Hydrating Cement Particle Interaction Model for Yield Stress Analysis

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Abstract. This study overviews existing methods for analyzing cement paste yield stress, and presents a new approach based on micro-structural computation. The proposed model explicitly considers cement particle interactions, both the colloidal and the nucleated gel ones. A new algorithm is proposed based on flocculating of poly-dispersed hard spheres in a simulation box, followed by nucleation of mono-sized nano-gel particles. The obtained virtual microstructures are than used as an input for a mechanical approach, which is conceptualized for simulating sliding kinematics needed to initiate the flow of the percolated solid network, i.e. to reach the paste yield stress. The microstructural modeling tool provides insights on how the localized gel is bridging the cement particles, responsible for the yield stress properties of bulk cement paste. Thus, it provides a promising new approach for quantifying the evolution of the bridging strength with nucleation (shear rest) time, enabling parametrization of the mechanical yield stress computation at micro-structural scale.

Keywords: Cement flocculation · Particle based model · Boundary nucleation and growth · Microstructure · Yield stress

1 Introduction

The time dependent behavior of cementitious materials has attracted the attention of many researchers [1–3], while modeling approaches are scarce [4–8]. In particular, Hattori and Izumi [6] explain the effect in terms of (de-)flocculation processes. In their approach, particle-connections are described by an analytical function for the coefficient of friction between particles. It considers the number of primary (dispersed) particles in a unit volume, the initial degree of agglomeration (defined as the ratio of the number of junctions to the number of particles), and the agglomeration rate. Their proposed equation can reproduce the different hysteresis loops observed in experiments with rheometers [3].

Flatt and Bowen [4] developed a yield stress model (Yodel) for particles forming an attractive, i.e. only non-contact, interaction network derived by means of statistical-geometrical considerations. The yield stress is expressed as a function of the particle volume fraction, percolation threshold, maximum attractive inter-particle forces, median particle radius calculated on a volume basis and the particle coordination

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number, which gives the number of contacts between particles. Maximum packing fraction and minimum inter-particle separation distance have to be used as fitting parameters. The model accurately predicts the dependence of yield stress on the solids volume fraction; however, the scaling of yield stress is not directly predicted from particle size, but from the radius of curvature at the point of particle contact. The Yodel considers the yield stress from colloidal stresses only, while contact between particles due to nucleation gel is not included.

Wallevik [7] used a semi-microstructural (statistical) approach to extend the so-called Hattori–Izumi theory [6] by adding different types of flocculation/nucleation connections, both reversible and permanent. This model is based on spherical and mono-dispersed particles and gives the number of particle connections, whose dynamic change is described by differential kinetic rate equations and interlinked with a continuum flow equation via apparent viscosities. Three types of yield stresses (and plastic viscosity) variables were introduced analytically, related to (1) the number of permanent linkages; (2) the number of reversible linkages and (3) the chemically formed breakable linkages.

Roussel et al. [5] considered a conceptual geometrical model where the nucleation gel links the monodispersed (d = 10 μm) cement particles as homogeneous cylinders, whose cross section (order of few nm) increases due to the ongoing formation of nucleation gel. This paper extends such an approach by employing a poly-dispersed particle model to explicitly describe flocculation and nucleation induced microstructures, for the first time.

Description of cement particle flocculation in 3D particle microstructural models was simulated using a Monte Carlo approach [9]. In [9], random moves of isolated cement particles and identified clusters are iterated, and according to the square-well potential, when any of two particles approach each other with a distance smaller than the critical, they will form a flocculated cluster.

This work presents a micro-structural computational approach for analyzing cement paste yield stress, explicitly considering cement particle interactions, including both the colloidal and the nucleated gel actions. The model is able to calculate the development of the micro-structure as a function of the particle size distribution, water cement ratio, size of maximal particle which flocculates (and minimum distance between flocculated particles), and volume of nucleated gel.

