

MODELLING HYDRATION PROCESS OF CEMENT NANOPARTICLES BY USING AN AGENT-BASED MOLECULAR FORMATION ALGORITHM

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ABSTRACT

This paper presents an agent-based modelling approach for hydration process of Portland cement taking place at the nanoscale. By following a combination of stochastic, deterministic and adaptive rules, cement system is allowed to evolve from an anhydrous separated state to a bond state with enhanced mechanical properties. We consider the two main chemical reactions producing C-H-S gel and portlandite, and identify the related anhydrous cement components as two autonomous agents, while water and hydration time are viewed as activator agents. The material representation consists of a geometrical configuration based on a two-dimensional granular fluid, which shows to be suitable when studying nanostructure formation. The resulting agent-based model is tested on a $10^3 \text{ m} \times 10^3 \text{ m}$ thin film with 20 μm thickness containing anhydrous cement. We evaluate the modelling approach after 7 days of hydration from comparison with experimental results, and agreement is good.

KEY WORDS

Nanoscale modelling, molecular formation, hydrated Portland cement, nanostructure prediction

1. Introduction

Nanotechnology is a revolutionary discipline in the field of science and technology and is expected to have a considerable impact on society [1]. It has already been used for a number of industrial applications, such as electronics, sensors and batteries. The extension of nanotechnology to the applications in material science has demonstrated its potential in the area of construction materials including traditional ones such as polymers, structural steel and concrete. Nanotechnology in civil engineering can be defined in the context of materials and structures as the synthesis, design and modification of materials with dimensions in the range of 1nm to 100 nm. Calcium-silicate-hydrate (C-S-H), a key product of hydrated cement paste, has particle sizes in the range of 1nm to 100 nm. Understanding the structure of C-S-H at nanoscale would help improving the performance of the

material. This new technology has a potential to significantly modify the intricate hydration mechanism of the cement-based materials and the properties of hardened concrete. It should be possible to more precisely control and modify the mechanical behaviour of existing systems or to tailor the performance of novel construction materials.

Portland cement is a multi-component system formed by a number of rather impure chemical constituents, the most important of which are the anhydrous compounds tricalcium silicate (C_3S , conventionally referred to as *õaliteõ*), dicalcium silicate (C_2S , *õbeliteõ*), tricalcium aluminate (C_3A) and an aluminoferrite phase approximating to the formula C_4AF [*]. All these compounds, in a finely powder form, readily react with water giving insoluble hydration products which, in a cement paste (a mixture of cement powder and water) or a concrete (a cement paste containing sand and aggregate filler), gradually replace the water in the spaces between the cement grains and aggregate particles and eventually provide a matrix that effectively binds the composite mass together.

The hydration process of cement is a sequence of overlapping chemical reactions [2] between anhydrous klinker components (C_3S , C_2S , C_3A , C_4AF), gypsum (CSH_2) and water (H), leading to continuous cement slurry thickening and hardening. These chemical equations have different kinetic, so that the products formation can be scaled looking at the timing of the process. In discussing hydration of Portland cements, five hydration stages are defined [3]: preinduction, induction, acceleration, deceleration and diffusion. The duration of preinduction period is only a few minutes, during and immediately following mixing. In this period, the wetting of the powder and a rapid initial hydration, a layer of C-S-H gel is formed over the anhydrous surfaces of cement

* In designating cement compounds, a shortened notation is used where C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃ and H=H₂O. Thus tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$ is written C_3S , for example.

particles. C-S-H precipitates on the surface of cement grains in the form of small sheets (typically $60 \times 30 \times 5 \text{ nm}^3$) [4]. Due to the presence of this layer, very little hydration activity is going on in the following induction stage, lasting a few hours at room temperature. At the end of the induction period only a small percentage of cement particles has hydrated.

