

Macroscopic Modelling of Concrete Aging Regarding Hydration and Temperature Effects

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ABSTRACT

A macroscopic model to account for the hydration and aging phenomena that occur during the early ages of concrete is proposed in this work. Assuming the percolation of water through the hydrates already formed as the dominant mechanism of cement hydration, a normalised variable called hydration degree is adopted in the model, which has an evolution law that can be easily calibrated through an adiabatic calorimetric test. This methodology allows an accurate prediction of the evolution of the hydration degree and the hydration heat production. The evolution of the compressive strength is related to the aging degree, a novel concept which accounts for the effect of the hydration degree and the influence of the curing temperature on the final mechanical properties of concrete, a feature not attended with classic maturity concepts. A wide set of experimental tests validates the proposed model for ordinary and high performance concretes. Fly ash admixture concretes with a large spectrum of cement substitutions can be also modelled with the proposed approach.

Keywords: Concrete (E), Hydration (A), Temperature (A), Aging (C), Modelling (E).

1. INTRODUCTION

Nowadays a rising tendency to use concrete as a structural material at early ages, that is, before completion of the hydration process, is observed. This is evident for precasting as well as for pre-stressed concrete, where anticipation of concrete loading provides economic benefits concerned with the re-using of formworks, as well as abbreviating the construction phase. Another field where high cadence in production is registered concerns Rolled Compacted Concrete dams, where production technologies resemble the ones usually adopted in road construction. The quality control inherent to these situations is a subject of major concern, since durability and functionality of the structures is greatly affected by undesirable damages like cracking, at early ages primarily associated with thermal and shrinkage effects, but that can be also amplified by the precocious stressing associated to the high rhythm of construction.

A domain of research to which the present paper is mostly concerned relates to the modelling of such phenomena in a format suitable for structural applications, namely by providing a mathematical representation of the observed macroscopic temperature and volume changes that take place in concrete associated to the hydration of cement, as well as the increase of strength and rigidity of the hardening paste due to aging. The model to be presented herein accounts for many of the relevant features of concrete's behaviour at early ages, but in order to make it appropriate for an implementation in the framework of the Finite Element Method, the kinetics of the chemical reaction will be viewed on a macroscopic level, that is, at the scale of the specimens tested on laboratory. Basically such approach corresponds to visualise the enhancement of the mechanical properties of concrete as due to a change in the concentrations of the many constituents existing at the microscale, rather than an actual change in the mechanical properties of such components, which might be considered as nonaging. Within this framework, the aging process is therefore linked to the formation of new hydrates, or in other words, to a rise in the concentration of the hardened cement gel. Consequently, the essential phenomenon which dominates the hydration kinetics is the diffusion of the free water between the layers of the already formed hydrates (Coussy (1995), Ulm and Coussy (1995,1996)), here reproduced via a normalised variable termed hydration degree. Its evolution obviously depends on the current value of the hydration degree, but owing to the thermo activated nature of cement hydration a strong dependency on the temperature is also observed, a feature usually accomplished by assuming an Arrhenius

type kinematics, easily calibrated through an adiabatic calorimetric test. Additionally an aging model is proposed to describe the evolution of the concrete compressive strength during the hydration process. This is based on the novel concept of aging degree, with a rate evolution here linked both with the hydration degree and the curing temperature. Like in models purely based on maturity concepts this allows to account for the influence of temperature on the compressive strength evolution, but additionally it is able to capture the effect on the final concrete strengths of the curing temperature history. Besides, the involved parameters are easily obtained on the basis of adiabatic or isothermal tests, and are consistent with standard entities actually in use in the field of cement and concrete research to describe the physics of the hydration and aging phenomena.

For the validation of the proposed model a wide set of experimental tests concerning the temperature evolution and the rising of the compressive strength of several concrete mixes under controlled casting temperatures will be presented. Besides, it will be demonstrated that the proposed model performs quite well either for ordinary concrete or for high performance concrete with silica fume admixtures. Exploratory applications to fly ash concrete with 50% and 70% cement substitutions seem also to validate the proposed model, although further research is still required on this field for complete clarification of this preliminary conclusion.

2. HYDRATION OF CONCRETE

2.1 Thermo-chemical model

The chemical processes associated to the hardening of concrete in the first days after casting are accompanied by significant temperature effects, since cement hydration is a highly exothermic and thermally activated reaction. Based on the theory of reactive porous media developed by Coussy (1995), as well as on its application to concrete under the macroscopic approach proposed in Ulm and Coussy (1995,1996), the thermo-chemical model to be presented next is based on the macroscopic interpretation of the cement hydration as a chemical reaction in which the free water is a reactant phase, which combines with the unhydrated cement to form hydrates as a product phase.

Since the dominant mechanism in the kinetics of the reaction is due to the dispersion of water, if one defines χ , the hydration extent, as the number of moles of water combined per unit volume, in the hypothesis of a closed chemical system, that is, without external supply or loss of water, this entity can be considered an internal variable of the system. For a more suitable practical handling and interpretation, let us define the hydration extent on a normalised format, in the form

$$\xi = \chi/\bar{\chi}_\infty \quad (1)$$

where $\bar{\chi}_\infty$ is the final value of χ (eventually equal to one in ideal conditions of the water/cement ratio and other factors ensuring full hydration) and ξ is what one could call the ‘hydration degree’, an indication of how much the hydration reaction of the mixture is already performed. In practical conditions the full hydration of the cement is not obtained, and consequently the hydration degree at infinite time is such that $\xi_\infty < 1$. By relating the final hydration degree with the water/cement ratio (w/c) of the mixture, the formula (Pantazopoulou and Mills (1995))

$$\xi_\infty = \frac{1.031 w/c}{0.194 + w/c} \quad (2)$$

can be used for estimation of ξ_∞ .

Following Ulm and Coussy (1995) the rate $\dot{\xi}$ is itself a function of the hydration degree, but since the combination of water with cement is a thermally activated reaction, an amplification based on the widely used Arrhenius type law will be also considered to account for the influence of the temperature (Acker (1988)). A positive evolution of the form

$$\dot{\xi} = \tilde{A}(\xi) \exp\left(-\frac{E_a}{RT}\right) \geq 0 \quad (3)$$

is therefore proposed (Ulm and Coussy (1995,1996)), where apart from the temperature T the Arrhenius exponential term incorporates the constant R for the ideal gases and the activation energy of the reaction E_a . Eq. 3 encompasses the direct influence of the actual value of the hydration degree on term \tilde{A} , a normalised affinity to be considered specific for each hydration reaction, and easily obtainable from an adiabatic calorimetric

test as will be clarified latter. In the definition of the normalised chemical affinity it is convenient to assume it as expressible as

$$\tilde{A} = A/\eta \quad (4)$$

that is, as the ratio between A , the chemical affinity strictly speaking, and η , the viscosity directly linked with the microdiffusion of the free water through the hydrates. By assuming that the percolation of the water is retarded with the growth of the hydrates such viscosity would have to increase with ξ , and consequently, induced by de Schutter and Taerwe (1995), it is here postulated that

$$\eta = \eta_0 \exp\left(\bar{\eta} \frac{\xi}{\xi_\infty}\right) \quad (5)$$

where η_0 and $\bar{\eta}$ are material constants.

