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Review Article

An Introductory Review of Simulation Methods for the Structure of Cementitious Material Hydrates at Different Length Scales

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ABSTRACT

Concrete is a very complicated, random, multi-scale and multi-phase material. It is important to know cement paste structure to understand its properties and damage mechanisms that can influence the properties of concrete. Recently, many researchers have focused on the simulation of hydrated cement microstructure to figure out how damage/deterioration might be initiated. Moreover, as the microstructure of hydrated cement is known, we are able to produce greener, stronger and more durable concrete. There is a critical need to survey previous research to direct future study. In recent years due to development of advanced computers, most researchers tend to study the atomistic structure of hydrated cement and to make a bridge between nano and macro scales. Various models have been developed to simulate cement structure. This paper is an introductory review of the most important studies proposed by researchers for simulation of hydrated cement at different scales varying from nano to macro. Impact of the latest advances in simulation methods and their applications for hydrated cement research is investigated. Salient issues are categorised into four main sections including numerical models, microstructural models for cement hydration simulation, atomistic simulations and multi-scale studies.

Keywords: Atomistic simulation, cement, C-S-H, hydration, microstructure, multi-scale

INTRODUCTION

Simulations are useful when the conditions of interest are difficult to achieve in the laboratory. Concrete structure simulation is difficult due to its complex microstructure, which is still not completely understood. A lot of studies have been conducted for cement/concrete materials to know about their structures at different scales. The nature of concrete is random over a broad range of length scales, from nano to macro. Although each length scale presents a random composite, concrete in its engineering uses is considered as a uniform material at the macro scale. Therefore, it is highly necessary

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to study concrete at each length scale to have a better insight into its structure and properties. To simulate multi-scale structures of concrete materials, various sciences including chemistry, materials, physics, strength of materials, heat transfer etc. are needed.

Simulating the hydrated cement microstructure makes it possible to predict different properties and damage/deterioration mechanisms of the hardened cement in relation to time. In this paper, the most major methods that are implemented to simulate hydrated cement microstructure at different nano to macro scales are introduced. In this paper, major methods are introduced and categorised into four methods including:

- numerical models,
- microstructural models for cement hydration simulation,
- atomistic simulations and
- multi-scale studies.

In following section, 'Numerical Models', three basic models used several times as references in later studies are introduced. These models are considered as first research in the field of concrete microstructure simulation. In section 'Microstructural Models for Cement Hydration Simulation', the discussion is provided under five sub-sections for better categorisation. In the sub-section, 'NIST models', there is a brief review of various models proposed by NIST researchers (National Institute of Standards and Technology, USA) that are related to cement microstructure. This sub-section also includes studies proposed by other researchers whose models are based on NIST models. The HYMOSTRUC (van Breugel, 1995a,b), IPKM (Navi & Pignat 1990), μic (Bishnoi, 2008) and De Schutter models (De Schutter & Taerwe, 1995) are introduced in separate sub-sections due to their great importance in the history of hydrated cement microstructure modelling. Colloidal models (CM-I and CM-II) proposed by Jennings (Jennings, 2000, 2008) are introduced in the last sub-section of section. Important concepts used in colloidal models have been used in the development of later models.

In section 'Atomistic Simulations', various research is introduced in three sub-sections depending on the method used for cement microstructure simulation at the atomistic scale. Molecular dynamics, molecular statics and the Monte Carlo method are the three main methods for evaluation of cement properties at the atomistic scale. Each method has specific applications for assessment of different types of cement paste property. Their applications are discussed in section and various research is introduced for each method. In section 'Multi-Scale Studies', research conducted simultaneously in different scales is surveyed. There are two different points of view for multi-scale modelling of cementitious materials: hierarchical and concurrent modelling. Introduction of these methods and their applications are scrutinized in section.

NUMERICAL MODELS

The first attempts to simulate concrete were conducted using the numerical methods. Numerical methods were used to model mechanical properties of concrete. Wittmann *et al*. (1984-85) proposed a method based on the morphological law suggested by Beddow and Meloy (1980), simulating two-dimensional random geometry of natural aggregates to generate realistic

composite structures. They predicted the elasticity modulus and the diffusion coefficient of 'numerical concrete', using the take-and-place algorithm and finite elements method. Using this generated structure the creep and shrinkage of porous composite materials was simulated.

A particle model for brittle aggregate composite materials (concretes, rocks or ceramics) was proposed by Bazant *et al*. (1999). They implemented the take-and-place algorithm for simulation of concrete structure to estimate the propagation of a crack and its location in concrete.

