Micro-Structural Modelling of Cementitious Materials using Vector Approach

S. Bishnoi, K.L. Scrivener
Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Abstract

Cement is not only the most widely used construction material in the world but probably also the most complex. Recent years have seen the development of micro-structural models as tools for understanding and prediction of the properties of cementitious materials. A model is of necessity a simplification of the actual system, but the various characteristics of cementitious materials, e.g. particle shapes and sizes, etc. pose severe challenges for microstructural modelling. The model developed at EPFL, which uses the so called vector approach applied to microstructure of cementitious materials, provides us with a tool that enables us to model cement particles in the form of vector shapes that do not suffer from resolution limitations. For example, this approach can enable accurate representation of porosity in the cement matrix even at later stages of hydration when the pore sizes go down to nano-metric levels, the modelled features varying in size from a few tens of micrometers to a few nanometres. This approach is, however, computationally more expensive which has limited its development to date. Optimised algorithms and recent programming techniques have been found to effectively reduce these computational costs to practically acceptable levels. Using this model the hydration of 2,000,000 particles can now be studied with only a few hours of computation. Here we present the model μic that is based on these developments. This model allows the user to experiment with simulations by incorporating his own ideas and theories in the calculations.

1. Introduction

The success of concrete as a construction material can in part be attributed to the large extent to which the material can be tailored to match specific needs. This capacity to be engineered perhaps also makes concrete the least understood construction material. Furthermore, since engineering doesn't always wait for science, newer technologies and materials continue to be incorporated in the construction industry, making the task of predicting the properties of the final product all the more difficult. Even as new analytical models predicting the properties of various cementitious mixes continue to be formulated, computer-based numerical models are playing an increasingly important role.

In the hundred odd year history of cement research, a number of studies have focussed on developing prediction models of cement behaviour. The compressive strength of cement has been the focal point of most of these studies and is still a critical parameter in determining the quality of a cement. Porosity has always been considered a major factor affecting strength and in 1958 Powers [1] proposed a relationship between total porosity and strength that is still widely used today. It is however well understood that microstructure plays a major role in strength development and to say that strength depends only on the total porosity is a gross generalisation. Microstructural models thus play a vital role in the development of cement science.

The complexity of cement microstructure and the limited knowledge we have about it necessitates numerical simplifications. It is however still possible to maintain the essence of processes that lead to microstructural development and the computed values can be used not only for prediction but also to better understand various processes underlying cement hydration.

Over the past decade a microstructural model of cement has been developed at EPFL [2]. This model simulates the microstructural development of cement with hydration and characterises the porosity and permeability of the cement using vector shapes that are resolution independent [3]. Until recently, however, this model was limited in its capacity. The large number of particles required to be simulated in order to represent actual particle size gradations of cement could not be handled. Recent developments [4] have, however, overcome this limitation and allowed representation of actual particle sizes. A new model called µic (short for microstructure and pronounced as Mike) has been developed with the aim of complementing and aiding, rather than substituting experiments. This study presents results calculated using the new model, underlining the strength of the vector approach and demonstrating the new possibilities introduced by µic.

2. Modelling of Cement Hydration

The recent developments in computer science and the introduction of computers in consumer domain have spurred the development of numerical models in practically all scientific fields. The simplifications in approach necessitated by the complex nature of cement have led the researchers to develop various simplified approaches in modelling cement hydration. Based on these approaches, cement hydration models can be broadly classified into three categories – discrete volume element approach, semi-empirical analytical approach and vector approach.

In the discrete volume element approach, the microstructure is simulated as a three dimensional grid of cubic voxels. CEMHYD3D [5] is

one of the best-known and widely-used models in cement based on discretization of computational volumes into cubic pixels, each occupied by a single phase of cement or a product. This model allows easy representation of spatial distributions of different phases and different shapes. However, only particles of particular sizes depending on the mesh-size can be modelled with increasing approximation as the particle size reaches the mesh size. Although this approach is known to be simple and effective in mechanical applications [6] the resolution of this model is limited to about 1 μm. However, since many relevant features of cement microstructure are smaller than the voxel size, some information is irretrievably lost. For example, a thorough representation of particles of some cements might require voxels of 0.1 μm size and thus one billion voxels in a typical computational volume making the computation too complex for most computers. Furthermore, an accurate representation of porosity and pore-connectivity might still not be possible as the average pore sizes continue to reduce with the progress of hydration.

