

Agent-Based Modelling for Cement Hydration

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The Agent-Based Modelling and simulation (ABM) is a rather new approach for studying complex systems with interacting autonomous agents that has lately undergone great growth in various fields such as biology, physics, social science, economics and business. Efforts to model and simulate the highly complex cement hydration process have been made over the past 40 years, with the aim of predicting the performance of concrete and designing innovative and enhanced cementitious materials. The ABM presented here - based on previous work - focuses on the early stages of cement hydration by modelling the physical-chemical processes at the particle level. The model considers the cement hydration process as a time and 3D space system, involving multiple diffusing and reacting species of spherical particles. Chemical reactions are simulated by adaptively selecting discrete stochastic simulation for the appropriate reaction, whenever that is necessary. Interactions between particles are also considered. The model has been inspired by reported cellular automata's approach which provides detailed predictions of cement microstructure at the expense of significant computational difficulty. The ABM approach herein seeks to bring about an optimal balance between accuracy and computational efficiency.

1 Introduction

Throughout history models have helped to understand the reality around us. Based on fundamental physical and chemical principles, models are mathematical constructs that mimic complex systems as galaxies, nuclear explosions, molecular structures, etc. Trying to answer fundamental questions, models build a virtual world as for example the atomic model of Democritus or Leonardo da Vinci's drawings of bridges. Of course, models are less complex than reality and each model is endowed with its own set of assumptions.

Material modelling tries to establish relationships between the structure, processing, properties and performance of materials. Today the design of ever more complex and ever bigger structures, such as skyscrapers, dams or bridges, requires us to satisfy conditions about stability, functionality, durability and aesthetics. But, for new types of materials, no reliable experience-based design rules are available, so models are needed and computer science is needed to run these models. Cementitious materials are one of the most widely used and most complex construction materials, being as they are sensitive to surrounding environment, with time dependent behaviour, many mineralogical phases and multi-scale structural features. It is therefore a modelling and simulation challenge to create a powerful predictive tool in order to assess design and building processes.

In the present work, the real process we want to mimic is the hydration of cement when it is mixed with water producing the cement paste and the microstructure development responsible for the bearing capacity acquired in this process.

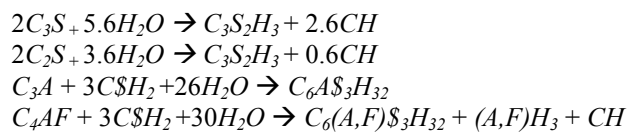
The objectives of the present paper are then threefold:

- To develop a mathematical model using the agent-based modelling approach related to cellular automata method used by Bullard (2007) to get detailed predictions of cement microstructure.
- To obtain the degree of hydration and the thickness of hydration products in terms of time.
- To study the influence of processing conditions like water/cement ratio, particle size distribution and curing temperature.

The rest of the paper is structured as follows: in Section 2 we review the basics of the cement hydration process and the microstructure development. In Section 3 we present a brief overview of cement hydration models. Section 4 is devoted to our agent-based modelling approach for cement hydration and finally we give conclusions and suggest future lines of work in Section 5.

2 Cement Hydration and Microstructure Development

Portland cement was invented 200 years ago but it is still relatively poorly understood. Cement is a multiphase material, its main phases being the tricalcium silicate C_3S or alite, the dicalcium silicate C_2S or *belite*, the tricalcium aluminate C_3A , the calcium ferroaluminate C_4AF and the gypsum $C\$H_2$. C stands for CaO , S for SiO_2 , A for Al_2O_3 , F for Fe_2O_3 , $C\$$ for $CaSO_4$ and H for H_2O . Cement is a multiscale material which has particles ranging from a $0.5 \mu m$ to about $100 \mu m$. Chemical composition and particle size distribution are in this way two of the factors influencing cement hydration and microstructure development when cement is mixed with water. During these processes chemical reactions and physical interactions occur giving as a result some hydration products. The main reactions are the following in which silicates, aluminates and gypsum react with water to give $C_3S_2H_3$, called *C-S-H* gel, Portlandite or CH and other products as $C_6A\$_3H_{32}$, known as ettringite (that becomes monosulfate when there is not enough sulphate available).