MICROSTRUCTURAL MODELS FOR CEMENT HYDRATION SIMULATION

NIST models

This section introduces important models proposed by NIST (National Institute of Standards and Technology, USA). Jennings and Johnson (1986) introduced a model to describe the hydration processes of C3S in three-dimensional space. In this model cement hydration was considered as nucleation and growth of spherical particles in 3D space. All spheres were shown by the coordinates of their radii and centres. Hydration was simulated as the decrement in the radii of the anhydrous phases and the concentric growth of Calcium Silicate Hydrates (C-S-H) layers on the surface of these particles. Calcium Hydroxide (CH) particles grew as new nuclei formed in the pore-space. Although this model could be used to incorporate some processes relating hydration to microstructural development, it could not be developed further due to limited computational power at the time of development.

Since the Jennings and Johnson model could not calculate mechanical properties of cement paste, NIST researchers, especially Edward J. Garboczi, tried to put the properties issue in context (Garboczi, 2013). Garboczi and Bentz *et al*. (1990) calculated concrete properties and developed a software called 'CEMHYD3D'. This model has two significant capabilities to develop starting 3D microstructures:

1. The embedment of particles of inert fillers, slag, CaCO3 etc. into the particle placement programme, and
2. Simplification of the chemical phase distribution process.

Other features of CEMHYD3D that enhance its capabilities are:

- Addition of the influences of limestone on hydration,
- Incorporation of elementary reactions for slag,
- Prediction of the concentration of the pore solution during hydration and its simultaneous effect on hydration rates,
- The capability to execute hydration under sealed or saturated conditions by specifying a number of cycles after which resaturation of the capillary porosity occurs,
- The ability to precipitate the C-S-H gel in either a random or a "plate" morphology, and
- The addition of a one-pixel dissolution bias that allows for the acceleration or retardation of the hydration rates of the smallest cement particles in the 3D microstructure (Bentz, 2005).

Although CEMHYD3D is still one of the most widely used and well known models in cement hydration, its disadvantage is that there is little kinetic information about the hydration process and requiring resolution, which inherently increases the computation cost of a relatively large volume cement paste (Tan, 2012).

A stochastic simulation model called HydratiCA has been developed for simulating temporal and spatial variations in aqueous mineral systems by Bullard at NIST. In this model nucleation, dissolution, solute transport and precipitation are governed by local probabilistic rules applied on a regular computational lattice. Moreover, the model can simulate ion diffusion in a dilute electrolyte. Consideration for the exponential temperature dependence of the reaction rate constants is shown to provide precise predictions of the effect of temperature on both the equilibrium and kinetics of reactions (Bullard, 2007a,b).

Bentz, Garboczi and Snyder (1999) developed a computer programme for simulating the microstructure of a 3D cubic volume of concrete called the 'HCSS Model' or three-dimensional Hard Core/Soft Shell microstructural model. Using HCSS, Interfacial Transition Zone (ITZ) regions are modelled by a soft gel that surrounds each particle located in a homogeneous matrix.

Recently, NIST researchers have integrated most of their programmes into the Virtual Cement and Concrete Testing Laboratory (VCCTL) that covers the micro to millimeter scales of concrete (Bullard 2011).

HYMOSTRUC model

This model was built by K. van Breugel (1995a,b). In this model, the cement hydration was simulated as a function of the particle size distribution and chemical composition of the cement, the water to cement ratio and the actual reaction temperature. This model was based on the assumption that reaction products were formed close to dissolving cement grains and the density of the reaction product (gel) in case of isothermal curing was constant throughout the hydration process. The model could simulate the development of properties of cement, such as proportional changes in particle size, compressive strength, embedded cement volume changes, porosity in the matrix aggregate ITZ, hydration rate and degree of hydration calculation.

In this model the evolution of hydrating product phases is less focused. This model does not do any calculation of interactions or overlaps between particles; therefore, the microstructural information is not considered in the simulations. Furthermore, the neighbourhood of particles is not considered for the calculation of reaction rates, and localised information at the level of particles, which is extremely important for microstructural properties such as pore connectivity, is lost. Another major criticism of this model is that nucleation of products in the pore-space is not accounted for. Since this model treats the entire microstructure in only a statistical fashion, localised information is lost and cannot be used for further analysis (Bishnoi, 2008).

