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10 **Hygro-Thermo-Chemical Modeling of High Performance Concrete. I:**
11 **Theory**

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6 **Abstract:** This study deals with the formulation, calibration, and validation of a new hygro-thermo-
7 chemical model for high-performance concrete (HPC) suitable for the analysis of moisture transport
8 and heat transfer at the early age and beyond. In Part I of this study the theoretical formulation
9 is presented and discussed in detail. Classical macroscopic mass and energy conservation laws are
10 written by using humidity and temperature as primary variables and by taking into account explicitly
11 various chemical reactions, such as cement hydration, silica fume reaction, and silicate polymerization.
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13 The effect of cement hydration is modeled through the classical concept of hydration degree. Silica
14 fume reaction and silicate polymerization are modeled by introducing the degree of silica fume reaction
15 and the concentration of silicate polymers, along with their evolution laws. The present model can
16 simulate early age phenomena, such as self-heating and self-desiccation, with great accuracy. Numerical
17 implementation, calibration and validation of the model by comparison with experimental test data are
18 postponed to Part II of this study [1].

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Keywords: Concrete, Early Age, Moisture, Temperature, Relative Humidity, Hydration, Silica Fume
35 Reaction, Polymerization.

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1 Introduction

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45 Durability and serviceability are nowadays two of the most important issues in concrete construc-
46 tions. Premature deterioration of reinforced concrete, due to corrosion of the reinforcing steel,
47 greatly affects the structural performance, shortens the service life of structures and increases
48 maintenance costs. To overcome this problem, since the early nineties, high-performance concrete
49 (HPC) mixes, characterized by low permeability and high strength, have been formulated and
50 used in design. Unfortunately, HPC constructions are more prone to cracking (especially at the
51 very early age) which produces a direct path for corrosive agents to reach the reinforcing steel
52 and completely defeats the beneficial effect of HPC low permeability. The most common cause of
53 cracking at the early-age is the restraint of concrete to volume changes. Typically three different
54 kinds of volume changes occur in concrete structures: (1) thermal expansion due to heat released
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6 by exothermic chemical reactions; (2) shrinkage due to release of water through external concrete
7 surfaces (drying shrinkage); and (3) shrinkage due to water consumption (autogeneous shrinkage)
8 during cement hydration and other chemical reactions, such as the silica fume (SF) reaction and
9 silicate polymerization. The effect of autogeneous shrinkage is small (and usually negligible) for
10 standard concrete whereas it is significant for HPC.
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13 As a consequence of the aforementioned volume changes, uniform and/or non-uniform stress
14 states develop in concrete even in the absence of external loads. This is the typical situation
15 occurring in composite bridges, in which the deck, subjected to shrinkage and restrained by the
16 girders underneath, undergoes tensile stresses, which in some cases reach the tensile strength
17 leading to transverse cracking. The overall scenario is complicated by the fact that, at an early
18 age, concrete strength is under development and the build-up of strength depends on the evolution
19 of the chemical reactions involved in the aging process, which, in turn, depends on temperature,
20 humidity, and admixture materials. Reliable and predictive analyses of the behavior of concrete
21 structures at early ages (and beyond) require the formulation of a consistent theoretical framework
22 that includes all of the various phenomena characterizing early age evolution of concrete.
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25 Many experimental, theoretical, and computational studies on the behavior of concrete at
26 the early age and, specifically, on self-heating and self-desiccation can be found in the literature.
27 Among others, Wittmann [2] calculated the moisture profiles in high strength concrete by adding
28 a sink term in the diffusion equation to account for endogenous drying. In the aforementioned
29 study, however, the effect of hydration heat was neglected. Ulm and Coussy [3] developed a
30 thermodynamics based theory for the description of cement hydration. This theory was refined
31 by Cervera [4], who proposed a coupled thermo-chemo-mechanical model to simulate the aging
32 effect on strength and damage. The focus of these studies was mainly the evolution of hydration,
33 and hygral phenomena (which are important for HPC) were neglected. Also Bažant et al [5]
34 developed a comprehensive material model for the simulation of cracking at early age considering
35 only temperature effects. More recently Gawin et al. [6] proposed a refined model based on
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the interpretation of concrete as a multi-phase porous material and on the use of homogenization techniques. Such model has showed a good capability in fitting experimental results, but it does not take into account the effect of SF reaction and silicate polymerization. Similarly, only hydration was modeled in the study by Oh and Cha [7], in which a model for moisture and temperature calculation in early-age concrete was developed.

Typical HPC mixes are characterized by low (<0.4) water-to-cement ratio, high cement content, and, most importantly, by the incorporation of SF or other pozzolanic materials [8]. The pozzolanic reaction associated with the presence of SF determines a denser microstructure and leads to increased performance of concrete in terms of strength and durability. In addition, SF is known to accelerate silicate polymerization [9], which is a gradual bonding of particles of calcium silicates hydrates (C-S-H). This increases the average degree of polymerization of the silicate chains and causes the so-called chemical aging of C-S-H [10]. Both pozzolanic reaction and silicate polymerization interact with cement hydration [9] influencing concrete mesostructure and, ultimately, concrete behavior at early age and beyond. None of the analytical models currently available in the literature can simulate the effect of SF reaction and polymerization on heat transfer and moisture transport in concrete.

The objective of the present study is to overcome the limitations mentioned above and to simulate moisture transport and heat transfer in HPC by taking into account explicitly the coupled effect of cement hydration, SF pozzolanic reaction, and silicate polymerization. In the present part I, only the theoretical formulation will be presented. The subsequent part II [1] will present the numerical implementation and will report the results of extensive calibration and validation activities performed on the basis of experimental data available in the literature.

