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Modeling of internal curing in maturing mortar

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ABSTRACT

Prediction of the influence of internal curing both on the material behavior during maturing and on its final physical properties is an important issue in concrete research. A novel, mechanistic-type numerical model of concrete is applied for modeling the chemo-physical phenomena taking place during internal curing. The model takes into account full coupling between chemo-thermal, hygral and mechanical phenomena in porous media (i.e., maturing cement paste or mortar). In this work, the recent development of the model for description of internal curing is presented along with the results of simulations. The model allows for description of the influence of internal curing on such phenomena as hydration, self-desiccation or autogenous shrinkage. The results of the simulations are compared with the experimental data concerning autogenous phenomena in low water-to-cement ratio mortars containing superabsorbent polymers.

1. Introduction

As an effect of the development of high-performance concrete (HPC) technology, an increasing interest in early-age phenomena taking place in maturing cement-based materials can be observed in the recent years, e.g. [1,2]. The reason for this fact is that these modern concretes are especially sensitive to the negative effects of maturing. Autogenous shrinkage which occurs in HPC due to their very fine pore structure and low water-to-cement ratio (w/c) may lead to early-age cracking and to a serious decrease of material durability [1].

Among various methods designed to reduce the sensitivity of concretes to the maturing conditions and prevent early-age cracking, internal curing is one of the most significant topics of ongoing research, e.g. [3–10]. The possible methods for providing internal curing were briefly reviewed in [3]. Most commonly, internal curing is provided by adding to the mixture pre-saturated light-weight aggregates (LWA) [4], or superabsorbent polymers (SAP) [5,6]. The SAP or LWA are supposed to become uniformly distributed in the mixture and act as internal water reservoirs to provide curing water to the cement paste, and thus promote its hydration and prevent the autogenous RH drop (self-desiccation). Especially with the use of SAP, it is possible to considerably limit or even completely prevent self-desiccation and autogenous shrinkage [6–9].

However, in order to enable a wider application of this method in the engineering practice, a better understanding of the phenomena taking place during internal curing is still necessary. Various experimental methods have been employed to explore the mechanisms of water migration from internal water reservoirs to the surrounding maturing cement paste, and on the way this extra water interacts with the cement paste [10].

The application of numerical modeling may be also very helpful in understanding phenomena taking place during internal curing [11]. An example of such approach is the recent work by Mönnig [12] who adapted the DuCOM model [13] for the description of hydration evolution and development of concrete properties during internal curing. However, there is yet no model able to describe the material behavior at the macroscopic level (e.g., strains of the material) from a point of view of water transport phenomena during internal curing. This is the motivation for the research reported in this paper.

The aim of this work is the application of the recently developed numerical model of concrete [14,15], based on a mechanistic-type approach, for modeling of complex phenomena in internally cured cement-based materials. The model was recently validated for the description of hygral and mechanical phenomena in concrete at early ages and beyond, e.g. [15–17]. For the purpose of internal curing description, the development of the model is proposed. The material is treated as homogenous, with volume-averaged constitutive relationships due to the presence of water reservoirs. The attention is in particular focused on the influence of the additional water on the hygral state of the medium, and further on hydration, self-desiccation and autogenous shrinkage.

In parallel, an experimental research was performed, concerning the influence of internal curing by means of SAP on early age phenomena in low w/c mortars.

The results of the simulations are compared with the obtained experimental data, concerning the hydration evolution, self-desiccation and autogenous shrinkage in the mortars.

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2. Experimental research

The experimental research carried out was aimed at determining the influence of internal curing by means of SAP on the early-age phenomena in low w/c mortars and involved: calorimetry, autogenous RH evolution and autogenous deformation measurements. Additionally, setting time was determined on the corresponding cement pastes. The experimental results are presented in Section 5, where they are used for the purpose of experimental validation of the proposed model.

2.1. Materials and mix preparation

Two types of mortars were examined in this research: a reference mortar with w/c of 0.3 (plain mortar), and a mortar with addition of SAP and an entrained water to cement ratio (w/c_e) of 0.04 (SAP mortar).

The cement pastes used for determination of the setting time had the composition corresponding to the appropriate mortars (i.e., exactly the same composition except for the aggregates).

The cement used was CEM I 42.5 N, with a specific surface of 277 m^2/kg and the following Bogue-calculated phase composition (by wt.%): C_3S: 73.5, C_2S: 3.3, C_3A: 5.7, C_4AF: 9.5, free CaO: 0.5.

The volume of the aggregates in the mortars was estimated as 40% and 38.4% for the reference mortar and the mortar with SAP, respectively. Alluvial sand composed of sandstone, limestone and metamorphic rocks, with well rounded particles of size 0.25–1.0 mm, was used.

To control the workability of the mortars, a liquid polycarboxylate-based superplasticizer, containing 29% of dry mass replaced a part of the mixing water in an amount of 0.5% by cement weight. Deionized water was used.

Solution-polymerized SAP with irregular particles of size 63–125 μm were used. The assumed absorption of 12.5 g/g allowed obtaining workability similar to the plain mortars. The SAP were added in an amount of 0.32% by cement weight.

The mortars for measurements of autogenous deformation and RH evolution were prepared in a 5 l Hobart mixer. The dry constituents (i.e., including SAP where applied) were first mixed manually for about 2 min, and then automatically for another 30 s. After the addition of water the duration of the mixing procedure was 4.5 min. The mixer vessel was filled with approximately 1 l of constituents.

The same mixture procedure was applied for the cement pastes used for the setting time measurements, with about 0.5 l of constituents filling the mixer vessel.

All the constituents had temperature of about 20 °C.

2.2. Measuring techniques

2.2.1. Setting time

Setting time of the cement pastes was determined by the Vicat needle [18] in a temperature-controlled room at approximately 20 °C. Directly after mixing, the pastes were placed in the PVC form, and a cover with thin plastic foil was provided during the whole measurement in order to prevent evaporation from the surface, without hindering the penetration of the needle. Two measurements were performed for each mixture, and the difference in measured setting times between two specimens did not exceed 10 min in any case. The average setting times for plain pastes were equal to 6 h 15 min and 7 h 20 min for initial and final setting, respectively. For SAP pastes delayed setting was observed, with 7 h 40 min and 9 h 15 min for initial and final setting, respectively.

