A MULTISCALE MODEL FOR PREDICTING THE MECHANICAL PROPERTIES OF CEMENT PASTE

S. Krishnya (1), Y. Yoda (2) and Y. Elakneswaran (1)

(1) Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University

(2) SHIMIZU CORPORATION, Shimizu Institute of Technology, Center for Construction Engineering

Abstract

Mechanical properties of cement paste are indispensable and frequent requirement in structural analysis of concrete and other cement-based materials, and therefore the theoretical predictions have obtained considerable attention in the field of material engineering. Despite of being an active research area, available models for accurately predicting the mechanical characteristics of Ordinary Portland Cement (OPC) are limited, and which remains an imperative requirement in the cement industry. In this paper, a multiscale computational model is proposed for evaluating the basic mechanical properties of cement paste such as compressive strength and Youngs Modulus. The entire model consists of two-phase: hydration model and multi-scale model. The hydration model which has been developed by chemical thermodynamic calculations using coupled PHREEQC is used to quantify the hydration products. Hence the multi-scale analytical scheme is used to predict the mechanical properties of cement paste. In this simulation, a unified procedure based on three hierarchal scales is developed, initiates from Calcium-silicate-hydrate (C-S-H) matrix (consist of two types of C-S-H, monolayer water and gel porous) and progresses consequently up to the cement paste (consist of hydration products, porous and unhydrated cement). Finally, the validity of the proposed multi-scale model is verified with set of experimental data available in the literature. In conclusion, the scheme presented in this paper can accurately predict the Young's modulus and compressive strength accurately with low average relative error.

Keywords: Cement paste, Multiscale model, Calcium-silicate-hydrate (C-S-H), Young's modulus, Compressive strength

1. INTRODUCTION

OPC is one of the prime materials in almost all the construction industries, revealing a versatile scope for wide range of applications. Mechanical characteristics of cement are frequently required in material selections, structural analysis and designing concrete and other

cement-based structures. Therefore, researchers are very intense to explore the cement behaviour, and for this reason, theoretical prediction of the mechanical properties of OPC is being marked as an active area of research. Within the last few decades, many studies have been carried out in this area including numerical predictions, analytical and empirical relationships developed from experimental studies for predicting the characteristics of cement material [1-4]. The numerical predictions are primarily based on the finite element methods with the aid of digital imaging, simulating the microstructure by spherical or real shape particles [4,5]. Most of the previously proposed analytical models are based on the homogenisation method [2, 6], and some of them are simplification of mathematical complexity by introducing reasonable assumptions [7]. For example, cement was frequently assumed to be isotropic elastic material, two-phase composite sphere, etc. In some models, only C-S-H and portlandite were employed as hydration products [4,6,7]; few models ignored the C-S-H, but instead considered the capillary porosity or gel space ratio for the prediction of mechanical properties [1]. Even though the proposed models attempted to represent the approximation of the reality, the assumptions and simplifications limit their application range. It is clearly perceived that due to the complexity in understanding the microstructural characteristics and behaviours, no studies have successfully demonstrated the precise mechanism for effectively predicting the mechanical characteristics of OPC.

Cement paste is comprised of three phases such as the stiff anhydrous cement grains, products of hydration and porosity. Typically, several products are formed during the hydration process of the OPC, and the product that contributes substantially to the mechanical properties is C-S-H (Calcium Silica Hydrate) which has a high specific surface area with a complex pore structure [8]. During the early stage of hydration, a loose-packed (LP) C-S-H forms with an open fractal structure consisting of a random agglomeration of C-S-H globules with relatively a low packing density [9]. With the passage of time, the LP C-S-H densifies to approach a stable jammed packing of globules and nucleates at the surface of unreacted cement grains, leading to the development of soft outer products called low-density (LD) C-S-H. While outer products are continuously formed, fresh C-S-H matrix would start forming within the space confined by the existing C-S-H layer, and this newly formed C-S-H has higher density. It should be noted that, in most of the previous predictions, the C-S-H has been incorporated in single form (in place of three actual forms) with average denseness, led to the increased relative errors in the simulations [1, 5].