2 Moisture Transport Governing Equation

Water can be found in concrete in various phases [11, 12, 13] that can be classified as follows: (a) capillary water, (b) water vapor, (c) adsorbed water, and (d) non-evaporable (chemically

bound) water. The capillary water is liquid water filling capillary pores (empty volume among cement particles) and its state can be described through the capillary pressure, which is governed by Kelvin's equation [14]. If capillary pores are not fully saturated, the capillary water is in equilibrium with air and water vapor, which can be assumed to behave as incompressible gases [14]. Near pore walls, van de Waals forces retain water molecules and cause them to form thin adsorbed water layers. The thickness of the adsorbed layers is an increasing function of the *relative humidity* h . In small micropores (gel pores) of few Å the adsorbed water layers cannot fully develop for high relative humidity conditions and, for this reason, they are referred to as hindered adsorbed water layers [13].

The mobility of water along adsorbed water layers is rather limited (especially for hindered adsorbed water) and the transport mechanism is completely different compared to the transport of capillary water and water vapor. In addition, all moisture transport mechanisms are influenced by concrete microstructure (in particular the microstructure of calcium silicates hydrates), which, in turn, depends on the extent of the chemical reactions that characterize concrete at early ages. Moreover, these chemical reactions often involve water, which may be subtracted from the system (e.g. during cement hydration) or released into the system (e.g. during silicate polymerization). When water is chemically combined with other chemical compounds, it loses its mobility completely and it cannot contribute to moisture transport. In the literature, the chemically bound water is typically referred to as non-evaporable water because it is retained even at temperature exceeding 105 °C.

In principle, the different water transport mechanisms should be modeled independently through the formulation of separate diffusion equations since each single mechanism has its own driving force (capillary pressure for the capillary water, vapor pressure for the water vapor, etc.). However, the complexity of the phenomena hampers this kind of approach and calls for a simplified approximated analysis. First of all, it is possible to simplify the problem by postulating the existence of local thermodynamic equilibrium ([13, 15, 6], among others). This assumption approximately

holds also in presence of a chemical evolution of the system (aging), since the characteristic times
 of the water transport mechanisms are much smaller than those associated with concrete chemical
 reactions. In Gawin et al. [6] two separate diffusion equations were used to model separately
 the transport of water vapor and the transport of capillary and adsorbed water. Although the
 approach is certainly worth mentioning, it seems that the increased complexity (and the increased
 number of material parameters to be calibrated) is not compensated by more accuracy in modeling
 experimental evidence. In addition, modeling capillary water transport and adsorbed water (free
 and hindered) transport through only one equation [6] is an approximation of the same order (at
 least at standard room temperatures) as combining phenomenologically all the transport mecha-
 nisms in one single phenomenological macroscopic equation ([13, 16, 60], among many others).

In this study, as widely accepted in the literature, the latter option is exploited and the overall
 moisture transport process under isothermal conditions is described through the Fick's law that
 expresses the flux of water mass per unit time \mathbf{J} as proportional to the spatial gradient of the
 relative humidity h

$$\mathbf{J} = -D_h(h, T) \nabla h \quad (1)$$

The proportionality coefficient $D_h(h, T)$ is called *moisture permeability* and it is a nonlinear func-
 tion of the relative humidity h and temperature T [16]. The choice of the relative humidity h as
 the state variable of the problem (in addition to the temperature T) is done here for convenience
 but other options can be equivalently adopted [15].

The moisture mass balance requires that the variation in time of the water mass per unit
 volume of concrete (water content w) be equal to the divergence of the moisture flux \mathbf{J}

$$-\frac{\partial w}{\partial t} = \nabla \cdot \mathbf{J} \quad (2)$$

The water content w can be expressed as the sum of the evaporable water w_e (capillary water,
 water vapor, and adsorbed water) and the non-evaporable (chemically bound) water w_n [18, 19].
 For reasons discussed later in this paper, it is reasonable to assume that the evaporable water is

a function of relative humidity, h , *degree of hydration*, α_c , and *degree of silica fume reaction*, α_s , i.e. $w_e = w_e(h, \alpha_c, \alpha_s)$ =age-dependent sorption/desorption isotherm [20]. Under this assumption the water content variation in time reads

$$\frac{\partial w}{\partial t} = \frac{\partial w_e}{\partial t} + \frac{\partial w_n}{\partial t} = \frac{\partial w_e}{\partial h} \frac{\partial h}{\partial t} + \frac{\partial w_e}{\partial \alpha_c} \dot{\alpha}_c + \frac{\partial w_e}{\partial \alpha_s} \dot{\alpha}_s + \dot{w}_n \quad (3)$$

where the total time derivatives of α_c , α_s , and w_n are used instead of the partial derivatives in order to stress the fact that these variables will serve as internal variables, as opposed to results from the solution of the boundary value problem. Note that total and partial derivatives of these quantities coincide since the mass conservation equation is written with reference to the initial (undeformed) spatial configuration.