2 Micro-structural Modeling Approach

The particle interaction fundamentals, responsible for time-dependent rheological behavior of cement suspensions, are modelled using in-house developed particle packing routines in Matlab. Micro-to-nano-sized particle structures are used as a starting point to develop new modules related to rheology. As part of this paper, a commonly used cement hydration particle model (e.g. [10, 11]) is extended with: (1) a flocculation algorithm, (2) an Boundary Nucleation and Growth (BN&G) module that describes the nucleation induced bridging of the binder particles and (3) a rheological module for early age rheological behavior of the obtained virtual microstructures (Fig. 1). All three modules are described further in detail.

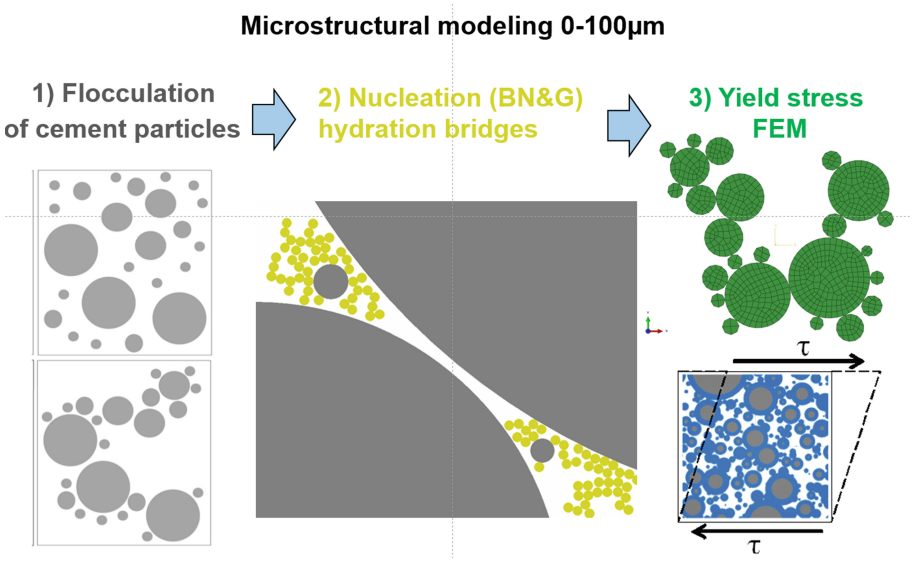

Fig. 1. The new poly-dispersed particle modeling approach proposed for elucidating time-dependent rheology ageing: interaction of cement and nucleation particles during the dormant hydration period.

2.1 Flocculation of Cement Particles

For implementing particle models, an initial randomly distributed cement particle structure is formed in a predefined representative volume element (RVE in 3D) or surface (in 2D) based on particle algorithm for non-overlapping placement of poly-dispersed particles [10] including periodic boundary conditions and a proposed flocculation algorithm. The starting point for the micro-scale particle modelling is that spherical particles are randomly positioned from bigger to smaller inside a predefined volume/surface (100 μm edge), following a certain particle size distribution. The number of particles per fraction is approximated by the Rosin-Rammler function [10]. The volume of all particles in a fraction of an individual component V is calculated by dividing the total fractional weight by its specific density. Then, dividing V by the volume of one single particle V_0, gives the number of particles in a certain fraction [10]. The selection of the lower particle size is based on computational time convenience, whereas the upper particle size depends on the size of the RVE. Every particle has its defined position (x and y in 2D) and radii. For cement particles below about 10 μm in diameter, colloidal properties will be considered, controlled by the action of the total (surface) potential energy. For larger particles ($d_c \sim > 10$ μm) the kinetic energy, or inertia, starts to dominate over the potential energy, so flocculation by soft colloidal linkages can be disregarded [2, 4, 5]. Flocculation of small cement particles to form larger agglomerates (flocs) is driven by van der Waals attractive forces [4, 5]. For flocculated systems, van der Waals inter-particle forces are dominating over Brownian forces, which are thus neglected. To speed up calculations and make them available for aggregation of nano-nucleation particles, particles are directly placed at equilibrium distances randomly around the outer surface of randomly chosen bigger cement particle.