2.2.2. Calorimetry measurements

The rate of heat release was measured on mortars with isothermal calorimetry at 20 °C using TAM Air Isothermal Calorimeter (Thermometric AB). The glass jars were filled with about 6 g of mortars, closed and placed in the calorimeter. The mixtures were mixed in the mixer, thus the initial peek was not measured, however this is of minor importance in view of the phenomena observed within this research. The measurements lasted for 5 days. Two specimens for each material were used, resulting in a difference for the cumulative heat release curves of less than 1%.

2.2.3. Autogenous RH measurements

Directly after mixing, mortars were put in plastic vials and placed in the Rotronic hygrometric chambers. The temperature in the chambers was controlled by means of water at 20 ± 0.1 °C circulating in their casings. At the age of approximately 20 h, the specimens were removed from the measuring chambers, crushed and put back in the chambers in order to avoid bleeding and condensation on the sensors. The sensors were calibrated before and after each measurement with four saturated salt solutions within the range of 75.47–97.59% RH. The measurements lasted for about 6 days.

Two specimens for each mixture were measured simultaneously. The difference in readings between two samples did not exceed about 1.6% RH and 0.25% RH for plain mortar and SAP mortar, respectively.

2.2.4. Autogenous deformation measurements

The measurement of autogenous strain of mortars was carried out using the manual dilatometer in accordance with the ASTM C 1698 standard [19]. Directly after mixing, the corrugated molds were filled with the mortars on the vibrating table. During the whole period of measurements the specimens were stored in a controlled temperature room at 20 ± 0.5 °C. Three specimens for each mixture were used. The measurements started at final set and lasted for about two weeks. The standard deviation did not exceed 14 μm/m and 8 μm/m for plain mortar and SAP mortar, respectively. The mass loss of the specimens after the end of measurements did not exceed 0.02 g in any case. According to [19], its contribution to the total shrinkage is approximately equal to 2 μm/m and well within the standard deviation.

3. Modeling phenomena in fresh concrete

The model [14,15] used in this work was described in detail in several publications. However, in order to discuss the necessary developments a brief description will be provided here. For a detailed description of model equations and their numerical solution, see [14,15].

The model is based on the so-called mechanistic type approach, thus the phenomena observed macroscopically are described in terms of their real physical origins. Such an approach should allow for application of the model in different conditions and for different purposes, as also shown by this work. In particular, the model has been recently used for modeling of hygral performance and creep and shrinkage of cementitious materials [15–17].

The use of this type of approach enables the description of couplings between the strongly non-linear phenomena of various chemo-physical natures that occur during maturing of concrete.

The balance and conservation equations are written considering concrete as a porous material, with pores filled partially with the liquid phase (bound water and capillary water) and partially with the gaseous phase (the mixture of dry air and vapor). The thermal, hygral and mechanical equilibrium state is assumed locally, with chemical processes (hydration) proceeding at a certain rate.

The model equations in the macroscopic formulation are obtained by means of the successive volume-averaging from the micro-scale with the Hybrid Mixture Theory developed by Hassanizadeh and Gray [20] and applied for building materials by Gawin [21]. After introducing the constitutive relationships, which account for various mechanisms of mass and energy transport characteristic for specific phases in concrete as well as for hydration process and mechanical performance, the final form of the macroscopic governing equations of the model is obtained [14]. These equations concern: two mass conservation equations (continuity equations), written for dry air and water species and involving the solid skeleton mass conservation, enthalpy conservation equation and linear momentum balance (mechanical equilibrium) equation. The equations are written in terms of the primary variables: gas pressure p^g, capillary pressure p^c (describing the hygral state), temperature T and displacement vector $\mathbf{u}$. The superscripts refer to the intrinsic values related to the single phase. The evolutionary variable of the model is the normalized hydration degree Γ_{hydr}. The concept of the normalized hydration degree originally applied in [14] is very convenient from the modeling point of view. Nevertheless, in this work the hydration degree α will be consistently used, defined as the amount of cement reacted respect to its initial content. This approach allows avoiding the estimation of the final hydration degree, which was necessary in [14].

It is worth mentioning, that the capillary pressure is able to describe the hygral state of the medium not only in the capillary moisture range, i.e., above about 40% RH [22], but also when actual capillary water is no longer present in pores. This requires a proper physical interpretation, where the thermodynamical potential of the physically adsorbed water multiplied by its density is formally treated as capillary pressure [14].

The governing equations are discretized in space by means of the Finite Element Method, e.g. [23]. The time discretization of model equations is carried out with the fully implicit scheme of the Finite Difference Method.

The question may arise if in the case of autogenous phenomena described at the macroscopic level, there is a need to use any sort of spatial discretization. Indeed, if the autogenous conditions as defined by Jensen [1] are analyzed (i.e., no external load, isothermal conditions and no moisture exchange with the environment), there is no need for the spatial analysis, since by definition no gradients of physical quantities are visible at the macroscopic level. Thus, it can be assumed that each point of the analyzed volume behaves in the same way. In such case only time discretization is necessary since the hydration proceeds at a certain rate. However, in realistic conditions (usually different than the autogenous conditions), the so called autogenous phenomena take place also in parallel to other phenomena, e.g. self-heating, temperature exchange with the environment or drying. For this reason, it is surely an advantage of the model, that it is capable to describe transport phenomena in space.

In view of description of the internal curing process, the key phenomena are those related to water migration in the inner structure of cement paste. The mass conservation equation for water species involving the solid skeleton mass balance proposed by Gawin et al. [14], and modified due to internal curing reads:

$$\begin{aligned} & n\left(\rho^w-\rho^{gw}\right)\frac{\partial S_w}{\partial p^c}\frac{\partial p^c}{\partial t}-\left\{\beta_s\rho^{gw}(1-n)(1-S_w)+\left[(1-n)\beta_s+n\beta_w\right]\rho^w S_w\right\}\frac{\partial T}{\partial t} \\ & +(1-S_w)n\left(\frac{\partial \rho^{gw}}{\partial T}\frac{\partial T}{\partial t}\right)+\left[\rho^{gw}(1-S_w)+\rho^w S_w\right]div\frac{\partial \mathbf{u}}{\partial t} \\ & -div\left[\rho^g\frac{M_a M_w}{M_g^2}\mathbf{D}_d^{gw}grad\left(\frac{p^{gw}}{p^g}\right)\right]+div\left[\rho^{gw}\frac{k\mathbf{I}k^{rg}}{\mu^g}\left(-grad\,p^g\right)\right] \\ & +div\left[\rho^w\frac{k\mathbf{I}k^{rw}}{\mu^w}\left(-grad\,p^g+grad\,p^c\right)\right]=\frac{\rho^{gw}}{\rho^s}(1-S_w)\dot{m}_{hydr} \\ & +\frac{\rho^w}{\rho^s}S_w\dot{m}_{hydr}-\dot{m}_{hydr}+\dot{m}_{IC} \end{aligned} \tag{1}$$