This paper proposes a two-phase model for the prediction of the compressive strength and elastic modulus of OPC paste by the means of cement chemistry and nano-micromechanics of cement. The hydration model is employed firstly to predict the fractions of hydration products, and subsequently, the multi-scale model is developed to assess the aforementioned mechanical properties. The multi-scale model initiates at nano-scale, and worth noting that the low-density C-S-H and high-density C-S-H are both taken into account to establish the model more accurately.

2. HYDRATION MODEL

2.1 Existing model: Introduction

The products of hydration and the compositions have the significant role in determining of mechanical properties of cement materials, but very few literatures have quantitatively dealt with those estimations through various mechanisms [3, 10,11]. Recently, Elakneswaran et al

[12] have found a valid thermodynamic model coupled with PHREEQC module to predict the weight assemblage of OPC hydrates, compared with experimental and semi-experimental results and demonstrated the applicability of several cements including OPC, slag-cement and ferrite-rich cement. However, the proposed model has only been established up to the prediction of hydrates by weight. But, as known, the mechanical behaviours of the materials significantly rely on the pores content i.e. the effect of capillary porosity, gel porosity and associated shrinkage. Therefore, in this study, the proposed coupled thermodynamic model is further expanded for the volumetric prediction of hydration products which are the inputs of the subsequent phase of the entire model.

2.2 Model expansion

As discussed earlier, there are two types of C-S-H: the LD C-S-H that tends to form as the outer product and HD C-S-H forms as the inner product of the cement gel. As for the computation of the volumetric fraction of each type of C-S-H, the relationship (Eq. 1) derived experimentally by Tennis and Jennings [8] is adopted herein.

$$M_r = 3.017.\frac{w}{c}.\alpha - 1.347.\alpha + 0.538 \quad (1)$$

where M_r is ratio of the mass of LD C-S-H to the total mass of C-S-H, w/c is water cement ratio and α is degree of hydration. The average densities of both C-S-H used for the calculations are obtained from the literature [13], 2000 kg/m^3 and 1700 kg/m^3 for HD and LD C-S-H respectively.

Volumetric prediction of chemical shrinkage is another important concern, which is typically caused as the molar volume of the products is relatively lower than that of products. The coefficients of chemical shrinkage of cement phases are obtained from the Table 1. The volumetric fraction of both capillary porosity and chemical shrinkage (the sum) can be expressed as given in Eq. (2).

$$V_{cp+cs} = V_i - (V_p + V_{rr}) \quad (2)$$

where, V_{cp+cs} is volume of capillary porosity and chemical shrinkage, V_i is initial volume of cement paste, V_p is volume of products and V_{rr} is volume of remaining reactants.

Table 1: Coefficients for chemical shrinkage [14]

Cement phase	Coefficient (g water/ g solid cement phase)
C_3S	0.0704
C_2S	0.0724
C_3A (Convert all C_3A to ettringite)	0.171
C_3A (Convert all C_3A to Monosulfoaluminate)	0.115
C_4AF (Convert all C_4AF to ettringite)	0.117
C_4AF (Convert all C_4AF to Monosulfoaluminate)	0.086

C-S-H gel, by its internal structure, has the pore spaces and which is generally defined as gel porosity. The porosity of C-S-H gel varies depending on the stiffness of the matrix, leading to the variation in gel porosity of LD C-S-H and HD C-S-H. From the literatures, they were respectively found to be 36% and 26% for LD and HD C-S-H [13].

2.3 Model verification

The expanded model for predicting the volume fractions of hydrates are verified for chemical shrinkage and capillary porosity. For the verification purpose, an independent set of experimental data are collected from the literature [15], which have been made of OPC for the water/cement ratio of 0.55. The computed chemical shrinkage and capillary porosity are shown and compared with the experimental data in Fig. 1-A and Fig. 1-B respectively.

