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Porosity development in a thermo-hygral finite element model for cementitious materials

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ABSTRACT

A numerical model for the thermo-hygral (TH) behaviour of cementitious materials is presented. The model includes a new approach to the evaluation of porosity during hydration in which a colloid model and stoichiometry are used to evaluate the volume of bound and unbound water forms. The advantage of the proposed porosity function is that it accounts for different cement types and concrete mixes and it gives a porosity evolution consistent with the moisture mass balance equation. Sink/source terms are introduced for the capillary water that account for the moisture entering/exiting the gel pores and the aggregate, whilst the standard capillary curve is modified to account for temperature and changing porosity with hydration. The numerical model considers as the primary variables the water degree of saturation of capillary pores and the temperature and is validated using several drying experiments. The results are generally in good agreement with experimental measurements.

1. Introduction

The early-age and long-term behaviour of cementitious materials is a topic of great importance since cement-based materials can be subjected to various harmful environmental conditions that may lead to their partial or total degradation. Such deterioration may be due to drying–wetting cycles, high temperatures caused by active nuclear wastes or corrosion agents. The common factor for all of these problems is moisture and heat flow within the material, which occurs once the hydration reaction begins and which is usually associated with either shrinkage or swelling. When these volume variations are restrained, microcracks can initiate and consequently the durability and strength of the material may be reduced. It is therefore a major challenge to develop a numerical model that is capable of rationally describing the behaviour of cementitious materials in a computationally tractable manner. Cementitious materials are unsaturated porous media which are usually mathematically modelled by means of coupled partial differential equations that describe the transfer of heat and moisture in the case of the thermo-hygral behaviour [1–4]. In ref. [2], no distinction is made between the different fluid phases and with this approach it is difficult to capture changes in density, porosity, permeability and strength. Such methods are sometimes described as 'phenomenological' [5] and in general involve depicting the complex physical and chemical processes with a limited number of empirical equations which depend upon a reduced set of parameters obtained from detailed experiments. By contrast, some authors, [5], have pursued a more mechanistic approach which introduces separate terms to account for all of the possible individual phenomena that govern transport behaviour. Distinct constitutive laws describe the evolution of the three interacting fluid phases: dry air, liquid water and water vapour, as well as the evolution of entropy and of the solid skeleton [5–8]. However, due to the complexity of the processes occurring within the material, the TH models cannot be entirely mechanistic and, in practice, it proves necessary to use a hybrid of the two approaches. Some researchers [9–11] have proposed and validated the idea that not all the fluid phases play a crucial role in the thermo-hygral processes and therefore the least influential phases may be disregarded with little effect. An alternative approach was developed by Ulm and Coussy [12] and Cervera et al. [13], in which the solidification of material and the role of water via a chemo-plastic approach was considered in order to model the early-age behaviour of cementitious materials. This method was predominantly used to predict deformation and cracking as it accounts for autogenous shrinkage, strength-growth and hydration heat without concentrating explicitly on the hygral transport.

The current paper proposes a mechanistic-phenomenological finite element approach to the prediction of the TH behaviour of cement pastes and concretes at early-ages and beyond for moderate environmental temperatures. The model introduces a porosity evolution function, based on the colloid model for C-S-H (calcium-silicate-hydrate) gels formulated by Jennings [14], and also takes into account fluid absorption by the aggregate. The hygral and thermal profiles are obtained using coupled mass and enthalpy balance equations. The colloid model is preferred because it captures the influence of the chemical composition of the cement upon porosity and provides a quantitative means of evaluating the volumes of both capillary and gel water. The porosity development model is important because, as the authors discovered, if the

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porosity evolution is simulated independently of the moisture mass balance, very inconsistent results can arise. Furthermore, there is often a lack of clarity in the literature on the definitions of capillary and total porosity and this ambiguity hinders the choice of adequate porosity parameters. In order to validate the model, a series of drying tests on ordinary cement paste and concrete specimens are simulated in both sealed and unsealed conditions.

This article is arranged as follows:

Section 2 Presents a summary of the colloid model and classifies the water forms populating the hydrates.
Section 3 Describes the mathematical model to be solved, the chosen variables and the constitutive laws used to describe the transfer processes.
Section 4 Describes the proposed method for estimating the water forms present in the hydrates.
Section 5 Addresses the development of porosity in the light of the colloid model and discusses the influence of the voids in the aggregate on the overall porosity.
Section 6 Presents the spatial and time discretisations for the present TH boundary value problem.
Section 7 Validates the thermo-hygral model by simulating various desiccation experiments.
Section 8 Draws conclusions about the proposed porosity development model and the accuracy and applicability of the combined TH model.