where the indices g, w, gw, s refer to gaseous phase, liquid water, water vapor, solid phase, respectively, t is time, $n=f(\alpha)$ is porosity, $S_w=f(p^c)$ is saturation degree of pores with liquid water (both capillary and physically adsorbed), $\rho=f(T)$ is density, β is the volumetric thermal expansion coefficient. The first three terms on the LHS of the Eq. (1) are the accumulation terms due to the moisture adsorption/desorption, thermal expansion, and density change with temperature, respectively. The remaining terms on the LHS of the Eq. (1) are the flux terms. The first of those terms is due to the whole medium deformations. The next term is due to the diffusive flow of water vapor in the gaseous mixture of vapor and dry air, described by Fick's law with M_π being the molar mass ($\pi=a, g, w$) and $\mathbf{D}_d^{gw}$ the effective diffusivity tensor [21]. The last two terms on the LHS are due to the advective flow of vapor and of liquid water, respectively. The advective flow is described with Darcy's law, with $k=f(\alpha)$ being the intrinsic permeability (assuming isotropy of the medium) and $\mathbf{I}$ the second-order unit tensor, $k^{r\pi}=f(S_w)$ being the relative permeability ($\pi=g, w$), and $\mu^\pi=f(T)$ being the dynamic viscosity ($\pi=g, w$). The RHS of the Eq. (1) describes the source terms, where the two first terms are the actual sources of skeleton due to the decrease of pores volume caused by the build-up of hydration products $\frac{\dot{m}_{hydr}}{\rho^s}$, the following term is the actual sink due to the mass of water consumed by hydrating cement $\dot{m}_{hydr}$, and the last term describes the additional source term due to internal curing $\dot{m}_{IC}$. The constitutive relationship describing the latter term is developed in the next section.

In Eq. (1) the movement of water due to the gravity has been neglected.

If one assumes that autogenous conditions are provided, as already mentioned, and integrates the Eq. (1) over the whole volume of analyzed material, the transport terms occurring in Eq. (1) will vanish (as the corresponding gradients will be equal to zero) as well as the terms due to temperature change (as isothermal conditions are maintained). In such case, the equation is obtained:

$$n\left(\rho^w-\rho^{gw}\right)\frac{\partial S_w}{\partial p^c}\frac{\partial p^c}{\partial t}=\frac{\rho^{gw}}{\rho^s}(1-S_w)\dot{m}_{hydr}+\frac{\rho^w}{\rho^s}S_w\dot{m}_{hydr}-\dot{m}_{hydr}+\dot{m}_{IC} \tag{2}$$

which states that the change of water content in the material is an effect of consumption of water due to hydration (sink), and of corresponding build up of hydration products in the pores (source), while additional water may be provided due to internal curing. It needs to be however underlined, that Eq. (2) was not employed in the further analysis and is only presented here to indicate in a clear way the origins of autogenous phenomena.

The rate of the mass of water consumed by hydrating cement may be described as [14]:

$$\dot{m}_{hydr}=\frac{\partial \alpha}{\partial t}m_{hydr\infty} \tag{3}$$

where $m_{hydr\infty}$ is the mass of non-evaporable water consumed at full hydration per unit volume of the material.

The evolution of hydration degree is modeled based on the affinity concept proposed by Ulm and Coussy [24] which states that the hydration kinetics of concrete under sealed conditions is governed by two constitutive laws: the rate of hydrating mass (or alternatively the rate of hydration) is a function of the affinity, and the affinity is a function of the mass hydrated (or alternatively hydration degree reached).

The expression for the hydration rate proposed initially by Ulm and Coussy [24], and modified for the influence of relative humidity by Gawin et al. [14], written in terms of the hydration degree α reads:

$$\frac{\partial \alpha}{\partial t}=\tilde{A}\beta_\varphi \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where $\tilde{A}$ is the normalized chemical affinity for the whole system of reacting cement, which may be described by means of an empirical relation [25]. The influence of temperature is described by means of the commonly used Arrhenius-type term, with E_a being the activation energy and R the universal gas constant. An initial value of hydration degree α_0 needs to be assumed in the simulation, which for the purpose of autogenous phenomena description corresponds to the time instant from which the material has already some shape rigidity and the creation of menisci can be observed in pores.

It is a commonly known fact, e.g. [1,26], that along with the decrease of RH in the pores, the hydration rate is decelerated. This effect is taken into account by means of the empirical function β_φ, derived based on experimental work by Bažant and Najjar [26]:

$$\beta_\varphi = \left[1 + a(1-\varphi)^4\right]^{-1} \tag{5}$$

where φ is relative humidity expressed as the absolute value (0 to 1), and a is an empirical parameter assumed in our simulations as $a = 12.5$.

The changes in the pore size distribution caused by the hydration evolution are believed to have an influence on the hygral behavior of the material. However, these phenomena still need some serious experimental investigation. In the absence of sufficient experimental data, the sorption isotherm is assumed as independent of hydration degree [27]:

$$S_w = \left[1 + \left(\frac{p^c}{a}\right)^{b/(b-1)}\right]^{-1/b} \tag{6}$$

where a, b are material parameters. The sorption isotherm is one of the cardinal characteristics of the capillary porous media, thus the parameters of Eq. (6) have a great influence on the results of the simulations. If drying at later ages is analyzed, the parameters of Eq. (6) may be directly determined based on the experimental data on sorption isotherms. For the purpose of autogenous phenomena description, where the aforementioned changes in the inner structure of material take place, such an approach may however not be applicable. Thus, for the initial period of concrete maturing, the parameters governing sorption isotherm may need to be determined separately. This may be done based on the hydration evolution measurements and parallel RH drop measurements.