A global indicator of the evolution of this process is the degree of hydration, α , defined as the ratio between the amount of reacted cement at time t and the initial amount of cement. This degree of hydration can be also defined in terms of the exothermic heat produced at time t . Cement being a multiphase material, the hydration process is a multivariate process: curves of degree of hydration versus time or heat rate versus time are different for different phases and different particle sizes. One of the difficulties is then to identify kinetics at particle level.

Structurally, cement paste is a dense suspension of particles in a liquid medium. As hydration proceeds, the size of anhydrous phases decreases, the amount of hydration products increases and the microstructure of the hardened cement paste evolves with time. Four main phases can be distinguished: unhydrated core grains, several forms of *C-S-H* gel (the phase mainly responsible for the cement's hardening), Portlandite particles with hexagonal aspect, and the so-called pore system, consisting in the remaining water plus water that is included in *C-S-H* nanopores. Porosity influences properties such as strength, shrinkage, creep and permeability. Information about microstructure is necessary to predict properties of cement paste such as, for example, strength, because it depends not only on the amount of pores, as is Power's model around 1960, but also on the size and location of pores. Nowadays, neither model can accurately relate microstructure to properties of cement paste.

Regarding the specific mechanisms of the process we would like to model, cement hydration consists of several coupled processes with different kinetics depending on both the nature of the process and the state of the system. It is usual to visualize the overall progress of hydration on a plot of heat rate versus time that can be divided into several stages defined by some special points as shown in Figure 1.

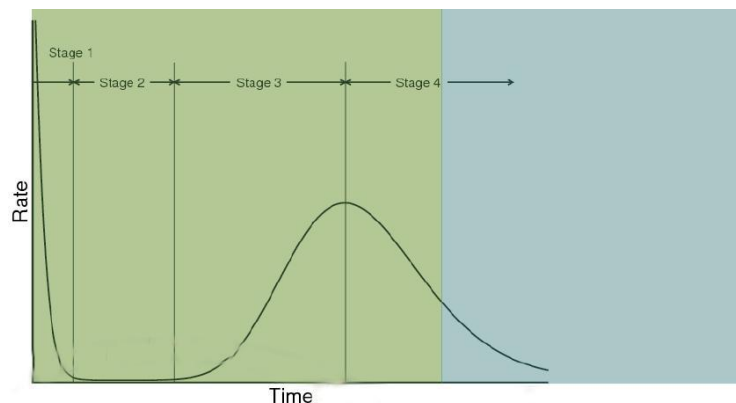


Figure 1. Rate of exothermic heat versus time (Taylor, 1997)

First stage is called pre-induction: just after being in contact with water, cement grains dissolve quite rapidly but the rate decreases very quickly passing to a dormant period, the induction stage in which the rate of dissolution remains low for a few hours. When some critical point is reached, precipitation of solids starts and growth of *C-*

S-H gel proceeds in the so-called acceleration stage. Finally, when impingement of domains reduces the available surface for growth, a diffusion process of transport of solution components controls kinetics in the deceleration stage. The reader who is interested in details about these mechanisms is referred to Bullard et al (2010).

One of the modelling needs about the cement hydration process is to elucidate where division points are located and what the mechanisms triggering each stage are. The other main challenge is to find a link between chemical kinetics and microstructure in order to be able to control the rate of reaction and thereby also control the hardening and heat generation as well as the structure and distribution of hydration products.

3 Modelling Approaches to Cement Hydration and Microstructure Development

We give now a brief summary of main modelling approaches to cement hydration process and microstructure development over the past 40 years as in the synthesis work (Thomas, J.J. et al., 2011).