The acceleration and deceleration periods (collectively known as setting period), represent the interval of most rapid hydration. During the acceleration period, solid CH crystallized from solution and C-S-H gel deposit into the available water-filled spaces. The hydrates inter-grow, a cohesive network is formed and the system begins to develop strength. Setting of the cement paste is so due to strengthening of the cement grains network by C-S-H nanoparticles precipitating at the contact points between the cement grains. The strength of the cement paste increases during the hydration process because of the augmentation of the number of contact points between the cement grains by the multiplication of C-S-H particles. Fig. 1.1 illustrates C-S-H gel formation and grain cements evolution during hydration of cement.

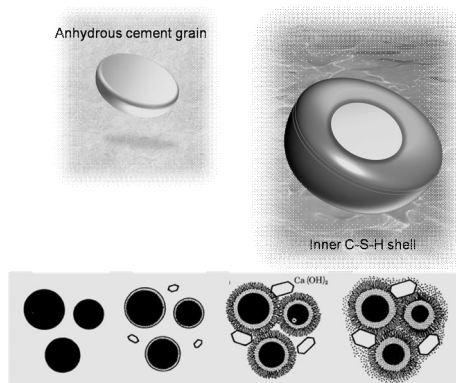


Figure 1.1.1. C-S-H gel formation

As consequence of the deposition of hydrates, the porosity of the system decreases. Eventually, the transportation of ionic species and water through the network of C-S-H gel is hindered, and the hydration rate decelerates. At ambient condition, these events occur within several days, the total degree of hydration reaching a value of about 30%. The hydration continues at slow pace owing to the ever-decreasing system porosity, the network of hydrated products becomes more and more dense, and strength increases. The duration of diffusion period is indefinite at ambient temperature. The total degree of hydration after 7, 28 and 90 days is about 40, 60 and 80% respectively.

1.2 Modelling the hydration process of cement at the nanoscale

Understanding phenomena at the nanoscale to improve the performance of the existing materials is a major part of the application of nanotechnology in construction

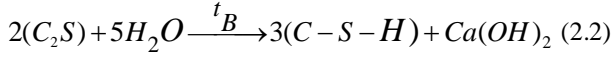
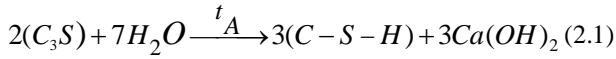
materials. It includes theoretical modeling of C-S-H nanostructure, nanocharacterization techniques and instrumentation. An investigation at the nanoscale provides a better understating on various issues associated with construction materials. Some authors, as Pignat [5], studied the water permeability of cement paste by simulation of the multiscale pore distribution including the sub-nanometre level. Research conducted by Garboczi and Neumann [6] combined the existing software developed at the Virtual Cement and Concrete Testing Laboratory (simulating the micrometre to millimetre size range of concrete) with molecular dynamics simulations of the C-S-H to understand the critical nanoscale structure and dynamics of the C-S-H. Bernard et al. [7] used a multistep micromechanics approach developed from the nanolevel of the C-S-H matrix. Also Kirkpatrick [8] examined the structuring of water on solid surfaces and in pores with dimensions of the order of nanometres to understand the cement hydration at the molecular scale. Simulation methods based on molecular dynamic has proven to be an useful framework of interactions between molecular and binding sites, as Griebel et al. [9] utilized to study the formation and structure of small cementitious C-S-H particles.

When constructing models that involve multiple types of particles and different timing scales, one may choose between two different classes of models: equation-based approaches that identify system variables and evaluate or integrate sets of equations relating these variables, and in the other hand, agent-based modelling which consists of a set of agents that encapsulate the behaviour of the various individuals that makes up the system, and execution consists of emulating these behaviours. In this study we have explored the latter approach, which requires the development of a meta-algorithm that serves as a framework for integrating heterogeneous units (agents) of a composite model, as the cement system is indeed. A virtue of this style of scheme integration is that there is possibility of dividing the whole system into *subsystems*, that is to say a degree of modularity can be assumed for each subsystem simulated using a particular algorithm. If this requirement is satisfied, one can expect an established and well-studied model to be useful when simulating the hydration process of cement.

