CONCRETE AS A HIERARCHICAL STRUCTURAL COMPOSITE MATERIAL

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Abstract: A multiscale modeling methodology that relates the nanostructure of concrete to its micro and macro properties is presented. This work aims to set a framework for the understanding of the relations among chemical composition, microstructure morphology, and the macroscale mechanical properties of concrete constituents. The simulation is based on four levels of hierarchal structural model, starting from the molecular dynamics simulation of hydrated cement solid nanoparticles (e.g. C-S-H, and CH), all the way up to concrete aggregates. To validate the theoretical model, a non-destructive testing technique, the Resonant Ultrasound Spectroscopy (RUS), is used to measure elastic constants of hydrated cement paste. The results showed a good agreement between theoretically predicted and experimentally measured properties.

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1. Introduction

Cement concrete is one of the world's most widely used materials. Unfortunately, the production of cement involves a thermal process that accounts for 5 to 10 percent of the world's total CO_2 emissions. Ulm and Constantinides (2007) studied the cement paste and found that the macroscopic strength of concrete appears to be linked to the nano-granular structure of its constituents, particularly the Calcium-Silicate-Hydrate (C-S-H) units, and not to its chemistry. They argued that if one can replace the constituents of conventional Portland cement with materials of the same or similar nanostructure, which can be produced without an intensive thermal process, then it open the door for a "green concrete" that can cut the global CO_2 emission. Therefore, a basic understanding of the nano/micro structure of concrete constituents, and how it is related to the macroscopic mechanical properties, are essential to the design of a new class of concrete that is high strength, yet green.

There have been only a few successful attempts to model the macroscopic mechanical properties of cement paste and concrete from their microstructure, as reported in the literature. The difficulty of simulation stems from the complex nano-porous structures, limited knowledge of the individual constituent properties, and the large variation in curing conditions. Among few researches, Ulm and Lemarchand (2003) developed a multiscale micromechanics hydration model, combined with intrinsic material properties, to predict the early age elastic properties of cement-based materials. In another study, Ulm and Heukamp (2004) treated concrete as a multiscale poroelastic material. Feng and Christian (2007) proposed a three-phase micromechanics model of cement paste, using theories of composite and poromechanics, to predict the properties of hardened cement pastes. They adopted existing literature values of solid phases, C-S-H, CH (calcium hydroxide), and cement. However, Low Density (LD) and High Density (HD) C-S-H were not distinguished and cement paste was treated only as a three-phase composite (C-S-H, CH and unreacted cement paste). Haecker, et al. (2005) predicted elastic modulus as a function of degree of hydration using a finite element based “microstructure development model”.

In this paper, we developed a multiscale modeling methodology to relate the nanostructural properties to the micro and macro performance of concrete. This study is built on a four-level microstructural model. At molecular and nano scale, fundamental mechanical properties of constitutive mineral crystals of cement, hydrated cement paste, sand, and aggregate are calculated by molecular dynamics (MD) simulation. These nanoscale properties are used as the input for the computation of sub-micro scale LD and HD C-S-H mechanical properties. At microscale, effective properties of cement paste and mortar are predicted with the help of micromechanics of composite theory and microstructural model of hydrated cement paste (HCP) developed by the authors. Void effect is introduced by empirical porosity-elastic property relation. To valid the model, RUS (Resonant Ultrasound Spectroscopy) is used to measure the elastic properties, which are compared to the simulation result for HCP. Finally, at macro (continuum) scale, both the lattice model and the generalized method of cells (GMC) are employed to compute the effective properties of concrete.

2. Multiscale Approach for Cement Concrete

Cement concrete may be viewed as different material from different scales. In nanoscale, its primary constituents are C-S-H and other similar crystals; in microscale, it is viewed cement paste; and in macroscale, it is investigated as concrete. To understand its mechanical properties, one needs to understand the structure of cement-based materials at all scales (levels).

Figure 1 illustrates a four level model to obtain macroscale properties for cement-based materials (Dormieux and Ulm 2005). Level 1 represents the nanoscale C-S-H solid phase which includes globules and nanopores. Level 2 includes LD and HD C-S-H and the gel pores, which has a dimension of 16.6 nm in diameter. Level 3 is cement paste which is composed of C-S-H matrix, residual cement clinkers, CH, and macropores. Monosulfate hydrate (AFm phase) has a minor effect on the structural properties of cement paste. In this paper, we replace it with CH for simplicity. Level 4 is a composite made of mortar or concrete.