The RH drop corresponding to the calculated capillary pressure is calculated by means of the Kelvin-Laplace's equation, e.g. [2]:

$$\varphi = \exp\left(-\frac{p^c M_w}{\rho^w RT}\right). \tag{7}$$

The stress state of the material is modeled by means of the so-called effective stress principle [28]:

$$\boldsymbol{\sigma}_e = \boldsymbol{\sigma} + (1-K_P/K_S)p^s\mathbf{I} \tag{8}$$

where $\boldsymbol{\sigma}_e$ and $\boldsymbol{\sigma}$ are the effective stress and the total stress tensors, respectively, $(1-K_P/K_S)$ is the Biot constant accounting for different values of bulk moduli of the skeleton K_S, and the porous body, K_P [17]. The effective stress accounts both for the externally applied load $\boldsymbol{\sigma}$, and the pressure exerted on the solid phase by the pore fluids p^s.

Thus, the effective stress may be treated as the effect of *externally* and *internally* applied load. In the case of autogenous conditions, no external load is applied, thus the first term on the RHS of Eq. (8) vanishes and the porous material is only *internally* loaded. A natural consequence of such approach is that it is possible to model creep strains accompanying autogenous shrinkage [2]. This is possible thanks to incorporating the effective stress principle in the microprestress-solidification theory by Bažant et al. [29,30]. The parameters governing deformation of the material are derived from the so-called B3 model [31]. The full description of the algorithm is beyond the scope of this paper and is presented in details in [15].

The pressure exerted by the pore fluids is calculated with the expression [15,17]:

$$p^s = p^g - \chi_s^{ws} p^c \tag{9}$$

which states that the increase of the absolute value of p^s is observed with the increase of the generalized capillary pressure. The latter one is due to the drop of saturation of pores with water caused by hydration (in the case of self-desiccation), or is due to the external conditions (in the case of drying, imposed in the form of boundary conditions).

In the formulation (9) adapted by Gawin et al. [15,17], the commonly used saturation degree S_w [28] was replaced with χ_s^{ws} which stands for the ratio of solid surface in contact with the thin adsorbed water film, and was assumed as a function of saturation degree S_w. Such approach is supposed by Gawin et al. [15,17] to better describe the behavior of materials with very fine pores and well developed internal surface, as concrete. Based on the experimental work by Baroghel-Bouny et al. [27], Gawin et al. [15,17] proposed empirical relations for $\chi_s^{ws}(S_w)$ for ordinary and high performance cement pastes and concretes. For a complete review about the different forms of effective stress tensor and the corresponding solid pressure, see [32].

4. Modeling of internal curing

The observation of water transport from internal reservoirs to the cementitious material may be carried out using the original model [14,15] directly at the mesoscopic level. For the analysis at this level, the concept of the so-called Representative Elementary Volume (REV) needs to be used. The REV is modeled as composed of two materials, which are treated themselves as homogenous: water reservoirs (LWA or swollen SAP) surrounded by the maturing cement paste, mortar or concrete. The analysis carried out by means of this kind of approach is able to provide interesting information in particular regarding the kinetics of water desorption from reservoirs and the kinetics of water migration in the cured surrounding cement paste. These phenomena are current topics of discussion [10] and their understanding is crucial for further analysis carried out at the macroscopic level.

Although an extensive analysis of the aforementioned phenomena at the mesoscopic level has been carried out [33,34], it is beyond the scope of this work.

Instead, the attention is focused on the influence of internal curing upon the autogenous phenomena observed macroscopically. Thus, in the analysis presented in this paper the macroscopic model described in previous section is used, where the material is treated as homogenous. However, a volume-averaged additional term due to internal curing $\dot{m}_{IC}$ (see Eq. (1)) was added to the original model [14,15].

Some important aspects derived from the meso-level analysis [34], serving as the assumptions for the macroscopic analysis will be highlighted here.

The additional source term can be obtained in two ways. First it can be explicitly derived from the meso-level analysis. For this purpose, the two-scale modeling scheme with the full two-directional linkage between the scale levels should be introduced, i.e., at each point of the macro-scale medium the underlying REV should be analyzed with the conditions derived from the macro-scale. The results from the REV concerning the hygral state would then be further averaged back into the macro-scale. This approach is somehow similar to the so-called FE^2 two-scale modeling scheme proposed by Feyel for description of mechanical response of composites [35].

However, this kind of analysis is very complex and computational time-demanding. Instead, as shown in this work, the additional source term may be introduced directly at the macroscopic level.

A problem that is being currently investigated [10,34,36–38] is the distribution of additional water respect to the distance from reservoirs. These investigations aim at defining the effective distance to which the internal curing water is supplied by the reservoirs. This is a crucial problem from the point of view of designing the size and distribution of reservoirs in practice. In modeling, since the volume-averaged source term introduced at the macro-level is used, it is not possible to properly take into account the distribution of the saturation degree with additional water at the meso-level. However as shown by some recent experimental evidence [36–38], this problem should be of secondary importance for the amounts of internal curing agents normally applied in practice (i.e., sufficient for optimal internal curing). Lura et al. [36] observed that water could travel up to 3 mm in a hardening cement paste (w/c 0.3). Trtik et al. used neutron tomography for observation of water migration from large SAP particles [37] and LWA [38] to maturing cement paste. They concluded that hardly any gradients of water content against the distance from the water reservoirs could be observed in a w/c 0.25 cement paste in the first day of hydration. The assumption of practically uniform distribution of curing water in the cured volume is also supported by recent numerical investigations [34].

Thus, it can be assumed that for the amounts of internal curing agents normally provided in practice, e.g. [5], the drop of saturation of pores due to self-desiccation is practically instantaneously compensated by the water transported from reservoirs and redistributed in the cured volume.

In further considerations it is assumed that the whole volume of cured paste is uniformly provided with curing water (until the water is used up), and thus the additional source term may be introduced directly at the macroscopic level.

For a proper description of an additional water source dependent upon the hygral state of the medium it is necessary to assume it as a function of capillary pressure:

$$\dot{m}_{IC}(p^c) = \frac{1}{1-\eta}\frac{\partial m_{IC}}{\partial p^c}\frac{\partial p^c}{\partial t} \tag{10}$$

where η is the volume ratio of the material occupied by water reservoirs (SAP in swollen state or porosity in the LWA) and $\partial m_{IC}/\partial p^c$ is the volume averaged mass of water transported from SAP to the unit volume of cured material due to the increase of capillary pressure in the paste. Thanks to such an approach, the additional source term will account for the internal curing compensation of water loss in the paste caused not only by self-desiccation, but by drying as well.

