

Multi-scale poro-elastic properties of cement-based materials

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ABSTRACT: The focus of this paper is a brief summary of (1) the multi-scale structure of cementitious materials in the light of microporomechanics theory; and (2) to present estimates of the poroelastic properties of cementitious materials (cement paste and mortar) by means of advanced homogenization techniques of microporomechanics. This microporomechanics approach allows us to deliver a blueprint of the elementary poroelastic properties of all cementitious materials, which do not change from one cementitious material to another, but which are intrinsic properties. These properties result from the intrinsic gel porosity of low density and high density C-S-H, which yield a base Biot coefficient of $0.61 < b \leq 0.71$ and a Skempton coefficient of $B = 0.20 - 0.25$. While the base Biot coefficient decreases gradually at larger scales, because of the addition of non-porous solid phases (Portlandite, ..., aggregates), it is shown that the Skempton coefficient is almost constant over 3-5 orders of magnitude.

Keywords: poro-mechanics, multi-scale modeling, homogenization.

1 INTRODUCTION

In this paper we attempt to address the modeling of cementitious materials within the framework of porous media theory. More precisely, we investigate whether concrete can be described in terms of the constitutive equations of poromechanics, e.g. the one of linear poroelasticity [Biot (1941), Coussy (1995)],

$$\Sigma_m = K_{hom} E - bp \quad (1)$$

$$\varphi - \varphi_0 = bE + \frac{p}{N} \quad (2)$$

$$\frac{1}{M} = \frac{b - \varphi_0}{K_s} + \frac{\varphi_0}{K_{s/fl}} \quad (3)$$

where $\Sigma_m = (1/3)\Sigma$:1= the macroscopic mean stress, p = pore pressure; $E = \epsilon$:1= the volume strain; $\varphi - \varphi_0$ = the porosity change, K_{hom} = drained bulk modulus; b = Biot-Willis parameter, N = Biot skeleton modulus, M = Biot modulus; and $K_{s/fl}$ = Bulk modulus of the skeleton/fluid.

Recent progress in experimental and theoretical microporomechanics makes it possible today to upscale poroelastic properties from very fine scales of heterogeneous materials. As nanoindentation has provided an unprecedented access to micromechanical properties of the elementary phases of cementitious materials [Constantinides & Ulm (2002)], it becomes possible to break down their complex microstructure to the scale where cementitious materials do no more change -in a statistical sense- from one mix proportion to another. With this colloidal scale in mind, we can employ advanced homogenization techniques of microporomechanics that became recently available [Dormieux (2003)], and adapt them to meet the requirements of the multiscale microstructure of cementitious materials. The results of this challenging endeavor are estimates of the poromechanics properties of cementitious materials at multiple scales. In this paper we briefly discuss these results, which have been developed in detail in Ulm et al (2004).

Table 1 presents the poroelastic material constants which are commonly employed in porous-media theory. It should be noted that 4 parameters of those presented, suffice to completely characterize the poroelastic problem of an isothermal-isotropic material, i.e. 2 parameters from group I, and 2 from group III – other combinations are possible. This is a consequence of the equations that link the three groups together and reduce the dimension of the problem.

Table 1: Poroelastic constants.

I. Drained	K_{hom}	Drained bulk modulus
	G_{hom}	Drained shear modulus
	E_{hom}	Drained Young's modulus
	ν_{hom}	Drained Poisson's ratio
II. Undrained	K_{hom}^u	Undrained bulk modulus
	G_{hom}^u	Undrained shear modulus
	E_{hom}^u	Undrained Young's modulus
	ν_{hom}^u	Undrained Poisson's ratio
III. Pressure effect	B	Skempton coefficient
	M	Biot modulus
	N	Biot skeleton modulus
	B	Biot-Willis coefficient

2 APPLICATION OF MICRO-PORO-MECHANICS TO CEMENT-BASED MATERIALS

2.1 Presentation of concepts

Concrete is a fairly complex heterogeneous composite material, with a random microstructure at different length scales ranging from the nanometer scale to the macroscopic decimeter scale. Continuum micromechanics offers a framework to address this heterogeneity. The underlying idea of continuum micromechanics is that it is possible to separate a heterogeneous material into phases with on-average constant material properties. The three elements of continuum micromechanics are [Zaoui (2002)]:

A. *Representation*, which deals with the geometrical description of the considered heterogeneous material system. Representation includes the identification of the different phases in a representative element volume V (r.e.v.), and their morphology. A phase, in the sense of continuum micromechanics, is not necessarily a material phase as used in physical chemistry, but a material domain that can be identified, at a given

scale, with a homogeneous deformation state, that is with on-average constant material properties. The classical poromechanics theory is based on a two-phase representation of a porous medium as a solid-fluid composite. Such a representation falls short in representing a multi-scale porous material such as concrete and an extension of theory is required.

B. *Localization*, which establishes the link between a macroscopic strain (or stress), prescribed at the boundary ∂V of the r.e.v., and the microscopic strain (or stress) in the individual (homogeneous) phases composing the r.e.v.

C. *Homogenization*, which is based on volume averaging over the r.e.v. of the constitutive relations defined at the scale of the phases. Homogenization delivers the macroscopic poroelastic properties of the r.e.v. as a function of the microscopic phase properties, their volume fractions, and their specific morphologies.

Application of these three elements to cement-based materials is detailed below. Special emphasis is placed on the representation of the material which masks the physics of the problem.

2.2 Representation of cement-based materials

The heterogeneity of cement-based material manifests itself at different scales. For purpose of poromechanical analysis, the microstructure can be broken down into four elementary levels, as sketched in Figures 1 and 2 [Constantinides & Ulm (2002)]. These scales are discussed below.

2.2.1 Level '0': Nanoporosity

The lowest level of a mechanical representation of the complex microstructure of cement-based materials is the largest scale at which the material properties do not change from one cement-based material to another. It is the scale, where physical chemistry meets mechanics; that is the material properties are solely defined by the physical chemistry of the formation process of the material. This scale is typically situated above the atomic scale. In the case of cement-based materials, it is the scale of the C-S-H (Cement chemistry notation: C=CaO, S=SiO₂, H=H₂O) solid that form at early

ages by the hydration of C_3S and C_2S . We refer to this scale as level '0', as explained below.

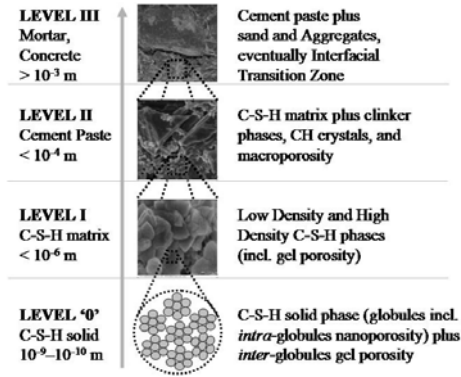


Figure 1: Multi-scale structure of cement-based materials.

This scale has been the focus of cement chemists' investigations. From a poromechanical point of view it suffices to note that: given the characteristic size of the interlayer space of less than ten water molecules in size (elementary dimension of water is distance between O-atoms 0.284×10^{-9} m), it is reasonable to say that the water in this space cannot be considered to be a bulk water phase, to which e.g. Stokes equations apply. Instead, the mechanical response at this scale is dominated by the surface properties of the C-S-H gel, and the water present is structural water. Very recently, Jennings in a number of papers [Jennings (2000), Tennis & Jennings (2000)], provided qualitative and quantitative evidence that this solid porosity which manifests itself at a scale smaller than the characteristic solid dimension of 2.2×10^{-9} m, is

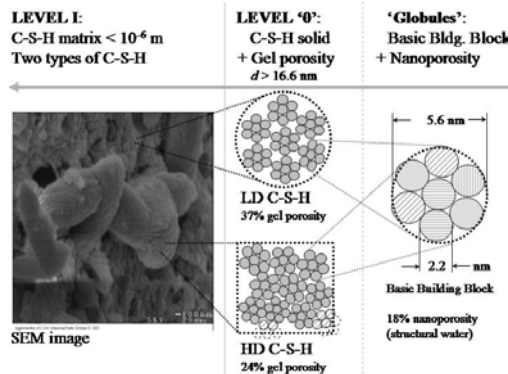


Figure 2: Details of Level I. Adapted from Jennings (2000).

