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# Modelling of Hydration and Microstructure Formation of Irregular-shaped Cement

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## ABSTRACT

The shape of cement powder particles plays a crucial role in particle packing and hydration of cement. However, cement powder is generally regarded as sphere for simplification in most cement hydration models. This paper aims to investigate the influence of cement particle shapes on hydration of Portland cement and microstructure of cement paste. A novel central growth model is proposed to generate cement particles with irregular shapes. The particle shape library for single particles and particle packing algorithm are then developed to reconstruct initial 3D microstructures. Afterwards, the hydration process of cement with different shapes are simulated using CEMHYD3D model. The simulated hydration heat, degree of hydration and setting of cement paste with water-to-cement (w/c) ratio of 0.35 are compared with experimental data. The results indicate that the reconstructed irregular-shaped particles have good description for real cement particles in terms of surface area, particle size distribution and geometry. The effect of particle shapes on hydration is significant due to difference in surface area and geometric discrepancy, whereas this effect becomes less obvious with decreasing w/c ratio. The cement hydration model accounting for irregular-shaped particles can serve as an effective tool to better understand cement hydration mechanisms and microstructure formation.

## 1. INTRODUCTION

The shapes of cement powder particles and aggregates play a critical role in their workability, mechanical performance and durability of cement-based materials [1,2]. Cement powders with any given fineness that are produced from same clinker or calcium sulphate particles by different grinding techniques (e.g., roller milling and ball milling) and grinding time have different water demands, setting time and viscosity, which are ascribed to the different particle shapes of cement [1]. An accurate characterisation and reconstruction of real irregular particle shapes is a crucial aspect in better understanding of hydration process, microstructural evolution and mechanical properties development of cement-based materials.

In recent years, different advanced techniques including 3D laser ranging [3] and X-ray computed tomography (XCT) [4] have been used to characterise and analyse the 3D shapes of coarse aggregates in concrete. Unlike coarse aggregates, the size of cement powder particles ranges from a few tenths of a micro-meter to dozens of micro-meters. It is still quite challenging to accurately capture the individual cement particle shapes in 3D using these techniques due to their limited resolution as well as the complicated and prohibitive sample preparation process. For example, there should be at least 10 voxels in any one dimension of a particle to obtain this particle's shape that can only be achieved using the best XCT synchrotron sources [4]. Computer simulation may provide a suitable methodology to reconstruct and analyse the 3D shapes of cement powder particles without such drawbacks, and thus to estimate the effect of particle shapes on cement hydration and microstructural evolution of cement pastes that have not been extensively studied to date.

The main purpose of this paper is to generate irregular-shaped particles and investigate the influence of shapes of cement particles on Portland cement hydration. A novel central growth model (CGM) based on the discrete method along with particle packing is proposed to rebuild cement particles with random irregular shapes and produce 3D representative volume element (RVE) of cement mixes with irregular-shaped cement particles, which is subsequently incorporated into the CEMHYD3D model to simulate the hydration and setting of irregular-shaped cement. A series of experiments are carried out to acquire the input parameters for simulations and measure some properties associated with cement hydration for validation of simulations. Afterwards, parametric analyses are conducted to estimate the effect of particle shape on particle packing, e.g., particle size distribution (PSD), and cement hydration process including hydration heat, degree of hydration and connectivity of solids and pores.

## 2. MODELLING AND SIMULATION

Figure 1 shows a flow chart of the generation of microstructure of irregular-shaped cement using the proposed discrete-based CGM, the entire procedure of which can be divided into five steps. Steps I and II are related to the generation of individual irregular-shaped cement particles, while steps III to V are associated with the random packing of these individual particles.

Step I: Initially, a 3D discrete box with the same resolution as that of RVE is constructed and used as growing space, which should be large enough to accommodate the single particle. The coordinates of the central point in this discrete growing space and a set of default eigenvectors for growing irregular-shaped particles are then transferred into a list. The values (0-100) of the eigenvector in each square (or cube) represent the growing probabilities of the particle in the corresponding dimension.