By substituting Eqs. 1 and 3 into Eq. 2 one obtains

$$\nabla \cdot (D_h \nabla h) - \frac{\partial w_e}{\partial h} \frac{\partial h}{\partial t} - F(h, \alpha_c, \alpha_s, \alpha_p) = 0 \quad (4)$$

and

$$F_h(h, \alpha_c, \alpha_s, \alpha_p) = \frac{\partial w_e}{\partial \alpha_c} \dot{\alpha}_c + \frac{\partial w_e}{\partial \alpha_s} \dot{\alpha}_s + \dot{w}_n \quad (5)$$

where $\partial w_e / \partial h$ is the slope of the sorption/desorption isotherm (also called *moisture capacity*), α_p is the concentration of silicate polymers, and the function $F_h(h, \alpha_c, \alpha_s, \alpha_p)$ expresses the effect of concrete aging on the the diffusion process. In particular, the first two terms account for the microstructural changes associated with concrete chemical reactions and the last term accounts for the internal “consumption” of water involved in the chemical reactions. When only cement hydration is accounted for, this last term is called *moisture sink* and it explains the well-known *self-desiccation* phenomenon observed in high-performance concrete. For old enough normal concrete one has $F_h(h, \alpha_c, \alpha_s, \alpha_p) \approx 0$, whereas $F(h, \alpha_c, \alpha_s, \alpha_p) \neq 0$ for early age normal concrete and, in general, for HPC.

The governing equation (Eq. 4) must be completed by appropriate boundary and initial

conditions. The initial conditions specify the relative humidity in the whole problem domain at time instant $t = 0$ and the boundary conditions specify either the relative humidity on the boundary Γ , $h(t)|_{\Gamma} = \bar{h}(t)$ (Dirichlet's type) or the moisture flux orthogonal to the boundary $-(D_h \nabla h) \cdot \mathbf{n}|_{\Gamma} = \alpha_h(h - h_{\infty})$ (Cauchy's type).

3 Temperature Evolution Due to Exothermic Chemical Reactions

The coefficients of the diffusion equation presented in Sec. 2 depend on temperature, therefore the temperature field needs to be calculated. Note that, since the chemical reactions associated with cement hydration and SF reaction are exothermic, the temperature field is not uniform for non-adiabatic systems even if the environmental temperature is constant.

Heat conduction can be described in concrete, at least for temperature not exceeding 100 °C [21], by Fourier's law, which reads

$$\mathbf{q} = -\lambda \nabla T \quad (6)$$

where \mathbf{q} is the heat flux, T is the absolute temperature, and λ is the heat conductivity. For the temperature range considered in this study ($T < 100^{\circ}\text{C}$), the heat conductivity λ of concrete is known to depend mildly on temperature, moisture content, and aging [22]. However, many authors in the past have obtained good numerical predictions by neglecting this dependence [16]. For the sake of simplicity, the same assumption is made herein. An average value of $\lambda = 2.3\text{W/m}^{\circ}\text{C}$ [21] will be used for the numerical simulations presented in Part II of this study.

The enthalpy balance equation can be written as

$$\rho c_t \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q} + \dot{Q}_c + \dot{Q}_s + \dot{Q}_p \quad (7)$$

where ρ is the mass density of concrete, and c_t (ranging from 840 to 1170 J/kg°C [22]) is the isobaric heat capacity (specific heat) of concrete. An average value of $c_t = 1100 \text{ J/kg}^{\circ}\text{C}$ can be generally adopted for all concretes. \dot{Q}_c , \dot{Q}_s , and \dot{Q}_p represent the rate of heat generation per unit

volume due to cement hydration, SF reaction, and silicate polymerization, respectively. Since, to the best of the authors knowledge, there is no evidence of temperature variation associated with the polymerization of silicates, $\dot{Q}_p = 0$ is adopted hereinafter.

If one assumes, as commonly accepted in the literature [3, 25, 4, 6] and confirmed by various theoretical and experimental investigations [23], that the latent heat of hydration reaction per unit of hydrated mass (\tilde{Q}_c^∞) is constant for a given concrete, then one can write [4]

$$\dot{Q}_c = \dot{\alpha}_c c \tilde{Q}_c^\infty \quad (8)$$

where $\dot{\alpha}_c$ is the rate of the hydration degree discussed in Sec. 4 and c is the cement mass content.

The temperature rise due to cement hydration (commonly referred to as self-heating) can be substantial, especially in massive structures; temperature increase up to 60°C has been reported, for example, in [24, 26].

Similarly to the hydration heat, also the heat generated by SF reaction can be expressed as [25]

$$\dot{Q}_s = \dot{\alpha}_s s \tilde{Q}_s^\infty \quad (9)$$

where $\dot{\alpha}_s$ is the rate of pozzolanic reaction degree, which will be discussed later in Sec. 5, s is the SF mass content, and \tilde{Q}_s^∞ is the latent heat of SF reaction per unit mass of reacted SF.

The hydration enthalpy, \tilde{Q}_c^∞ , can be measured by conducting calorimetric tests at complete hydration; typical values range from 400 kJ/kg to 550 kJ/kg, depending upon cement composition [24]. If the exact phase composition of the cement is known, \tilde{Q}_c^∞ can be determined from weighted average of the heat of hydration of each single compound

$$\tilde{Q}_c^\infty = Q_{C_3S}^\infty W^{C_3S} + Q_{C_2S}^\infty W^{C_2S} + Q_{C_3A}^\infty W^{C_3A} + Q_{C_4AF}^\infty W^{C_4AF} + \dots \quad (10)$$

where Q_i^∞ is the individual enthalpy of reaction for each compound, and W^i is the initial percentage weight for each compound.

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6 The enthalpy of SF reaction, \tilde{Q}_s^∞ , can be assumed to be constant and equal to 780 kJ/kg [26].
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8 By substituting Eqs. 6, 8, and 9, into Eq. 7 one obtains
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17 where $F_T(\alpha_c, \alpha_s) = \dot{\alpha}_s s \tilde{Q}_s^\infty + \dot{\alpha}_c c \tilde{Q}_c^\infty$. For old enough concrete $F_T(\alpha_c, \alpha_s) \approx 0$.
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19 The energy conservation governing equation (Eq. 11) must be completed by appropriate bound-
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$$\nabla \cdot (\lambda \nabla T) - \rho c_t \frac{\partial T}{\partial t} + F_T(\alpha_c, \alpha_s) = 0 \quad (11)$$

where $F_T(\alpha_c, \alpha_s) = \dot{\alpha}_s s \tilde{Q}_s^\infty + \dot{\alpha}_c c \tilde{Q}_c^\infty$. For old enough concrete $F_T(\alpha_c, \alpha_s) \approx 0$.