DuCOM [7] is a well known example of the second category – the semi-empirical analytical models. DuCOM focuses on predicting the durability of concrete structures and has been integrated with a finite-element package making it possible to make simulations on specimens close to structural scale under various conditions. The weakness of this approach lies in its semi-empirical nature. This approach requires painstaking analysis of a broad array of experimental results making the entire process of modelling tedious. Furthermore, since this approach relies on present knowledge in the form of fixed equations, it affords little space for incorporation of developments in knowledge.

The vector approach [8,9,2] involves the storage and processing of vector information, as opposed to discrete voxels, the resolution of this approach is limited only to the precision of the computer. Johnson and Jennings [8,10] first presented the concept of modelling cement hydration as nucleation and growth of spherical particles in three-dimensional space and developed a program to achieve this goal in late 1980s.

HymoStruc [9] and Integrated Particle Kinetics Model [2] are two of the models using this approach. Both these models essentially simulate cement hydration as particle growth with overlaps. The main difference in the models lies in the fact that while the former relies completely on product deposition on the surface of reacting particles, the latter can also model the nucleation and growth of products in the pore space. The vector approach also allows the simulation of reactions of individual particles, based on the properties of each particle and their surroundings. For example, as implemented in the Integrated Particle Kinetics Model, the reaction rate of each particle can be governed by a set of equations based on particle size, deposited product layers and surface interactions.

The vector approach is not without its disadvantages. Since the vector approach is known to be computationally more demanding its applicability is limited. A feasible implementation of this approach thus requires the development of optimal algorithms reducing computational costs.

3. The Vector Approach and µic

µic derives its basics from the work by Navi and Pignat [2,3] that is essentially restricted to the hydration of C_3S. While the basic structure of the model, with the reactants and the products being modelled as vector spheres, has been kept the same, µic aims at achieving results closer to reality and extending the model to Portland cement and other binders.

Earlier implementations of the vector approach emphasised how computational restrictions limited the capacity of simulations. For example, due to practical restrictions, the simulations of the Integrated Particle Kinetics Model was restricted to twelve thousand particles limiting the size of the smallest particle simulated to several micrometers. The main advantage of the vector approa ch – that particles of all sizes can be modelled – was thus lost.

The new model is based on new object oriented programmes developed in Java using new specialised algorithms. Table 1 summarises the efficacy of the new programmes.

Table 1: Summary of improvements achieved

Before	***After***
Programs in Fortran	Object Oriented in Java
10,000 particles in a few days	2,000,000 particles in a few hours
Time $\propto n^2$	Time $\propto n \bullet \log(n)$
Platform: Unix Workstation	Platform independent

Not only do the new algorithms improve the speed and capacity of the model, but also improve the maintainability and flexibility of the code creating newer possibilities in hydration modelling. The next obvious step to the simulation of C_3S hydration is the extension of the model to Portland cement. However, given the complexity of the problem and the gaps in our understanding of cement, the model has to be evolutionary in nature. In fact a model that aids the interpretation of experimental results and design of new experiments would contribute more than one that attempts to predict based on incomplete information. µic is thus a model that has been developed keeping in mind the needs of a researcher to provide him a tool to interpret experimental results and to test new hypotheses he might formulate based on these results.

In order to achieve this objective the Cement Hydration Tool-kit [4] was developed. This tool-kit provides a pluggable interface to the model that makes the task of experimentation with the model semi-trivial. Though the primary objective of this tool-kit is to model Portland cement, it can be equally well used to model any other particulate reaction. Figure 1 shows the basic structure of the tool-kit. This tool-kit provides a set of tools that a user can use to build the reactions that he needs to simulate. For example, the user can define custom reactions between materials that the user has defined as well.