Level 1 C-S-H plays a central role in the study of cement-based material properties. A widely accepted C-S-H colloidal model is by Jennings and his co-worker (Tennis and Jennings, 2000; Jennings, 2004; Jennings, 2000), in which he assumed that two types of C-S-H, LD and HD, exist in cement gel. LD and HD C-S-H have 37% and 24% gel porosity, respectively. Both LD and HD C-S-H are formed by the basic building blocks called ‘globules’. The globules have a dimension of 5.6 nm and nanoporosity of 18%, which is usually filled with structural water.

Gel porosities of C-S-H and nanoporosity of globules are intrinsic properties of concrete. The volumetric proportion of LD C-S-H and HD C-S-H changes from one cement paste to another, depending on the water to cement ratio and curing condition. In the development of the microstructure of cement, HD C-S-H usually formed around residual cement clinkers while CH generally formed in between LD C-S-H and adjacent to macropores (Dormieux and Ulm, 2005).

There are two types of multiscale modeling techniques: hierarchical and concurrent methods. Hierarchical modeling starts the computation from the lower level materials such as crystalline structure of C-S-H, and the computed lower level properties are used as input data for the next level computation, and so on. In the concurrent modeling, various methods such as finite element (FE), molecular dynamics (MD), etc., are applied to regions of different scales of the material at the same time. In this paper, we employed the hierarchical modeling method to simulate cement-based materials (concrete and mortar) as shown in Fig. 1.

3. Hydrated Cement Paste Model

The micromechanics model for cement paste and mortar discussed in this paper is based on the following two observations (Dormieux and Ulm 2005): 1) unreacted cement is generally rimmed by HD C-S-H; and 2) CH tends to grow in between LD C-S-H sheets The scheme for this proposed hydrated cement model is illustrated in Fig. 3. In this model, LD C-S-H and CH are assumed to form a LD/CH composite, which can then be the inclusion of the next level of hydrated cement composite (composite 2). Unreacted cement is enclosed by HD C-S-H to form a HD/Cement composite (composite 1-1), which can be the matrix of composite 2. Mortar (composite 3) is considered to be composed of sand particles and composite 2.

For the multiscale computation, molecular dynamics (MD) is utilized to simulate the mechanical properties of nanoscale solid phase C-S-H (C-S-H structural related mineral crystals tobermorite 14A and jennite), calcium hydroxide (CH) and sand (alpha quartz). Then the properties of low density (LD) and high density (HD) C-S-H gels are calculated using microporomechanics theories (Wu, et al., 2008). Next, the effective properties of two-level composites—composite 1 (1-1, and 1-2) and composite 2—are calculated using the Mori-Tanaka method (M-T). Finally M-T theory was applied to obtain the homogenized properties of mortar (composite 3). In order to account for the presence of voids in the mortar (mortar porosity), empirical elastic properties-porosity relations are used to calculate the effective properties of mortar. Figure 2 illustrate the scheme of the multiscale model of C-S-H, cement paste, and mortar. However, the volumes of major phases in the cement paste model need to be determined prior to the homogenization process.

The volume of major hydrated cement phases was presented by Powers (1948, 1960) and Jennings and Tennis (1994). Whereas Powers' model can only predict the volume of unreacted cement, Jennings' model can estimate the relative amount of unreactd C-S-H and CH. The highlights of Jennings model are summarized as Eqs. (1)-(4):

$$V_{unreacted\_cement} = c(1-\alpha_{total})\left(\frac{1}{\rho_{cement}}\right) \qquad (1)$$

$$V_{CH} = c(0.189\alpha_1 p_1 + 0.058\alpha_2 p_2) \qquad (2)$$

$$V_{AFm} = c(0.849\alpha_3 p_3 + 0.472\alpha_4 p_4) \qquad (3)$$

$$V_{CSH\_Solid} = c(0.278\alpha_1 p_1 + 0.369\alpha_2 p_2) \qquad (4)$$

where $V_{unrelacted\_cement}$, V_{CH}, V_{AFm}, V_{CSH_Solid} are the volumes of unreacted cement, CH, AFm and solid C-S-H material in 1g of cement paste, respectively, c is the initial weight of the cement, defined by:

$$c = \frac{1}{1 + w_0 / c} \qquad (5)$$

p_i is the percent of ith phase (C_3S: $i = 1$, C_2S: $i = 2$, C_3A: $i = 3$ and C_4AF: $i = 4$) in the unreacted cement, and α_i is the degree of hydration of the four cement constituents, which is expressed as:

$$\alpha_i = 1 - \exp\left(-a_i (t - b_i)^{c_i}\right) \qquad (6)$$

In the above, a_i, b_i and c_i are constants determined by Taylor (1987) and *t* is the age of the hydrated cement. The composition of cement used in this paper is shown in Table 1. The water to cement ratio w_0 / c used in this study is 0.4. We distinguish two types of C-S-Hs: LD and HD, with the ratio 1:1, based on the Dormieux and Ulm (2005). The calculated volume fractions of different components using Jennings' model are shown in Fig. 3.