This model was later modified to account for random parking of particles (Koenders & van Breugel, 1997). In this extended version of the model, the pore-structure constant was determined by analysis of two-dimensional slices from the simulations. The model was extended for calculating autogenous shrinkage of hardening cement paste based on the pore structure using a combination of various empirical equations using pore-parameters calculated from the model (Bishnoi, 2008). Another pixel-based method to analyse pores was later added to the model (Ye *et al*., 2003).

Based on the HYMOSTRUC model, Liu Xian *et al*. made an improvement to take account of the addition of limestone to cement as no-expanding particles and an inert filler without taking part in the hydration process (Tan, 2012).

IPKM Model

The integrated particle kinetics model (IPKM) was developed at EPFL by Navi and Pignat (1990). IPKM simulates 3D model of the evolution of C-S-H microstructure during hydration using the vector approach similar to that used by Jennings and Johnson earlier. This model clearly takes into account the influence of inter-particle contacts and the accessibility of water in pores on the rate of hydration and on microstructure formation.

Unlike the HYMOSTRUC model, it simulates the hydration of every individual particle using kinetics laws that depend not only on the size of the particle, but also on the neighbourhood of each particle. This model also supports the growth and nucleation of new nuclei in the pore space (Bishnoi, 2009). Due to the explicit calculation of all possible interactions, the simulations using IPKM are slow, which leads to the simulations only within relatively small numbers of particles (Tan, 2012).

μic

Like IPKM, a computer programme for modelling the hydration of cements named 'μic' (pronounce Mike) was developed, which preserves the multi-scale nature of the cement microstructure. Support libraries built into the framework enable fast simulation of systems containing millions of particles, allowing every single particle in a system to be modelled and all the interactions to be calculated. It was found that it is possible to explain the hydration kinetics during the first day using a nucleation and growth mechanism when a loosely packed C-S-H with a lower bulk density is assumed to form (Bishnoi, 2008, 2009).

De Schutter Model

G. De Schutter proposed a kinetic hydration model, which carries out adiabatic hydration tests on concrete. It was developed based on the adiabatic and isothermal hydration tests and it is valid both for Portland cement and blast furnace slag cement. This hydration model enables the calculation of the heat production rate as a function of the actual temperature and the degree of hydration. However, the interactions between the cement hydration and the reaction of mineral admixtures are not considered in the model (De Schutter & Taerwe, 1995).

Colloidal Models: CM-I and CM-II

CM-I was introduced by Jennings for the structure of C-S-H as it is formed during the hydration of cement. In this model, the basic building block is a unit of C-S-H that is roughly spherical and flocculates to form larger units. This model describes the structure of the basic units and how they pack to form larger structures and microstructures. CM-I provides a method of the predicting nitrogen accessible gel porosity, density and associated surface area of C-S-H in

cement pastes. The basis for the model is that C-S-H forms as one of two types of cement, high- or low-density C-S-H. (Tennis & Jennings, 2000; Jennings, 2000).

A second-generation model for the C-S-H nanostructure based on the explanation of water absorption isotherms is CM-II. The cornerstone of the model is a description of the globules as small brick-like particles, which consist of solid C-S-H and internal water, and the distribution of water in the small pores between them. Using this model, the properties of C-S-H gel could be estimated; this helps to establish quantitative relationships between the nanostructure and bulk properties (Jennings, 2008).

ATOMISTIC SIMULATIONS

In atomistic simulations, one has essentially infinite control over the specific configuration and geometry of the material. Simulations provide an easier and straighter way to study atomic mechanisms in spite of the advance in resolution of length and time scales in experiments. Observing individual atoms still remains by definition a trivial task in atomistic simulations.

The use of atomistic simulations for cementitious materials is a new field. It is worth noting that molecular modelling studies recently have focused primarily on the structural properties of the cementitious phases rather than the inherent kinetic aspects of cement hydration. However, the precise structural information gained from these atomistic modelling studies may serve as valuable input for the kinetic models (Subramani, 2008).

Two main procedures are used to sample the energy surface and search for the equilibrium configuration of atoms or molecules. Monte Carlo (MC) simulations generate configurations of a system by making 'smart' random movements of the atoms, while Molecular Dynamic (MD) simulations follow the physical time evolution of system by integrating Newton's laws of motion (Selvam *et al*., 2009).

Molecular Dynamics

Molecular dynamics (MD) is a strong simulation technique for studying the chemical and physical properties of solids, liquids, biological molecules and amorphous materials.