Further, taking into account, that the sorption isotherms for SAP is written in terms of p^c, in accordance with Eq. (6), it is possible to determine the function $\partial m_{IC}/\partial p^c$ directly at the macro-level:

$$\dot{m}_{IC}(p^c) = \frac{\eta}{1-\eta}\rho^w\frac{\partial S_w^{IC}}{\partial p^c}\frac{\partial p^c}{\partial t}. \tag{11}$$

The function $S_w^{IC} = f(p^c)$ is obtained in accordance with Eq. (6), with parameters determined based on the experimental determination of sorption isotherms for SAP or LWA.

Another possible description of the additional source term considers it as a hydration-degree dependent function. Unlike in the previous approach, where it was natural to describe the desaturation of internal sources in terms of the capillary pressure (i.e., in accordance with the sorption isotherm), here some additional discussion will be presented on the character of the additional source term.

First, taking into account the aforementioned observation that water from the reservoirs is being uniformly distributed, internal curing may be considered as a simple ‘demand-supply’ mechanism. This corresponds to the assumption that internal reservoirs supply water that instantaneously and completely fills empty pore spaces, until all the water contained in the reservoirs is consumed. Following this kind of approach, the kinetics of desorption is assumed to be independent of the growth of capillary suction, as in the previous approach, and to be controlled only by the free space availability in the pores of the paste.

This leads to the simple conclusion, that the saturation degree of pores with water is maintained on the initial level of 100%, until all the water from the reservoirs is consumed due to hydration. In other words, the extra water supplied by reservoirs is assumed to completely compensate the chemical shrinkage of the paste. This is in agreement with the conclusions by Lura et al. [36], who observed the transport of water from pumice to the cement paste by X-ray adsorption measurements, and in parallel measured the chemical shrinkage of the pastes. According to their observation, the desaturation of water reservoirs is approximately proportional to the chemical shrinkage of the paste.

Instead of writing the additional source term, it can just be imposed, that the RHS of the Eq. (1) is zeroed (i.e., the additional source term is equal to the opposite of the remaining terms on the RHS of Eq. (1)) as long as the condition holds:

$$\left(1-\frac{\rho^w}{\rho^s}\right)m_{hydr\infty}(\alpha-\alpha_0) \le \frac{\eta}{1-\eta}\rho^w \tag{12}$$

where the LHS is due to the chemical shrinkage of the paste compensated by internal curing (assuming $S_w = 1$), and the RHS term stands for the total mass of entrained water. One should note that the amount of water supplied by the SAP presented on the LHS of Eq. (12) is smaller than the amount of water consumed by the hydration process $m_{hydr\infty}(\alpha-\alpha_0)$. This is because, at the same time a corresponding build-up of hydration products takes place in pores, thus less water than is consumed is needed to completely fill the pore spaces. It should be however underlined, that with the use of the latter approach, where the source term is in fact a function of hydration degree, it is no longer possible to account for the presence of internal curing during drying, where the desaturation of pores is no longer an effect of hydration process only. On the other hand, as shown by the results of our simulations, this kind of approach better describes the kinetics of water desorption from the internal reservoirs in autogenous conditions, than the capillary suction mechanism.

In Section 5, the results obtained in simulations with the two approaches presented here are compared.

5. Experimental validation

In order to experimentally validate the approach presented in the previous section for the description of the influence of internal curing upon the autogenous phenomena, simulations were carried out based on the experimental research described in Section 2. Thus, the hydration degree evolution, self-desiccation and self-desiccation shrinkage of low w/c mortars were analyzed. The reference mixture had w/c of 0.3, while in the mixture with SAP, an additional w/c$_e$ of 0.04 was entrained. The water-entrained porosity due to SAP was estimated as 3.7%.

For calculation of the hydration degree, based on the cumulative heat of hydration measurements, the total heat of hydration was necessary. It was calculated based on the Bogue-calculated composition of the cement, and on the values of heat of hydration for individual clinker phases [39], as equal to 528 J/g of cement.

The starting point of the simulations corresponds to the age of 12 h after water addition, i.e., the time instant at which the hydration degree was equal to 0.185. This point was chosen based on the fact that that it was the time instant from which a RH drop was observed in the reference mixture. Thus, the experimental results for the autogenous strains of the reference mortar were zeroed at this age.

In the case of autogenous deformation measurements, initial swelling, reaching approximately 80 μm/m, was observed for mortars with SAP for approximately 15 h from final setting. From this point on, shrinkage was observed. The origin of the early expansion phenomenon is still under investigation. Sant et al. [40] suggested crystallization pressure of calcium hydroxide as the possible mechanism contributing to the initial expansion. It is however necessary to realize, that assuming such approach, although it gives some understanding of the swelling origins, it is still hardly possible to quantitatively describe this process. Thus, this mechanism was not taken into account in the presented model. Instead, in order to analyze autogenous shrinkage only and in particular how it is impacted by internal curing, the experimental results for autogenous strains of SAP mortars were zeroed at the point of maximal expansion, i.e., at the age of 24 h from water addition (i.e., about 15 h from final setting).

The initial conditions were assumed as 99.9% RH, $T_0 = 20\,°C$ and $\alpha_0 = 0.185$. Autogenous conditions were provided (i.e., isothermal conditions with $T = 20\,°C$ and no exchange of moisture with the environment). The length of the time steps varied during the computation from 1 s for the first hours of maturing, up to 120 s at later ages.

As the first step of analysis, the parameters of the reference (plain) mortar were calibrated based on the experimental data in accordance with [14,15]. The initial and final porosity values were estimated based on Powers' model [2].

For the description of internal curing, two approaches discussed in Section 4 were applied, i.e., the capillary suction mechanism, with the sorption isotherm for SAP presented in Fig. 1a, and the 'demand-supply' mechanism. The character of sorption isotherm for SAP, especially at RH greater than about 97%, where very steep desaturation takes place, is an important aspect in the simulations using the capillary suction mechanism. However, it should be noticed that the exact character of the desorption curve above 97% RH is not known since it is extremely difficult to determine it experimentally [6]. Although the type of SAP used in the experiments was different than that investigated by Jensen and Hansen [6], the sorption isotherm determined by them was used in the simulations.