4. Nanoscale: MD Simulation of Nanoparticles

Understanding the properties of basic constitutes of materials is the first step in multiscale modeling. With the recent advancement in experimental techniques, more insight has been gained into concrete's nanostructure.

At the nanoscale (see Level 1 in Fig. 1), the mechanical properties of nanoparticles of C-S-H, CH, cement constituents, and sand are calculated using molecular dynamics simulations. The corresponding crystalline structures of these materials are shown in Fig. 4.

Molecular dynamics is a computational technique that models the behavior of molecules. The force fields of computational chemistry and material science are applied for studying small chemical molecular systems and material assemblies. The common feature of molecular modeling techniques is that the system is at the atomistic level; this is in contrast to quantum chemistry which applies quantum mechanics and quantum field theory ("Quantum chemistry," Wikipedia: The free encyclopedia). The main benefit of molecular modeling is that it allows more atoms to be considered as compared to quantum chemistry during the simulation, starting with a small number of molecules, and keeping on increasing the unit cell size until we reach a periodic system, which represents the full scale material properties. The procedure recommends simulating unit cells with 3000 atoms or more in order to reach the periodic unit cell that represents the infinite system.

For Molecular Dynamics simulation, commercially available software Materials Studio (Accelrys Inc., 2008) was utilized to estimate the mechanical properties of nanoparticles of Portland cement and hydrated cement nanoparticles. More detail on MD simulations are reported in Wu, et al. (2008a, b).

5. Sub-Microscale: Microporomechanics Calculation of Effective Properties of LD and HD C-S-H

Microporomechanics is a useful tool to study the mechanics and physics of multiphase porous materials (Dormieux, et al., 2006). At the second level of this study (see Fig. 1), properties of C-S-H gels are computed using microporomechanics. C-S-H gel is a porous material with 37% (LD) and 24% (HD) porosity. According to Dormieux and Ulm (2005) the poroelastic properties of LD and HD C-S-H can be calculated using the following relations:

$$K = G_s \frac{4(1-\phi_0)}{3\phi_0 + 4(G_s / K_s)} \qquad (8)$$

$$G = G_s \frac{(1-\phi_0)(8G_s + 9K_s)}{6\phi_0(2G_s + K_s) + 8G_s + 9K_s} \qquad (9)$$

where *K* and *G* are effective bulk and shear moduli, G_s and K_s are shear and bulk modulus of the solids obtained from MD simulation, and ϕ_0 is the porosity. The properties of LD and HD C-S-H are estimated in Wu, et al. (2008).

6. Microscale: Homogenization of HD C-S-H with Residual Cement and HD C-S-H with CH

The two-phase sphere micromechanics model (Abudi, 1991) is utilized to estimate the effective properties of level 3 composites: composite 1 (1-1, and 1-2). The volume fraction of unreacted cement in the composite 1-1 is given by:

$$Vf_{unreacted\_cem} = \frac{12\%}{12\% + 23.5\%} = 0.338 \qquad (10)$$

Obtained results for composite 1 (1-1, and 1-2) are shown in Table 2.

In order to compute the effective properties of cement paste, the Mori-Tanaka micromechanics model is used to homogenize two composites: unreacted cement-HD C-S-H and CH-LD CSH shown in Table 2. The volume fraction of inclusion (CH-LD CSH) in this model $VF_{CH\text{-}LDCSH}$ is taken as *0.68*. Therefore, the effective properties of cement paste with zero porosity (e.g. Young's modulus, E_o, Poisson's ratio, v_o, bulk modulus, K_o , and shear modulus, G_o) are calculated as:

$$E_0=43.1\ GPa \qquad v_0=0.3 \qquad K_0=35.9GPa \qquad G_0=16.6GPa$$

7. Macroscale: Effective Properties of Mortar and Concrete

Elastic Properties-Porosity Relation

Porosity is one of the most important factors which affect the strength of cement paste. Many analytical or semi-analytical equations may be used to describe the moduli-porosity relation of a porous material. A good summary of these equations is given by Yoshimura, et al. (2007). For reference, selected relations are listed in Table 3:

Knudsen (1959) proposed an empirical equation to define the relation between the mechanical strength and the porosity. Relation no. 1 in Table 3 is the Knudsen law which is one of the most widely used relations.

The effective properties of hydrated cement paste calculated using Equations 1-4 in Table 3 are given in Table 4. The Young's moduli of hydrated cement paste (HCP) fall in the range of 15.4-23.7 GPa. Poisson's ratio computed by Eqs. 3 and 4 is 0.27. The results in Table 4 are used as the input parameters for next level computation to obtain properties of mortar.