2. An agent-based model for hydration process of Portland cement

The hydration process of Portland cement is driven by several chemical equations which have different kinetic [2]. In this first attempt at agent-based modelling for hydration process of cement, we will start by considering the two main chemical reactions that involve the formation of C-S-H gel and portlandite, Ca(OH)_2 . Therefore, the reactive phases considered, alite - C_3S - and

belite -C₂S-, when interacting with water will follow the equations:



where t_A and t_B respectively represent the time needed for reaction (2.1) and (2.2) to be completed, being $t_A < t_B$.

We identify an agent with an anhydrous cement particle. Initially, each agent coincides, at random, with one of the two types of particles; type A for C₃S, or type B for C₂S. As the simulation proceeds, the agent changes to represent stable portions of the system that can be considered locally strength. Each agent, during the simulation, can undertake one of the following actions: (i) keep chemically inactive, (ii) react with water, or (iii) stop to reacting with water. The rules for keeping chemically inactive are deterministic as they depend on the type of particle along with the time lasted. If the hydration time is less than t_A all the agents are chemically inactive. If the time is larger or equal than t_A only the agents whose identity coincides with particle type A (agent-A) can choose to react with water. And, finally, if the time is even larger or equal than t_B also the agents type B are allowed to choose the same action. Reacting with water is also deterministic by the amount of water available. If the number of water molecules is enough to complete equation (2.1), the agent-A will decide to react and produce C-S-H gel and portlandite, as will do the agent B to complete its equation (2.2) if the amount of water fits. Therefore, time and water will act as other agents but with the roll of activating the agents A and/or B, when the conditions are appropriated.

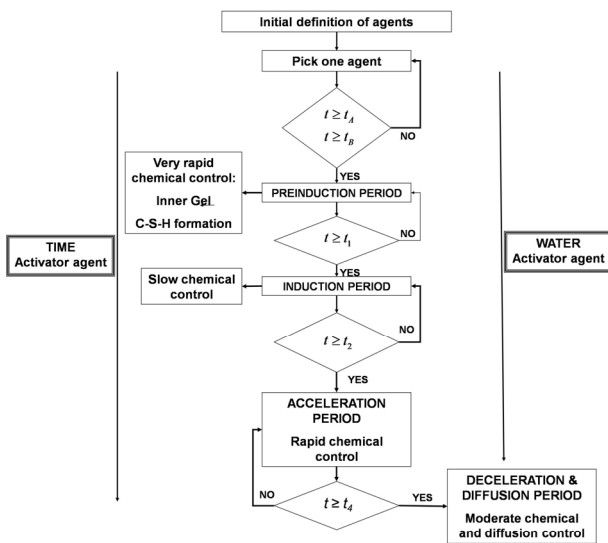


Figure 2.1 Flow-chart representation of the agent-based model

Going on considering the rules imposed for water as activator agent, both the agents type A and B can decide to stop reacting and become chemically inactive for a period of time. That fact occurs when hydration time is larger or equal than a certain t_1 . During this time, the induction period takes place while there is a physical diffusion barrier formed by the reaction products that does not allow the hydration process to proceed at the same rate, the whole process speeds down. Finally, when the induction period is finished, at certain time t_2 , the agents can come back to the second state and react with water if it is available. The acceleration period starts and hydration process can continue faster, until products layer thickness reaches a critical value. When that fact occurs, being time t_4 , the deceleration period controls the hydration process at moderate rate. The overall agent-based model algorithm takes the form outlined in Fig. 2.1.

3. Algorithm description

The material representation used in this study is based on the Stroeve's work [10], which simulates the granular structure of cement at the microlevel as a partial distribution of spherical particles (anhydrous cement) diluted in a aqueous matrix (water). However, while Stroeve's model considers the particles and water confined in a cuboidal volume, this paper will present a non-investigated system configuration based on a two-dimensional granular fluid. Initially, anhydrous cement particles are located at random throughout a thin film with rectangular base and very small thickness. Once water is added to the cement particles, the spatial restriction changes to a cylinder-shaped thin film whose height coincides with the thickness used before. The cement particles are not allowed to overlap any previously placed particle. The initial and final geometrical configurations are shown in Fig. 3.1 and Fig. 3.2. respectively.