The energy conservation governing equation (Eq. 11) must be completed by appropriate boundary and initial conditions. The initial conditions specify the temperature in the whole problem domain at time instant $t = 0$ and the boundary conditions specify either the temperature at the boundary Γ , $T(t)|_\Gamma = \bar{T}(t)$ (Dirichlet's type) or the heat flux orthogonal to the boundary $-(\lambda \nabla T) \cdot \mathbf{n}|_\Gamma = \alpha_T(T - T_\infty)$ (Cauchy's type).

4 Cement Hydration

Cement hydration is characterized by the reaction of free-water with unhydrated cement particles, which are mainly composed by calcium silicates (C_3S and C_2S), calcium aluminates (C_3A), and calcium aluminoferrites (C_4AF). The products (cement hydrates) of this reaction are mainly calcium silicates hydrates (C-S-H), calcium hydroxide (CH), ettringite (Aft), and monosulfate (Afm) [9]. Although cement hydration has been studied for many years [9, 22], the exact stoichiometry of the chemical reactions involved is not known and their mutual interaction as well as the influence of external factors (such as temperature, relative humidity, etc.) is not completely understood. As a consequence, in the literature, studies that consider each chemical reaction independently are very limited [7] whereas many authors [27, 3, 28, 25, 29] have studied cement hydration with reference to an overall hydration process. The present study adopts the latter approach.

When a cement grain is immersed in water, a layer of soft gel (composed by cement hydration products) forms on the surface of the grain. As hydration progresses, this layer grows both inward and outward around a hard core of unhydrated cement. In order for the hydration to continue, water needs to reach the unhydrated grain core and therefore the water diffusion process through

the layer of hydrated compounds is typically considered the dominant mechanisms governing
 the hydration kinetics. According to the thermodynamics based model proposed by Ulm and
 Coussy [3, 28] and later revisited by Cervera et al. [4], the hydration kinetics can be described
 by postulating the existence of a Gibb's free energy dependent on the external temperature T
 and the *hydration extent* χ_c . The latter represents, in the case of a closed chemical system, the
 number of chemically combined moles of water per unit volume of concrete and it expresses the
 thermodynamic imbalance between the chemical constituents. The hydration extent can be also
 used to define a normalized measure of the hydration process, the *hydration degree*, as

$$\alpha_c = \frac{\chi_c}{\bar{\chi}_c^\infty} \quad (12)$$

where $\bar{\chi}_c^\infty$ is the theoretical asymptotic values of the hydration extent in ideal hygrometric conditions. The actual asymptotic value of hydration extent, χ_c^∞ , is always smaller than the theoretical value, $\bar{\chi}_c^\infty$, since, in practice, ideal hygrometric conditions are never met. The ratio between the actual and the theoretical asymptotic values is the asymptotic degree of hydration $\alpha_c^\infty = \chi_c^\infty / \bar{\chi}_c^\infty$, which has been shown to be always smaller than the unity [24].

By assuming that the thermodynamic force conjugate to the hydration extent, called the *chemical affinity*, is governed by an Arrhenius-type equation and that the viscosity governing the diffusion of water through the layer of cement hydrates is an exponential function of the hydration extent [3], Cervera et al. [4] proposed the following evolution equation for the hydration degree

$$\dot{\alpha}_c = A_c(\alpha_c) e^{-E_{ac}/RT} \quad (13)$$

and

$$A_c(\alpha_c) = A_{c1} \left(\frac{A_{c2}}{\alpha_c^\infty} + \alpha_c \right) (\alpha_c^\infty - \alpha_c) e^{-\eta_c \alpha_c / \alpha_c^\infty} \quad (14)$$

where $A_c(\alpha_c)$ is the so called *normalized chemical affinity*, E_{ac} is the hydration activation energy, R is the universal gas constant, and η_c , A_{c1} , A_{c2} are material parameters. The ratio E_{ac}/R can be

6 experimentally determined and it ranges from 3000 to 8000 K for concrete. In the present study
7 the value $E_{ac}/R = 5000$ K will be adopted when specific measurements are not available. The
8 parameters η_c , A_{c1} , A_{c2} can be calibrated, for example, by simulating the temperature evolution
9 during adiabatic tests as it will be discussed in Part II of this study [1].
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12 Moreover, it is well known from experiments that if the relative humidity decreases below a
13 certain value ($h \approx 75\%$), the hydration process slows down and may even stop [12, 30]. This
14 phenomenon can be taken into account [6] by rewriting Eq. 13 as
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$$24 \quad \dot{\alpha}_c = A_c(\alpha_c) \beta_h(h) e^{-E_{ac}/RT} \quad (15)$$

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$$30 \quad \beta_h(h) = [1 + (a - ah)^b]^{-1} \quad (16)$$

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34 The function $\beta_h(h)$ is an empirical function that was first proposed for the definition of the
35 equivalent hydration period by Bažant and Prasannan [30]. The parameters a and b can be
36 calibrated through the analysis of experimental data but the constant values $a = 5.5$ and $b = 4$
37 can be generally adopted [6, 30].
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44 5 Silica Fume Reaction