Effective Properties of Mortar

M-T micromechanics theory is used to compute the effective properties of composite mortar (composite 2 in Fig. 3) in which sand (alpha quartz) is considered the inclusion and cement paste is the matrix. The volume fraction of the sand used in the calculation is 1/3. The homogenization results for mortar are given in Table 5.

Effective Properties of Concrete

Two micromechanics models are used to calculate the effective properties of concrete: Generalized Method of Cell (GMC) (NASA, 2002; Aboudi, 1989; Aboudi, 1996) and the lattice model. Both methods may be applied to composites with irregular shape inclusions and different packing arrangements.

The lattice model (spring network) has been utilized to compute effective elastic moduli and simulate crack formation in materials (Ostoja-Starzewski, 2002; Alzebdeh, et al., 2008; Al-Ostaz, et al., 2008; Alkateb, et al., 2008). In this paper, regular triangular lattices with linear central springs (Fig. 5) are adopted. Elastic moduli of individual phases are mapped into spring stiffness according to the formula:

$$C_{ijkl} = \frac{\alpha}{2\sqrt{3}} \sum_{n=1}^{6} l_i^n l_j^n l_k^n l_l^n \qquad (11)$$

where $l_1 = \cos\theta$, $l_2 = \sin\theta$ are the direction of the spring, α is spring constant.

The springs' stiffnesses are assigned according to the following criteria: if the spring falls within the inclusion boundary it is assigned a stiffness k_i; if it falls within the matrix boundaries it is assigned a stiffness k_m, and for any bonding spring connecting both phases, it is assigned a stiffness k_b . The values of k_i and k_m are calculated according to the individual phase's elastic properties according to Eq. (12):

$$C_{1111} = C_{11} = \frac{3\sqrt{3}}{8}\alpha, \quad C_{1122} = C_{12} = \frac{\sqrt{3}}{8}\alpha, \quad C_{1212} = C_{66} = \frac{\sqrt{3}}{8}\alpha \qquad (12)$$

A lattice used in the computation is shown in Fig. 6.

The effective properties of concrete are computed by GMC and lattice model, and are given in Table 5. The Young's moduli given by GMC and lattice model are 42 GPa and 36.3 GPa, respectively.

8. Results Validation

To validate our numerical results, Resonant Ultrasound Spectroscopy is employed to measure the elastic constants of hydrated cement paste. RUS is a modern nondestructive acoustic technique which can be used to measure the elastic properties of solids with high-precision (Migliori, et al., 1990, 1993). RUS measures the eigenmodes of vibration of parallelepiped, spherical, or cylindrical samples. A RUS instrument is shown in Fig. 7.

RUS test samples were prepared and cured according to ASTM standard C192. Although the samples can be of different shapes, we used accurately shaped parallelepiped samples such as the one shown in Fig. 8. The water cement ratio for the samples is the same as used in the concrete specimens, that is 0.4.

To perform the test, the two corners of the test sample were carefully placed between two transducers. Next, one of the two transducers applied the vibrations to the sample using the frequency sweeping technique and the other recorded the frequency amplitude of the sample's response in terms of the natural frequencies. Finally, we were able to determine the elastic constants (Maynard, 1996).

The elastic constants measured by RUS for a hydrated specimen with 0.4 water-cement ratio and porosity of 8.1% are: elastic modulus E is 21.55GPa, and the Poisson's ratio ν is 0.22, which agree quite well with the computed results in Table 3.

The Young's modulus of concrete was obtained by ASTM C469 standard test method for static modulus of elasticity and Poisson's ratio of concrete in compression using concrete compression machine. Laboratory tests give the results of Young's modulus for concrete as 38.2GPa, which matches the values given by GMC and lattice model: 42GPa and 36.3GPa.

9. Conclusions

A multiscale simulation methodology was developed to relate the nanoscale constituent properties of cement concrete to its micro and macro scale properties. Nanoscale properties are obtained using Molecular Dynamics simulation, microscopic properties are obtained using microporomechanics theory, and macroscopic properties are obtained using Mori-Tanaka composite theory. Concrete properties are obtained using GMC/HFGMC approaches. Throughout the simulations, lower scale results were used as the input data for higher scale simulations. The input parameters for Molecular Dynamics simulation were obtained from the fundamental physics-chemical properties of constituting elements. The simulated results are compared with experimental results and showed quite good agreement at each calculation level. Therefore, it is demonstrated that the hierarchical approach used in this study can be a powerful tool to investigate the properties of cement concrete from nanoscale to macroscale. Ultimately, the goal is to utilize such tools for the design of concrete that is more environmentally friendly, and with better strength.