The particle flocculation algorithm is proposed as follows:

1. Randomly place bigger particles (d_c>1-10μm)
2. If d<d_crit: Random attachment on smaller particles
   a. Random pick of a placed cement particle
   b. Random positioning on circumference of the picked (bigger) particle
   c. Overlap?
      i. Yes: GOTO step b)
      ii. No: store *Particle*(x, y, *radii*)
3. Loop (a-c) until all *cement particles are* placed

2.2 Nucleation Hydration: Nano-Particle Bridging of Cement Particles

After having generated the initial (flocculated) cement particle structure, hydration algorithms are invoked to simulate the stepwise evolution of the particle hydration process by the associated addition of nucleation 'nano-'particles following boundary nucleation and growth (BN&G) mechanism, whilst forming a nucleating virtual microstructure. Nucleation bridges as a function of hydration (rest) time is simulated by invoking the particle flocculation algorithm described in Sect. 2.1, extending it for (BN&G) aggregation of 'nano-'particles, based on volume balance and morphology approach for nucleation of (e.g. C-S-H and ettringite cement hydration products) on particle surfaces, both cement and nucleate particles. Therefore, initially cement particles are biased, i.e. have higher probability to be picked, as there are more of them than gel particles. Latter, with increasing degree of hydration, gel particles are becoming more and more biased, as the number of gel particles very soon prevails over the initial cement particles. The volume balance approach is simply based on expansion factor and density of gel nucleates [10, 11]. Incremental volume for each reaction iteration step is calculated proportionally to the degree of hydration (*DoH*), which is linearly increased (stepwise, e.g. in 10 steps) until reaching the maximum value of about *DoH* = 5% [11]. This maximum value for hydration degree corresponds to end of dormant (workable) period, i.e. begin of cement setting. Because of such a low reaction degree, and uncertainties about densities of nucleation gel, volume change of cement particles due to dissolution reaction was neglected. From the incremental gel volume, the number of nucleate gel particles for iteration step is obtained by defining their monodisperse size to be d_{nano} = 5 nm [11], or bigger for computational convenience. The amount of aggregated nucleation gel particles is numerically quantified (e.g. using a neighbour search algorithm) and analysed for local nano-structure morphology. This bridging morphological information is then correlated to the strength of the bridges between cement particles.

2.3 Yield Stress Computational Analysis

The virtual particle structure is transformed into a network of interacting cement particles, using FEM (Fig. 4) and/or DEM, where the cement particles are connected by (initially only) van-der-Walls attractive forces and/or with hydration gel bridges. Those

inter-particle connections, being weaker for the attractive forces and increase in strength with nucleation, still exhibit the weakest point of the elements forming the percolated network of particles. The FEM shear simulation on this network of connected cement particles can simulate the shear force needed to initiate the flow of the microstructure, i.e. the cement paste yield stress. Microstructural system is sheared by applying an external shear force using slow (stepwise) deformations, so the stress is spread only through the percolating network. In a general case, having a random angle Θ between the applied shear and the particle interaction orientation, the shear stress, which can effectively be used to separate the two cement particles is multiplied by a factor of $\cos(\Theta)$. This means that the stress is equal to zero (or maximum) if the cement particles are aligned in (or perpendicular to) the direction in which stress is applied.

3 Results and Discussion

The effect of flocculation is demonstrated by running two simulations (Fig. 2). The first one mimics a fully dispersed case (Fig. 2 down parts) obtained by fully random placement of cement particles for all sizes. On the other side, the upper figures show the flocculated case, where the cement particles having $d_{crit.} < 5$ μm are positioned using the above proposed flocculation algorithm. Results show formation of flocculated percolated network, which is connected via soft colloidal (van-der-Waals) forces.