For the description of the effective stresses, the constitutive relationship for $\chi_s^{ws}(S_w)$ (see Eq. (9)) proposed by Gawin et al. [15,17] for HPC was used. The material parameters assumed in the simulations are summarized in Table 1.

Table 1
Parameters of the material used in simulations.

Parameter/Property	Value
Cement content, kg/m^3	972
Non-evaporable water content, g/g	0.233
Specific density, kg/m^3	2400
Initial porosity, %	29.0
Final porosity, %	17.6
Parameter a in Eq. (6)	$1.45 \cdot 10^6$
Parameter b in Eq. (6)	9.0
Young modulus, GPa [43]	30
Compressive strength, MPa [42,43]	56
Poisson's ratio [42]	0.20

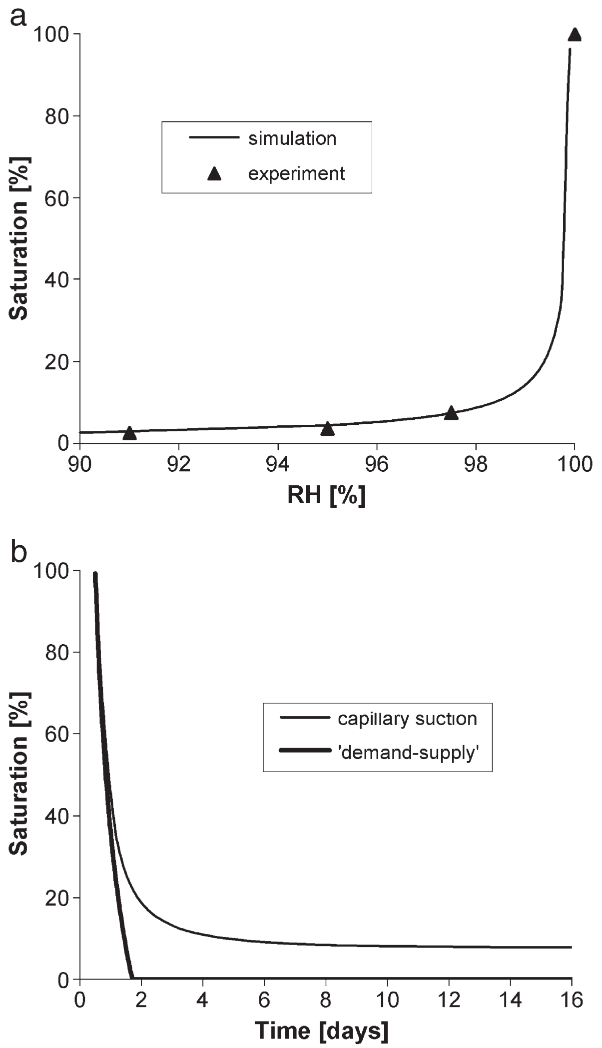

Fig. 1. Hygral characteristics of SAP: sorption isotherm for SAP assumed in simulations compared with [6] (a), and saturation degree of water entrained pores during maturing of mortar for two approaches describing the additional source term (b). Time from water addition.

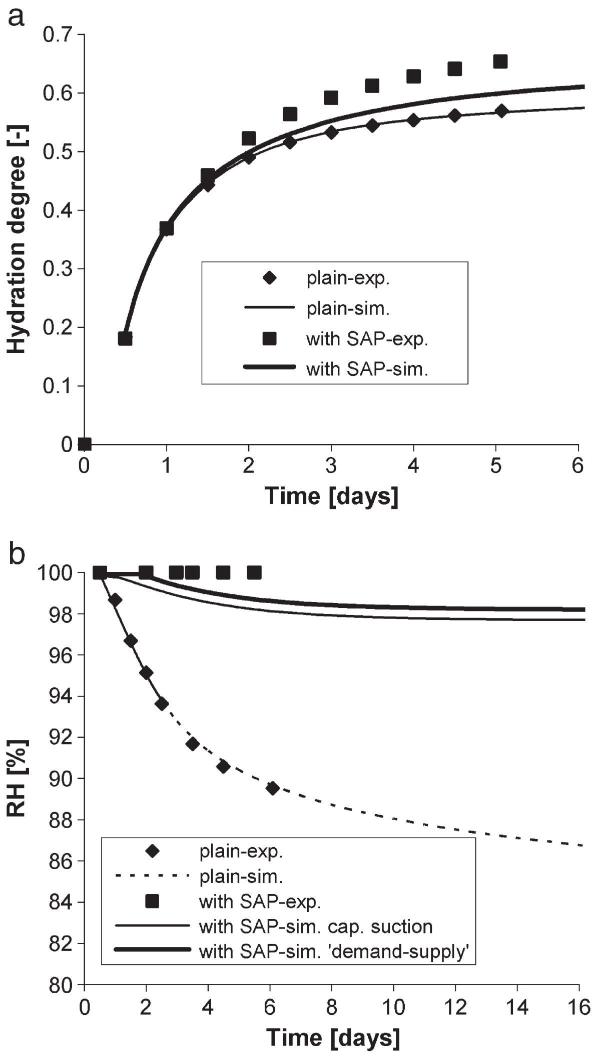

Fig. 2. Comparison of the experimental and simulation results, concerning: hydration degree evolution (a) and autogenous RH evolution (b). The simulation results for hydration evolution for mixtures with SAP for the capillary suction approach and 'demand-supply' approach are overlapping. The experimental results for RH evolution are scaled to 100% RH due to the dissolved salts [2]. Time from water addition. The experimental results are the average of two samples.

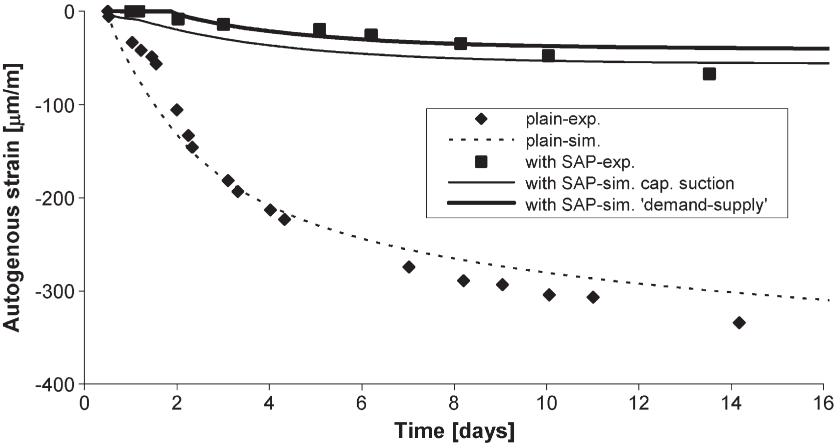

Fig. 3. Comparison of the experimental and simulation results concerning evolution of autogenous strains in plain and SAP mortars. Time from water addition. The experimental results are the average of three samples.