Step II: Firstly, the coordinates of the first node in the list (i.e., central point) are read and the corresponding pixel is turned into a blue particle pixel. Its eight neighbouring pixels highlighted in yellow colour are then activated and a set of eight probability values between 0 and 100 are generated for them sequentially based on Monte Carlo simulation. The eight probability values are then compared with the corresponding characteristic values of the special irregular particles respectively. If the pointed cell has a probability value smaller than its corresponding characteristic one, the cell is turned into a part of the particle. These steps are repeated on the activated neighbouring pixels until the target area of this particle is achieved. Figure 2f shows an individual particle with irregular shape, where the simulated cement particle is plotted in green.

Step III: Due to the similar orientation of particles produced by the same eigenvector, the grown cement particle needs to be rotated by a random angle $\alpha$ in the growing space to keep its random orientation in the RVE.

Step IV: Boolean operations are used to eliminate “sieve holes” after rotations.
Step V: The individual particle with a random orientation (see Figure 2) is then thrown into RVE of cement mixes using random placement algorithm from the largest to smallest ones.

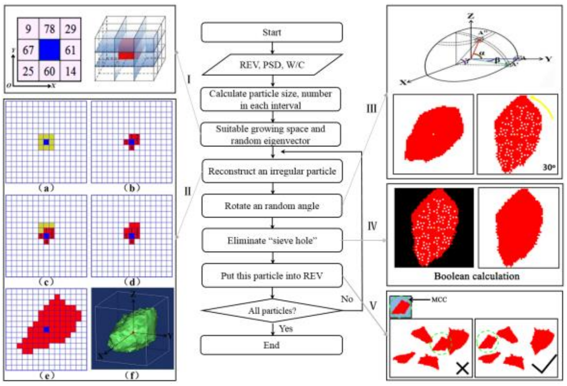

**Figure 1.** Flow chart for the generation of an irregular-shaped particle and particle packing.

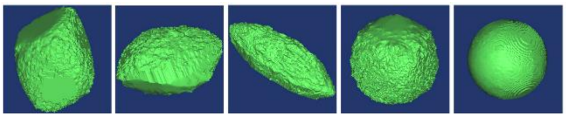
**Figure 2.** Schematic diagram of four typical irregular (M1, M2 and M3) and spherical (DS) shapes of particles selected from particle shape library.

With the measured PSD of cement powders via laser particle analysis, the initial microstructures of cement mixes (w/c = 0.35) with different shapes of cement particles are generated using the developed random placement algorithm, as shown in Figure 3, where red particles present cement clinkers and grey particles are gypsum (5 wt% of cement). The cement particles with sizes are randomly placed into the RVEs from the largest to smallest particles that are not allowed to contact with each other. Compared to that containing spherical cement particles, the initial microstructures consisting of cement and gypsum particles with an irregular shape are randomly located without a certain orientation.

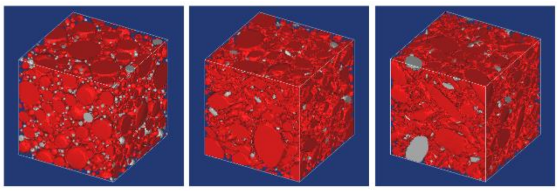
**Figure 3.** Initial 3D microstructures of cement mixes with spherical (DS), intermediate (M2) and elongated-shaped (M3) particles at w/c ratio of 0.35 (red and grey colours stand for cement and gypsum particles respectively).

The simulated PSD of cement mixes composed of spherical and irregular-shaped particles is compared with experimental data (see Figure 4), which shows the simulated PSD for irregular-shaped particles fits very well with experimental data. This implies that the real PSD can be accurately simulated using irregular-shaped cement particles. However, the simulated PSD for spherical particles fluctuates with particle diameter and is not strictly consistent with experimental PSD, especially for relatively larger particles (> 35 μm).