Acknowledgement

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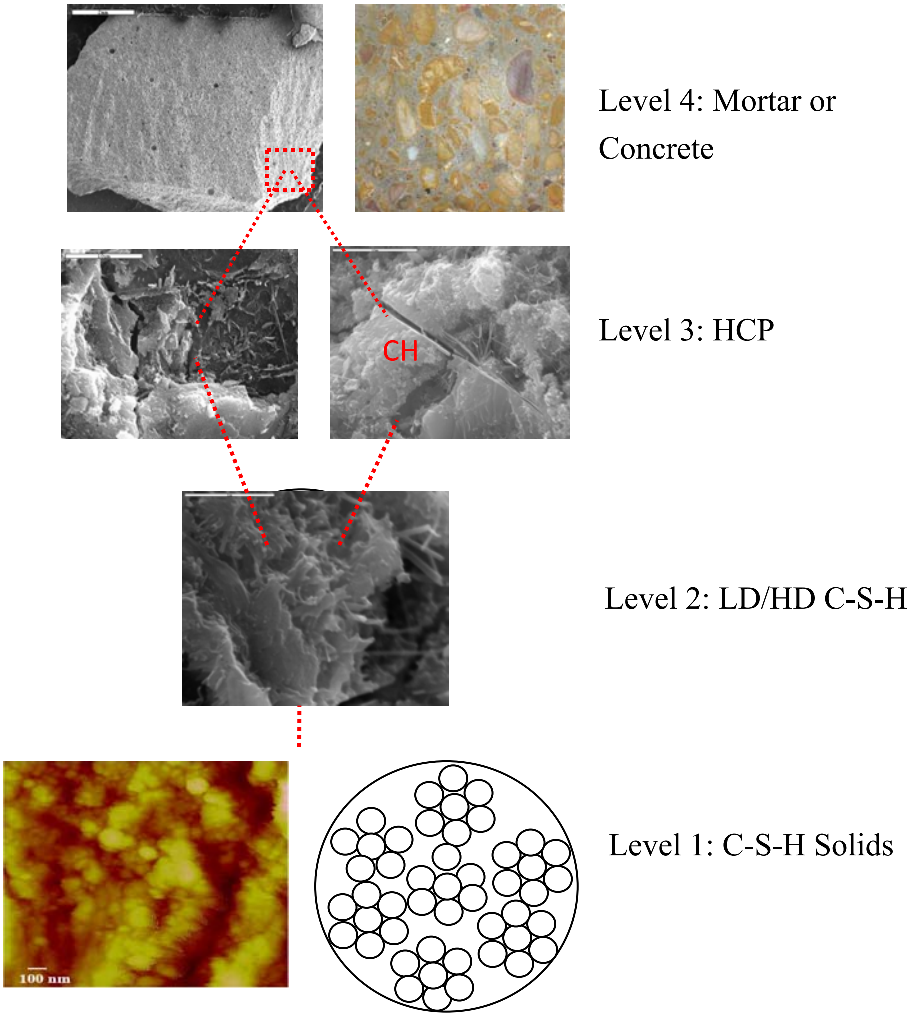


Fig. 1. Multi-level microstructure images of cement-based materials (AFM image of C-S-H solids (Mondal, et al., 2005))