Single-particle models were the first to appear around 1960. Kondo and Kodama (1967) developed a model of alite hydration, considering growth and diffusion processes and assuming a uniform and concentric layered growth of hydrates on a single spherical cement particle. With this model, the overall rate of reaction is taken to be that of the slowest reaction step. The model is easy to implement and capable of predicting the degree of hydration. Twenty years later, Pommersheim, Clifton and Frohnsdoff (1982) described another single-particle model for alite hydration, similar to the previous one, but more mathematically rigorous, handling diffusion at phase boundaries through solving time-dependent diffusion equations in spherical coordinates. Some limitations of single particle models are that they do not consider particle interactions, they do not take into account particle size distribution effect and their predictions could be valid only for cement mixes equivalent to those used to calibrate the parameters of the model.

Nucleation and growth models were developed first around 1940, based on experimental observations, suggesting that the rate of formation of *C-S-H* hydration product is rate controlling at early stages of hydration. In these models nucleation and growth are often considered as a single general process by which one phase transforms into another. In the early stages of the process the volume of transformed phase increases following a simple power law but at later times, behaviour gets more complex due to the impingement of adjacent regions of growing product. Assuming that nuclei are randomly distributed, Avrami (1939), Jonhson and Mehl (1939), and Kolmogorov (1937), proposed, independently, the well known Avrami or JMAK equation:

$$X(t) = 1 - \exp[-(kt)^m] \quad (1)$$

where $X(t)$ is the volume fraction transformed at time t , k is a combined rate constant of growth and nucleation, and $m=p/s + q$, where p is the growth dimensionality ($p=3$ for isotropic growth i.e. spheres), s is the type of rate control ($s=1$ for phase boundary and $s=2$ for diffusion) and q is the type of nucleation ($q=0$ for site saturation and $q=1$ for continuous nucleation). This equation fits well to C_3S hydration kinetics until the peak on Figure 1 but fitted parameters have limited physical significance and no particle size distribution effects are considered.

In 2007, a boundary nucleation and growth model, developed by Thomas (2007) and proposed by Cahn (1956), assumes that nuclei form only on planar boundaries based on the observation that *C-S-H* nucleates on mineral surfaces. Formulation of the model is more complicated and it does not account for impingement effect but it provides a better fit than the JMAK equation and it has being recently used to analyse temperature and pressure effects on hydration kinetics.

Single-particle and nucleation and growth models are not capable of simulating phenomena such as strength development, porosity and distribution of multiple cement phases. Hydration simulation models, starting with the model of Jennings and Johnson (1986), were designed to simulate microstructure development and most of them give only an approximation of kinetic aspects.

The Jennings and Johnson model uses an off-lattice approach, addressed recently as vector approach which represents shapes by using properties that are not discretized into a grid. Cement particles are seen as equally-spaced spheres in a cubic volume represented by coordinates of their centres and radii, and hydration is simulated as the reduction in their radii and the uniform growth of *C-S-H* layer on their surface. The model uses mass and volume balance rules, as well as a statistical approach to reaction rates rather than following the hydration of each individual particle. It accounts for particle size distribution and location of nuclei as well as impingement

effects, by the redistribution of products in space. However, due to computational limitations, it could not be developed further.

Following a vector approach similar to that proposed by Jennings and Johnson, Van Breugel (1991) developed another microstructural simulation model called HYMOSTRUC. The model relates microstructural changes with time through a finite difference model that takes into account temperature and water related effects:

$$\frac{\Delta\delta_{x,j+1}}{\Delta t_{j+1}} = K_0(\cdot)\Omega(\cdot)F_1(\cdot)\left[F_2(\cdot)\left(\frac{\delta_{tr}}{\delta_{x,j}}\right)^\beta\right]^\lambda \quad (2)$$

where $\delta_{x,j}$ is the depth of hydration product, j is an integer identifying the time interval, $K_0(\cdot)$ is a rate factor, $\Omega(\cdot)$ resumes water-related microstructural changes, the F terms depend on the curing temperature, δ_{tr} is the transition thickness triggering transition to the diffusion stage, β is an empirical parameter and $\lambda=0$ until $\delta_{x,j}$ reaches δ_{tr} . Parameters of the model are experimentally based so it requires recalibration for cement mixes outside the experimental data base.