18% irrespective of the type of C-S-H. Instead, it is intrinsic to the C-S-H solid phase, and is often referred to as nanoporosity. Beyond this scale, there is a second type of porosity, the gel porosity, but which was found to differ from one type of C-S-H to another, as detailed below. Hence, from a poromechanics point of view, it is appropriate to consider this solid phase which includes a 18% intra-solid porosity filled by structural water (and not bulk water), as the elementary solid phase of a poromechanics representation of cement-based materials. This solid phase, which are described by Jennings as 'globules', and which is sketched in Figure 2, has been found to be of a characteristic size of 5.6×10^{-9} m.

2.2.2 Level I: Gel porosity

The solid phase of level '0' together with gel-porosity forms two types of C-S-H phases. These phases manifest themselves in units roughly larger than 16.6×10^{-9} m, as sketched in Figure 1. We refer to this level as level I, as it represents the smallest material length scale that is presently accessible by mechanical testing, i.e. nanoindentation. At the considered Level I, it is now well established that the C-S-H exist in, at least, two different forms, a low density (LD) and a high density (HD) form (see Figure 2). The difference between the two types of C-S-H relates to the gel porosity of roughly 24% for HD-C-S-H, and 37% for LD-C-S-H [Tennis & Jennings (2000)], due to the different packing density of the C-S-H solid of the two types of C-S-H; in addition to the 18% nanoporosity within the C-S-H solid phase (at level '0'); see Figure 2. In contrast to the nanoporosity, the gel porosity has a characteristic dimension of the solid phase, i.e. on the order of 5.6×10^{-9} m, in which the water present can be considered as a bulk water phase, in the sense of the poromechanics theory. It should be noted that the gel porosity values appear to be intrinsic to all cement-based materials: they are a consequence of the formation process of C-S-H in the course of hydration. That what changes from one cement paste material to the other is the volumetric proportion of HD C-S-H and LD C-S-H, within the C-S-H matrix. In contrast to the intrinsic porosity

values, the C-S-H matrix porosity (nanoporosity excluded) depends through the volume fractions on the mix proportions (and cement fineness). The ultimate mechanically intrinsic building block of the C-S-H is the HD- and LD-C-S-H phases, for which the porosities do not change from one material to the other, nor the solid composition. This has been shown by nanoindentation tests by Acker [Acker (2001)] and Constantinides et al. [Constantinides & Ulm (2001)], who obtained the same stiffness values for the two types of C-S-H by nanoindentation of different cement-based materials (different w/c-ratio). These mean stiffness values are independent of the type of cementitious materials; instead they are intrinsic to cementitious materials in general.

2.2.3 Level II: Capillary porosity

Level II refers to the cement paste, which manifests itself at a characteristic length scale of 10^{-6} - 10^{-4} m (see Fig. 1). At this scale, the porous C-S-H matrix together with the unhydrated cement products (i.e. the four clinker phases C_3S, C_2S, C_3A, C_4AF), large Portlandite crystals ($CH = Ca(OH)_2$), aluminates and the macro-porosity ϕ_0 (which is often referred to as capillary porosity, and which is generally present only in high w/c- materials) form the cement paste. The porosity of a cement paste (excluding the nanoporosity), in which the water is a fluid phase in the sense of the poromechanics theory, as well as the solid volume fractions can be determined by advanced hydration models [Tennis & Jennings (2000)]. At this scale, the intrinsic phases (i.e. phases that do not change from one cement-based material to the other) are the four clinker phases, the Portlandite crystals, and the water phase saturating the pore space. Their material properties are well known by now thanks to nanoindentation: the stiffness values of the clinker phases have been determined by Velez et al. (2001), the one of Portlandite crystals by Acker (2001), and confirmed by Constantinides & Ulm (2002). From a morphological point of view, the composite cement paste consists of inclusions (clinker-phases, A-phase, CH-phase and porosity) embedded into a porous C-S-H matrix, which -at a level below- is composed of the two C-S-H-phases.