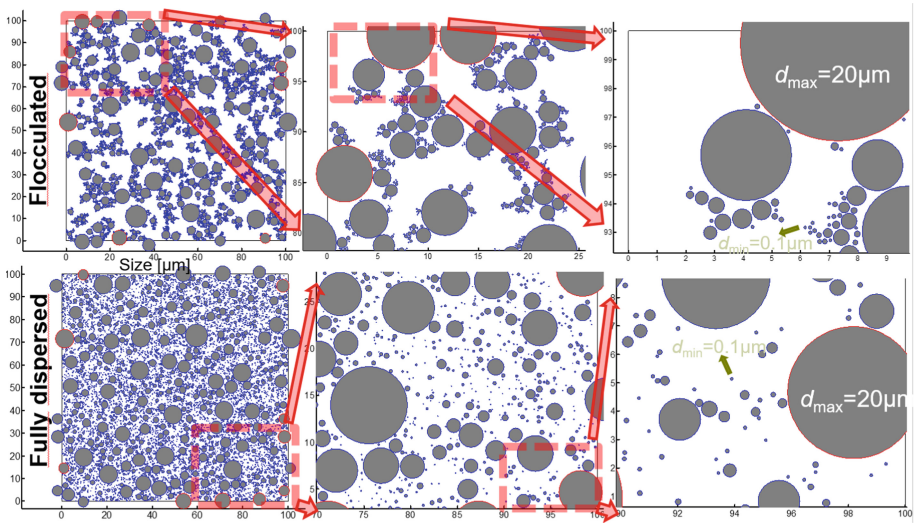

Fig. 2. Flocculation effects on cement microstructure (left: 100 μm × 100 μm simulation boxes, water-cement ratio of 0.45): (down) fully dispersed cement particles; (up) cement particles having $d_{crit.} < 5$ μm flocculate forming a percolated network via soft colloidal (van-der-Waals) interactions.

Figure 3 shows typical results from boundary nucleation and growth (BN&G) simulation, where the yellow nano-particles are aggregated by their sequential positioning near the surfaces of existing cement or gel particles. The simulation was run on the same initial flocculated microstructure from Fig. 2 (top), using 100 μm × 100 μm simulation box having a water-to-cement ratio of 0.45. The nucleation simulation was run until achieving a degree of hydration DoH = 5%, where the amount of aggregated gel particles was calculated based on a volume expansion factor (3.24) and nucleate density (1.2 g/cm^3). The results with zoom-in show how the yellow nucleation gel nano-particles are linking the cement particles to form a percolated rigid network. With the increasing degree of hydration (DoH = 0%–5%, not shown here but one can compare Figs. 2 and 3 for DOH = 0 and 5%), increases the number of the yellow nucleation gel particles. This results in an increased strength of each individual interaction bridges in a unique way, which can now be correlated with this microstructural configuration, as discussed in next.

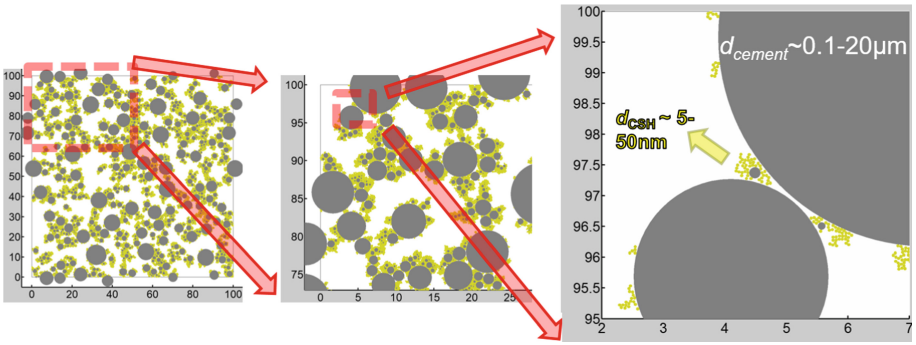

Fig. 3. Boundary nucleation and growth (BN&G) simulation by aggregation of (yellow) nano-particles. Nucleation particles are linking the cement particles to form a percolated rigid network; with increasing the degree of hydration (DoH = 0%–5%) increases the number of nucleation particles, resulting in increased strength of interaction bridges. (Color figure online)

In the case of nucleated bridges, the microstructure for yield stress analysis has to be simplified (Fig. 4). This is done by considering only an assembly of cement particles explicitly (Fig. 4 middle and right). The huge number of nano-particles (yellow, left in Fig. 4) is taken into account (up-scaled) implicitly via the interaction forces (strength of the bridges), as described in Sect. 2.3, where the bridging strength between cement particles is correlated with the local morphological configuration of the nano-particle aggregates. Morphological information on percolated nucleation hydration bridges is used to quantify the increased strength of interaction bridges with hydration to get the cement particle interaction input parameters for FEM yield stress microstructural analysis. On a cement particle scale, one applies an external shearing force, and calculates the changes in interaction energy and stress-strain distributions throughout the interconnected particle network.