Most recently, a new implementation of the vector approach has been developed by Bishnoi and Scrivener (2009), derived from the earlier model of Navi and Pignat (1996). The microstructural modelling platform called μc uses new support libraries allowing the user to fully customize the simulations and to model the hydration of a few million particles in a few hours on a personal computer. Still growth of multi-layered spherical particles is used to represent the microstructural evolution; solution phase chemistry is not taken into account. It appears to be a useful tool for the investigation of the mechanisms of hydration.

In contrast to the vector models described above, Bent and Garboczi (1991) used a lattice-based approach based on digital images to develop a 3D microstructure simulation tool called CEMHYD3D. They considered a uniform cubic lattice assigning to each voxel of the lattice some material, and changes on this virtual microstructure are simulated following some empirical and local rules that mimic the processes involved in hydration such as dissolution of solids, diffusion, etc. Many properties can be determined as hydration proceeds, spatial simulation of microstructure is good and computations on the system are fast. However the time scale has to be recalibrated for new cement mixes and rules are set for a fixed pixel size, so simulations do not converge when pixel size is reduced.

Trying to avoid kinetic limitations of CEMHYD3D, Bullard (2007) developed the stochastic simulation model called HydratiCA applying Cellular Automata approach started with von Neumann in 1966. In CA modelling a physical system is idealized as a discrete lattice whose cells can take a finite number of values and classical differential equations are replaced by rules governing agents' behaviour. HydratiCA's rules follow fundamental kinetic principles based on CA modelling of reaction-transport processes developed by Karapiperis and Blankleider (1994) that converge to standard reaction-transport equations in the continuum limit. Each stoichiometric solid phase, like C_3S , water and each aqueous solute species is modeled as a separate chemical component. These are discretized on cells of a regular cubic lattice. The occupation number of cells of a given component at some lattice point gives its concentration there. A large number of fundamental material parameters are required for input but there is no explicit dependence on cement mixes. Stochastic rules simulate chemical and structural changes for each time interval getting convergence for time steps that are small enough. In this way, detailed predictions of the microstructure development and the kinetics of phase changes can be obtained and the simulation model can be used to elucidate mechanisms of hydration but the approach is quite computationally expensive due to the large number of intervals of time required for convergence.

All the models described until now require input data related to thermochemical, physical and structural properties of material, as well as input reaction rate data. These data must be obtained from experiments or more fundamental computations using molecular-scale techniques. Molecular-scale simulation is a recent field in which materials are simulated at atomic level by quantum mechanical simulations or force field methods. These kinds of simulations could be used as a valuable input for kinetic models. Both approaches are computationally expensive and are focused on structural properties of cementitious materials without having exploited simulation of dissolution and growth processes whereas such as methods have been successfully applied on Geochemistry.

Agent-Based (AB) modelling is a rather new approach for simulating complex systems with interacting agents. It can be considered as a generalization of Cellular Automata (CA). In AB simulation the model system is not required to be on a lattice, state variables can be discrete or continuous, and the rules can include deterministic, stochastic and adaptive elements. In general, an Agent-Based simulation model is a hybrid discrete-continuous simulation model with proactive autonomous and interacting entities. In the recent past they have been applied to social networks, markets, flows, biology, chemistry, archaeology and material science as described in Chan et al., (2010). In the context of physical phenomena, these models have been used to describe flow dynamics and diffusion and percolation processes, as well as molecular self-assembly (Troisi et al., 2005). One advantage of rule-based models is their computational efficiency compared with differential equation models and their ability to mimic emergent behaviours from the bottom. The AB simulation model for hydration cement described in the following section is based on previous work (Cerro-Prada et al., 2009) and it is inspired on CA approach by Bullard (2007).