2.2.4 Level III: Mortar and Concrete

Level III of a characteristic length scale greater than 10^{-3} m refers to mortar and concrete; that is a composite material composed of a porous cement paste matrix, and sand particle inclusions in the case of mortar, or aggregate inclusions in the case of concrete. Some authors consider in addition the Interfacial Transition Zone (ITZ) between inclusions and matrix, which has been focus of many micromechanical modeling attempts (e.g. Garboczi (1993), Hashin & Monteiro (2002), Heukamp & Ulm (2002)); but which will not be pursued further in this investigation. From a poromechanics point of view, the cement paste matrix is a porous matrix, while -except for special applications- any porosity contained in the aggregates is rather of occluded nature.

The intrinsic density, porosity and stiffness values of the different constituents of cement-paste materials over the range of length scales considered are known by now (e.g. Constantinides & Ulm (2002)), and will serve as input parameter for the homogenization model of the poroelastic properties developed below. In this context, it is worth noting that the four levels described above respect the separability of scale condition; that is each scale is separated from the next one by at least one order of length magnitude. This is a prerequisite for the application of continuum micromechanics.

2.3 Localization

The breakdown of the multi-scale heterogeneous microstructure of cement-based materials into the four level microstructure, separated on-average by one or several order of length magnitude, allows us to consider each level as a r.e.v., V , composed of n homogeneous phases (in a micromechanical sense) of constant material properties per phase (obtained by nanoindentation).

Following continuum micromechanics, each level is considered to be subjected to a homogeneous strain boundary condition of the Hashin type:

$$\text{on } \partial V : \xi(x) = E \cdot x \quad (4)$$

where $\xi(x)$ is the microscopic displacement and x denotes the microscopic position vector. Furthermore, the microscopic strain in the different

phases is assumed to be linked to the macroscopic strain by a linear strain localization condition:

$$\varepsilon(x) = \mathbf{A}(x) : E \quad (5)$$

with $\mathbf{A}(x)$ the 4th order localization tensor, which satisfies the compatibility condition:

$$E = \langle \varepsilon \rangle_V \Leftrightarrow \langle \mathbf{A} \rangle_V = \mathbf{I} \quad (6)$$

where $\langle y \rangle_V = (1/V) \int_{\text{xdV}}$ stands for the volume average of quantity y over domain V ; and \mathbf{I} is the 4th order unit tensor. For a heterogeneous material composed of homogeneous phases, it is convenient to introduce a linear phase strain concentration of the form:

$$\langle \varepsilon \rangle_V = \langle \mathbf{A} \rangle_V : E; \sum_{r=1}^n f_r \langle \mathbf{A} \rangle_{V_r} = \mathbf{I} \quad (7)$$

where $f_r = V_r/V$ stands for the volume fraction of the phase. In the isotropic case, $\langle \mathbf{A}(x) \rangle_{V_r}$ reduces to:

$$\langle \mathbf{A} \rangle_{V_r} = \mathbf{A}_r^v \mathbf{J} + \mathbf{A}_r^d \mathbf{K} \quad (8)$$

where \mathbf{A}_r^v and \mathbf{A}_r^d represent the volumetric and the deviatoric strain localization coefficient; \mathbf{J} is the volumetric part of the 4th-order unit tensor \mathbf{I} , and $\mathbf{K} = \mathbf{I} - \mathbf{J}$ is the deviator part.

The morphology encountered at all different levels of cement-based materials is of the Eshelbian-type, that is an ellipsoidal inclusion embedded in a reference medium [Eshelby (1957)], for which estimates for the localization tensor $\langle \mathbf{A}(x) \rangle_{V_r}$ are provided by several schemes of which the most well known are the Mori-Tanaka and the Self-consistent scheme. In this paper the Mori-Tanaka scheme is used [Mori & Tanaka (1973)].