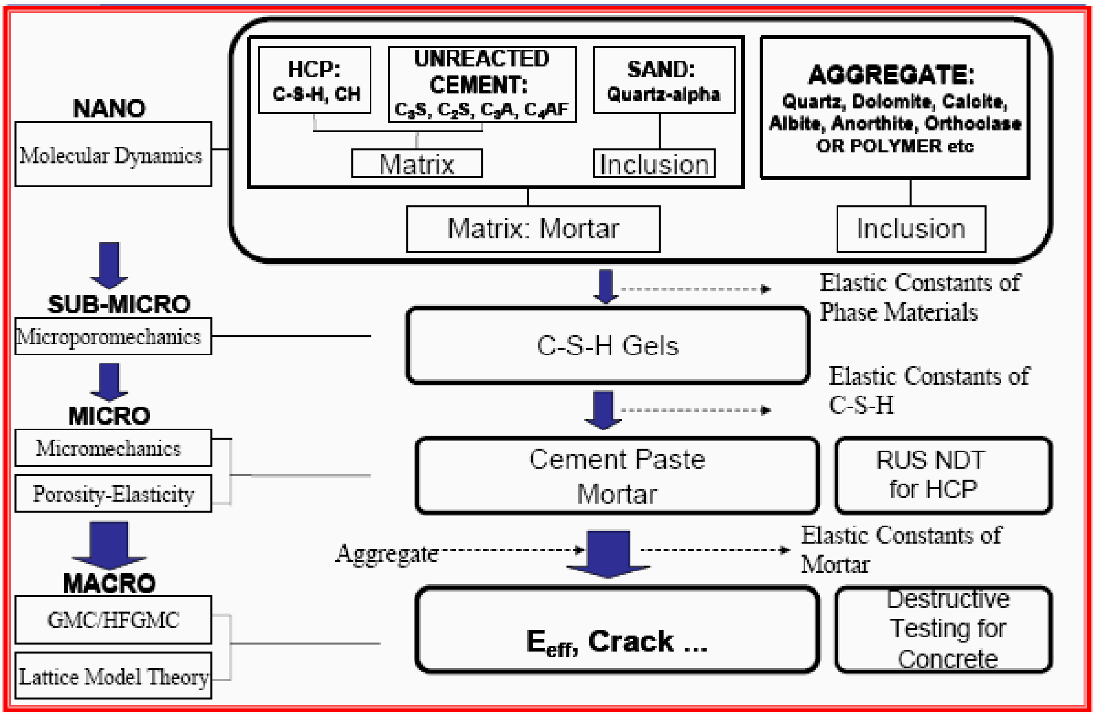


Fig. 2. Scheme of multiscale modeling of concrete.

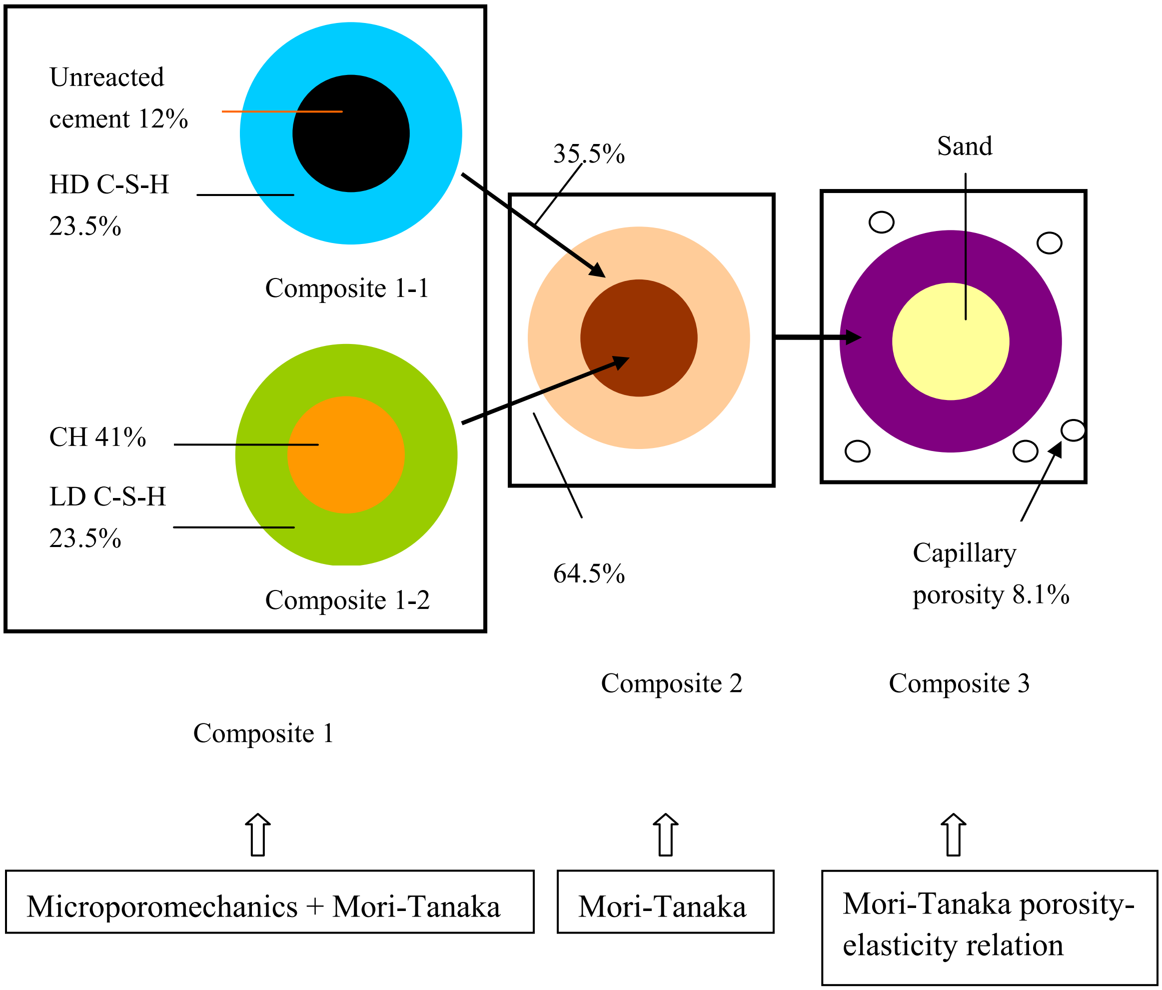
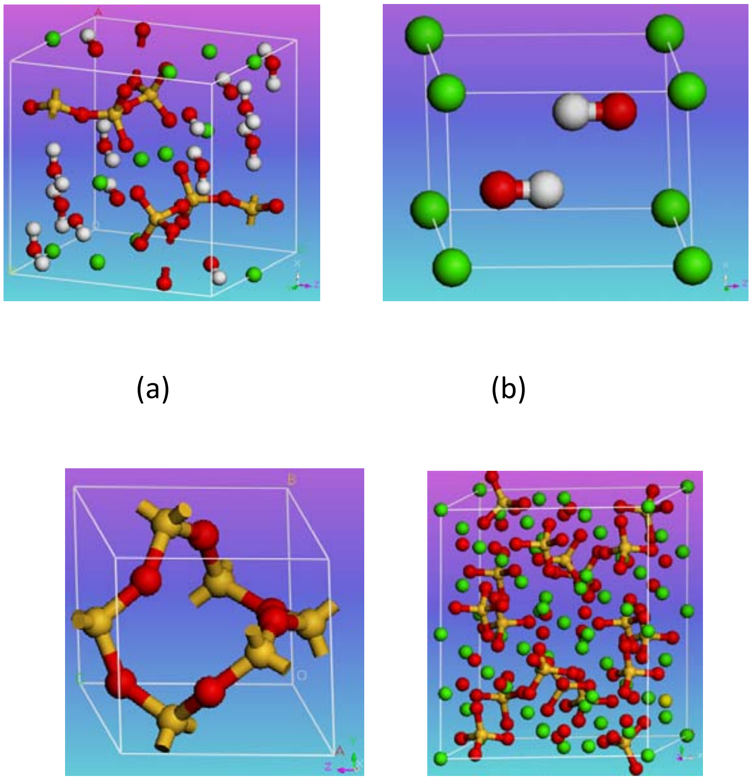