4 Agent-Based Modelling (ABM) for Cement Hydration

The agent-based simulation model for cement hydration we have developed is a microstructural model aiming to simulate the hydration kinetics and the microstructure development as hydration evolves at the cement particle scale, using localized rules to mimic the hydration process. Calcium silicate phases are considered as agents of the system, while time and water play the role of activator agents and temperature acts as a determiner agent. Our agent-based computational approach comprises a set of rules which come from a systematic ab-initio study of hydration process (Van Breugel, 1991). The kinetic laws drive an initial phase-boundary reaction in which a layer of *C-S-H* gel is formed over the surfaces of non-hydrated cement particles, ending at a certain critical time when the product layer around each cement particle reaches the transition thickness. When that fact occurs, the deceleration period controls the hydration process at moderate rate. Kinetic rules follow integrated kinetic formula (2) proposed by Van Breugel (1991), however, our model considers interactions between particles by pseudo-randomly assigning to each cement particle its own transition thickness as well as its own rhythm for decreasing, depending on the size and composition of the particle, coherently built from experimental data.

The overall agent-based model algorithm takes the form outlined in Figure 2. An initial distribution of particles of type A (alite) and B (belite) is generated. During the simulation, each agent can keep inactive, react with water, or stop reacting with water. The rules for staying chemically inactive are deterministic as they depend on the type of particle along with the time lasted. Reacting with water is also determined by the amount of water available.

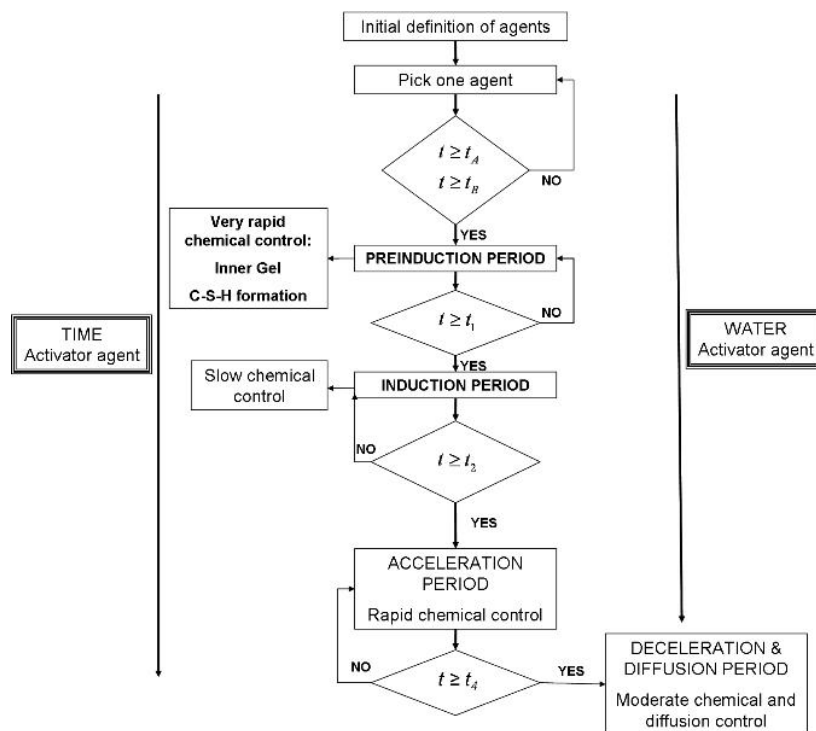
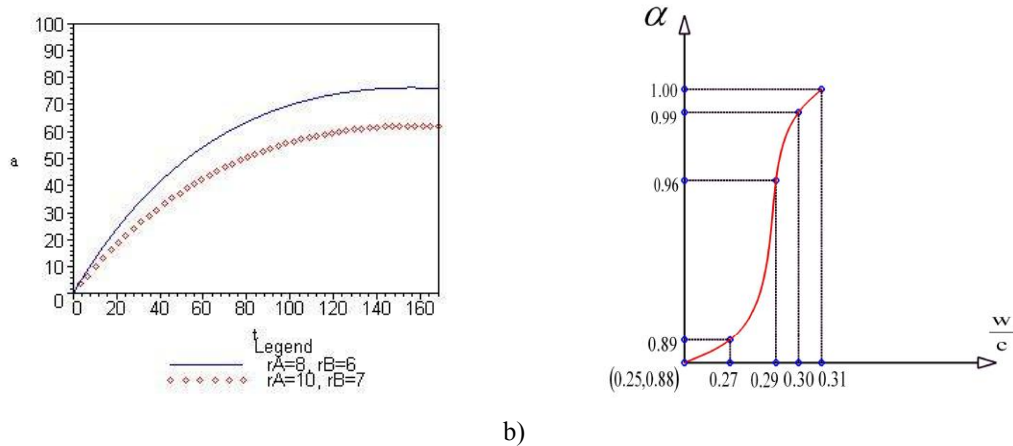