Molecular dynamics is used for a better understanding of chemical and physical interaction between atoms and to gain basic properties in the atomistic level. It is good to calculate the time-dependant quantities. In this method the interaction between atoms are approximated and related through empirical interatomic potentials. This approximation provides means to study several nano phenomena using millions of atoms. The interaction between the atoms is governed by Newtonian dynamics. From the time evolution of the atoms and their interactions at specific temperatures, the thermodynamical and mechanical properties and stress-strain relationship can be derived (Gopalakirishan *et al*., 2011).

Manzano *et al*. (2007) performed energy minimisation studies to calculate the key mechanical properties of cement based materials using different crystalline hydro silicates of calcium models. They concluded that the shear (G), bulk (K) and Young's Modulus (E) decreased slightly when calcium to silica ratio of C-S-H increased and when more water molecules entered the composition of C-S-H. In addition, their calculations showed that the mechanical properties of C-S-H structures with dimer or pentamer silicate chains were lower

than the mechanical properties for C-S-H with infinite silicate chains. Subramani (2008) has shown that weak bonds in the Tobermerite structures can be broken to C-S-H blocks by molecular dynamics. The attack of magnesium salt on cement hydrates microstructure using Hamid's (1981) Tobermorite 11 A° crystal structure was also investigated. Murray *et al*. (2010) calculated the stress strain of C-S-H structures by using the molecular dynamics method. Murray *et al*. (2010) and Selvam *et al*. (2009) computed the relationship between stress and strain in C-S-H through the basic block of the C-S-H structure that proposed by Subramani *et al*. (2009). Murray *et al*. (2010) computed the mentioned relationship at nano scale.

Simulation of the structure of C-S-H by MD was investigated by Faucon *et al*. (1996). They studied C-S-H structures with Ca/Si ratios between 0.66 and 0.83. They identified structural instability in the mechanisms causing breaks in the Si-O chains. Dolado *et al*. (2007) studied the formation and the structure of C-S-H by means of molecular dynamics simulation of the polymerisation of Si(OH)2 in the presence of solvated Ca(OH)2,4H2O.

Shahsavari *et al*. (2011) introduced an empirical force field for complex C-S-H layered materials named CSH-FF that was a re-parameterised version of Clay-FF for prediction of C-S-H properties more efficiently and less computationally intensive. Qomi *et al*. (2014) used this force field to optimise the properties of cement hydrates.

Al-Ostaz *et al*. (2010) and Hajilar and Shafei (2015) predicted the mechanical properties of major constituents of cement-based materials using MD. Introducing the COMPASS force field, they investigated the effects of the force field and super-cell size. The results showed that the MD method was capable of providing a good prediction of the mechanical properties of the cement paste.

Molecular Statics

This method uses traditional classical mechanics to model molecular systems. Classical mechanics is used to describe the motion of macroscopic objects according to Newton's second law. In molecular static (MS) modelling, energy minimisations are performed on the atomic structure as explained in Leach (2001). This minimisation will yield an equilibrium structure based on the closest local minima of the initial atomic structure. However, the optimised structure thus obtained may characterise one possible equilibrium or stable structure of the many that could exist. The bulk properties of material like electrical properties, vibrational properties and mechanical properties depend on the curvature of the energy surface.

Subramani *et al*. (2008) showed that molecular statics could be used to determine the energy potential of the crystalline C-S-H structures. They used the computed energy potential to determine key mechanical properties such as Poisson's ratio and Young's modulus of the crystalline C-S-H structure.

GULP code (Gale & Rohl, 2003) was used by many researchers to calculate mechanical properties of C-S-H amorphous structure (Manzanao *et al*., 2007a, Subramani *et al*., 2009) or C-S-H related crystal structure (Gmira *et al*., 2004). This method was also used by Subramani *et al*. (2009) and Manzano *et al*. (2007) to find the possible amorphous atomic structure of C-S-H (Gopalakirishan *et al*., 2011).

Monte Carlo Method

The Monte Carlo (MC) method is a technique to sample the infinite number of available configurations of a material (Binder & Heermann, 2002). In principle, the MD method is one route to obtain such a sample, but there are cases where the MD method is not sufficiently efficient, particularly when sampling configurations that can only evolve dynamically at an extremely slow rate. The Monte Carlo (MC) method is used to model the physical phenomena through probabilities (Leach, 2001). This method does not have time evolution and thus, it is the application of nano science modelling to understand the atomic structure of C-S-H much faster than molecular dynamics. The method is also applied to study film-growth type problems and is called MC for non-equilibrium systems. Similar to MD, this method can also be used to calculate thermodynamical properties. The method can skip high barriers with several local minima faster than MD (Gopalakirishan *et al*., 2011).