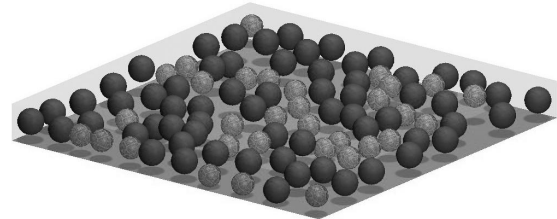


Figure 3.1. Initial distribution

We will distinguish the two types of anhydrous particles considered in the model by differencing their radius. Particle type A, representing C₃S, will have larger radius than particle type B, C₂S. The proportions that these particles represent within the whole material are set as they are normally presented in Portland cement composition [11]; C₃S represents 50% out total mass, C₂S represents 25%, and the remaining proportion 25%

represents other particles that complete the Portland cement system.

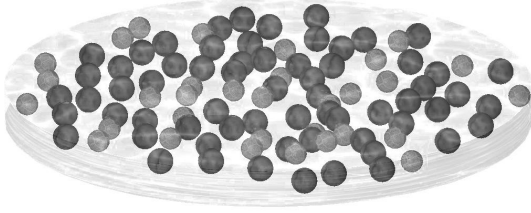


Figure 3.2. Final distribution

Now, we briefly describe the main steps of the algorithm, as are shown in Fig. 3.3.

Step 1. Initial distribution.

An initial distribution of particles of type A and B is generated. It consists of spheres of two different radius $r_A > r_B$, located at random in a 2:1 ratio throughout a cuboid (a rectangular prism) with very small height regarding to lengths of the sides of its base. Spheres can not overlap each other and they are all completely included in the cuboid. A 25% of the volume of the cuboid is free of spheres, representing this percentage the rest of components of Portland cement

Step 2. Water addition

A number of smaller spheres corresponding to water molecules are added to the previous configuration, in such a way that the water/cement ratio is a given number ϕ in this work we take 0.5 as the w/c ratio-. The water is one of the activator agents of this system. The consequent increment of volume does not increase the previous thickness of the cuboid, but it results in a distribution of the three types of spheres throughout a cylinder with same height as the cuboid. A simple calculation of volumes shows that the radius of the cylinder must be at least $\sqrt{\frac{5.15}{2\pi}xy}$, xy being the area of the base in the cuboid.

Step 3. Particles redistribution.

Starting from the cylinder distribution, the model for the dynamics of spheres A and B is a Brownian motion described by a stochastic differential equation of Langevin type [12]. This can be explained as a first effect of the four agents of the system interacting together. In this kind of equation some terms that represent stochastic friction, are added to the Newtonian motion's equation:

$$m \frac{dv}{dt} = F(x) - \beta v + \eta(t) \quad (2.3)$$

Here, the second term represents a viscous force proportional to the velocity of particles, and the third term is the so called *noise term*, due to the shocks between water molecules and type A and B molecules.

As a consequence of these dynamics, the hydration process starts and the preinduction period takes place. When a certain time t_A is reached, agents of type A choose to react with water agent producing C-S-H gel that can be interpreted as a new agent with the responsibility of concentrating locally the mechanical strength of the system. A uniform consumption of water is assumed. Geometrically, the radius of A-spheres decreases while a spherical shell of inner C-S-H gel grows uniformly around them. The rules for this process follow Van Breugel's *basic rate formula* [13, 14] which allows to calculate the decreasing of the volume in an individual cement particle. In this step, the decreasing of particle's radius is assumed to be directly proportional to time, according with van Breugel's phase-boundary reaction. The same scheme happens also for B-agents, starting at a time t_B larger than t_A , due to the slower hydration kinetic of C_2S .

Step 4. Induction period.

When hydration time is larger or equal than a certain t_1 , preinduction stage finishes and the induction period takes place. There is very little chemical activity for an interval of time, but the Brownian dynamic continues controlling the movement of the particles.

Step 5. Acceleration period.

