental results reveal the linear correlation between the Ca(OH)<sub>2</sub> content and the degree of hydration.

Neither the curing temperature nor the w/c ratio affects this correlation, at least within the range of temperatures and w/c ratios studied.

When looking at the very early ages, Fig. 9 reveals a threshold in the appearance of crystallized Ca(OH)<sub>2</sub>, showing a significant precipitation of this product in the cement paste. This threshold appears at the same degree of hydration ( $\alpha \approx 7\%$ ) for all the cement pastes investigated here. Moreover, from this threshold the Ca(OH)<sub>2</sub> content is linearly linked to the degree of hydration.

Eqs. (12) and (13) modelling makes it possible to achieve a good estimation of the Ca(OH)<sub>2</sub> formation rate in the cement pastes from 0 to 40%. The slope of the modelled curve is consistent with the slope of the curve formed by the experimental results. However, a difference is observed between the computed and experimental values because, Ca(OH)<sub>2</sub>, which is considered, in the chemical equations and according to Lea's [4] data, as forming during C<sub>3</sub>S hydration, is assumed to precipitate from the very start of the hydration process (Eq. (2)). This

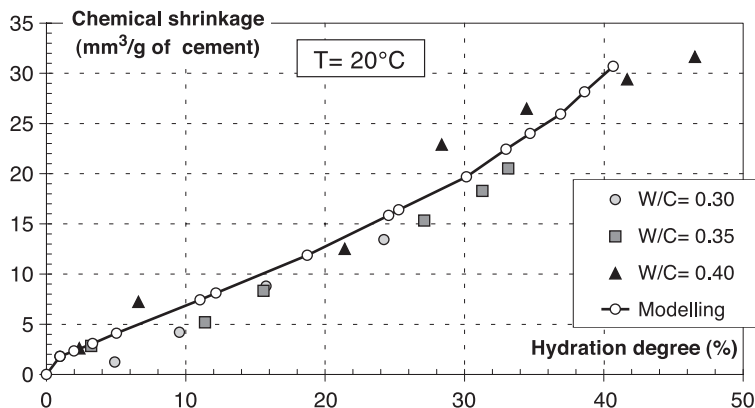


Fig. 8. Evolution of the chemical shrinkage of cement pastes with w/c=0.30, 0.35, 0.40 cured at 20 °C as a function of hydration degree—Comparison between experimental and simulated results.

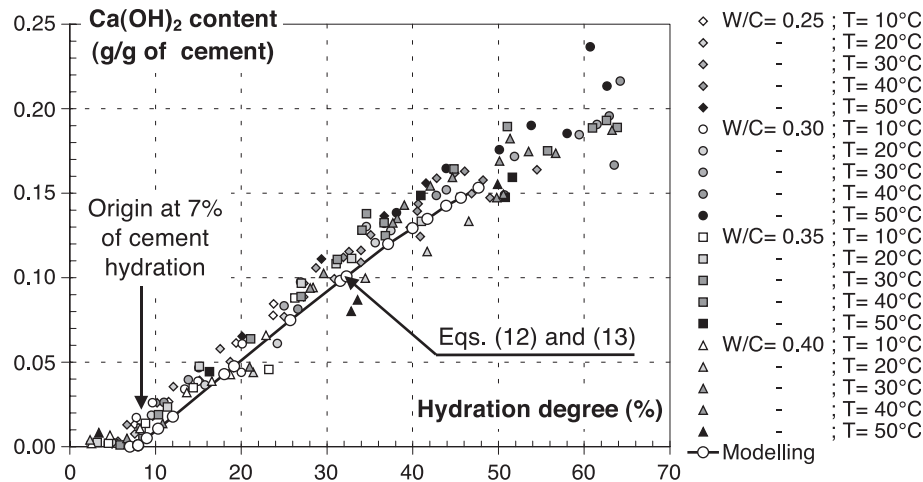


Fig. 9. Evolution of the  $\text{Ca(OH)}_2$  content of different cement pastes as a function of hydration degree—Comparison between experimental and simulated results (the origin of  $\text{Ca(OH)}_2$  appearance has been considered at 7% of hydration degree for the simulation).

assumption, however, is not true since we know that the precipitation of  $\text{Ca(OH)}_2$  is not immediate and occurs only a few hours after cement and water contact (when the calcium ion concentration of the interstitial phase reaches a maximum [4]).

The consideration of this retardation in  $\text{Ca(OH)}_2$  precipitation implies to adjust the origin of the modelled curve at 7% of hydration, which corresponds to the threshold of the  $\text{Ca(OH)}_2$  formation as detected by TGA. In this case, Fig. 9 shows that the modelled curve fits the experimental results very well.

## 5. Conclusions

The main conclusions that can be drawn from this study are the following:

- The correlation between the chemical shrinkage and the hydration degree (measured using TGA) of cement pastes with w/c ratios within the range 0.30–0.40 and cured at 20 °C can be predicted with good accuracy (from 0 to 40% of hydration) by the semiempirical model presented here and based on the hydration reactions equations.
- The computed  $\text{Ca(OH)}_2$  content values are consistent with the experimental values obtained on cement pastes with w/c=0.25, 0.30, 0.35 and 0.40 cured at 10, 20, 30, 40 and 50 °C, if we consider that  $\text{Ca(OH)}_2$  precipitation occurs at a certain hydration degree (here, 7% of cement hydration).

Therefore, the same modelling approach can be applied to the determination of both chemical shrinkage and  $\text{Ca(OH)}_2$  content. From the knowledge of the cement composition, it is possible to predict the chemical shrinkage of cement paste. The next step now is the prediction of the

autogenous shrinkage of cement paste at early and very early ages of hydration, a research work currently in progress within our laboratory.

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