Now, by defining the chemical affinity with a format like (Cervera *et al.* (1999))

$$A = k \left(\frac{A_0}{k \xi_\infty} + \xi \right) (\xi_\infty - \xi) \quad (6)$$

where A_0 is the initial affinity of the reaction (that is, when $\xi=0$) and k is an additional parameter, handling Eqs (3-6) the final form for $\dot{\xi}$ reads

$$\begin{aligned} \dot{\xi} &= \frac{k}{\eta_0} \left(\frac{A_0}{k \xi_\infty} + \xi \right) (\xi_\infty - \xi) \exp\left(-\bar{\eta} \frac{\xi}{\xi_\infty}\right) \exp\left(-\frac{E_a}{RT}\right) = \\ &= \tilde{A}(\xi) \exp\left(-\frac{E_a}{RT}\right) \geq 0 \end{aligned} \quad (7)$$

Form the observation of this rate equation it becomes evident that the thermal activation expressed by the Arrhenius factor is of primary importance at the beginning of the reaction, but as the hydration proceeds considerable attenuation is introduced by the viscosity exponential term as well as by factor $(\xi_\infty - \xi)$, cancelling the evolution as the hydration degree reaches the final value $\xi = \xi_\infty$. Therefore, and beyond the required positiveness for $\dot{\xi}$, the evolution expressed in Eq. (7) contains the basic requisites for a realistic modelling of the hydration reaction.

2.2 Thermal evolution

Following standard energetic reasonings, and without entering into details that are out of the scope of this work, it is relevant to note that the thermodynamic equilibrium of a body undergoing thermal changes is ruled by a field equation of the form

$$C \dot{T} = \dot{Q} + H + \mathcal{e} + D \quad (8)$$

where C denotes the heat capacity per unit volume, Q is the heat associated to an internal source, H is the external heat source and D is the energy dissipation (all associated to an unit volume). \mathcal{e} accounts for thermal conductivity effects. Focusing on the simulation of the hydration problem we will assume that C is constant, whereas the dissipation D , essentially linked with the chemical reaction, is usually taken as negligible when compared to the other terms in Eq. 8. Furthermore, the internal heat source Q is provided by the hydration reaction itself, and according to many authors (Reinhardt *et al.* (1982), Rostassy *et al.* (1993), Torrenti *et al.* (1994), de Schutter and Taerwe (1995)) we will assume here that $\dot{Q} = Q_\xi \dot{\xi}$, where Q_ξ is a constant. Therefore Eq. 8 turns into

$$C \dot{T} = Q_\xi \dot{\xi} + H + \mathcal{e} \quad (9)$$

Due to the dependency of $\dot{\xi}$ on T , an iterative procedure is usually required to solve this equation in space and time for general situations. However, in this work we are mostly concerned with the validation of the proposed model on the basis of adiabatic and isothermal experimental tests, where solution of Eq. 9 can be readily simplified (a unique exception applies to the semi-adiabatic tests which will be invoked in Section 2.5).

Adiabatic test conditions

Under adiabatic conditions $H = \mathcal{e} = 0$, and consequently Eq. 9 turns

$$C \dot{T} = Q_\xi \dot{\xi} \quad (10)$$

Denoting by T_0 the initial temperature the solution can be expressed as

$$T = T_0 + \frac{Q_\xi}{C} \xi \quad (11)$$

which points out the intrinsic equivalence between the evolution of temperature and the hydration degree under adiabatic conditions. This result can be substituted into Eq. 7 to render

$$\xi = \tilde{A}(\xi) \exp\left(-\frac{E_a/R}{T_0 + Q_\xi/C \xi}\right) \quad (12)$$

which is a nonlinear equation in terms of ξ . To integrate it let us consider a numerical procedure where ξ_n refers to the hydration degree to be computed for time step $t_n = n \Delta t$, whereas ξ_{n-1} concerns to an already solved time step $t_{n-1} = (n-1) \Delta t$, with Δt being the time spacing between two consecutive time steps. Writing Eq. 12 for time t_{n-1} and assuming that $\dot{\xi}_{n-1} = (\xi_n - \xi_{n-1})/\Delta t$ (forward-Euler integration scheme) an explicit expression is obtained for ξ_n :

$$\xi_n = \xi_{n-1} + \Delta t \tilde{A}(\xi_{n-1}) \exp\left(-\frac{E_a/R}{T_0 + Q_\xi/C \xi_{n-1}}\right) \quad (13)$$

This result can be used recursively to obtain a final formula to update the hydration degree during an adiabatic test:

$$\xi_n = \Delta t \sum_{i=1}^{n-1} \tilde{A}(\xi_i) \exp\left(-\frac{E_a/R}{T_0 + Q_\xi/C \xi_i}\right) \quad (14)$$

Concerning the temperature rise under adiabatic conditions, it suffices to substitute into Eq. 11 the hydration degree obtained from Eq. 14.

Isothermal test conditions

Under isothermal conditions the thermal field is known *a priori*, since a constant temperature \bar{T} is observed throughout. Under these conditions the Arrhenius term in Eq. 7 is constant, and consequently, by invoking the same reasonings as for the derivation of Eq. 14, the hydration degree is computed according to the formula

$$\xi_n = \Delta t \exp\left(-\frac{E_a}{R\bar{T}}\right) \sum_{i=1}^{n-1} \tilde{A}(\xi_i) \quad (15)$$

2.3 Experimental identification of model parameters

At the end of an adiabatic test Eq. 11 would render

$$T_{\infty} = T_0 + \frac{Q_{\xi}}{C} \xi_{\infty} \quad (16)$$

which can be used to evaluate the average value of constant Q_{ξ} , that is,

$$Q_{\xi} = \frac{C}{\xi_{\infty}} (T_{\infty} - T_0) \quad (17)$$

since T_{∞} is directly measured at the end of the adiabatic test and the other entities are constants.