2.4 Homogenization

Homogenization methods for elastic and thermoelastic properties of composite materials have been around for quite some time (see review in Zaoui (2002)). By contrast, homogenization of poromechanics properties is more recent. The most recent contribution to micro-poromechanics is due to Dormieux and co-worker (see e.g. [Chateau & Dormieux (2002), Dormieux et al (2002), Dormieux & Bourgeois (2003)]), on which we base our derivations of the poroelastic properties of cement-based materials. The complete details of the upscaling schemes are provided in Ulm et al

(2003). For the purpose of this brief description it suffices to recall that homogenization delivers the macroscopic poroelastic properties of the r.e.v. as a function of the microscopic phase properties, their volume fractions, and their specific morphologies, i.e:

$$K_{\text{hom}}, G_{\text{hom}}, B, b = \mathfrak{F}(g_r, k_r, f_r, A_r) \quad (9)$$

where k_r, g_r are the bulk modulus and shear modulus of the individual phases (n), f_r their volume fractions and A_r estimates of the stress/strain localization coefficients. It should be noted that the effect of morphology is masked inside these localization coefficients and suitable estimates are provided by the Mori-Tanaka scheme [Mori & Tanaka (1973)]. Estimates of the remaining poroelastic coefficients (Table 1) are provided by the equations that link the three groups indicated in Table 1. The process is demonstrated in Ulm et al (2004).

3 APPLICATION TO CEMENTITIOUS MATERIALS

3.1 Materials

The materials we consider here are a cement paste and mortar prepared at a water/cement ratio of $w/c=0.5$, using an ordinary Type I Portland cement. The mortar composition is characterized by a water-cement-sand mass ratio of $w/c/s=1/2/4$, using a fine Nevada sand of density $\rho=2,650 \text{ kg/m}^3$, $d_{60}=0.23 \text{ mm}$ and $d_{30}=0.17 \text{ mm}$. These materials have been under investigation at MIT for several years, and is well characterized by mechanical testing at multiple scales, from nanoindentation [Constantinides & Ulm (2002)], ultrasonic measurements of the elastic properties [Constantinides & Ulm (2003)], to triaxial strength and deformation properties [Heukamp et al (2001), Heukamp & Ulm (2002)].

3.2 Results

The volume fractions of the individual chemical constituents as well as their intrinsic elastic properties are known and serve as input parameters to our homogenization schemes. Volume fractions and elastic properties are conveniently provided by advanced cement chemistry models and indentation

studies respectively. A summary of the theoretical predictions obtained using the upscaling homogenization methods of poroelasticity are provided in Table 2.

Table 2: Experimental measurements and theoretical predictions of poroelastic properties at different scales.

	Level I		Level II	Level III
	HD C-S-H	LD C- S-H	Cement paste	Mortar
E_{ST}^* [GPa]			18.6	21.6
E_{RF}^{**} [GPa]	-	-	21.7	25.2
E_{UPV}^{***} [GPa]	-	-	22.8	26.5
E_{hom} [GPa]	-	-	21.7	30.1
E_{hom}^u [GPa]	-	-	22.3	30.8
v_{hom}	0.24	0.24	0.24	0.26
v_{hom}^u	0.25	0.25	0.28	0.28
b	0.61	0.71	0.69	0.54
B	0.24	0.25	0.22	0.24
N [GPa]	85.9	93.1	95.5	143.2
M [GPa]	8.7	5.8	5.3	9.4

* ST=Static

** RF=Resonance Frequency

*** UPV=Ultrasound Pulse Velocity

4 DISCUSSION

The developed upscaling scheme delivers estimates of the poroelastic properties of cementitious materials at multiple scales, that are difficult to assess experimentally. Particularly, static tests in which simultaneously the mean stress and the pore pressure are monitored are difficult to perform in the purely elastic range, and involve very early on plastic deformation. The static stiffness that is reported from such tests is often much smaller than the dynamic stiffness measured on the same material. By way of example, Table 2 reports the dynamic Young's modulus determined by Ultrasound Pulse Velocity (UPV) and Resonance Frequency (RF) of the cement paste and mortar we consider in this study, together with the static stiffness obtained from the unloading branch

of a uniaxial compression test. From this Table, it is readily seen that the static modulus is some 10-20% smaller than the dynamic stiffness. Hence, a consistent comparison with the estimated stiffness values obtained by upscaling should be made with the dynamic stiffness values.

