Estimating the mechanical properties of hydrating blended cementitious materials: An investigation based on micromechanics

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ABSTRACT

The hydration model of Parrot & Killoh (1984) has been extended to blended cements and coupled to a micromechanical scheme similar to that of Pichler & Hellmich (2011) to estimate the Young modulus and the compressive strength of cementitious materials as a function of time. A finite aspect ratio of 7 is introduced to describe the shape of the hydrates and improve the estimate of the early age strength by the micromechanical scheme. Furthermore, accounting for the stress fluctuations in the cement partly explains the fact that the compressive strength of a concrete can be lower than that of its cement paste. Finally, the estimated physical properties are compared to numerous experimental measurements from the literature and new experimental measurements on blended cement pastes featuring significant weight fractions of limestone filler, fly ash or silica fume. It is shown that the present model slightly overestimates the dilution effect.

1. Introduction

Deriving the mechanical properties of cementitious materials from their compositions is a matter of interest for the design of optimized formulations and accurate estimates of stresses and strains in structures. Standards models often rely on the measurement of the compressive strength at 28 days $f_{c,28}$ as the sole indicator of the mechanical performance of the concrete. An empirical formula is therefore applied to estimate the secant Young modulus of the concrete E_{28}. For instance, the one of the Eurocode 2 [3] for concrete containing quartzite aggregates is $E_{28} = 22 \, (f_{c,28}/10)^{0.3}$, where E_{28} is in GPa if $f_{c,28}$ is provided in MPa. The Young modulus can be 20% higher for basalt aggregates or 10% to 30% lower for limestone and sandstone aggregates. While the influence of the aggregate type is accounted for, this formula cannot be applied to lightweight aggregates or recycled aggregates. Indeed, a corrective factor $\eta_E = (\rho/2200)^2$, where ρ is the dry density of the concrete in kg/m³, is introduced to handle the case of lightweight aggregates ($\rho < 2200$ kg/m³). The standard itself considers this correction as inaccurate and requires an effective measurement of the Young modulus whenever this property becomes critical. The ACI 318 standards [4] specifies a similar equation, except that the exponents are very different:

$$E_{28} \approx 21 \left(\frac{\rho}{2300}\right)^{1.5} \left(\frac{f_{c,28}}{20}\right)^{0.5}.$$

(1)

The ACI 318 standards also points out that the modulus for concrete is sensitive to the modulus of the aggregates and that the measured values range typically from 120 to 80 % of the estimated value [4]. Moreover, it is well-known that this equation often overestimates the Young moduli of concretes featuring compressive strengths above 41 MPa [5]. Lastly, these empirical formulae require a prior knowledge of the compressive strength of the concrete. Consequently, they become inadequate to design optimized formulations.

Models have been proposed in order to improve the accuracy of the estimates of the mechanical properties by relying on material sciences. For instance, Freyssinet proposed in 1933 that the strength and stiffness of cementitious materials are related to what is nowadays called the gel-space ratio [6]. Following the same reasoning, Powers later assumed that the strength of cement gel is the sole source of strength of the porous cement paste and uncovered a practical relationship between the gel-space ratio and the compressive strength of cement pastes [7]. Such models can address the heterogeneous nature of cementitious materials, the changes of their microstructures due to the hydration reactions, the stiffness of the components involved at microscopic scale and the failure mode if the compressive strength is estimated. At first, different homogenization schemes were introduced to estimate the properties of concrete starting from those of the cement paste [8–11]. Then, coupling the existing knowledge about the chemical reactions occurring in concrete [12–14] and measurements of the stiffness of individual phases by nanoindentation [15] allowed the

development of multiscale homogenization procedures dedicated to cementitious materials [2,15-21], in which the cement paste itself is considered as an heterogeneous material. Furthermore, numerical simulations of the microstructure of the cement paste have been achieved [22–24]. Such numerical simulations require some data about the particle size distribution of the cement. Then, the generated artificial microstructures may be used as inputs of 3D numerical simulations so as to estimate the Young modulus or the strength of the material [25,26]. Nevertheless, these computations can prove time-consuming: optimizing a formulation, validating the model against experimental results or using it for every element of a finite-element model of a structure still are intricate challenges. Consequently, the mean-field homogenization models based on a scalar description of cement hydration remain valuable for their ease of use and their low computational demand [27]. Indeed, extending these models to account for new evidences is often straightforward.