Figure 2: Algorithm overview for the agent-based model

This AB model allows to analyse the degree of hydration and the growth of the *C-S-H* gel as functions of time, taking into account the effects of particle size distribution, water-cement ratio and curing temperature.

We have previously applied this agent-based approach for modelling the cement hydration process in Cerro-Prada et al. (2009), through an algorithm that produces the degree of hydration, the water consumption and the thickness of the *C-S-H* gel in terms of time, considering not only hydration of alite but also including belite in ordinary Portland cement, upon constant ambient temperature. Particle size and water-cement ratio were taking as parameters of the model. The computation achieved good agreement with reported experimental results. Figure 3 and Figure 4 depicted some results obtained from the mentioned computational model.



a) b)
 Figure 3. Degree of hydration in terms of particles size: rA is the radius in micras of alite spherical particles and rB is the radius in micras of belite spherical particles (a) and ultimate degree of hydration curves in terms of water/cement ratio (b).

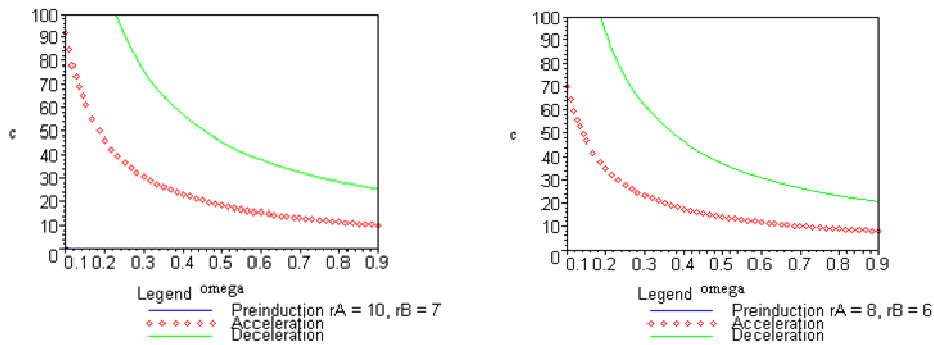
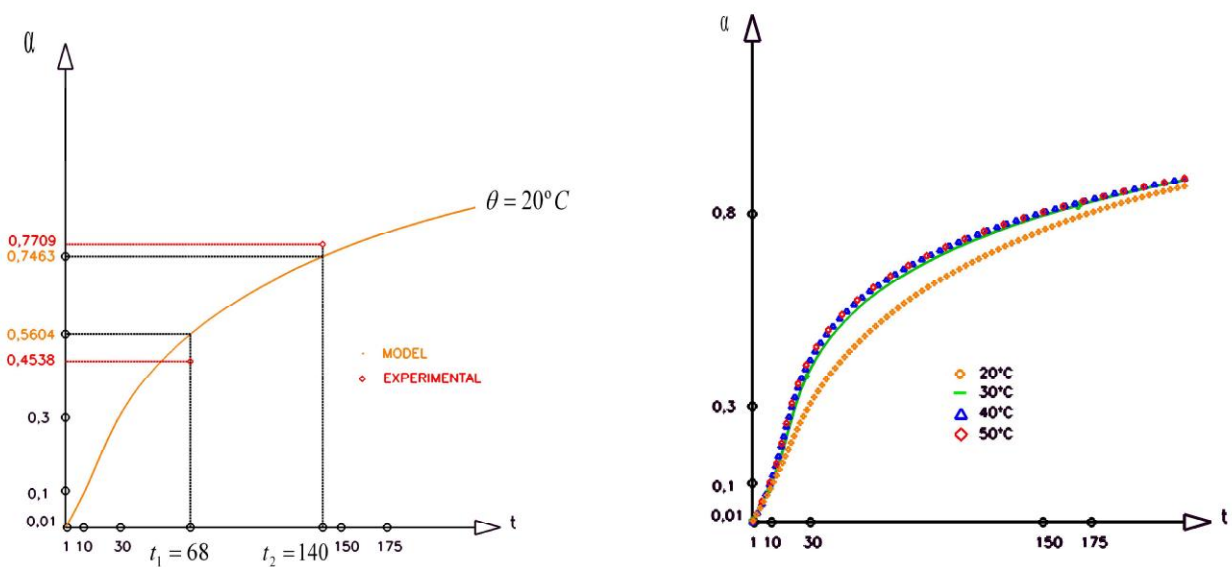


Figure 4. Relative consumption of water in terms of water/cement ratio for two different particle sizes distribution.

We have extended the model considering the effect of curing temperature, and its influence on the morphology and density of the hydration products, by taking into account the decreasing ratio between the volume of the products and the volume of the reactants as addresses in (2), as well as including that ratio within the rules that govern the agents. The model validation is conducted by comparison between computed and experimental results achieved on ordinary cement pastes with different water-cement ratios cured at various temperatures (Figure 5). The thermal effects on the density of different cement pastes are analysed with the thermogravimetric analysis (TGA).