Furthermore, the normalised affinity \tilde{A} , an essential entity of the hydration model, is also directly ‘measurable’ during the adiabatic test. By substituting Eq. 3 into Eq. 10 owing to Eq. 17 one obtains

$$\tilde{A}|_{test} = \frac{\xi_{\infty} \dot{T}}{T_{\infty} - T_0} \exp\left(\frac{E_a}{RT}\right) \quad (18)$$

This equation allows to compute the normalised affinity by measuring the temperature rate \dot{T} along the experiment, together with the adiabatic temperature itself. If a discrete measurement of temperatures is performed during the test a discrete form could be attributed to Eq. 18 through the identification of \dot{T} with $\Delta T/\Delta t$. Therefore, the three parameters k/η_0 , A_0/k and $\bar{\eta}$ involved in Eq. 7 can be adjusted by fitting the ‘model’ affinity with the experimental one obtained from an adiabatic calorimetric test through Eq. 18.

As for the ratio E_a/R it can be also experimentally determined, ranging within the interval 3,000-8,000°K for concrete. Also, and according to Hansen and Nielsen (1985) and van Breugel (1992), the activation energy remains almost constant above 20°C, and consequently we will assume E_a/R as a constant, tuned in order to match the temperature rise under an adiabatic calorimetric test.

2.4 Application to ordinary and high performance concretes

Insight on the ability of the proposed model to reproduce the hydration reaction is provided by Fig. 1, where the adiabatic tests conducted by Benz *et al.* (1998) for an ordinary Portland concrete (OPC) and for a high performance one (HPC) are reproduced. Table 1 resumes the values adopted for the various parameters involved in the numerical model. In this figure, as well as in the forthcoming ones, dots correspond to the experimental values, whereas solid lines indicate the predictions from the above described model. From observation of Fig. 1a it becomes evident that a good fitting with the temperature rise measured experimentally is obtained for the ordinary Portland concrete with a ratio $w/c = 0.35$; the same applies for Fig. 1b, where the normalised affinity adopted in the model is compared with the inferred experimental one. Figs 1c,d provide a similar comparison for the high performance concrete, where $w/c = 0.45$ and a silica fume/cement ratio $s/c = 0.2$ are considered. Good agreement is therefore obtained for both concretes.

TABLE 1

Material properties for Bentz *et al.* (1998) tests.

	ξ_{∞}	k/η_0 ($10^8 h^{-1}$)	$\bar{\eta}$	A_0/k (10^{-5})	E_a/R ($^{\circ}K$)	Q_{ξ} ($10^8 J/m^3$)
OPC	0.66	0.35	6.0	1.0	5000	2.39
HPC	0.72	0.15	4.0	0.5	5000	1.73

$C = 2.33 \times 10^6 J/m^3^{\circ}C$ $T_0 = 21^{\circ}C$

2.5 Application to fly ash cement concretes

In Sánchez de Rojas *et al.* (1993) various hydration heat measurements were performed for different samples of concrete, tested by using the Langavant calorimeter method. Among those tests the ones concerning different additions of fly ash are of great interest, since at early ages the fly ash cement mixtures exhibit low activity and generate less hydration heat than in the OPC and HPC concretes. Three cement/fly ash addition mixtures are considered – 100/0, 50/50 and 30/70 –, for which the temperature rises on the Langavant calorimeter are represented in Fig. 2.

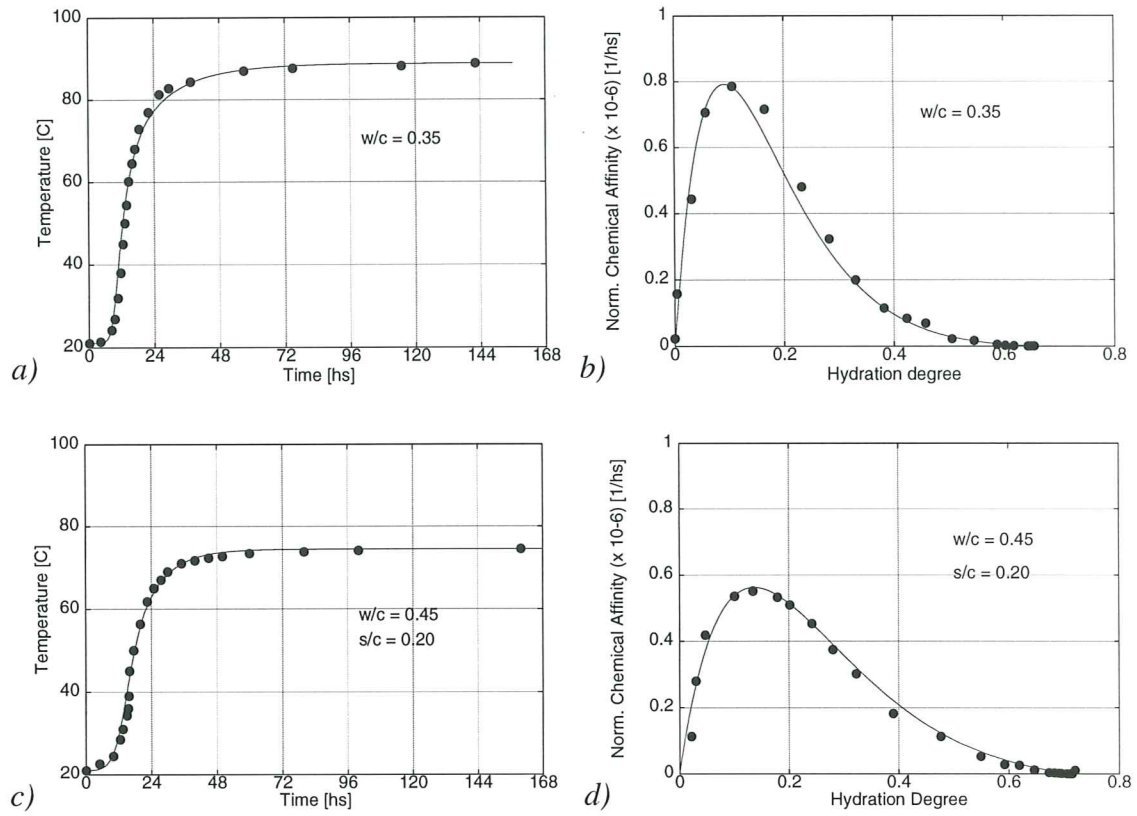


Figure 1. Temperature evolution and normalised affinity for Bentz *et al.* (1998) adiabatic tests (dots – experimental values, solid lines – model predictions).