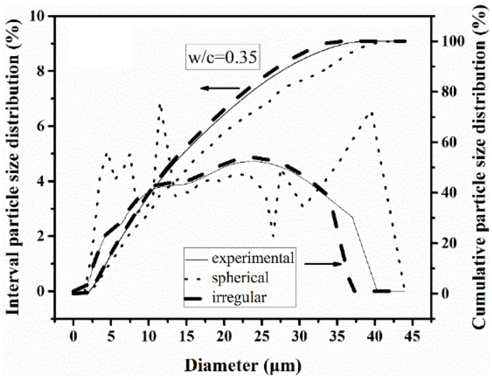


**Figure 4.** Particle size distribution of cement mixes with w/c ratio of 0.35.

## 3. RESULTS AND DISCUSSION

Figure 5 shows the simulated hydration heat together with experimental data. The hydration heat of irregular-shaped system in the early period up to 60 h is much higher than that of spherical system, which can be ascribed to the corresponding larger specific surface area. The released heat of spherical-shaped system at 60 h is approximately 80% of that of intermediate-shaped system, while the released heat of elongated-shaped system is slightly higher to that of intermediate-shaped system. This implies that the equiaxed cement particles with similar chemical composition and PSD can contribute to the reduction in heat release rate.

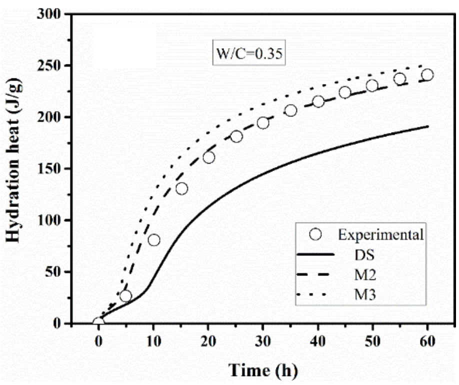


**Figure 5.** Experimental and simulated hydration heat of cement pastes with spherical (DS), intermediated (M2) and elongated-shaped (M3) particles at w/c ratio of 0.35.

Figure 6 shows the simulated DoH of cement pastes with spherical, intermediate and elongated shaped particles at = 0.35 as a function of curing time. The simulated DoH of intermediate-shaped system fits very well with experimental DoH based on non-evaporable water content. The DoH of elongated-shaped system is the greatest, followed by intermediate-shaped system, while the DoH of spherical system is the lowest. This can be attributed to the difference in their surface areas. The elongated-shaped particles have the largest surface area, while the surface area of spherical particles is the smallest. In the early period up to 6 h, the DoH of elongated-shaped system is 0,18, which is about 5 times that of spherical system. At 28 d (i.e., 672 h), the DoHs of systems with different particle shapes tend to be similar to each other and reach 0.64.

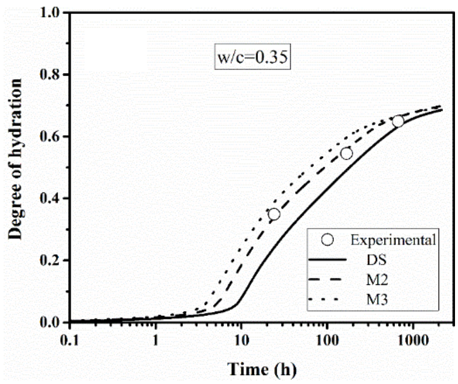


**Figure 6.** Experimental and simulated degree of hydration of cement pastes with spherical (DS), intermediated (M2) and elongated-shaped (M3) particles at w/c ratio of 0.35.

Figure 7 depicts the simulated 3D microstructure and pore structure of hydrating cement paste with various shapes of cement particles. As seen in the 28 d microstructures of cement pastes, the initial shapes of cement particles cannot be clearly distinguished and the simulated complex microstructures of cement pastes look similar to each other. At 28 d of hydration, cement pastes with different shapes have similar DoH at w/c = 0.35. At the same time, the surfaces of anhydrous cement particles in any shaped systems all become more spherical with time, which implies that any discrepancies resulting from cement particle shape during hydration process would be reduced as hydration proceeds. In addition, the pore structure of irregular-shaped system is more complex than that of regular-shaped (i.e., spherical) system.

