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Assessment of diffusive and mechanical properties of hardened cement pastes using a multi-coated sphere assemblage model

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Abstract

This paper addresses the problem of the estimation of the diffusive and mechanical properties of hardened cement pastes by means of a simplified multi-coated sphere assemblage model. This model relies on a microstructure description involving the main hydrated products (portlandite, C–S–H, and aluminous compounds) and accounts for the physical properties of each phase as well as their volume fraction and to a certain extent their size and relative disposition. The basic idea is that any initial cement grain hydrates partly to form an external (outer) layer of C–S–H and partly an internal (inner) layer of C–S–H, both having different properties. The multi-coated sphere model, due to Hashin for its 2-phase version, is then used and applied to calculate the diffusion coefficient and Biot coefficient of such an assemblage. The evolutions of the diffusive properties when the initial material is subjected to lixiviation and calcite formation are estimated on the basis of simplified description of these degradation mechanisms; the issue of expansion due to internal pressure generated by crystal growing (crystallization pressure) in the context of sulfate attack is also analyzed.

Keywords: Diffusion; Mechanical properties; Sulfate attack; Numerical simulation; Modeling

1. Introduction

The long-term behavior of cementitious materials is a topic of great concern in many applications of civil engineering. In particular, such materials are already widely used for radioactive waste conditioning and containers and could become an attractive option for the construction of disposal engineering barriers, surface structures and underground structures for interim and long-term storage, respectively [1,2]. In this context the French Atomic Energy Commission (CEA) has developed research programs aiming at analyzing and characterizing the long-term behavior of cement-based materials. Several degradation scenarios have been identified and analyzed in condition of water immersion or flow (as a consequence of ground water), for which the diffusive and mechanical properties are of particular importance. In this study we focus our attention on these two properties and their evolutions induced by the following chemical attacks (or the consequences of these chemical attacks), in the case of saturated cement pastes: leaching (decalcification), carbonation and swelling due to sulfate attack.

Whereas many studies have been devoted to the analysis and the characterization of physical properties of concrete viewed as a heterogeneous material made up of aggregates surrounded by cement paste matrix with or without interfacial transition zone (see e.g. [3–5]), few address this problem at the level of the cement paste. However, a better understanding of the global performance of complex materials such as Portland cement-based ones requires investigations and knowledge at a microstructural level [6]. In particular, if we examine the case of two cement pastes made with CEM I and CEM V cement, respectively, both having the same water to cement ratio (w/c), experimental results show a higher global porosity for CEM V material, whereas the diffusive coefficient is one order greater for CEM I paste (see e.g. Ref. [7]). This observation indicates that the total porosity, which is a macroscopic quantity, cannot be considered as a suitable parameter for assessing the diffusion parameter when dealing with different materials.

The microstructure description of the hydrated cement paste adopted in this study is based on a very simple microstructure

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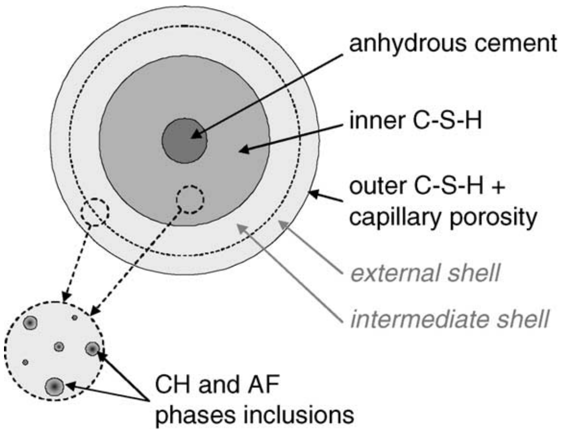

Fig. 1. Elementary description of the composite sphere forming the hydrated cement paste; spherical inclusions of portlandite and aluminous phases are distributed through both inner and outer C–S–H.

description of the cement paste involving only the four following components: internal and external calcium silicate hydrate phase (C–S–H), calcium hydroxide (CH), aluminous phases (AF) and anhydrous compounds. It relies on the basic idea that any initial cement grain hydrates in a first stage to form an external (outer) layer of C–S–H. When the available space becomes limited for the hydrated products to develop, together with the fact that the water reaches the anhydrous cement with more and more difficulty (due to the C–S–H layer growing), then a more compact internal (inner) C–S–H layer forms [6,8]. Both CH and aluminous phases are supposed to be dispersed as inclusions of different sizes in the two C–S–H layers. We investigate and propose to model the changes of diffusive properties under steady-state and saturated conditions when the material is subjected to leaching (decalcification of the hydrated products) and carbonation. Further, we propose to apply our approach to give a comprehensive and theoretical description of the material expansion due to an internal crystallization pressure generated by sulfate attack.