a) b)
 Figure 5. Model versus experimental degree of hydration in terms of time (a) and degree of hydration curves in terms of time for different curing temperatures (b).

This modelling approach for cement hydration is implemented on Maple© and MATLAB© obtaining a computationally fast algorithm: the first 8 hours of hydration, for 50.000 particles, can be simulated in a few minutes using a standard personal computer.

5 Conclusions

The present work shows how an agent-based (AB) simulation model can be used to study the cement hydration process and the microstructure development. Alite and belite cement particles are considered as spheres confined in a computational volume. Their behaviour is governed by kinetic rules based on a statistical approach to reaction rates, but assigning to each particle its own transition thickness to trigger on diffusion stage and its own rate factor at this period. Effects of particle size distribution, water/cement ratio and curing temperature are taken into account.

Globally, AB modelling produces results on degree of hydration in terms of time, as well as water consumption and *C-S-H* thickness, being in agreement with reported experimental results. We believe that one of the great advantages of this computational technique is that the emergent phenomena can be modelled through very simple rules, by governing the behaviour of each agent. Moreover, the model is flexible to allow the addition of more reacting phases and hydration products. Computational effort is low compared to models that take into account solution phase chemistry.

Future lines of work will focus on improving accuracy when modelling and simulation, without losing computational tractability, by applying kinetics rules closer to fundamental principles. Lattice approaches are also considered in which interactions between particles can be taken explicitly into account, in order to achieve a better insight into cement hydration process.

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