Once the induction period gets finished at certain time $t_2 > t_1$, the agents can react again with available water. The acceleration period starts and hydration process proceeds at high rate. This process gives rise to a decreasing radius of A-spheres and B-spheres. With the same rate, the thickness of the surrounding shell gets thicker. Simultaneously, hexagons based particles, corresponding to portlandite, are added to the configuration in this hydration stage, placed close to the spheres. The volume of water goes down. The agents follow the same kinetic rules considered in step 3. For a third time $t_3 > t_2$, two different parts can be distinguished in each shell, an inner one that remains active and an outer one that keeps size but still contributes to develop mechanical strength in the cement paste. Thus, decreasing of water agent present in the system can be translated in a differentiation of C-S-H gel, main hydration product that is considered to be essential for the properties of the final system. In this way, in the presence of the activator agents - enough amount of water and suitable time-, either A-agents or B-agents react with water giving the same hydration products: gel shells and portlandite crystals. We then consider this agent as a new one locally and globally responsible for the development of mechanical strength.

Step 6. Deceleration and diffusion period.

Deceleration and diffusion period starts once products layer thickness reaches a critical value. The decreasing of volume of cement particles is now driven by the diffusion controlled reaction characterised by the critical thickness [13, 14], resulting a degree of hydration at which the rate of reaction decelerates.

The algorithm goes on until computation of remaining water volume ends. Therefore, in the presented model for hydration process, both water and time agents have to cooperate in a certain way in order to activate the subsystems given by A- and B-agents respectively.

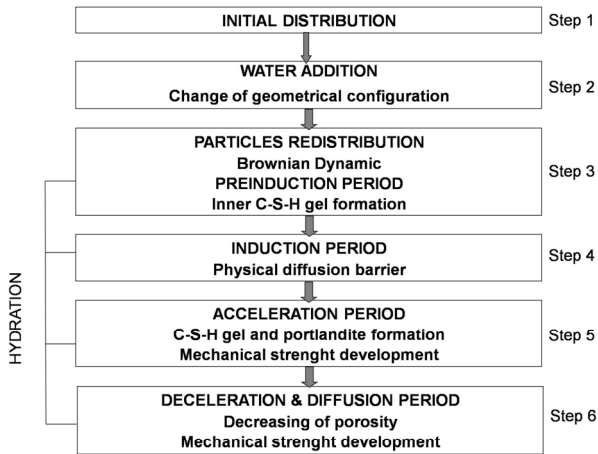


Figure 3.3. Flowchart of the algorithm

In Fig. 3.4, we sketched the time schedule during a simulation that illustrates how this activator agent controls the behaviour of the rest of the agents. For every stage in steps 3 to 6, variations of involved radius and consumption of water are computed for each subsystem giving information about the behaviour of the whole system.

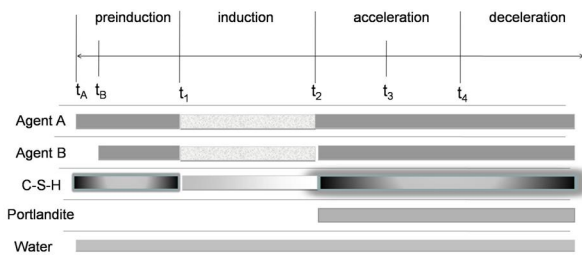


Figure 3.4. Time schedule for the algorithm

4. Experiments and discussion

At the nanoscale, nature manifests itself in a discrete way, so its description requires, at least, an implicit molecular assumption. Our calculations presented in this paper are *ab-initio* calculations, which are, *a priori*, the most suited to study nanoscale phenomena. For input and output geometries, partials changes on molecule shapes were obtained using the Microstation [15] program with a basis scheme, because shape evolutions are less dependent on the underlying theoretical method used to compute them. We wrote out the algorithm by the use of Maple [16], a

symbolic computation software with many capabilities. The method for using the agent-based algorithm developed in the cement hydration system followed the following steps:

- Material preparation: prepare the initial configuration data sets.
- Select parameters, such as water to cement ratio and the thin film dimensions.
- Construct a fineness function to measure algorithm effectiveness.
- Execute a set of agent-based algorithm runs.
- Select the run with results than most closely match the experimental results.
- Refine parameters and algorithm to a succinct form.