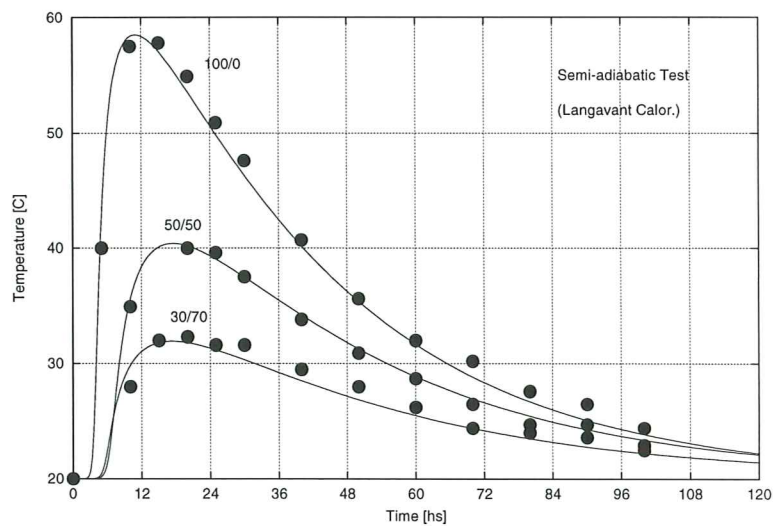


Figure 2. Temperature evolution for concrete with fly ash (Langavant Calorimeter, Sánchez de Rojas *et al.* (1993)).

Note that a wide range of cement substitutions is considered. The base cement used on the mixtures is of Type I/45 A, according to [UNE (1988)] classification. Concerning the simulation of the present semi-adiabatic problems, the thermal field equation (9) was solved numerically by simulating the concrete sample inside the calorimeter with the Finite Element Method. Table 2 resumes the parameters adopted for the hydration model. From Fig. 2 it becomes evident the progressive reduction on the temperature rises which is obtained by increasing the fly ash substitutions. The ability from the macroscopic hydration model to capture the temperature evolution for the three mixtures is also quite evident, both in the initial rising branch and for the post-peak descending one.

TABLE 2

Material properties for Sánchez de Rojas *et al.* (1993) tests.

	ξ_{∞}	k/η_0 ($10^9 h^{-1}$)	$\bar{\eta}$	A_0/k (10^{-7})	E_a/R ($^{\circ}K$)	Q_{ξ} ($10^8 J/m^3$)
100/0	0.69	3.30	6.0	1.0	6000	1.64
50/50	0.69	2.05	6.0	1.0	6000	1.10
30/70	0.69	2.30	6.0	1.0	6000	0.69

$C = 2.16 \times 10^6 J/m^3^{\circ}C$ $T_0 = 20^{\circ}C$

3. AGING MODEL AND TEMPERATURE EFFECTS

3.1 Hydration degree and maturity

From a phenomenological standpoint the development of the mechanical properties of concrete at early ages has to be linked with the hydration degree, as this entity may be looked as an indicator of how much the inherent chemical reaction has already advanced. However, much experimental data puts into evidence that temperature plays also a significant role in the development of concrete strength during the curing process. To account for this influence of temperature T many aging models have been defined in terms of ‘maturity’ or ‘equivalent age’ concepts, basically through the definition of an artificial age for the concrete, which may be superior or inferior to the real one

depending on if the actual temperature history has accelerated or retarded the aging process (in comparison with what would occur under a reference temperature T_r , typically 20°C). Two possible definitions of equivalent ages t_e are the ones from Saul and from Freiesleben and Perdersen, revisited in Kim *et al.* (1998),

$$t_e^{\text{Saul}} = \frac{\sum_i (T_i - T_d)}{T_r - T_d} \Delta t \quad (19a)$$

$$t_e^{\text{F&P}} = \sum_i \exp \left[\frac{E_a}{R} \left(\frac{1}{T_r + 273} - \frac{1}{T_i + 273} \right) \right] \Delta t \quad (19b)$$

where T_d is called the datum temperature. Apart from the fact that the kinetics of the hydration degree is not directly visible in these definitions, the influence of temperature on the curing process is only accounted on an accumulative manner, that is, different thermal curing conditions could result in the same maturity irrespective to the temperature history.

However, as demonstrated in Kim *et al.* (1998) and referred also in Kjellsen and Detwiler (1993) and Carino (1981), much experimental observation puts into evidence that concrete strength is affected not only by the accumulative temperature history but also by the history itself. Typically, if a temporary rise on the curing temperature is produced during the first day after casting a noticeable acceleration of the hydration process is observed, effect which, however, is progressively reduced if the rise in temperature is produced at later ages. Conversely, temporary drops on the curing temperature lead to a retarding effect in the hydration reaction, but the influence is also attenuated as the temperature reduction is produced at later times.

A complementary effect of temperature concerns with the fact that a rise in the early curing temperature improves the early concrete strength, but at the latter time a reduction of the final strength is observed. This phenomenon, reported in Kim *et al.* (1998), is attributed by Kjellsen and Detwiler (1993) and Carino (1981) to the fact that the acceleration produced in the hydration rate due to a temperature rise leads to an increased porosity inside the cement paste, attributable to a nonhomogeneous microdiffusion of the hydration products and to differences in the thermal expansion coefficients of the many concrete constituents. On the other hand, through the lowering

of the curing temperature at the first ages a retarding of the hydration kinetics is observed, which produces a decay on the initial mechanical properties of concrete, eventually with a subsidiary rise on the limit strength owing to the greater uniformity on the distribution of the hydration products and to the reduced porosity. These reasonings put into evidence the limited ‘memory’ proficiency of traditional formulae like the ones reproduced in Eq. 19, since concretes cured under different temperature histories could have the same maturity or equivalent age and, consequently, the same final strength, an assumption that is in contradiction with the experimental evidence. Therefore, a realistic aging model should account for the influence of the hydration degree, but the effect of the curing temperature would have to be explicitly included as well.

Focusing in the concrete compressive strength, let us introduce an internal variable κ such that

$$f(\kappa) = \kappa f_{\infty} \quad (20)$$

where f stands for the current strength and f_{∞} denotes the final compressive strength at the reference temperature. As defined here variable κ can be considered a normalised strength, which hereinafter will be referred to as the ‘aging degree’. Since we intend to account for both the hydration degree and the temperature effects on the evolution of the compressive strength of concrete, let us postulate a rate equation for the aging degree of the form

$$\dot{\kappa} = \lambda_T(T) \lambda_{\xi}(\xi) \dot{\xi} \quad (21)$$

where $\lambda_T \lambda_{\xi} \geq 0$. Factor λ_{ξ} is supposed here to obey to a linear expression of the form

$$\lambda_{\xi} = A \xi + B \quad (22)$$

where A and B are material parameters. Factor λ_T accounts for the influence of temperature, here reproduced by the expression

$$\lambda_T = \left(\frac{100 - T}{100 - T_r} \right)^a \quad (23)$$

where T_r is the reference temperature for the determination of f_{∞} and the exponent a is a model parameter that serves to regulate the thermal incidence on the evolution of the aging degree. Note that for $T > T_r$ term λ_T becomes lesser than one, thus attenuating

the strength increase; conversely for $T < T_r$ it results $\lambda_T > 1$, thus enhancing the evolution of the aging degree. Fig. 3 depicts the typical evolutions obtained for ξ and f when the curing occurs under three different isothermal conditions: 5°C, 20°C and 40°C.