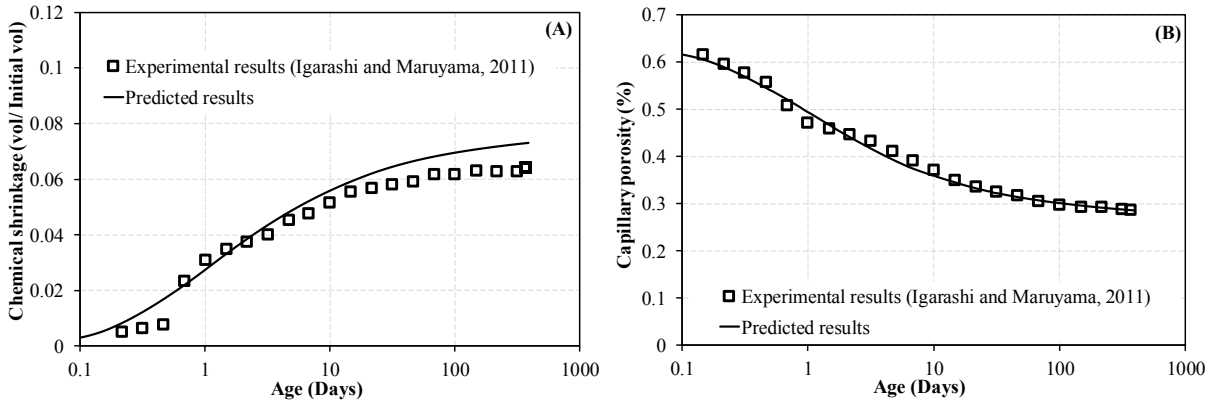

Figure 1: Comparaison of model results with experimental results of (A) chemical shrinkage and (B) capillary porosity for W/C 0.55

It can be seen from Fig. 1-A and Fig. 1-B that the predicted results are in a very good agreement with the experimental results. The predicted chemical shrinkage after 1 day and 320 days are 2.8 % and 7.2 % respectively, and the experimental results are 3.1 % and 6.4 % for the same aging. For the capillary porosity, predicted results after 1 day and 320 days are 49.15 % and 28.7 % while the experimental results are 47.4 % and 28.7 %. It is also observed that the capillary porosity gradually decreases, as expected. Typically, at the very early stage, the matrix could consist of stiff anhydrous cement grains and softer hydrates in a slight suspension form. With the time, due to the consumption of water, hardening of the cement matrix occurs, leading to the decrease in porosity.

3. MULTI-SCALE MODEL

3.1 Model description

In order to compute the compressive strength and Young's modulus of the cement paste, a multi-scale model is proposed. In this analytical scheme, the hydrated cement paste is considered in three levels, initiating at nano-scale C-S-H matrix, expanding to C-S-H foam and finally to cement paste. The volumetric fractions predicted from the hydration model are the inputs of this multi-scale scheme.

In the first level, the Young's modulus and compressive strength of C-S-H matrix is predicted at the characteristic scale of 1-100 nm. At the presence of two types of C-S-H, the Young's modulus of the matrix can be expressed as,

$$E_{CSH} = E_{LD\_CSH} + (E_{HD\_CSH} - E_{LD\_CSH})\Phi_{CSH-HD} \quad (3)$$

where the E_{LD_CSH} and E_{HD_CSH} are found to be 22 GPa and 27.5 GPa [16]. Φ_{CSH-HD} is the volume fraction of HD C-S-H in the total C-S-H, and which was estimated based on the results obtained from hydration model.

For the prediction of compressive strength of C-S-H matrix, the Griffith theory [17] is employed in this study. As the behavior of hydrated cement is brittle, the Griffith strength ratio ($\sigma_c/\sigma_t = 8$, where σ_c is the compressive strength and σ_t is tensile strength) is well applicable, and the compressive strength of C-S-H matrix ($f_{c,CSH}$) is indirectly obtained from its tensile strength ($f_{t,CSH}$). The tensile strength of C-S-H matrix can be expressed in terms of its packing density (η_{CSH}) (Eq. 4) [18].