Fig. 3. Proposed cement paste model.



(a) (b)

(c) **(d)**

Fig. 4. Unit cell of crystalline structure of (a) jennite (C-S-H), (b) calcium hydroxide (CH), (c) alpha quartz (sand), and (d) C_3S (cement).

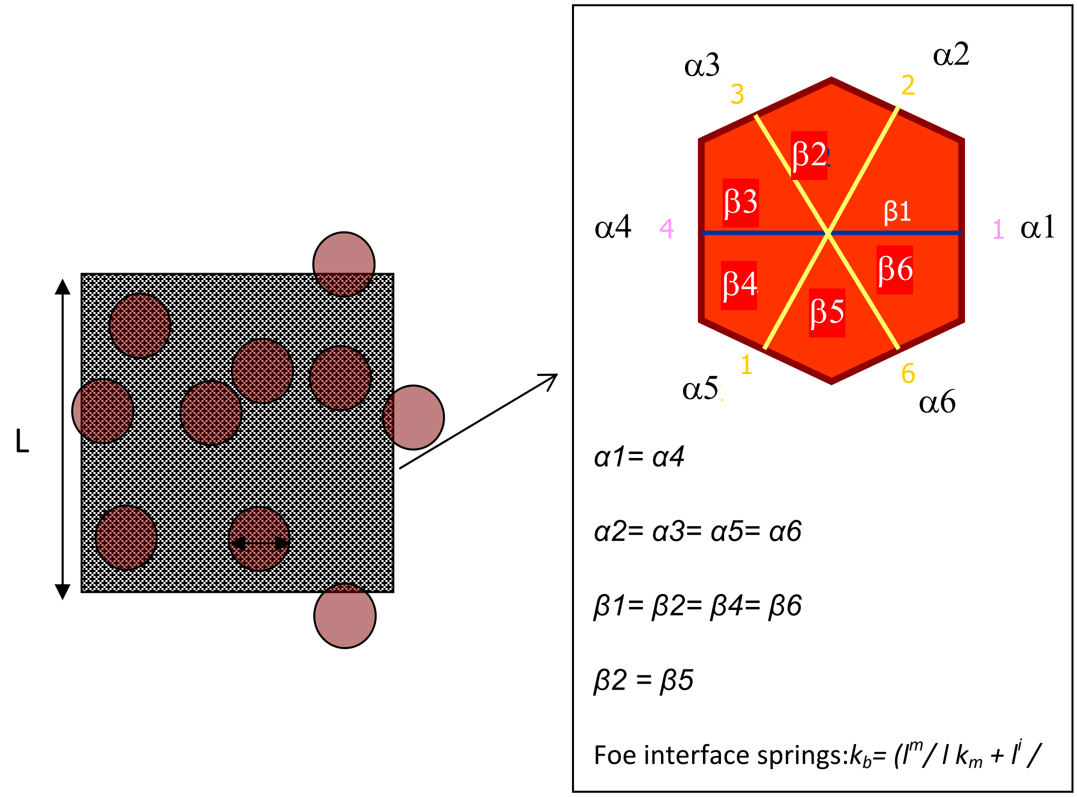


Fig. 5. Fine mesh spring network with a zoom-in for a unit cell.