As can be seen in Fig. 2, a very good agreement with the experiments was obtained for the reference mortar, concerning both hydration evolution and autogenous RH evolution.

The values of Young modulus [41], Poisson's ratio [42] and compressive strength [42,43] assumed in simulations based on some published experimental data (Table 1) allowed obtaining a very good agreement of the results concerning strains of the reference mortar, Fig. 3. The compressive strength was needed as a parameter for the calculation of strains according to the B3 model [31], adopted in the model [15].

In Fig. 1b the desorption of SAP during maturing of mortars is compared for the two approaches analyzed. The use of the 'demand-supply' mechanism leads to a full consumption of the curing water from the SAP, while for the capillary suction mechanism, the capillary suction is maintained on the levels which do not allow for full desaturation of the SAP.

As can be seen in Fig. 2a, the influence of internal curing upon the evolution of the hydration degree is underestimated. For the appropriate description of this phenomenon, an extended investigation of the dependence of hydration evolution upon RH would be necessary.

For the description of the self-desiccation process, the use of the 'demand-supply' mechanism leads to a better agreement with experimental results than the capillary suction mechanism, especially qualitatively, since it is possible to simulate the initial period when hardly any self-desiccation takes place.

As can be seen, a very good agreement of the results was obtained for the autogenous shrinkage for the mixture with internal curing, described by means of the 'demand-supply' mechanism, Fig. 3. This concerns both the character of the shrinkage curve, with initial plateau, attributed to the period when no self-desiccation occurs, and the magnitude of the strain. The agreement obtained for the capillary suction mechanism can also be found very satisfying, since it accurately describes the magnitude of the influence of internal curing upon autogenous shrinkage strains.

6. Conclusions

This paper presents a mathematical model of concrete [14,15] applied for description of phenomena taking place during internal curing. The proposed approach is based on introducing the additional water source term into the macroscopic balance equation for water species. This is based on the assumption that the additional curing water from the reservoirs is uniformly distributed within the whole volume of cured material and that it is provided almost instantaneously compared to the desaturation caused by hydration process. This is in agreement both with recent experimental data [36–38] and with numerical investigations [34].

Two mechanisms are proposed to describe the mass source term due to internal curing. The first one is the capillary suction mechanism, based on the statement, that the desaturation of internal water sources is a capillary pressure-governed mechanism. This mechanism is however strongly dependent upon the character of sorption isotherms for internal reservoirs at high relative humidities, which especially for SAP are difficult to determine experimentally. The advantage of such approach, however, is that it is able to account also for external drying and not for self-desiccation only.

The second approach proposed, which better agrees with the experimental observations in autogenous conditions, is the so-called 'demand-supply' mechanism. This approach assumes that all the empty pore volume created due to the hydration process (i.e., the chemical shrinkage) is instantaneously filled with extra water. This process of full compensation for self-desiccation takes place until all the water is consumed from the reservoirs.

The results of the simulations performed with the two proposed approaches are validated against the experimental data obtained for low w/c mortars with SAP. The results of the simulations show that the effect of SAP addition on limiting self-desiccation and autogenous shrinkage are described by the presented model with a very good agreement, both from a qualitative and a quantitative viewpoint.

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References

[1] O.M. Jensen, Autogenous phenomena in cement-based materials, Aalborg University, Denmark, 2005.

[2] P. Lura, O.M. Jensen, K. van Breugel, Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms, Cem. Concr. Res. 33 (2) (2003) 223–232.

[3] O.M. Jensen, P. Lura, Techniques for internal water curing of concrete, Mater. Struct. 39 (9) (2006) 817–825.