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48 A certain amount of SF is often added in concrete mixture in order to produce HPC [31, 32]. SF
49 belongs to the category of highly pozzolanic materials and it consists of silica in noncrystalline
50 form with a high specific surface and exhibiting high pozzolanic activity.
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53 From the chemical-physical point of view, three principal mechanisms have been suggested
54 in the literature to explain SF effects on concrete: (1) SF particles cause pore blockage in the
55 hydrating cement producing a denser hydrating gel structure [33]. (2) Pozzolanic reactions occur
56 between the silica-rich SF particles and the portlandite (CH) generating Calcium Silicate Hydrates
57 (C-S-H) [34]. (3) SF particles act as nucleation sites for cement hydration, accelerating the hy-
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dratation process [35]. While the CH is relatively weak and brittle, the C-S-H phase formed by the pozzolanic reaction has a microscopic morphology similar to that developed by cement hydration [36]. Consequently, the additional C-S-H produced by the pozzolanic reaction leads to higher strength, lower porosity, and improved chemical resistance [8].

The exact stoichiometry of pozzolanic reaction between SF and CH is not known exactly, especially in relation to the water stoichiometry coefficient. On this issue the current literature shows dissonant results. According to Sellevold [37] the amount of water bound in the C-S-H formed by the pozzolanic reaction should be the same as that contained in the CH. Other experimental investigations [38], however, suggest that the chemically bound water per gram of cement increases in cement pastes containing SF. In contrast to these findings, Li et al. [39] found a reduction of chemically bound water in concrete mixes containing SF. In addition, experimental results by Papadakis [40] suggest that the reaction takes place without additional water.

A possible reason for the contradictory results reported above is that the presence of SF accelerates and amplifies the process of polymerization of C-S-H gel phase [41] which leads to a release of the water previously combined during cement hydration (reduction of the chemically bound water) and a consequent increase of the free water [42]. In the present study, C-S-H polymerization will be addressed separately as discussed in Sec. 6 and it is assumed that no water is involved (consumed or released) in the SF pozzolanic reaction (Sec. 8).

The effect of SF on moisture transport phenomena is here modeled through the introduction of the degree of SF reaction, α_s , defined as the ratio between the amount of reacted SF and the total amount of SF. Since the kinetics of the pozzolanic reaction can be assumed to be a diffusion controlled process [43, 44, 45], the theory adopted in Sec. 4 to describe cement hydration can be exploited here to describe the evolution of SF reaction. Accordingly, one has

$$\dot{\alpha}_s = A_s(\alpha_s) e^{-E_{as}/RT} \quad (17)$$

and

$$A_s(\alpha_s) = A_{s1} \left(\frac{A_{s2}}{\alpha_s^\infty} + \alpha_s \right) (\alpha_s^\infty - \alpha_s) e^{-\eta_s \alpha_s / \alpha_s^\infty} \quad (18)$$

where A_s is the SF normalized affinity, E_{as} is the activation energy of SF reaction, and α_s^∞ is the asymptotic value of SF reaction degree. $E_{as}/R = 9700$ K can be generally assumed [24]. The material parameters A_{s1} , A_{s2} and η_s can be calibrated similarly to the parameters governing cement hydration [1].

Contrarily to cement hydration, the pozzolanic reaction of the SF seems to be less sensitive to the relative humidity and it is able to continue to near completion even in presence of very low relative humidity [46, 47]. Consequently, the rate of SF reaction degree is assumed not to depend on h .

When a sufficient amount of SF is available in concrete, all the CH produced by cement hydration can be consumed by the pozzolanic reaction. For a water-to-cement ratio, w/c , of about 0.5 (normal concrete), about 16% of SF is required to consume all the calcium hydroxide during the pozzolanic reaction [49]. For lower values of w/c , the required amount of SF, $(s/c)_{req}$, to consume all the calcium hydroxide is reduced proportionally and the proportionality coefficient of 0.4 can be used as confirmed by experiments on carbonation shrinkage [49]. One can write

$$(s/c)_{req} = \min(0.16, 0.4 w/c) \quad (19)$$

If the amount of SF exceeds the minimum required amount of SF to consume all the calcium hydroxide, the asymptotic degree of SF reaction is smaller. Assuming a linear relationship between α_s^∞ and the inverse of s/c , the asymptotic degree of SF reaction degree can be estimated as

$$\alpha_s^\infty = SF^{eff} \min \left[1, \frac{(s/c)_{req}}{s/c} \right] \quad (20)$$

where SF^{eff} is the "efficiency" of SF, i.e. the mass ratio between the SiO_2 mass content and the total mass of SF. Since only the SiO_2 participates to the pozzolanic reaction, the remaining part

of SF does not participate in any chemical reaction and has the role of an inert filler. Typically, SF_{eff} ranges from 0.85 to 0.92 [9].

6 Silicate Polymerization

Many experimental investigations [9] revealed that C-S-H particles bond together over time, increasing the average degree of polymerization of the silicate chains and causing the C-S-H to become stiffer, stronger, and denser. The key reaction for linking the C-S-H gel hydrolyzed molecules together is the condensation. In condensation reactions, covalent bonds are rearranged in such a way that two monomers are connected to form a polymeric cluster and water is “condensed” out.

Portland cement contains, among other things, silicates, which are minerals that contain silicate anion and various cations (e.g., calcium, sodium, magnesium, iron, aluminum ions). In presence of water, silicates become hydrated and some of the oxygens form a covalent bond with a hydrogen nucleus from the water. Since the hydrated silicates contain Si-OH bonds, condensation is possible along with the creation of a polymerized silicate framework. This process occurs slowly at standard room temperature, but it can be greatly accelerated by curing at elevated temperature and it may be induced also by drying [50, 51]. This chemical aging process of C-S-H can thus affect many of the physical properties of cement paste and concrete, such as permeability, strength capacity, shrinkage and creep behavior [52].