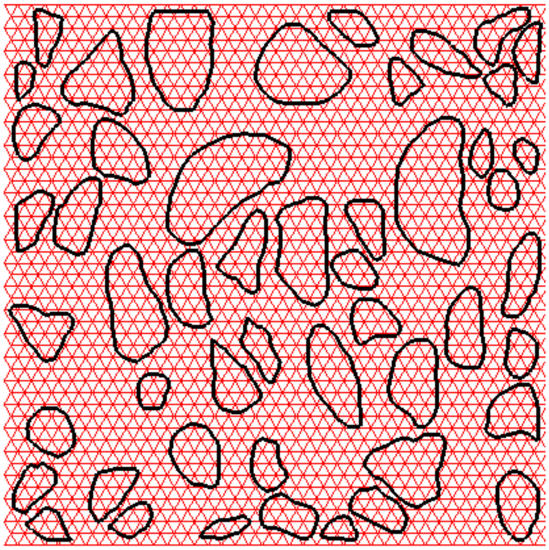


Fig. 6. Spring network mesh of concrete.

Fig. 7. A room temperature RUS system.

Fig. 8. A 1.378cm×1.1956cm×0.964cm parallelepiped shape cement paste sample.

Table 1. Composition of Cement Constituents

Phases	***WP (%)***	***VP (%)***
C_3S	73.9	73
C_2S	12.3	10
C_3A	6.3	8.8
C_4AF	7.5	8.2

WP: Weight Percentage   VP: Volume Percentage

Table 2. Computation of Mechanical Properties of Composites Unreacted Cement /HD CSH and CH/LD C-S-H

Composite (inclusion/matrix)	VF_i	E_i	v_i	E_m	v_m	E_{eff}	v_{eff}
Unreacted cement /HD CSH	0.281	56.6§	0.29	41	0.3	44.87	0.3
CH /LD CSH	0.662	50.02	0.31	30.8	0.29	42.31	0.3

§ Cement particles porosity effect considered.

Unit in this table is GPa except for *VF* and ν.

Table 3: Selected Elastic Constants-Porosity Relations

Eq.	Author (year)	Elastic Constants-Porosity Relation
1	Knudsen (1959)	$E = E_0 e^{(-k\phi_0)}$
2	Helmuth and Turk (1966)	$E = E_0(1-\phi_0)^k \quad k=3$
3	Kerner (1952)	$G = G_0(1-\phi_0)(7-5\nu_0)/[\phi_0(8-10\nu_0)+7-5\nu_0]$ $K = 4K_0G_0(1-\phi_0)/(4G_0+3\phi_0K_0)$
4	Hashin (1962)	$E = E_0(1-\phi_0)/\{1+(1+\nu_0)(13-15\nu_0)\phi_0/[2(7-5\nu_0)]\}$ $G = G_0(1-\phi_0)/[1+2(4-5\nu_0)\phi_0/(7-5\nu_0)]$ $K = K_0(1-\phi_0)/\{1+(1+\nu_0)\phi_0/[2(1-2\nu_0)]\}$

Constant k in equation 1 follows Velez et al. (2001) and k=3.4

K_0, G_0 and v_0 are from the calculated results of cement paste in section 4.2.3.

Porosity in this study $\phi_0 = 8.1\%$

Table 4. Effective Properties of Hydrated Cement Paste

No	E_0 (GPa)	Eq. In table 3	E_{hcp}	v_{hcp}
1	43.1	1	16.1	-
2		2	15.4	-
3		3	23.7	0.27
4		4	23.7	0.27

Table 5: Effective Properties of Mortar

Case	Matrix	(Cement Paste)		Inclusion (Sand)			Mortar	
	E	*K*	*G*	*E*	*K*	*G*	*E*	*v*
1	23.7	17.17	9.33	98.66	42.05	44.48	47.4	0.21
2	23.7	17.17	9.33	62.5	42.05	44.48	39	0.24

Unit in this table is GPa except for Poisson’s Ratio.

Table 6: Effective Elastic Moduli of Concrete by GMC and Lattice Model Theory

E_{mortar}	39
E_{agg}	46.6
E_{con_eff} : GMC	42
E_{con_eff} : Lattice	36.3

E_{con_eff}: Effective Young's Modulus of concrete