$$f_{t,CSH} = f_{t,glob}\, exp\left(\frac{1.293(\eta_{CSH}^{13.011} - 1)}{\eta_{CSH}}\right) \quad (4)$$

where $f_{t,glob}$ is the apparent tensile strength of C-S-H globule, and that is found to be 320 Mpa [10]. The packing density of C-S-H matrix (η_{CSH}) can be expressed as follows,

$$\eta_{CSH} = \eta_{LD\_CSH} + (\eta_{HD\_CSH} - \eta_{LD\_CSH})\Phi_{HD\_CSH} \quad (5)$$

where the packing densities of the LD C-S-H (η_{CSH-LD}) and HD C-S-H (η_{CSH-HD}) are obtained from the literatures, which are 0.63 and 0.76 respectively [19].

In the second level, the Young's modulus and compressive strength of C-S-H foam is computed at the characteristic scale of 100 nm-10 μm, and this C-S-H foam consists of C-S-H matrix and capillary porosity. The expression for the Young's modulus of C-S-H foam can be obtained from [10] as

$$E_{CSH\_foam} = E_{CSH}\, exp(A\frac{\Upsilon_{CSH}^{B} - 1}{\Upsilon_{CSH}}) \quad (6)$$

where Υ_{CSH} is C-S-H space ratio, can be expressed as shown in Eq. (7), in which the volume fraction of C-S-H (Φ_{CSH}) and capillary porosity (Φ_{cap}) are obtained from the previous hydration model. A and B are the factors expressed as given in Eq. (8) and Eq. (9) respectively.

$$\Upsilon_{CSH} = \frac{\Phi_{CSH}}{\Phi_{CSH} + \Phi_{Cap}} \quad (7)$$

$$A = 0.82\, exp\,(-4.949\,\frac{\beta^{0.02} - 1}{\beta^{2.8}}) \quad (8)$$

$$B = 1.818\, exp\,(4.310\,\frac{\beta^{0.02} - 1}{\beta^{2.8}}) \quad (9)$$

The compressive strength of C-S-H foam (f_{c,CSH_foam}) can be expressed as shown in Eq. (10) [10].

$$f_{c,CSH\ foam} = f_{c,CSH}\, exp\,(-\frac{C(1 - \Upsilon_{CSH}^{D})}{\Upsilon_{CSH}}) \quad (10)$$

Here, the compressive strength of C-S-H matrix ($f_{c,CSH}$) which has been already computed in first level is implemented for the above calculation. C and D are factors respectively defined by Eq. (11) and Eq. (12).

$$C = 1.101\ exp\ (-\frac{0.296(\beta-1)}{\beta}) \quad (11)$$

$$D = -11.058\beta^{1.987} + 16.191\beta \quad (12)$$

The factor of C-S-H distribution is defined as β. Typically, the distribution factor can be within the range 0.4-1.0, depends on several factors such as heterogeneous nucleation, precipitation of C-S-H and cement finess [10].

In the third level, cement paste is modelled to predict its Young's modulus and compressive strength. The cement paste model comprises the C-S-H matrix, capillary porosity, unreacted clinker and other hydrates at the characteristic scale of 10-100 μm. The Young's modulus of the cement paste (E_{cp}) is predicted from the following expression [10] by implimenting the results obtained from the second level,

$$E_{cp} = E_{CSH\_foam}\ (1 + \Phi_{inclusion}\left(0.0102E_{incl} + 0.278E_{CSH_{foam}}^{0.2}\right)) \quad (13)$$

where $\Phi_{inclusion}$ is the volume fraction of hydrates excluding C-S-H, estimated from the hydration model. E_{incl} is the Young's modulus of solids excluding C-S-H in hydrates. Finally, the compressive strength of the cement paste is derrived from the Eq. (14).

$$f_{c,cp} = f_{c,CSH\ foam}(0.758 + (1 - 0.758)\ exp(-29.3\Phi_{inclusion})) \quad (14)$$

3.2 Model verification

The comparison between the predicted results and experiment results of Maruyama and Igarashi [20] are illustrated in Fig. 2 (A) and Fig. 2 (B) for Young's modulus (Eq. 13) and compressive strength (Eq. 14) respectively. To emphasize the impact of involving two types of C-S-H, predicted results considering the C-S-H as single matrix are compared together in both Fig. 2. From Fig. 2 (A), it can be seen that the predicted Young's modulus increases with the increase in aging, and that fits well with the ultrasonic and loading test results. It can be clearly perceived that when the C-S-H was modelled to be a single matrix, the prediction is approximately 17 % lower than the experimental results after 360 days, which could be attributed to the variation caused in capillary porosity and volume of C-S-H matrix.