[4] A. Bentur, S. Igarashi, K. Kovler, Prevention of autogenous shrinkage in high-strength concrete by internal curing using wet lightweight aggregates, Cem. Concr. Res. 31 (11) (2001) 1587–1591.
[5] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials: I. Principles and theoretical background, Cem. Concr. Res. 31 (4) (2001) 647–654.
[6] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials II: Experimental observations, Cem. Concr. Res. 32 (6) (2002) 973–978.
[7] M. Geiker, D.P. Bentz, O.M. Jensen, Mitigating autogeneous shrinkage by internal curing, in: J.P. Ries, T.A. Holm (Eds.), High Performance Structural Lightweight Concrete, ACI Special Publication, vol. 218, 2004, pp. 143–154, Farmington Hills.
[8] V. Mechtcherine, L. Dudziak, J. Schulze, Internal curing by super absorbent polymers (SAP) – Effects on material properties of self-compacting fibre-reinforced high performance concrete, in: O.M. Jensen, P. Lura, K. Kovler (Eds.), Proceedings of the International RILEM Conference - Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Publications SARL, 2006, pp. 87–96.
[9] P. Lura, O.M. Jensen, S.-I. Igarashi, Experimental observation of internal water curing of concrete, Mater. Struct. 40 (2) (2007) 211–220.
[10] P. Lura, K. Friedemann, F. Stallmach, S. Mönnig, M. Wyrzykowski, L.P. Esteves, Kinetics of water migration (chapter 4), in: V. Mechtcherine, H.W. Reinhardt (Eds.), Report of the RILEM Technical Committee Application of Super Absorbent Polymers in Concrete Construction, 2011, in print.
[11] D.P. Bentz, E.A.B. Koenders, S. Mönnig, H.W. Reinhardt, K. van Breugel, G. Ye, Materials science-based models in support of internal water curing, in: K. Kovler, O.M. Jensen (Eds.), RILEM Report 41 Internal Curing of Concrete, RILEM Publications SARL, 2007, pp. 29–43.
[12] S. Mönnig, Superabsorbing additions in concrete – applications, modeling and comparison of different internal water sources, PhD Thesis, University of Stuttgart, 2009.
[13] K. Maekawa, R. Chaube, T. Kishi, Modelling of concrete performance, Hydration, microstructure formation and mass transport, E&FN Spon, London, 1999.
[14] D. Gawin, F. Pesavento, B.A. Schrefler, Hygro-thermo-chemo-mechanical modelling of concrete at early ages and beyond. Part I: Hydration and hygro-thermal phenomena, Int. J. Numer. Methods Eng. 67 (3) (2006) 299–331.
[15] D. Gawin, F. Pesavento, B.A. Schrefler, Hygro-thermo-chemo-mechanical modelling of concrete at early ages and beyond. Part II: Shrinkage and creep of concrete, Int. J. Numer. Methods Eng. 67 (3) (2006) 332–363.
[16] D. Gawin, M. Wyrzykowski, F. Pesavento, Modeling hygro-thermal performance and strains of cementitious building materials maturing in variable conditions, J. Building Phys. 31 (4) (2008) 301–318.
[17] D. Gawin, F. Pesavento, B.A. Schrefler, Modelling creep and shrinkage of concrete by means of effective stress, Mater. Struct. 40 (6) (2007) 579–591.
[18] ASTM C191 - 08, Standard test methods for time of setting of hydraulic cement by Vicat needle, ASTM International, West Conshohocken, 2008.
[19] ASTM C1698 - 09, Standard test method for autogenous strain of cement paste and mortar, ASTM International, West Conshohocken, 2009.
[20] S.M. Hassanizadeh, W.G. Gray, General conservation equations for multi-phase systems: 1. Averaging procedure, Adv. Water Res. 2 (1979) 131–144.
[21] D. Gawin, Modelling of coupled hygro-thermal phenomena in building materials and building components (in Polish), 853, Editions of Łódź Technical University, 2000, Łódź.
[22] T.C. Hansen, Physical structure of hardened cement paste. A classical approach, Mater. Struct. 19 (114) (1986) 423–436.
[23] O.C. Zienkiewicz, R.L. Taylor, The Finite Element Method, The Basis, vol. 1, Buttterworth-Heinemann, Oxford, 2000.
[24] F.J. Ulm, O. Coussy, Strength growth as chemo-plastic hardening in early age concrete, J. Eng. Mech. 122 (12) (1996) 1123–1132.
[25] M. Cervera, R. Faria, J. Oliver, T. Prato, Numerical modelling of concrete curing, regarding hydration and temperature phenomena, Comput. Struct. 80 (2002) 1511–1521.
[26] Z.P. Bažant, L.J. Najjar, Nonlinear water diffusion in nonsaturated concrete, Mater. Struct. 5 (25) (1972) 3–20.
[27] V. Baroghel-Bouny, M. Mainguy, T. Lassabatere, O. Coussy, Characterization and identification of equilibrium and transfer moisture properties for ordinary and high-performance cementitious materials, Cem. Concr. Res. 29 (8) (1999) 1225–1238.
[28] W.G. Gray, B.A. Schrefler, Thermodynamic approach to effective stress in partially saturated porous media, Eur. J. Mech. A/Solids 20 (2001) 521–538.
[29] Z.P. Bažant, A.B. Hauggaard, S. Baweja, F.J. Ulm, Microprestress-solidification theory for concrete creep. I: Aging and drying effects, J. Eng. Mech. 123 (11) (1997) 1188–1194.
[30] Z.P. Bažant, A.B. Hauggaard, S. Baweja, F.J. Ulm, Microprestress-solidification theory for concrete creep. II: Algorithm and Verification, J. Eng. Mech. 123 (11) (1997) 1195–1201.
[31] Z.P. Bažant, S. Baweja, Justification and refinements of Model B3 for concrete creep and shrinkage 1. Statistic and sensitivity, Mater. Struct. 28 (7) (1995) 415–430.
[32] W.G. Gray, B.A. Schrefler, F. Pesavento, The solid phase stress tensor in porous media mechanics and the Hill-Mandel condition, J. Mech. Phys. Solids 57 (2009) 539–554.
[33] M. Wyrzykowski, Modeling coupled thermo-hygral processes in maturing concrete exposed to internal and external curing, PhD Thesis, Technical University of Lodz, 2010.
[34] M. Wyrzykowski, P. Lura, F. Pesavento, D. Gawin, Modeling of water migration during internal curing with superabsorbent polymers, Journal of Materials in Civil Engineering (2011), submitted for publication.
[35] F. Feyel, Multiscale FE^2 elastoviscoplastic analysis of composite structures, Comp. Mater. Sci. 16 (1) (1999) 344–354.
[36] P. Lura, D.P. Bentz, D.A. Lange, K. Kovler, A. Bentur, K. van Breugel, Measurement of water transport from saturated pumice aggregates to hardening cement paste, Mater. Struc. 39 (9) (2006) 861–868.
[37] P. Trtik, B. Münch, W.J. Weiss, G. Herth, A. Kaestner, E. Lehmann, P. Lura, Neutron tomography investigation of water release from superabsorbent polymers in cement paste, International Conference on Material Science and 64th RILEM Annual Week, September 6–10, 2010, Aachen, Germany.
[38] P. Trtik, B. Münch, W.J. Weiss, A. Kaestner, I. Jerjen, L. Josic, E. Lehmann, P. Lura, Release of internal curing water from lightweight aggregates in cement paste investigated by neutron and X-ray tomography, Nucl. Instrum. Methods. Phys. Res. Section A: Accelerators, Spectrometers, Detectors and Associated Equipment (2011), doi:10.1016/j.nima.2011.02.012.
[39] H.F.W. Taylor, Cement chemistry, second ed. Thomas Telford Publishing, London, 1997.
[40] G. Sant, B. Lothenbach, P. Juilland, G. Le Saout, W.J. Weiss, K. Scrivener, The origin of early age expansions induced in cementitious materials containing shrinkage reducing admixtures, Cem. Concr. Res. 41 (3) (2011) 218–229.
[41] P. Simeonov, S. Ahmad, Effect of transition zone on the elastic behavior of cement-based composites, Cem. Concr. Res. 25 (1) (1995) 165–176.
[42] C.C. Yang, R. Huang, A two-phase model for predicting the compressive strength of concrete, Cem. Concr. Res. 26 (10) (1996) 1567–1577.
[43] A. Boumiz, C. Vernet, F. Cohen Tenoudji, Mechanical properties of cement pastes and mortars at early ages: evolution with time and degree of hydration, Adv. Cem. Bas. Mat. 3 (3–4) (1996) 94–106.