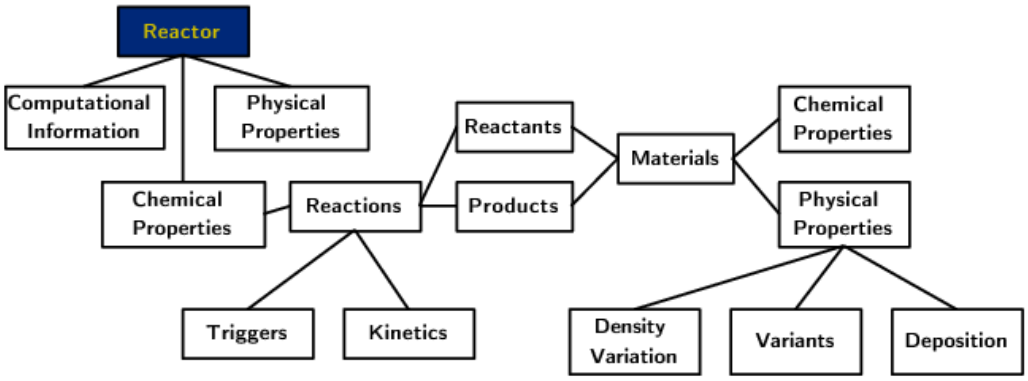

Figure 1: Structure of the Cement Hydration Tool-kit

3.1 Reactions

The user can define a set of reactions based on different properties specific to the application. Each reaction can have its own set of properties that define its behaviour. For example, the user can define particulate reaction kinetics that suit the specific application the best. Each reaction can have a set of particle reaction kinetics attached with it along with rules to choose the applicable kinetics at any instant of time. Though for most properties a library of common implementations is provided more specific or complex implementations can be simply plugged into the programmes. The reactants and products essentially point to the material of the reactants and the ratios in which they react or form.

3.2 Materials

Materials can also be tailored by the user based on specific needs. A generic implementation of materials has been provided in the tool-kit. This class stores various properties of the material, for example its name and diffusion coefficient, and can be plugged in with various behaviours. For example, materials can be plugged in with density variation profiles, which would allow the density of a reaction product to change depending on different conditions. Different materials can be inter-linked in various ways. For example, inner and outer C-S-H can be linked to indicate that they are

variants of the same material and rules for the generation of either of the variants can be defined.

The tool-kit supports three basic types of materials, viz. diffuse, discrete and universal. While discrete materials are present in the form of discrete particles, diffuse materials are represented as uniformly mixed in some other material or present universally throughout the pore-space.

3.3 Particles

All particles are defined as spherical grains having an arbitrary number of concentric shells of different materials. The shells can be defined by the user or produced as a result of reactions based on the input from the user. For example, if a user defines a product that deposits on a reacting particle, a new shell of the material of the product will be formed. At the start of the simulation, a set of particles of reactive and non-reactive particles are distributed in the representative volume based on laws defined with different materials. More particles are nucleated in the pore-space as the reaction progresses based on nucleation and growth laws defined with the materials.

3.4 Implementation

In this model, spherical particles are packed into a numerical volume to represent different phases of cement. While different phases may be interspersed in varying proportions in the particles and be present as concentric layers, they can also be present as separate particles. Reactions can be defined as the consumption of defined proportions of user-defined materials and the production of other materials. The products can then either be deposited over the grains already present or be deposited in new clusters in the pores. Plugins can be used to define the amounts of materials being used up from different particles and the distribution of products in the available space.

The most important of these plugins are reaction kinetics. Reaction kinetics are defined to control the rate of consumption of materials according to laws based on experimental observations. Other plugins can be used to define various other factors such as the choice of places where materials are consumed or deposited, triggers or poisoning effects for reactions, etc.

Plugins can be used to simulate many laws in the model. Using one of these plugins, the products can be deposited in varying proportion over different types of grains. For example, CSH can be allowed to deposit over Alite grains, filler particles or even as new clusters in pore space, all with different properties. This is achieved by defining the three types of CSH as different materials linked to each other. The proportion of CSH deposited

in the three places can be controlled by managing the produced amounts of the three types of CSH. These proportions are also not static and can be calculated at each moment using the plugin. Furthermore, another plugin can be attached to CSH to allow the production of CSH to increase the density of the particles already present, rather than just increasing the size of the particles.

Although most of the plugins are not obligatory to define and default and library implementations are provided for all of them, the full power of the model can be realised by using all its features.

3.5 Examples

The Cement Hydration Tool-kit provides tools necessary to define and simulate a reaction and allows the user to program custom reactions on materials with customised properties. A user can implement the relatively simple example of Alite hydration with the following steps:

- Create a new reactor with given properties (size, boundary conditions, etc.)
- Define a reaction named “Alite Hydration”
- Define materials named “C3S”, “Water”, “Inner CSH”, “Outer CSH” and “CH” with different properties
- Add C3S and Water to “Alite Hydration” as reactants and the other materials as products
- Link “Inner CSH” and “Outer CSH” as variant materials
- Define different possible reaction kinetics of the reaction
- Define the particle size distribution of “C3S” grains
- Define the nucleation parameters for “CH”
- Start the simulation of the reaction in the reactor