Silicate polymerization is much more pronounced in the presence of SF because the SF pozzolanic reaction increases the content of C-S-H gel. When the water consumed by cement hydration is less than the water condensed by silicate polymerization, one can observe a reduction of the non-evaporable water content starting after 2-3 months [49, 54]. Zhang and Gjørv [54] observed, for cement paste containing SF and characterized by various water-to-binder ratios, an increase of non-evaporable water content for up to 90 days, and a reduction of the non-evaporable water content after 550 days. This reduction was higher for higher SF content. This implies that, even if for standard concrete silicate polymerization can be neglected, it needs to be considered in

presence of SF. Silicate products of portland cements will generally be polymerized over time with
 an increase of the average chain length of polysilicates in C-S-H gel and with water release. The
 polymerization process can be modeled through the relative concentration of silicate polymers,
 α_p , defined as the ratio between the mass of polymeric species and the mass of C-S-H gel. The
 rate of the relative concentration of silicate polymers can be formulated as

$$\dot{\alpha}_p = A_{p1} A_p(\alpha_p) B_p(\alpha_c) e^{-E_{ap}/RT} \quad (21)$$

and

$$A_p(\alpha_p) = \alpha_p^\infty - \alpha_p \quad B_p(\alpha_c) = H(\alpha_c - \alpha_c^0) \quad (22)$$

where the term $A_{p1} e^{-E_{ap}/RT}$ describes the kinetics of the chemical reaction, the coefficient $A_p(\alpha_p)$ expresses the fact that the rate of polymerization is reduced as polymerization progresses and it eventually vanishes when the polymerization is complete ($\alpha_p = \alpha_p^\infty$, where $\alpha_p^\infty = 1$), the coefficient $B_p(\alpha_c)$ takes into account the effect of cement hydration (hydration products need to be present for the polymerization to occur), and $H(\cdot)$ is the Heaviside step function, used here to set a threshold value of hydration degree, α_c^0 , below which the polymerization process can be neglected. According to the experimental results of Hirljac et al. [50] on the alite (C_3S), the value of $\alpha_c^0 = 0.1$ can be adopted. Brough et al. [53] found an Arrhenius energy of 35 kJ/mol for dimeric reactions and of 100 kJ/mol for reactions producing higher polymeric species. In this study it is assumed an averaged value of 50 kJ/mol, which gives $E_{ap}/R = 6000K$.

The material parameter A_{p1} can be calibrated on the basis of experimental data on the evolution of the polymerized species, as discussed in Part II of this study [1].

7 Asymptotic Hydration Degree

As mentioned earlier the asymptotic (ultimate) hydration degree, α_c^∞ , is always less than one [24]. This is due to the fact that the unit value can be reached only in ideal conditions, i.e. with an

adequate water-to-cement ratio to ensure full hydration and perfect contact between the water and the cement grains. In practice, these conditions are never fulfilled during curing and complete hydration of concrete is never achieved [12, 55].

Pantazopoulou and Mills [19] proposed to calculate α_c^∞ on the basis of a mass balance between water needed to ensure saturation conditions and total water content. At infinite time, this balance equation reads

$$w_0 + \Delta w_c^\infty = w_e^\infty + w_n^\infty \quad (23)$$

where $w_0 = (w/c)c$ is the initial water content (neglecting the amount of entrained air content), w_e^∞ and w_n^∞ are the asymptotic evaporable water and chemically bound water, respectively. Δw_c^∞ is the amount of water that needs to be provided in order to maintain full saturation conditions during hydration and that corresponds to the so-called chemical shrinkage caused by the fact that hydration products have a lower volume than the sum of anhydrous cement and water [19]. Experimental studies [18] have shown that per each gram of hydrated portland cement: (a) approximately 0.253 g of water is chemically bound ($w_n = 0.253c\alpha_c$); (b) the evaporable water is proportional to the chemically bound water and the coefficient of proportionality can be estimated as $3.83w/c$ ($w_e \approx 3.83(w/c)w_n$); (c) the amount of water that needs to be supplied to overcome the chemical shrinkage and maintain saturation is $\Delta w_c = 0.065c\alpha_c$. Based on these observation and by using Eq. 23 Pantazopoulou and Mills [19] obtained

$$\alpha_c^\infty = \frac{1.031 w/c}{0.194 + w/c} \quad (24)$$

The presence of SF further reduces the ultimate achievable hydration degree because, due to the formation of additional C-S-H gel from the pozzolanic reaction, extra water is hindered into the gel pores and it becomes unavailable for cement hydration [24]. In addition, the specific surface of the C-S-H gel increases and unhydrated cement grain cores become less accessible. Note that this does not imply that the overall amount of C-S-H created is less (actually the opposite is true) because the C-S-H coming from the SF pozzolanic reaction must be added to the one coming from

the hydration.

The effect of SF on the water balance equation at saturation (Eq. 23) can be taken into account by considering (1) on the right hand side, an increased quantity of water held in the gel due to the pozzolanic reaction plus water released during silicate polymerization (roughly 0.50 g/g of reacted SF according to [56]) and, (2), on the left hand side, the amount of water that needs to be provided in order to maintain saturation conditions and that corresponds to the chemical shrinkage caused by pozzolanic reactions (roughly 0.22 g/g of reacted SF according to [56]). The SF pozzolanic reaction is considered not to consume water as discussed in Sec. 5.