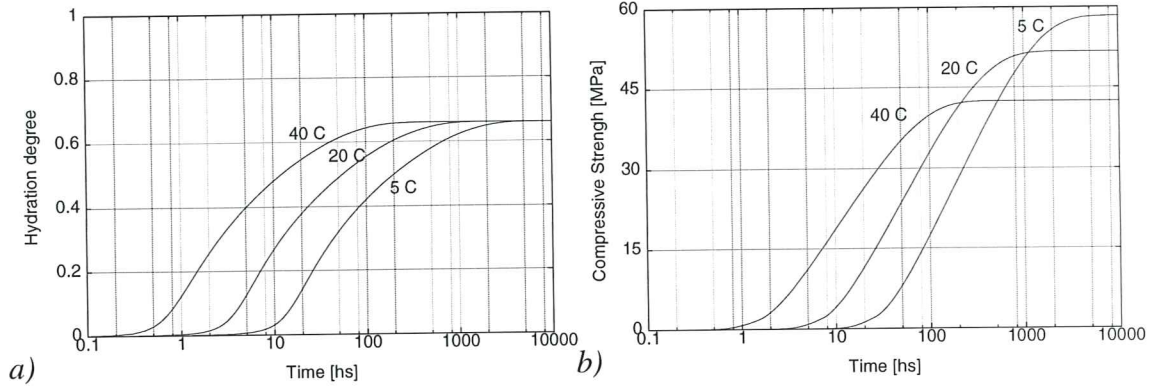


Figure 3. Influence of temperature on hydration and aging phenomena.

Note in Fig. 3a that the final value for the hydration degree is the same for the three curing temperatures, and consequently the maturity and equivalent age models can only reproduce the ascending branch of the compressive strength evolution reproduced in Fig. 3b, not the change on the final plateau. In fact, such models can be recovered by fixing $\lambda_T = 1$, which is equivalent to express Eq. 21 as

$$\dot{\kappa} = \lambda_{\xi}(\xi) \dot{\xi} \quad (24)$$

an evolution law that could be integrated in the form

$$\kappa = \Gamma_{\xi}(\xi) \quad (25)$$

In such conditions Eq. 20 would reduce to

$$f(\xi) = \Gamma_{\xi}(\xi) f_{\infty} \quad (26)$$

that is, the evolution of concrete strength would depend solely on the hydration degree, and consequently for $\xi = \xi_{\infty}$ the same final strength would result for the three curing conditions. By differentiating Eq. 25 with respect to time, through identification with Eq. 24 one would also conclude that

$$\lambda_{\xi} = \partial \Gamma_{\xi} / \partial \xi \quad (27)$$

which explains that the linear format assumed in Eq. 22 for λ_ξ is consistent with the parabolic definitions usually adopted in literature for Γ_ξ .

Eqs. 7,22 and 23 can be substituted into Eq. 21, which allows for the aging degree to be integrated in time according to

$$\kappa_n = \Delta t \sum_{i=1}^{n-1} \left[\left(\frac{100-T_i}{100-T_r} \right)^a (A\xi_i + B) \tilde{A}(\xi_i) \exp\left(-\frac{E_a}{RT_i}\right) \right] \quad (28)$$

where T_i and ξ_i are obtained as described in Section 2.2.

3.2 Application to Kim *et al.* (1998) tests

This section is dedicated to the simulation of the experimental tests reported in Kim *et al.* (1998), which were performed to evaluate the influence of temperature on the evolution of the compressive strength of concrete at early ages, as well as on its final values. The curing was carried out under controlled isothermal conditions during the first 28 days, namely at the temperatures of 5°C, 20°C and 40°C, as depicted on the first three shadowed rows of Fig. 4.

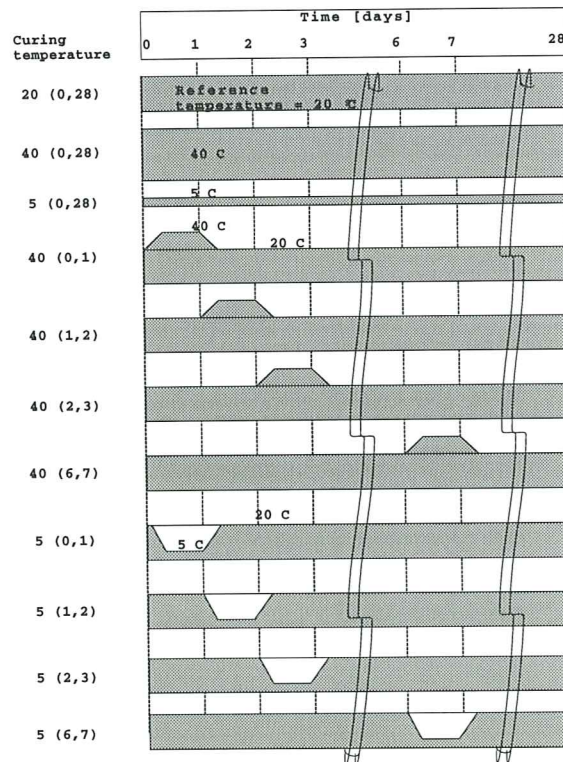


Figure 4. Curing temperature histories in Kim *et al.* (1998) tests.

Furthermore, a complex experimental program was pursued around the curing temperature of 20°C, consisting in raising it up to 40°C or lowering it until 5°C during just one day, and returning to the reference temperature of 20°C during the remaining 27 days. Of great relevance is the fact that the temperature perturbation is produced at different ages, as also depicted in Fig. 4. To ensure a clear identification of the different curing conditions for these tests we will retain the notation adopted in the above cited reference: 40(*d,d+1*) point out that a raise from 20°C to 40°C is produced between days *d* and *d+1*, whereas 5(*d,d+1*) indicate a decay from 20°C to 5°C during the same period (see also Fig. 4 for clarification). It is here emphasised that in spite of the temporary variations introduced in the curing temperature these tests can be considered as ‘step-wise’ isothermal, and consequently a minor adaptation is required in Eq. 15 to apply for the present application: the Arrhenius term should be considered as an argument of $\Sigma(\cdot)$, since \bar{T} should be adjusted to the step varying temperature. Two different *w/c* ratios of 0.35 and 0.55 were considered for the above referred tests. As for the cement, a Portland ASTM Type I was used. Table 3 resumes the material properties assumed in the macroscopic model.