The flexibility of the tool-kit can be understood from the following simple set of steps that can be used to add a Pozzolanic-reaction (say Fly-Ash) in the above implementation:

- Create a new material named “Fly-Ash”
- Define a new reaction named “Pozzolanic Reaction”
- Add “CH” and “Fly-Ash” to “Pozzolanic Reaction” as reactants and “Outer CSH” as product
- Make any changes to the nucleation and growth laws for “Outer CSH”
- Define reaction kinetics for “Pozzolanic Reaction”
- Start the simulation of the reactions in the reactor

The above example illustrates the simplicity and power of the tool-kit. It can also be seen how a user can change any law underlying the model and test hypotheses based on comparison of different results.

4. Example Experiments on µic

The model was used to study the effect of a non-reactive filler on the hydration of C_3S. It has been reported that the addition of non-reactive fillers to cement pastes leads to faster hydration rates and a finer pore-structure [11]. This can be explained by considering that in the presence of non-reactive surfaces in the system, a part of the CSH produced from the hydration of C_3S, that would otherwise have deposited on reacting C_3S particles, will deposit on the non-reacting filler surface. This reduces the accumulation of the product on the reacting particles and the impedance offered to diffusing ions. The reaction rates are thus higher in the presence of inert fillers. At the same time, since more product is deposited in the pores around the filler grains, the porosity is filled in a more uniform way, rather than just close to the reacting particles.

Five different microstructures with different extents of filler replacements and filler sizes were studied using µic. The control microstructure was simulated with C_3S particles of radii ranging from 20.2 µm to 0.3 µm (specimen A). In the other microstructures, the C_3S was replaced by filler particles as listed in Table 2. While in some specimens a part of the produced CSH was allowed to deposit on the filler surface, one of the specimens was simulated with no deposition of CSH on the filler surface (specimen D). Table 2 lists the properties of the specimens simulated. The initial microstructures of the specimens are shown in Figure 2. The number of particles in the simulations range between 100,000 and 500,000 particles.

Table 2: Microstructures studied

Name	***Replacement***	***Size of filler***	***CSH deposits on filler***
A	0%	-	-
B	10%	0.3 µm	Yes
C	5%	0.3 µm	Yes
D	10%	0.3 µm	No
E	10%	0.525 µm	Yes

4.1 Heat evolution

Since the simulation is carried out using real kinetics, the calorimetric curves from the simulations can be produced (Figure 3). The results clearly show an increase in heat evolution in specimens with filler replacement. The effect was more in specimen B, where the filler was finer and the replacement was to a higher extent. It is noteworthy that the effect of the larger filler (specimen E) was found to be quite close to that of the finer filler replaced to a lesser extent (specimen C). In case of specimen D, where no deposition of CSH was allowed on the filler

surface, the heat evolution rates were found to be lower that those in the control specimen (A) as expected.