Moreover, a good agreement is shown between experiment results and the predicted compressive strength (of LD and HD C-S-H model) (Fig. 2 (B)). For instance, the predicted strength of cement paste reached 42.8 MPa on 28th day and 59 MPa after 360 days, while the experimental results are 45.6 MPa and 58 MPa respectively. It can also be seen that the model slightly underestimates the compressive strength of cement paste at early stage compared to the experimental data. On the other hand, the predicted compressive strength from single C-S-H model shows nearly a 15 % deviation from the experimental results by the end of 360 days hydration.

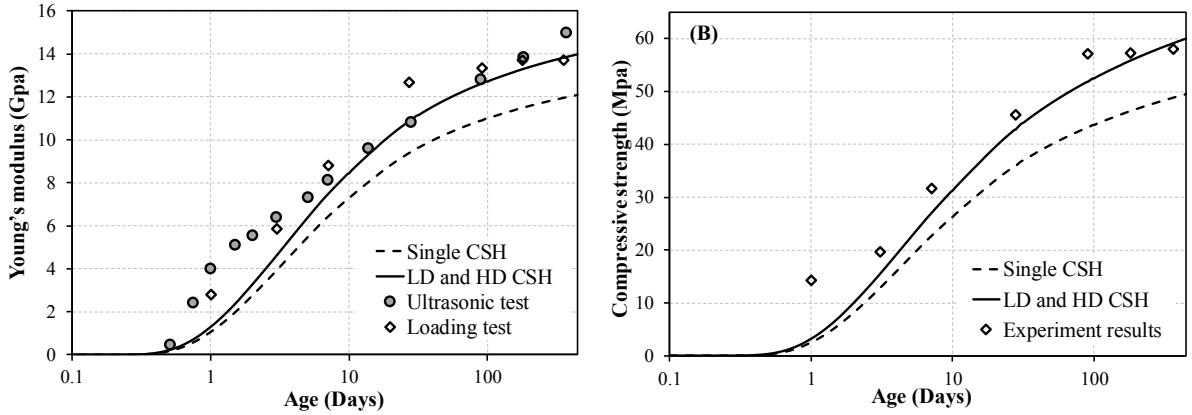

Figure 2:Development of (A) Young's modulus and (B) compressive strength of cement paste for W/C 0.55.

The results demonstrate that the model involved both LD and HD C-S-H could accurately predict the Young's modulus and compressive strength, whereas the conventional approach (C-S-H modelled as single matrix) has been shown to significantly deviate. Generally, the water/cement ratio of cement pastes used in most of the practical use is between the range of 0.4 and 0.6 [7]. In this paper, the proposed model is validated only for the cement paste with high water cement ratio of 0.55. To fully verify the feasibility of this model, further validation is recommended for the cement paste with low water cement ratio (for example, 0.4), and which is left for the future work.

4. CONCLUSIONS

A simple two-phase model has been developed for predicting Young's modulus and compressive strength of the cement paste. The volumetric fractions of hydration products are predicted thermodynamically in the first phase (hydration model), followed by an analytical scheme (multi-scale model) for computing Young's modulus and compressive strength. In this proposed model, the mechanical properties are predominantly related to the C-S-H product, as the C-S-H contributes more to strength development than other hydration products; and that is considered distinctly in the forms of LD C-S-H and HD C-S-H. The validity of the model predictions has been well verified with independent set of experimental data found in the literature. However, to make the proposed model fully feasible, further verifications are essential for different water cement ratios, comparing the predictability with more experimental data.

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