A group of researchers (Pellenq *et al*., 1997; Delville & Pellenq, 2000), assuming that C–S–H gel had a layered structure, used atomistic Monte Carlo simulations to gain insight into the electrostatic attraction force between layers.

Gilmer (1976, 1977) used this method successfully to study crystal growth in the 1970s and during the following decade Lasaga and co-workers applied the Monte Carlo method to the study of crystal dissolution (e.g. Wehrli, 1989).

MULTI-SCALE STUDIES

Concrete research topics include complex failure processes. These phenomena are scaled in a bottom-up manner from atomic to continuum scales. Thus, to fully represent cement concrete behaviours, a single-scale modelling method is not suitable as it is difficult to address cross-scale complex behaviour from material scale to structural scale. To look at a problem simultaneously from several different scales and levels of detail is a more mature way of doing modelling (Lu, 2011).

There are two different points of view for multi-scale modelling of cementitious materials: hierarchical modeling (Maekawa *et al*., 1999, Raabe, 2009, Jennings & Bullard, 2011, Sindu *et. al*, 2014) and concurrent modelling (Li *et. al*, 2009a,b, Lloberas-Valls *et al*., 2012 , Ghosh & Chaudhuri, 2013,). In hierarchical methods, results from the lower scale are transmitted to a higher scale, after which single-scale calculations are performed to gain macro scale results (Lu, 2011). Concurrent simulation implements increased resolution of the material scale at certain areas of interest (Lloberas-Valls *et al*., 2012). For instance, the constituents of concrete must be modelled around the fracture process zone while a macroscopic description is used elsewhere. In this method, the whole fine scale region is considered in the computation as opposed to hierarchical methods where the behaviour of a reduced fine scale area is representative for the one at a larger scale (Ghosh & Chaudhuri, 2013).

Hierarchical simulation methods proceed from the smallest scales to the continuum scale. Therefore it named the 'bottom-up' approach (Jennings & Bullard, 2011). In this method, bridging between scales can be done using various methods (Raabe *et al*., 2009).

Maekawa *et al*. (1999) proposed an integrated programme named DUCOM (DUrability COncrete Model), which is a Finite-Element based computational programme to evaluate

various durability properties of concrete. It traces the development of concrete hardening, structure formation and several associated phenomena from casting of concrete to a period of several months or even years. This model can be used to study the effect of ingredient materials and environmental conditions as well as the size and shape of structure on the durability of concrete (Maekawa *et al*., 1999, 2003). However, the DUCOM model did not consider in detail the chemical aspects of the hydration of binary cements.

Recently, a virtual lab called the 'DelftCode', a multi-scale modelling lab, was developed with the aim to line up the models that have been developed for their particular scale-level and to make the results compatible and interchangeable within the modelling framework. The result is a multi-scale simulation tool that covers 10 orders of magnitude and allows including various scale effects to be involved in the calculations. The tool can be used not only for design but also for repair assessments of concrete structures (Koenders *et. al*, 2008, 2012).

FUTURE POSSIBLE RESEARCH

Although good advances have been achieved so far, there are remaining gaps in the simulation results. Some probable studies that might be done to fill these gaps include: realistic quantum mechanical models of clinker phases, effects of impurities on the surfaces of particles, similar studies on the aluminate and ferrite phases, quantification modelling of clinker fracture across multiple levels, studying creep at the mesoscale, finding reasonable relationships between nano, meso and macroscale physical and mechanical properties, evaluation of reversible shrinkage, fracture at the mesoscale, modelling porosity in atomistic scale and determination of the role of water within C-S-H gel nanoparticles (Ulm *et al*., 2014).

Many open questions exist in the mind of researchers that may not be mentioned above. But we can certainly say that all of the future studies would complete the puzzle of cement structure information and more realistic models would be proposed to realise desired economic, environmental and structural needs.

CONCLUSION

This paper is an introductory review of some methods of simulation of cement hydration products. Most of the major methods implemented for simulation of the cement hydration microstructure at various scales from atomistic to macro scales were introduced. Recent studies have shown great potential for improving hydration simulations by providing information on processes occurring at atomic or nanometer length scales. These models will help us to have a better understanding of the behaviour of cement hydration microstructure and will provide more insight into modifying the properties of hardened cement paste at the nano to macro levels.

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