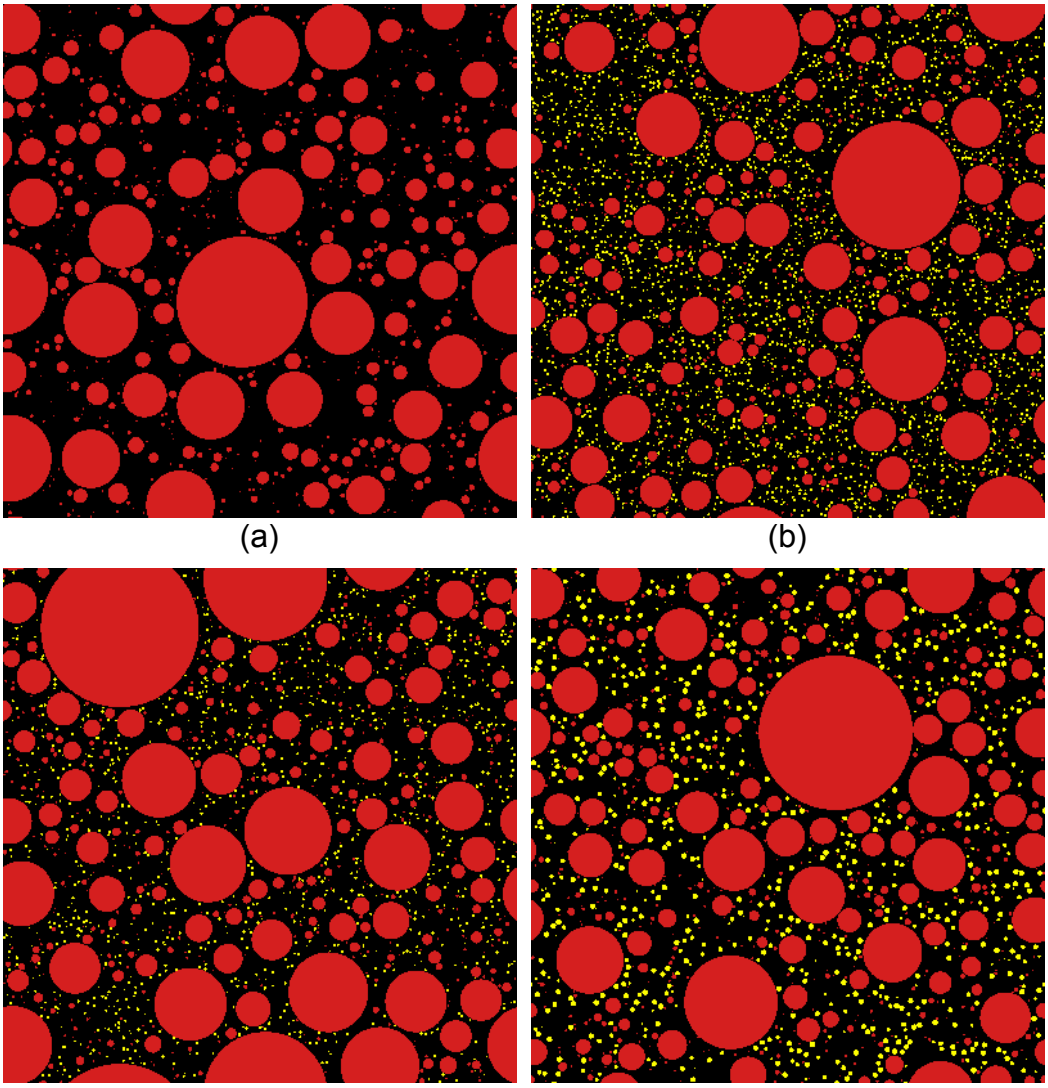

Figure 2: Initial microstructures of (a) specimen A, (b) specimen B, (c) specimen C and (d) specimen E

4.2 Porosimetry

The pore sizes of the specimens at 24 hour hydration were calculated using 3D erosion with pixel size of 0.1 μm. It must be noted here that this technique has only been used for faster results for this case study. The model includes programmes that characterise porosity using vector shapes [3] and work on the optimisation of these programmes to bring their performance at par with the hydration modules is in progress.