The initial configuration was prepared by choosing type A and B anhydrous cement particles randomly distributed in space confined in a $10^3 \text{ m} \times 10^3 \text{ m} \times 20 \text{ m}$ cuboid. The film dimensions were chosen in order to make sure that the average size radius of anhydrous cement (10 m radius) is smaller than the film thickness. The Fig. 4.1 shows the scanning electron microscopy (SEM) image of the 500 m radius circular thin film of hydrated cement nanoparticles formed after water (0.5 w/c) is added on a 1 mm^2 cuboidal distribution of type I Portland cement. We therefore reproduce experimentally the change of geometrical configuration of the 2D granular fluid as it is considered in the computer simulation.

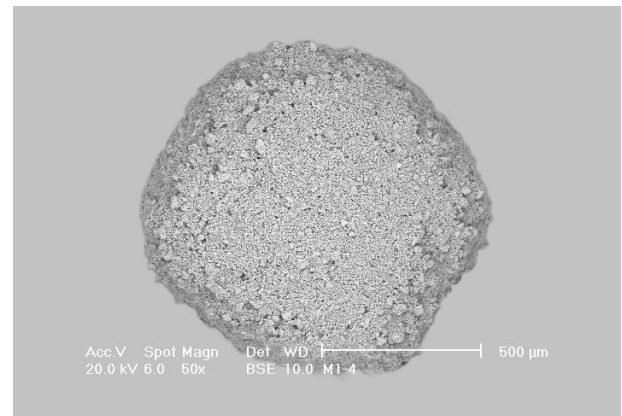


Figure 4.1. SEM image of hydrated cement nanoparticles distributed within circular pattern with 10^3 m diameter formed after water is added.

The degree of hydration and water consumption are been simulated by the agent-based algorithm considering different basic rate factors for each individual particle. The transition thickness is also evaluated for each cement particle on run time. The simulation computes along the final layer thickness of the resulting C-H-S nanoparticles after each step of hydration. The results are shown in Tables 4.1 and 4.2 respectively. The agreement with van Breugel's references [13] is good.

Hydration Stage	20 min Preinduction	28 horas Aceleration	7 days Deceleration
Degree of hydration	0.50	37.2	56.8
Water consumption	0.30	22.3	34.5

Table 4.1. Ratio between volume of reacted cement and volume of water with their initial values, respectively.

Hydration stage	20 min Preinduction	28 horas Aceleration	7 days Deceleration
Particles A	0.06-0.07	4 ó 5	9 ó 10
Particles B	0.007-0.017	0.5 ó 1.5	3 ó 5

Table 4.2. Layer thickness (in μm) of C-S-H nanoparticles precipitated on cement particles A, B respectively, during hydration process

5. Conclusions

This agent-based algorithm for simulation of cement Portland hydration process at nanoscale can be helpful for better understanding and controlling the behaviour of the resulting mechanical system. The great advantage of this computational technique is that the emergent phenomena can be modelled through very simple rules governing the behaviour of each agent. The equations of hydration are replaced by rules that govern the discrete evolution of the system configuration, and in this case, the method has provided an excellent description of the complex nanostructure of the hydrated cement.

A key feature is the material representation considered in this work, with a very high surface to volume ratio. This geometrical configuration is ideal for studying nanostructures for future applications in thin films or nanocoatings.

This work has shown that the agent-based molecular formation algorithm developed for the study of hydration of cement Portland is compatible with the current understanding of the physical-chemical behaviour of the cement grains when they are in contact with water. It is proven to be an efficient algorithm for the inclusion of new constrains or more particles to take part in the physical process, as this novelty modular approach allows including more contributions. We have shown that it is possible to devise a combination of stochastic, deterministic and adaptive rules that lead an anhydrous separate system to organize itself in a bond aggregate-matrix with emerging mechanical properties. This first attempt presented here, is resulting in an efficient computer implementation that reproduces hydrated cement nanostructure after 7 days of hydration. From comparison with experimental results we resume that agreement is good.

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