2. Classification of water forms

Many properties of cement-based materials, including the mechanical and mass transport, originate from the nanostructure level of the hydrated cement paste. The chemical reaction between cement and water gives rise to a complex configuration where hydration products, pores and unreacted cement grains are found. The principal chemical compound formed in cementitious materials is the C-S-H gel, which is assumed to dictate the inner structure of the hardened cement paste. The calcium-silicate-hydrate gel is a nanometric non-crystalline product that incorporates both solid particles and pores (full of water in the saturated state or partially empty in the non-saturated state). Because of their location, these voids are generally termed gel pores and form the so-called gel porosity. However, as will be discussed later, the behaviour of water located in the largest gel pores is considered similar to that of the water in the capillary network. Thus, these voids are included in the capillary porosity rather than in the gel porosity.

The present work follows Jennings' description of C-S-H gels [14], which assumes that they are essentially particulate in nature. Jennings originally used the term ‘globule’ to describe these particles [15], although he later suggested the term globule was inadequate to describe the units. We will follow his practice and use the term *globule* whilst fully acknowledging its inadequacy.

This section now proceeds with a summary of the authors' interpretation of the colloid model proposed in ref. [14], which deals with the classification of water forms in cement paste and, in particular, in C-S-H gels. In this colloid model, the basic unit block of the calcium-silicate-hydrate gel has a platelet shape and an internal sheet-like structure comparable to that of tobermorite and jennite, but less well-ordered than these two minerals. This basic silicate globule comprises Ca^{2+}, Si^{2+} and O^{2-} ions which constitute the *solid skeleton of reacted clinker* (SSRC), OH^- groups strongly bound to the solid skeleton representing the *non-evaporable/chemically bound water* (CBW) and water molecules that can be slowly removed during drying conditions less intense than for OH^- groups and which correspond to the *globular evaporable water*. This potentially mobile aqueous phase is situated in intraglobular pores and interlayer spaces, both less than 1 nm in size and will be referred to from now on as *intraglobular* (IGW) and *interlayer water* (ILW), respectively. The globular evaporable water is subjected to strong adsorption forces, has a high density (1200 to 2000 kg/m^3) and some of it, that is, the ILW, collapses the globule when it is removed.

The silicate globules are surrounded by *adsorbed water* (AW) with the same thermodynamic behaviour as the globular evaporable water. During hydration, the globules pack in flocs ranging between 30 and 60 nm in size that have variable densities (low, LD, and high, HD) and that encapsulate *small gel pores* (SGP) (1–3 nm) filled with *constrained water*. This aqueous form together with the sum of the adsorbed, interlayer and intraglobular water represents the *effective gel water*, which in this study is taken into account when assessing the gel porosity. The *large gel pores* (LGP), on the other hand, are between 3 and 12 nm in diameter and separate two neighbouring globule flocs. They contain H_2O molecules that form a meniscus at the interface with the gaseous phase and behave similarly to the bulk/capillary water situated outside the gel boundaries.

As far as the capillary network is concerned, its presence is due to the colloid precipitates that are too dense to fill all the available space and that entrap regions of pore solution during the short-term syneresis [16]. After the setting of the paste though, the newly created non-gel phases restrain the contraction of the solid network in the absence of heat treatment, thus preventing further syneresis. Thereafter, the volume of the capillary pores begins to decrease as a consequence of the ongoing hydration. A schematic representation of the water forms enumerated above is given in Fig. 1. In this paper, the classification of water forms corresponding to C-S-H was also extended to the reaction products resulting from the hydration of aluminate and aluminoferrite.

Recent work by Müller et al [17–19], in which H NMR Relaxometry was used to explore the nanoscale morphology of C-S-H, cast doubt over the existence of the large gel pores and suggests that there are only two water forms within the C-S-H gel nanostructure. Their findings also suggest that the volume of capillary pores may be less than predicted by previous models. The validity of our work does not depend on the veracity of these findings, although the descriptions of our ‘grouped’ water forms and the relative humidity (RH) boundaries between these water forms (see Sections 4, 5) would need to change for our model to be wholly compatible with Müller et al.'s description of the nanostructure of C-S-H and its evolution during hydration.

3. Mathematical model

The prediction of moisture evolution is obtained in this investigation by solving a boundary value problem comprising mass and energy balance equations. The physical phenomena describing the existing hygral transfers should take into account the migration of liquid water, dry air and water vapour through the pore network. Nevertheless, based on previous numerical and experimental investigations, some simplifying assumptions are considered in order to reduce the number of principal variables and the complexity of the mathematical formulation.

Before proceeding with the governing conservation equations, it is necessary to define some physical quantities related to the cement hydration. The degree of hydration, $\Gamma(t)$, is defined as the mass of hydrated material at time t divided by the mass of hydrated material at theoretical complete hydration [5]. Schindler and Folliard suggest in ref. [20] that this quantity can be equivalently expressed by

$$\Gamma(t) = \frac{H(t)}{H_{tot}} \tag{1}$$

in which $H(t)$ represents the heat released at time t and H_{tot} is the total heat released when all the cement has reacted.