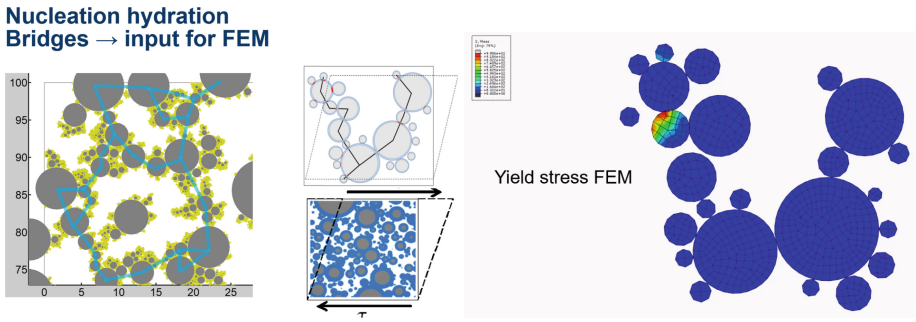

Fig. 4. Morphological information on percolated nucleation hydration bridges is used to quantify the increased strength of interaction bridges with hydration to get the cement particle interaction input parameters for FEM yield stress microstructural analysis. (Color figure online)

4 Conclusions

This paper proposes a micro-structural computational approach for analyzing cement paste yield stress. The approach explicitly considers cement particle interactions including both the colloidal and the nucleated gel interactions between particles.

A new flocculation particle based algorithm is described, based on placement of poly-dispersed hard spheres in a box, followed by nucleation of mono-sized nano-gel particles. A Boundary Nucleation and Growth process was considered, capturing the importance of morphology during evolution of the nano-scale gels. The model is able to calculate the development of the micro-structure as a function of the particle size distribution, water cement ratio, size of maximal particle which flocculates, minimum distance between flocculated particles, and volume of nucleated gel. A mechanical approach on this percolated particle network is proposed for simulating sliding kinematics needed to initiate the flow of the microstructure, i.e. to reach the paste yield stress. The model provides insights on how the localized colloidal and gel bridges are percolating cement particles, responsible for the yield stress properties of bulk cement paste. Currently, research is ongoing on how to parametrize the FEM yield stress using the bridging gel configurations, to correlate the amount and morphological configuration of nucleation particles (bridging the cement particles) with the micro-mechanical properties of the cement particle interactions.

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References

1. Ahari RS, Erdem TK, Ramyar K (2015) Thixotropy and structural breakdown properties of self consolidating concrete containing various supplementary cementitious materials. Cem Concr Comp 59:26–37

2. Zingg A et al (2008) The microstructure of dispersed and non-dispersed fresh cement pastes —new insight by cryo-microscopy. Cem Concr Res 38:522–529
3. Banfill PFG (2006) Rheology of fresh cement and concrete. Rheol Rev 61:61–130
4. Flatt RJ, Bowen P (2006) Yodel: a yield stress model for suspensions. J Amer Ceram Soc 89:1244–1256
5. Roussel N et al (2012) The origins of thixotropy of fresh cement pastes. Cem Concr Res 42:148–157
6. Hattori K, Izumi K (2007) A rheological expression of coagulation rate theory. J Disper Sci Tech 3:129–145
7. Wallevik JE (2009) Rheological properties of cement paste: thixotropic behavior and structural breakdown. Cem Concr Res 39:14–29
8. Wallevik J, Rheocenter I, Iceland IC (2011) The particle flow interaction theory–thixotropic behaviour and structural breakdown. In: Proceedings of 36th conference on our world of concrete and structures, pp 978–981
9. Zheng J, Zhang J, Scherer GW (2012) Prediction of the degree of hydration at initial setting time of cement paste with particle agglomeration. Cem Concr Res 42:1280–1285
10. Ukrainczyk N, Koenders E (2014) Representative elementary volumes for 3D modeling of mass transport in cementitious materials. Model Sim Mater Sci Eng 22(3):035001:1–24
11. Prabhu A et al (2018) A multi-scale approach for percolation transition and its application to cement setting. Sci Rep 8(1):15830