Focusing on the first three curing conditions of Fig. 4, Figs 5*a,b* allow to compare the evolutions of the compressive strength predicted by our model with the ones obtained during the experimental tests, for the two different *w/c* ratios. The overall agreement of the aging model predictions with the test results is fairly good, since it captures the double influence of the curing temperature: (*i*) as an activator of the hydration reaction and (*ii*) as a conditioning factor of the final concrete strength.

TABLE 3

Material properties for Kim *et al.* (1998) tests.

<i>w/c</i>	ξ_∞	k/η_0 ($10^{10}h^{-1}$)	$\bar{\eta}$	A_0/k (10^{-5})	E_a/R (°K)	Q_ξ ($10^8 J/m^3$)	<i>A</i>	<i>B</i>	ξ_{set}	f_∞ (MPa)	<i>a</i>
0.35	0.66	4.33	5.8	1.0	7000	1.25	3.79	-1.17	0.2	52	0.7
0.55	0.76	1.20	7.5	0.1	6500	1.25	3.72	-1.85	0.3	42	0.9

$C = 2.07 \times 10^6 J/m^3 \text{ } ^\circ\text{C}$ $T_0 = 21^\circ\text{C}$ $T_r = 20^\circ\text{C}$

In Figs 5*c,d* the final concrete strengths predicted by the aging model are compared with the experimental ones on a normalised format, and as a function of the hydration

degree. The standard deviation (S.D. in figures) from the model predictions with respect to the experimental average values is 0.06, therefore quite small if compared to the average error of the test measurements, which stood between 0.03 and 0.04 for both w/c ratios. Figs 5e,f provide a similar comparison as in Figs 5c,d, but the influence of temperature on Eq. 21 is neglected by assuming $a = 0$ in Eq. 22: the model predictions worsen considerably, exhibiting now a standard deviation of 0.13 in comparison with the average experimental measurements, which emphasises the importance of accounting for the influence of the curing temperature on the final concrete strength.

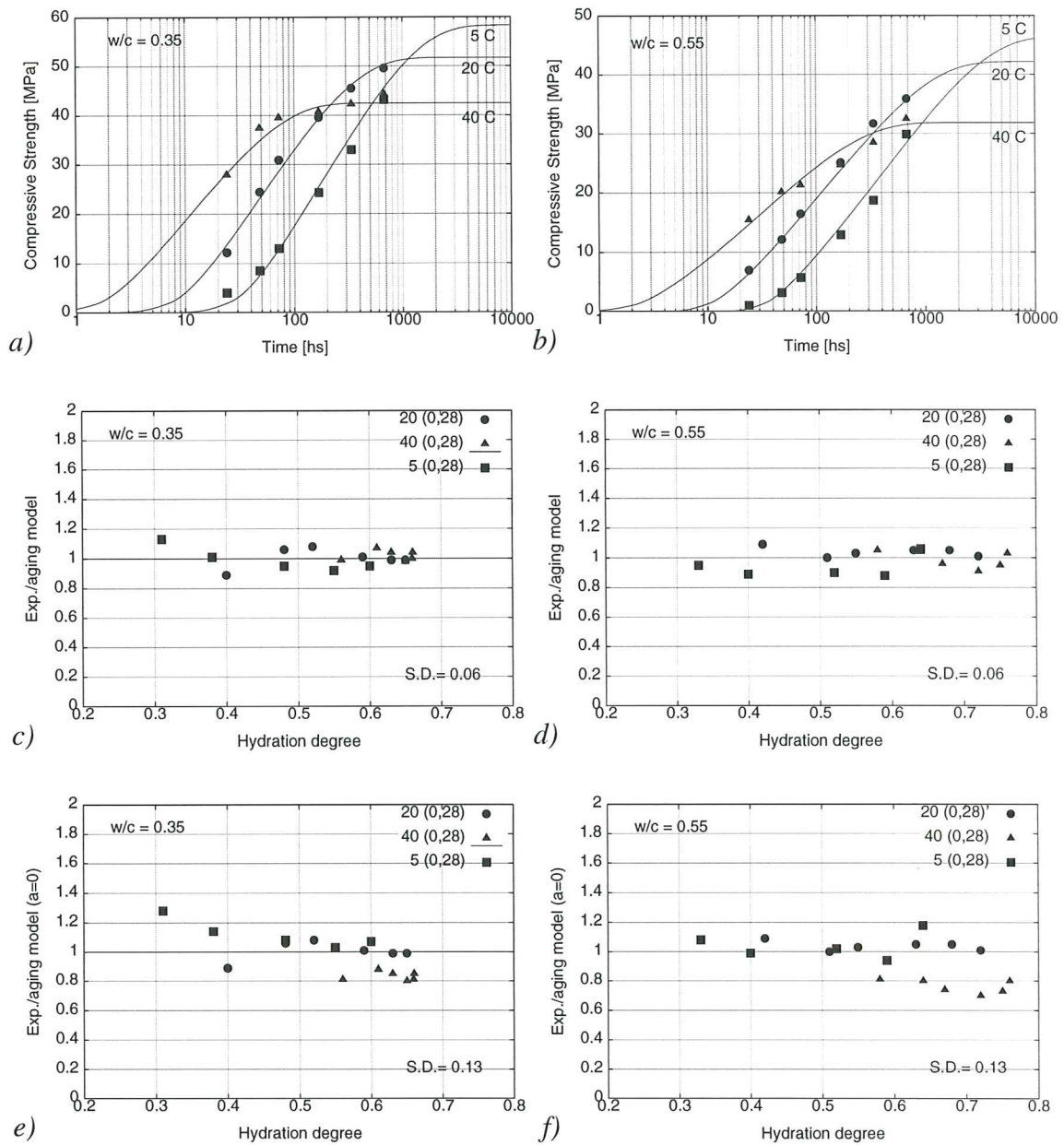


Figure 5. Strength evolution for the isothermal Kim *et al.* (1998) tests.