Based on these observations, the balance equation (Eq. 23) can be rewritten as

$$w_0 + 0.065 c \alpha_c^\infty + 0.22 s \alpha_s^\infty = 0.253 (3.83 w/c + 1) c \alpha_c^\infty + 0.5 s \alpha_s^\infty \quad (25)$$

where s is SF content and α_s^∞ is the asymptotic SF reaction degree given by Eqs. 19 and 20.

Solving Eq. 25 for the asymptotic degree of cement hydration, one obtains

$$\alpha_c^\infty = \frac{1.032w/c - 0.279(s/c)\alpha_s^\infty}{0.194 + w/c} \quad (26)$$

The asymptotic degree of hydration must be positive and so Eq. 26 holds only if $w/c > 0.27(s/c)\alpha_s^\infty$. This condition is always fulfilled by typical HPC mixes (e.g., for $w/c = 0.3$ and $s/c = 0.1$ one gets $0.3 \gg 0.279 \times 0.1 \approx 0.028$).

8 Non-Evaporable Water

As discussed previously, the non-evaporable water is the amount of water that is chemically bound as consequence of cement hydration, SF reaction, and silicate polymerization. In general, one can write

$$w_n(\alpha_c, \alpha_s, \alpha_p) = \kappa_c \alpha_c c + \kappa_s \alpha_s s - \alpha_p (\kappa_{pc} c + \kappa_{ps} s) \quad (27)$$

The first term represents the effect of cement hydration and κ_c is the mass ratio of non-evaporable water at full hydration. It can be assumed $\kappa_c = 0.253$ [12, 18, 20]. The second term represents the effect of SF reaction and, according to the discussion in Sec. 5, it can be assumed $\kappa_s = 0$. The third term characterizes the effect of polymerization and the negative sign traduces the fact that during silicate polymerization water is released in the system and the chemically bound water is reduced. Experimental studies showed that the addition of SF increases the rate of polymerization of C-S-H gel (for a C₃S paste at an age of 28 days, the mean chain length was 2.6 in the absence of SF, and 3.6 if SF was present [57]) and that the C-S-H gel formed by the SF reaction is highly polymerized [58]. Because of these reasons, for regular concrete mixes without the addition of SF the effect of the polymerization is rather small and it can be neglected by assuming $\kappa_{pc} \approx 0$. On the contrary the value of κ_{ps} can not be assumed equal to zero and must be determined from the analysis of experimental data [1].

9 Sorption/Desorption Isotherm and Moisture Capacity

The relation between the amount of evaporable water and relative humidity is called “sorption isotherm” if measured with increasing relativity humidity and “desorption isotherm” in the opposite case. Even though sorption and desorption isotherms are not exactly the same [59] their difference is generally neglected [60]. For this reason, in the following, “sorption isotherm” will be used with reference to both sorption and desorption conditions. The shape of the sorption isotherm for HPC is influenced by many parameters, especially those that influence extent and rate of the chemical reactions and, in turn, determine pore structure and pore size distribution (water cement ratio, cement chemical composition, SF content, curing time and method, temperature, mix additives, etc.).

In the literature various formulations can be found to describe the sorption isotherm of normal concrete. The most popular are the Brunauer-Emmett-Teller (BET) model [61], derived from statistical thermodynamics of adsorption, and modifications of the BET equation (the BDDT

model [62]; the FHH model [63]; Hillerborg's formula [64]; and the BSB model [65]).

However, in the present paper the semi-empirical expression proposed by Norling Mjornell [20] is adopted because it explicitly accounts for the evolution of hydration reaction and SF content. This sorption isotherm reads

$$w_e(h, \alpha_c, \alpha_s) = G_1(\alpha_c, \alpha_s) \left[1 - \frac{1}{e^{10(g_1\alpha_c^\infty - \alpha_c)h}} \right] + K_1(\alpha_c, \alpha_s) [e^{10(g_1\alpha_c^\infty - \alpha_c)h} - 1] \quad (28)$$

where the first term (gel isotherm) represents the physically bound (adsorbed) water and the second term (capillary isotherm) represents the capillary water. This expression is valid only for low content of SF. This also justifies the fact that the evaporable water content does not depend on the relative concentration of silicate polymers, α_p . The material parameter $g_1 > 1$ governs the shape of the sorption isotherm.

The coefficient $G_1(\alpha_c, \alpha_s)$ represents the amount of water per unit volume held in the gel pores at 100% relative humidity, and it can be expressed [20] as

$$G_1(\alpha_c, \alpha_s) = k_{vg}^c \alpha_c c + k_{vg}^s \alpha_s s \quad (29)$$

where k_{vg}^c and k_{vg}^s are material parameters.

The maximum amount of water per unit volume that can fill all pores (both capillary pores and gel pores), $w_{e1}(\alpha_c, \alpha_s) = w_e(h = 1, \alpha_c, \alpha_s)$, can be calculated, for a certain degree of hydration, by subtracting from the initial water content the difference between the chemically bound water and the amount of water that needs to be provided to compensate chemical shrinkage while maintaining saturation conditions ($0.253\text{g/g} - 0.065\text{g/g} = 0.188\text{g/g}$ for cement and $0\text{g/g} - 0.22\text{g/g} = -0.22\text{g/g}$ for SF, see Sec. 7). One can write

$$w_{e1}(\alpha_c, \alpha_s) = w_0 - 0.188c\alpha_c + 0.22s\alpha_s \quad (30)$$

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6 By using Eq. 30 and Eq. 28 with $h = 1$, and solving for $K_1(\alpha_c, \alpha_s)$ one obtains
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$$K_1(\alpha_c, \alpha_s) = \frac{w_0 - 0.188\alpha_c c + 0.22\alpha_s s - G_1 [1 - e^{-10(g_1\alpha_c^\infty - \alpha_c)}]}{e^{10(g_1\alpha_c^\infty - \alpha_c)} - 1} \quad (31)$$