Recent advances on our understanding of cement hydration are to be incorporated in the model that is introduced in the present article. First, the products of the hydration of C_4AF, a phase of cement, have to be updated according to new evidences [28,29] and the conditions for the formation of calcium monocarboaluminates have been defined by a thermodynamical framework [30]. Second, the effect of pozzolanic additions such as silica fumes and fly ashes can be modeled by accounting for the pozzolanic reactions [31]. Indeed, most of the existing multiscale homogenization models are focused on plain cements, while modern formulations often includes these additions to improve the durability or the mechanical performances, reduce the costs or the environmental footprint. Third, the effect of the fineness of cement and fillers, the relative humidity and temperature on the kinetic of the chemical reactions are modeled so as to provide an estimate of the mechanical properties as a function of time, not as a function of the hydration degree. Finally, the present model is validated against measurements published in the literature. The accuracy of the hydration model can be verified by XRD-Rietveld analysis, thermogravimetry and calorimetry. The estimates of compressive strength and Young modulus are also compared to the corresponding measurements. In addition, new measurements have been performed on blended cement pastes so as to extend the database of useful experimental results. The formulations and experimental procedures are detailed in order to help further validations of homogenization models.

1.1. Evolution of the volume fractions of constitutive phases

At early age, the evolutions of the mechanical properties of concrete are driven by the progressive hydration of the cement paste. In the present section, the volume fraction of the constitutive phases of concrete are estimated as functions of the time. First, an isothermal hydration model is introduced in order to rapidly produce an estimate of the volume of each phase of a cement paste. Then, the effect of temperature and relative humidity are accounted for. Lastly, the pozzolanic reactions are introduced.

1.1.1. The hydration of the cement

The considered hydration model is similar to that of Thiery et al. [32] as modified by Nguyen [33]. It is combined to the empirical expressions of the hydration rate of clinker phases described by Parrot & Killoh [1,30,34]. By describing the reaction rates as a function of the remaining amount of reactant and other environmental parameters, the present hydration model is fully compliant with the concept of chemical affinity [16]. New evidences regarding the products of cement hydration [28–30] have been incorporated as updates.

The constitutive phases are the unhydrated reactants of cement, water, the products of the chemical reactions and filler. The different phases are listed in Table 1, along with some of their physical properties. The hydration reactions are then listed in Table 2 along with their volume changes per mole of solid reactant ΔV_r and balances of capillary voids per mole of solid reactant $\Delta V_{r,cap}$. The volume change ΔV_r is related to the chemical shrinkage: products need less space than the reactants if water is included. Yet, since solid products need more space than the solid reactants, hydration reactions progress at the expense of the capillary porosity.

The kinetics of the reactions at the constant temperature of 20 °C is to be described. The model of hydration of Thiery et al. [32] makes use of the power laws adjusted by Papadakis et al. [35] to describe the rate of hydration of clinker compounds C_3S, C_2S, C_3A and C_4AF. The kinetics introduced by Nguen [33] is more complex so as to account for the induction period, a period of nucleation and growth of hydrates and a period during which the kinetics of hydration is controlled by the diffusion of ions. The empirical hydration rates of Parrot and Killoh [1], used by existing hydration models [30,34], also distinguish physically based limiting factors for the hydration rate, but it ensures that the

Table 1
The constitutive phases of the cement paste. Cement notation are used except for calcite: C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3; $\overline{S}$ = SO_3; $\overline{C}$ = CO_2. Molar masses are computed according to the python module `pyisocalc`, based on the data gathered by IUPAC [118].

Name	Formula	Molar mass	Density	Molar volume	Enthalpy of formation	C_p
		g/mol	g/cm^3	cm^3/mol	kJ/mol, @ 25 °C	J/mol/K, @ 25 °C
Cement Bogue composition						
Alite	C_3S	228.335	3.15	72.5	(−2929.2)	171.88
Belite	C_2S	172.258	3.27	52.7	(−2307.5, β)	(128.78, β)
Tricalcium aluminate	C_3A	270.194	3.03	89.2	−3587.8	209.87
Tetracalcium aluminoferrite	C_4AF	485.96	3.71	131.0	−5090.3	396
Gypsum	$C\overline{S}H_2$	172.172	2.31	74.5	−2022.6	186.02
C–S–H	$C_{1.7}SH_4$	227.496	2.1	108.3	(−3283)	(297)
Portlandite	CH	74.093	2.26	32.8	−986.1	87.49
Ettringite	$C_6A\overline{S}_3H_{32}$	1255.108	1.78	705.1	−17539	2174
MonosulphoAluminate	$C_4A\overline{S}H_{12}$	622.519	2.02	308	−8778	942
Iron(III) oxide-hydroxide	FH_3	213.734	2.2	97.2	(2 × −832.616)	(2 × 101.671)
Fe-Si hydrogarnet	$C_6AFS_{2.18}H_{19}$	1071.43	2.18	491.5	−14088	1682
Hydrogarnet	C_3AH_6	378.285	2.52	150.1	−5548	459
Water	H	18.015	1.0	18.0	−285.83	75.291
Amorphous silicate	S	60.103	2.22	27.1	−903.49	44.4
C–S–Hp	$C_{1.1}SH_{3.9}$	192.048	1.9	101.1	(−2841)	(297)
Calcite	$C\overline{C}$	100.087	2.71	36.9	−1128.79	81.88
Calcium monocarboaluminate	$C_4A\overline{C}H_{11}$	568.449	2.17	262.0	−8250	881