The next figures concern the remaining tests sketched in Fig. 4. Fig. 6 is dedicated to the 40(0,1), 40(1,2), 40(2,3) and 40(6,7) tests, whereas Fig. 7 reproduces the 5(0,1), 5(1,2), 5(2,3) and 5(6,7) ones, all of them plotted in parallel with the 20(0,28) curve to highlight the differences attributable to the one-day variations on the isothermal 20°C curing temperature. In order to explore the capabilities of the proposed model on different w/c ratios, Fig. 6 refers to $w/c = 0.35$ while Fig. 7 corresponds to $w/c = 0.55$. Predictions from the aging model compare remarkably well with the experimental observations for the whole set of experimental tests, namely in what concerns: (i) the accelerating effect introduced on the evolution of the compressive strength due to the elevation of the curing temperature above the 20°C, or conversely, the retarding effect produced on concrete aging due to reducing the temperature to 5°C, (ii) the progressive attenuation of the influence of the one-day thermal variations as such variations are produced on latter ages, practically cancelling after the 6-7th day, irrespective to the w/c ratio and the step-wise thermal change.

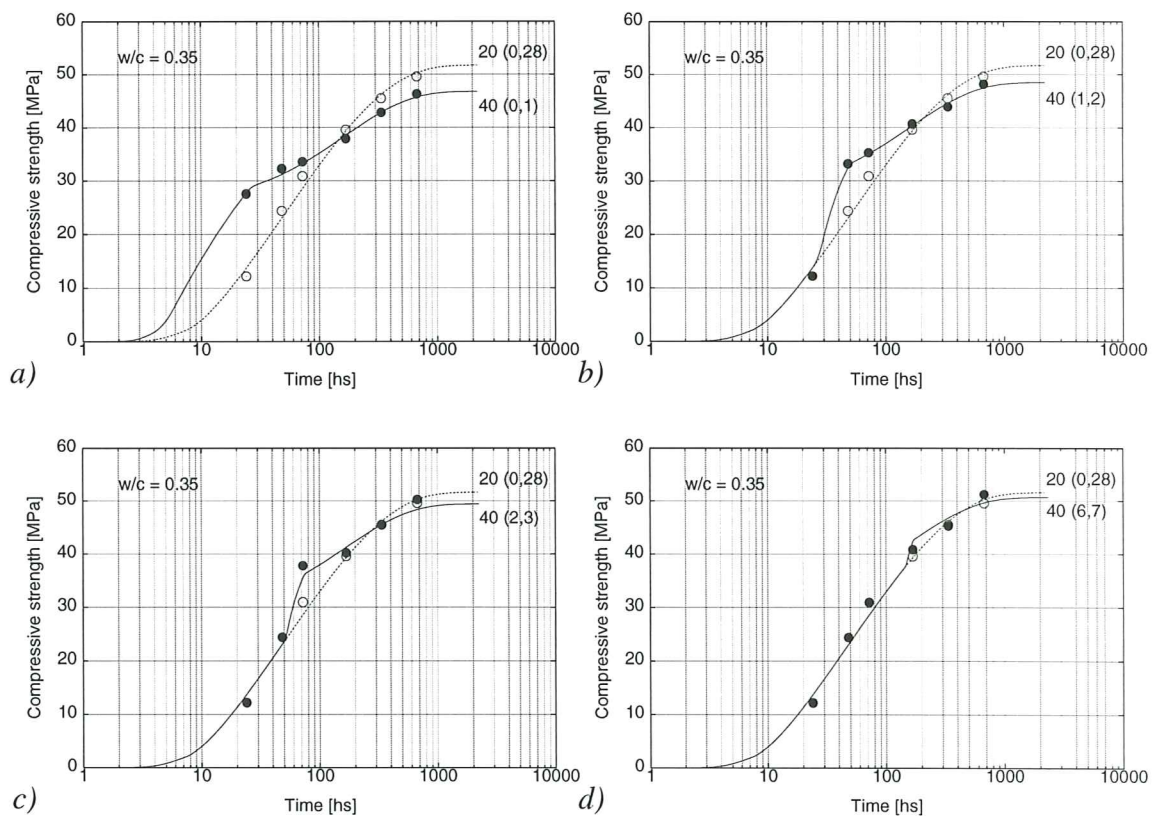


Figure 6. Strength evolution for the $w/c = 0.35$ Kim *et al.* (1998) tests.

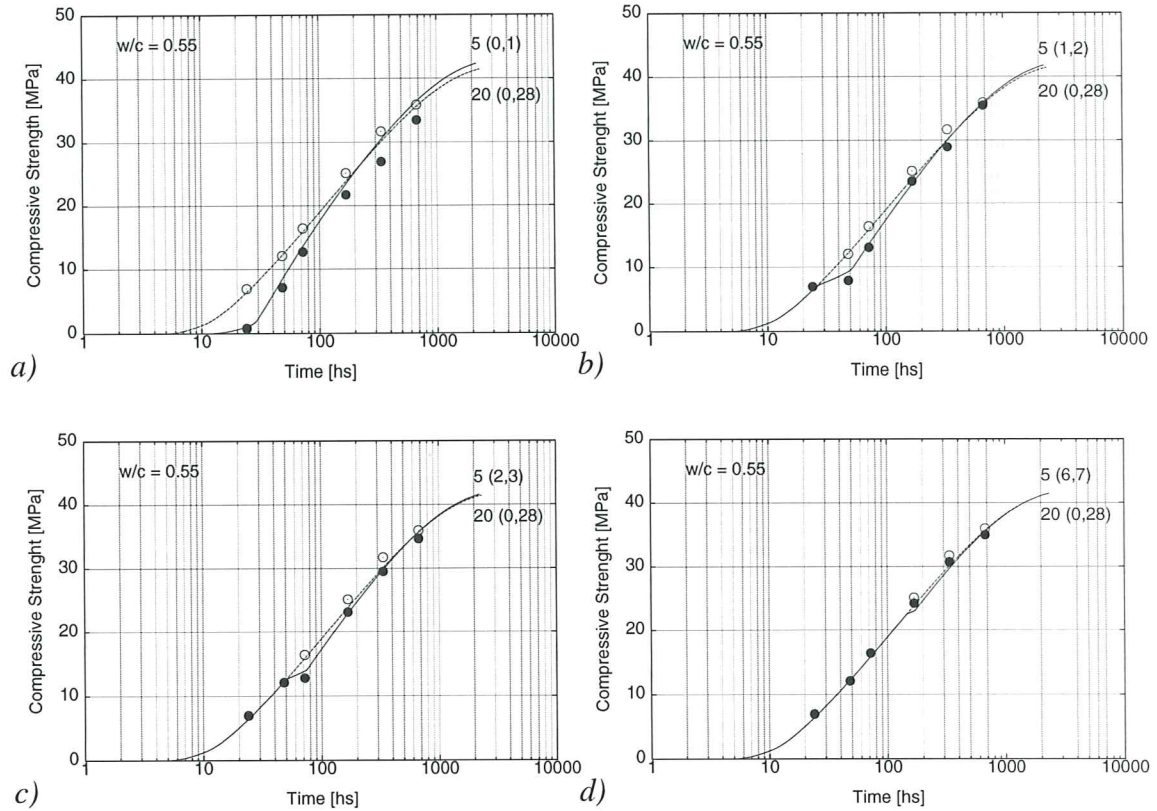


Figure 7. Strength evolution for the $w/c = 0.55$ Kim *et al.* (1998) tests.