14 The material parameters k_{vg}^c , k_{vg}^s , and g_1 can be calibrated by fitting experimental data relevant
15 to free (evaporable) water content in concrete at various ages [1, 20].
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18 The moisture capacity $\partial w_e / \partial h$ (derivative of the sorption isotherm with respect to h) that is
19 needed in Eq. 1 can be calculated numerically.
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23 24 25 10 Permeability

26 Moisture diffusion in concrete depends on various diffusion mechanisms that characterize the
27 mobility of different water phases present in concrete and that are influenced by the pore structure
28 of concrete. Three main distinct transport mechanisms may be identified: molecular diffusion,
29 Knudsen diffusion, and surface diffusion [66, 67].
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38 The molecular diffusion process dominates in macro-pores, which are characterized by a diam-
39 meter size from 50 nm to 10 μm [68]. Pores of this size constitute only a small portion of concrete
40 porosity and, therefore, molecular diffusion occurs only occasionally and cannot be considered the
41 dominant mechanism [67].
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45 The largest portion of concrete pores is composed of meso-pores (characteristic size from 25
46 to 500 Å) and micro-pores (characteristic size < 25 Å). In these pores, frequent collisions among
47 water molecules as well as between water molecules and pore walls provide the main diffusion
48 resistance (Knudsen diffusion), for which the diffusion resistance is related to pore size.
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56 The surface diffusion process (movement of water molecules along layers of adsorbed water)
57 occurs in certain mesopores and micropores featuring parallel walls and it poses much greater
58 resistance to transport than Knudsen diffusion for typical concrete pore sizes. Thus, in general,
59 the surface diffusion can be neglected in comparison to Knudsen diffusion unless most of the water
60 is adsorbed water, as it occurs at very low relative humidity.
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Although each individual mechanism is reasonably understood, it is not always easy to make an accurate prediction of the total diffusivity because it is difficult to describe and simulate the details of concrete pore structure formed by randomly oriented pores with variable pore radii and with various degree of tortuosity and connectivity. In addition, the scenario is further complicated by the dependence of the pore structure on water-to-cement ratio, cement content, SF content, age, etcetera.

In this work, as typically done in the literature [16], the above mechanisms are described phenomenologically through Fick's law (Eq. 1) which is characterized by the moisture permeability. The proposed formula for the moisture permeability is given by

$$D_h(h, T) = \psi(T) D_1 \left[1 + \left(\frac{D_1}{D_0} - 1 \right) (1 - h)^n \right]^{-1} \quad (32)$$

where

$$D_0 = \tilde{D}_0 \left(\frac{w}{c} \right)^3 \left(1 - \frac{s}{c} \right)^2 ; \quad D_1 = \tilde{D}_1 \left(\frac{w}{c} \right)^{2.5} \left(1 - \frac{s}{c} \right)^2 \quad (33)$$

and

$$\psi(T) = \exp \left(\frac{E_{ad}}{RT_0} - \frac{E_{ad}}{RT} \right) \quad (34)$$

In Eq. 32, the coefficient $\psi(T)$ takes into account the effect of temperature on permeability [69] as earlier proposed by Bažant and Najjar [16], D_0 and D_1 represent moisture permeability for a completely dry situation ($h = 0$) and completely saturated situation ($h = 1$), respectively. The exponent n governs the rate at which permeability transitions from D_0 to D_1 . The exponents of the power laws in Eq. 33 have been obtained by analyzing drying data gathered from the literature [1]. In Eq. 34, T is the absolute temperature, T_0 is the reference room temperature ($T_0 = 296$ K) and $E_{ad}/R \approx 2700$ K [16].

The moisture permeability parameters \tilde{D}_0 , \tilde{D}_1 , and n should, in principle, depend on aging but, at this point in time, there is not sufficient experimental evidence to investigate this dependence. A good fitting on a large range of experimental data can be achieved, as presented in Part II

of this study [1], by neglecting the aging dependence. This assumption was used successfully by Bažant and coworkers in [66].

The material parameters \tilde{D}_0 , \tilde{D}_1 , and n can be calibrated by fitting experimental data relevant to moisture diffusion as discussed in Part II of this study [1].

11 Closing Remarks

In this study a new hygral-thermo-chemical model for the simulation of moisture transport and heat transfer in HPC has been formulated. The model is characterized by the following features:

1. Moisture transport is described by one diffusion equation governing the evolution of pore relative humidity.
2. The diffusion equation is coupled with the heat balance equation which describes the evolution of temperature and takes into account the heat released during hydration and silica fume reaction.
3. The hydration process is modeled through the degree of hydration already used in [3, 4, 6].
4. The mass balance used in [19] to compute the asymptotic hydration degree is extended to include the effect of silica fume.
5. The aging effect associated with the silica fume is modeled through the degree of pozzolanic reaction, formulated for the first time in this study.
6. The aging effect of silicate polymerization is modeled introducing the concentration of silicate polymers, also formulated for the first time in this study.
7. The phenomenological model of K. Norling Mjönell [20] is adopted to simulate aging and silica fume effects on the sorption isotherm.
8. The chemically bound (non evaporable) water is modeled through an expression that takes into account hydration and silicate polymerization.

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6 9. Moisture permeability is modeled by a novel expression, which depends on three parameters
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8 with a clear physical interpretation.
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11 The model developed here needs to be calibrated and validated by comparisons with experi-
12 mental data. This task is pursued in Part II of this study which follows.
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