In UPV-tests, the stiffness is determined from the velocity with which a wave travels through the sample (for details see e.g.[Constantinides & Ulm (2002)]). Given the high frequency (in the 500 kHz - 1,000 kHz), it is unlikely that liquid mass can escape the sample; and the conditions can be assumed to be approximately undrained. Hence, UPV-measurements are suitably compared with the undrained stiffness values.

In RF-tests, a saturated sample is brought into vibration, and the stiffness is determined from the frequency response (for details see e.g. Constantinides & Ulm (2002)). Given the time it takes to reach a constant frequency, it is likely that the conditions are not completely undrained, and in a first approximation the values obtained can be associated with drained stiffness values, which explains that RF-stiffness are generally 1-1.5 GPa smaller than UPV-measurements.

Table 2 also summarizes the stiffness values (and poroelastic constants) obtained by upscaling. It is interesting to note that the undrained stiffness values of the cement paste almost coincides with the UPV-stiffness; and also the drained stiffness values almost coincide with the RF-measurements. This good agreement is a clear indication of the predictive capabilities of the homogenization scheme for the cement paste that is the capability of the model to capture the strain localization in the solid phases.

By contrast, the stiffness values obtained by homogenization of the mortar are slightly greater than the experimental values for both the undrained and the drained case. This is an indication of an additional micromechanical feature which adds a compliance to the composite material of non-negligible magnitude (difference on the order of 10-15%), and which has not been taken into account in our upscaling scheme. Several contributions in the open literature hint to the role of an Interfacial transition zone (ITZ) in between

the inclusions and the cement paste matrix, which may well explain this difference. This zone is known to be -on average- a zone of a higher porosity than the cement paste matrix. The Biot coefficient determined by neglecting the ITZ, therefore, appears as a lower bound of the actual Biot coefficient of the mortar.

It should also be noted that the poroelastic estimates for the LD and HD C-S-H are intimately related to their pore structure. Given the intrinsic nature of their microstructure, these poroelastic constants can be considered to be universal constants for all cementitious materials. While it was expected that the LD C-S-H with a higher porosity has a lower Biot coefficient than the HD C-S-H, it is interesting to note that the Skempton coefficient of both C-S-H phases is approximately the same, that is both C-S-H phase are similar sensitive to undrained loading conditions.

5 CONCLUDING REMARKS

Continuum Micromechanics and advanced microstructure modeling of cement chemistry together with advanced micromechanical testing (such as nanoindentation) provide a rational means today to estimate the poroelastic properties of highly heterogeneous materials, such as cement-based materials, and to confirm that cement-based materials are poromechanics materials that are sensitive to the pressure that develops in the porosity of these materials at multiple scales.

If we admit that the gel porosity is the smallest pore space in cement-based materials in which water occurs as a bulk water phase, the poromechanical effect of this porosity dominates over capillary porosity effects. The gel porosity of 24% and 37% in HD and LD C-S-H, which is the same for all cement-based materials, confines the Biot coefficient within $0.61 < b \leq 0.71$. Except for the case of an excessive capillary porosity, this base Biot coefficient decreases gradually at larger scales, because of the addition of non-porous solid phases (Portlandite, ..., aggregates), but is generally expected to be larger than twice the (bulk water) porosity. This relatively high value of the Biot coefficient indicates that the deformation of

cementitious materials is not only governed by the deformation of the solid phases, but also by a change of the porosity, particularly of the gel porosity in the C-S-H, which is on the same order as the macroscopic deformation. In a similar way, a pressure build-up or a pressure decrease (e.g. capillary pressure) also entails a non-negligible change of this gel porosity, resulting in swelling or shrinkage of these materials.

The Skempton coefficient B, which is a measure for the sensitivity of porous material to undrained and undrained conditions, is almost constant over several orders of magnitude, starting from the scale of the LD- and HD-CSH (level 0), to the scale of the cement paste (level II), and mortar or concrete composite (level III). It is on the order of $B=0.20-0.25$, which is a rather small value for a porous material with such a high porosity. In turn, this rather small value explains the little difference between drained and undrained elastic porosities, and may well explain the little consolidation effect that cement-based materials generally experience.

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