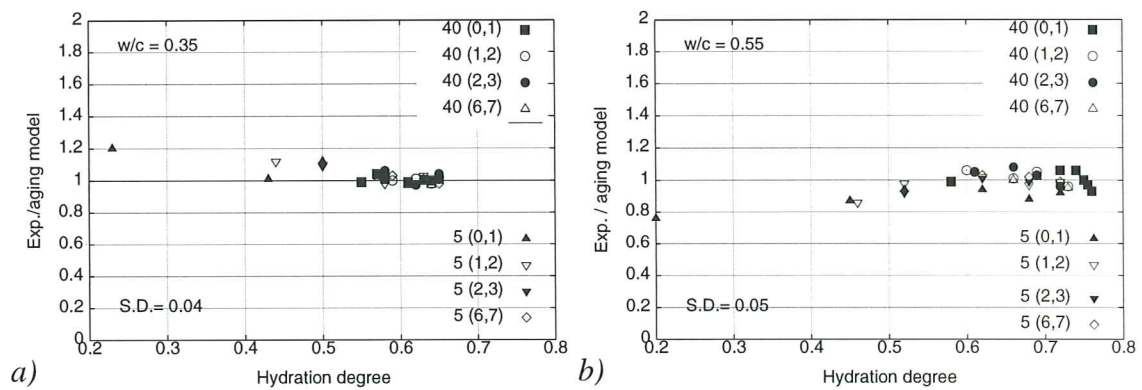


Figure 8. Comparison of the aging model with the experimental Kim *et al.* (1998) results.

The final compressive strengths obtained in the whole set of the Kim *et al.* (1998) experimental tests are presented in Fig. 8, together with the predictions from the proposed aging model. The standard deviation from the model predictions with respect to the experimental average values is 0.04 in Fig. 8a and 0.05 in Fig. 8b. If the influence of temperature was disregarded on the proposed aging model these standard deviations

would be practically doubled, attaining the 0.08 mark, which once more underlines the importance of temperature on the concrete strength that is attainable at the end, a feature not captured by classical maturity or equivalent age models.

CONCLUSIONS

With a format suitable for structural applications, a model that accounts for the hydration phenomenon on a macroscopic level is proposed in this work. It calls for a normalised variable termed hydration degree, for which an evolution law is proposed. Through comparison with experimental tests performed for ordinary and high performance concretes, as well as for concretes with fly ash additions, accurate predictions for the evolutions of the hydration degree and the hydration heat production are obtained. As for the development of the compressive strength the novel concept of aging degree is introduced, accounting for both the hydration degree and the temperature effects on the aging of concrete during the curing process. An important feature not attended in classic maturity concepts, but easily captured by the proposed aging model, is the influence of temperature on the final strength of concrete, that is, at the end of the hydration reaction.

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REFERENCES

- P. Acker. Comportement Mécanique du Béton: Apports de l’Aproche Physico-Chimique. Raport de recherche N. 152, Laboratoire Ponts et Chaussées, Paris, France, 1988.
- D. P. Bentz, V. Waller, F. de Larrard. Prediction of adiabatic temperature rise in conventional and high-performance concretes using a 3D microstructural model. Cem. Concr. Res. 28(2) (1998) 285-297.

- N. J. Carino. Temperature Effects on the Strength-Maturity Relation of Mortar. Report NBSSIR 81-2244, National Bureau of Standards, Washington DC, 1981.
- M. Cervera, J. Oliver, T. Prato. A thermo-chemo-mechanical model for concrete. I: Hydration and aging. *J. Engrg. Mech., ASCE*, 125(9) (1999).
- O. Coussy, *Mechanics of Porous Media*. John Wiley & Sons, Chichester, England, 1995.
- G. de Schutter, L. Taerwe. General hydration model for Portland cement and blast furnace slag cement, *Cem. Concr. Res.*, 25(3) (1995) 593-604.
- P. F. Hansen, A. Nielsen. Method for quick calculation of temperature differences in concrete members. VTT Symposium 61, Espoo, 1985.
- J.-K. Kim, Y.-H. Moon, S.-H. Eo. Compressive strength development of concrete with different curing time and temperature. *Cem. Concr. Res.*, 28(12) (1998) 1761-1773.
- K. O. Kjellsen, R. J. Detwiler. Later-age strength prediction by a modified maturity model. *ACI Mat. J.*, 90(3) (1993) 220-227.
- Norma UNE 80 301. Cementos. Definiciones, Clasificación y Especificaciones. 1988.
- S. J. Pantazopoulo, R. H. Mills. Microstructural aspects of the mechanical response of plain concrete. *ACI Mat. J.* 92(6) (1995) 605-616.
- H. W. Reinhardt, J. Blaauwendraad, J. Jongedijk. Temperature development in concrete structures taking account of state dependent properties. *Proc. Int. Conf. of Concrete at Early Ages*, 1982.
- F. S. Rostassy, A. Gustsch, M. Laube. Creep and relaxation of concrete at early ages. Experiments and mathematical modelling. *Proc. 5th. Int. RILEM Symp. on Creep and Shrinkage of Concrete*, H. Mang, N. Bicanic and R. de Borst (Eds.), E&FN Spon, 1993, pp. 453-458.
- M. I. Sánchez de Rojas, M. P. Luxán, M. Frías, N. García. The influence of different additions on Portland cement hydration heat. *Cem. Concr. Res.*, 23(1) (1993) 46-54.
- J. M. Torrenti, I. Ghenot, P. Laplante, P. Acker, F. Larrand. Numerical simulation of temperatures and stresses in concrete at early ages. *Proc. Int. Conf. Comp. Modelling of Concr. Struct.*, Z. P. Bazant and I. Carol (Eds.), Pineridge Press, Swansea, 1994, pp. 559-568.

- F. J. Ulm, O. Coussy. Modelling of thermochemomechanical couplings of concrete at early ages. *J. Engrg. Mech., ASCE*, 121(7) (1995) 785-794.
- F. J. Ulm, O. Coussy. Strength growth as chemo-plastic hardening in early age concrete. *J. Engrg. Mech., ASCE*, 122(12) (1996) 1123-1132.
- K. van Breugel. Hysmostruc: a computer based simulation model for hydration and formation of structure in cement based materials, in: A. Nonat, J. C. Mutin (Eds.), *Hydration and Setting of Cements*, RILEM, London, 1992, pp. 361-368.