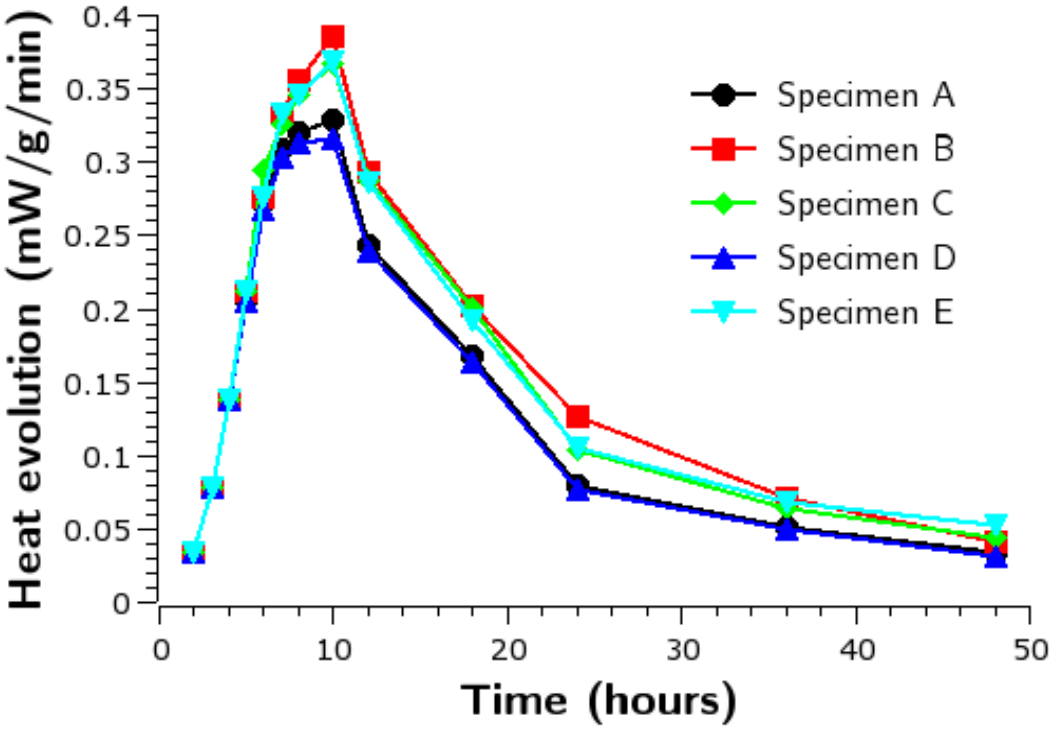

Figure 3: Heat evolution curves

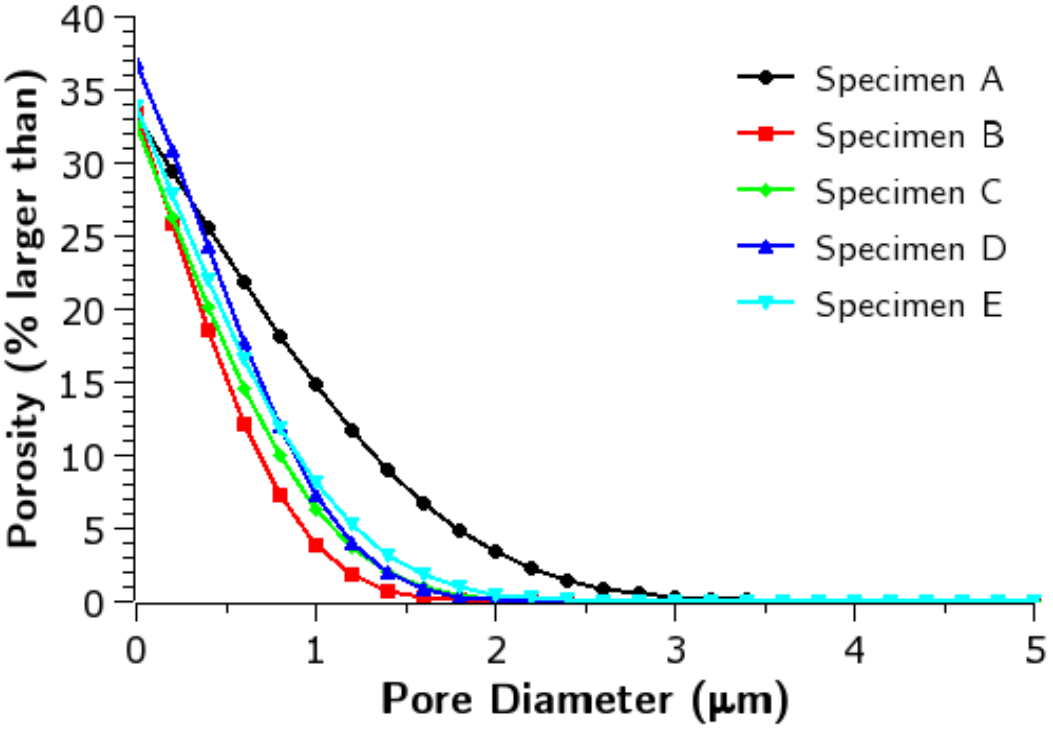

Figure 4: Pore sizes at 24 hours

The simplified analysis of the microstructures shows the effectiveness of fillers in breaking up the porosity even at early ages. Although the total porosity in all the specimens was almost the same, the pores in specimen B were found to be the finest. Once again, the results from specimens C and E were close. The porosity was relatively higher for specimen D where CSH was not allowed to deposit on the fillers while the total amount of C_3S was reduced due to the replacement.

The results show how well the model simulates behaviour observed in reality and its strength in obtaining results from hypothesis that would otherwise be too complex to verify otherwise.

5. Conclusions

The objective of this study is the development of a model that complements and facilitates, rather than replace experiments. The model µic has been developed as new object oriented Java programmes using algorithms that tremendously improve the performance of the vector approach. The model is based on the Cement Hydration Tool-kit that provides a pluggable architecture to the model and does not limit the model to the knowledge of the developers. The model allows experimentation with ideas and could prove to be a crucial platform where experimenters could watch their hypotheses in action and compare them against reality. A simple demonstrative example studying the filler effect was presented and it was seen that the model can be used to well emulate physical phenomena.

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