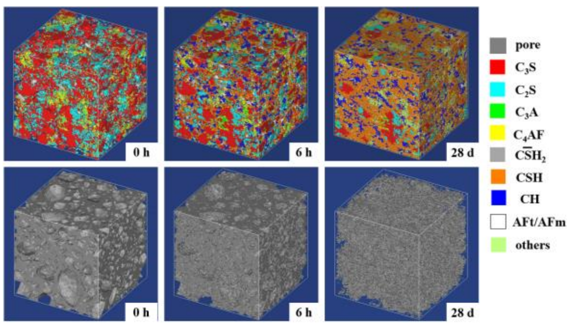


**Figure 7.** Simulated 3D microstructure and pore structure of cement paste (w/c = 0.35) at 0 h, 6 h and 28 d with intermediate-shaped cement particles.

To estimate the influence of particle shapes on percolation of solid phases regardless of kinetics of cement hydration, the connectivity of solid phases is plotted as a function of DoH in Figure 8. The connectivity of solid phases increases with increasing DoH. At w/c = 0.35, the solid percolation curves are quite similar to each other for microstructures of hydrating cement paste with spherical and intermediate cement particle shapes and the solid percolation thresholds for them are found to be around 0.014 DoH, which is approximately two times that for elongated-shaped system. Owing to geometric attributes, the elongated-shaped particles in initial microstructure tend to interconnect with each other, which accordingly results in a lower solid-to-solid spacing.

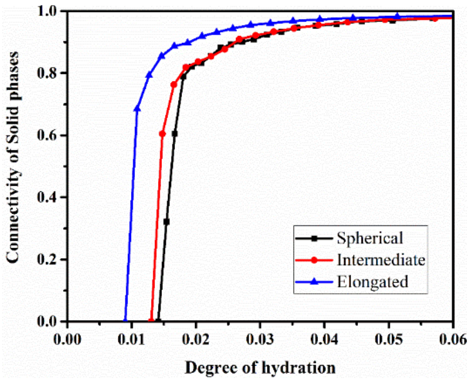


**Figure 8.** Connectivity of solid phases in hydrating cement paste (w/c = 0.35) with various cement particle shapes.

Figure 9 shows the connectivity of capillary pores in hydrating cement paste with various particle shapes. As expected, the connectivity of capillary pores decreases with increasing DoH due to the continuous formation of hydration products. The de-percolation of capillary pores occurs firstly in elongated-shaped system, followed by that in intermedia system and spherical system, which can be attributed to the relatively smaller solid-to-solid spacing.

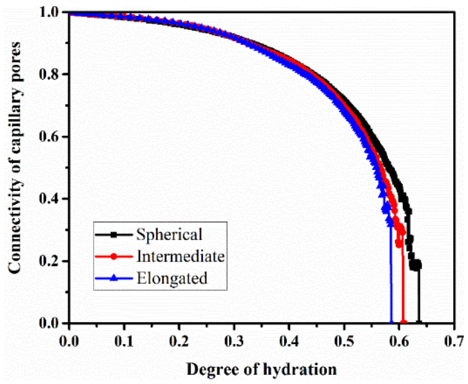


**Figure 9.** Connectivity of capillary pores in hydrating cement paste (w/c = 0.35) with various cement particle shapes.

## 4. CONCLUSIONS

In this paper, an integrated modelling approach consisting of central growth model, particle packing algorithm and cement hydration model is presented to estimate the influence of cement particle shape on cement hydration and microstructural characteristics of hydrating cement paste. Based on the findings of this study, the following conclusions can be drawn:

(1) The proposed central growth model can well reconstruct irregular-shaped cement particles. The generated particles are not only shape-random from the perspective of morphology but shape-controllable in terms of classification on the condition of sufficient constituent elements. Two shape descriptors, i.e., sphericity and normalized semi-axes lengths of equivalent inertia ellipsoid, can be used as criteria to generate unique irregular-shaped particles and create the corresponding shape library of particles. The proposed model can easily determine particle geometric attributes and effectively achieve desired packing density.

(2) The simulated particle size distribution and specific surface areas of initial microstructures made up of irregular-shaped cement particles are in good agreement with experimental data, while a large discrepancy exists between those for regular-shaped cement particles and experimental data.

(3) The shape of cement particles has a significant influence on hydration heat, degree of hydration and percolation of solid phases in hydrating cement paste, which is mainly due to the difference in specific surface area and solid-to-solid spacing between regular and irregular-shaped particles.

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