2. Bases of the model

The approach adopted in this study for describing the microstructure of the Portland cement paste relies basically on the assumption that the cement grains are initially spherical (typically in the range 0.1 to 100 μm and more [9,10]) and that they hydrate in two main components (inner and outer C–S–H) to form an assemblage of doubly coated spheres, in which are inserted other minor hydrated products (CH and AF phases) as spherical inclusions, supposed to be perfectly bonded to the C–S–H matrix. The core corresponds to the anhydrous part of the cement grains remaining (or not) after complete hydration and is surrounded first by the inner C–S–H layer and second by the outer one, both forming concentric shells (Fig. 1).

The porosity is assumed to be of two types: the capillary porosity (with a size domain starting from about 0.2–0.3 μm) constituting a material phase and the nanoporosity (sizes inferior to 0.2–0.3 μm) supposed to be intimately mixed with C–S–H to form the C–S–H matrix phase. The outer layer is divided into an external and intermediate shell, both having different capillary porosity volume fraction but identical C–S–H matrix properties. The CH and AF phases are homogeneously, but with different total volume fractions, distributed within each of the two C–S–H phases as spherical inclusions of various radii, the highest size of which is supposed to be small compared to the dimensions of shells; this latter hypothesis is supported by experimental evidence (see e.g. Ref. [6–8]). The capillary porosity is also assumed to be embedded in the outer layer and will receive a special treatment in particular when addressing the diffusion problem. The composite spheres possess exactly the same volume fraction for each of the elementary phases and occupy the entire volume of the material, implying a distribution in their sizes ranging to the infinitesimally small (a two-dimensional representation of such a construction is given in Fig. 2). This assumption is introduced for the sake of simplicity and because it leads to assemblages having certain exact effective properties results. For real materials, the smallest of the composite spheres do not probably exist and we assume these ones do not affect significantly the global behavior. All the initial phases are supposed to be isotropic and homogeneous and so is the macroscopic behavior of the material. The resulting well-known composite sphere model has been introduced in a two-phase version by Hashin [11] and then has been extended to multi-coated spheres by numerous researchers for evaluating physical properties such as conductivity (or diffusion) and mechanical parameters for multiphase materials (see e.g. Refs. [12–16]). It is worth noting here that by diffusion we mean mass transfer generated by concentration gradients of aqueous species; the porous medium is considered totally saturated and we neglect electrodiffusive phenomena due to electric charge of the ionic particles.

The evaluation of the effective physical properties for the material needs the knowledge of properties of each elementary phase. It means that a multiphase effective-medium approximation is required for assessing the properties of both inner and outer phases, where CH and AF spherical inclusions are

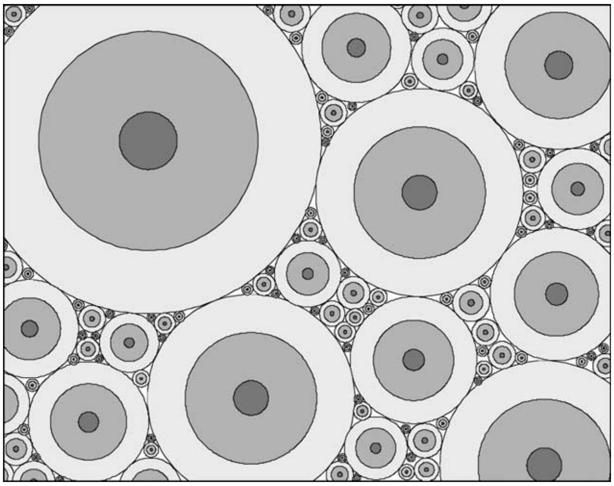

Fig. 2. Two-dimensional representation of the composite sphere assemblage describing the hydrated cement paste.