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2018-08-29

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Recommended Citation

Introducing a new cement hydration and microstructure model, Niall Holmes, Anselm Griffin, Bernard Enright and Denis Killiher, *Civil Engineering Research in Ireland (CERI) Conference 2018, University College Dublin*.

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Introducing a new cement hydration and microstructure model

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ABSTRACT: This paper presents a new cement hydration model to predict the microstructure evolution of hydrating tricalcium silicate (C3S). The model is written in MATLAB and employs the continuum approach and integrated particle kinetic relationships to show the change in C3S and the growth of Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide (CH) in the pore space over time.

Cement hydration is a highly complex process. While hydration models should never completely remove experimental analysis, they are an aid to better understand cement hydration and microstructure development by providing a method to analyse a large number of pastes with different cementitious make-ups in a relatively short time. This model uses spherical particles to represent the C3S with customizable input files such as cumulative weight distributions (CWD), to determine the particle size distributions, PSD), w/c ratio, C3S, C-S-H and CH phase densities, kinetic rates, stoichiometries and enthalpy values.

The current study presents simulated microstructures and demonstrates the versatility of the model, while still in the development stage, to simulate cement hydration and microstructure development over 100 days. With further development, it can become a flexible tool for both academia and industry that can easily incorporate the inclusion of supplementary cementitious materials etc.

KEY WORDS: cement; hydration; microstructure; modelling; MATLAB

1 INTRODUCTION

Cement hydration and microstructure development is a complex process. However, the advances in computing power and range of programmable software in recent years has made the modelling of cement hydration achievable. While computer modelling should never completely replace experimental analysis, it does provide valuable insights into the process particularly with the increased use of supplementary cementitious materials. Model outputs can now be directly compared with experimental analysis provided accurate input data is used throughout. A complete and accurate hydration simulation would enable materials engineers not only to predict the performance of concrete in the field, but also to troubleshoot performance problems and even to help design new cementitious materials. Despite significant effort and progress, the ability to perform such a complete simulation has not yet been developed, mainly because cement hydration is one of the more complex phenomena in engineering science.

This paper presents a new model written in MATLAB® to undertake cement hydration and microstructure simulations over any time-period with all input parameters changeable by the user. Changeable parameters include cumulative weight distributions (CWD), cement properties (including w/c ratio, cement phase density and enthalpy) and hydration and microstructure kinetic rates. The model employs the vector approach, which permits a large range of cement phase diameters to be modelled computationally effectively while

taking advantage of the inbuilt mathematical functions within MATLAB. The vector approach has been used in several previous hydration models [1–8].

This paper presents the initial design of the model for the hydration of tricalcium silicate (C3S)¹ which represents the greatest contribution of the four cement phases towards strength development. The approach used to develop the model are presented along with results from a number of simulations using different particle size distributions (PSD) as well as the versatility and flexibility of the model for the user.

2 CURRENT CEMENT HYDRATION AND MICROSTRUCTURAL MODELS EMPLOYING THE VECTOR APPROACH

The development of cement hydration and microstructure models have used either the discretization or the vector approach. [9] gave a comprehensive review of the most well-known models employing the vector approach and brief overview of these models is presented below.

2.1 Jennings & Johnson microstructure simulation model

This model used spherical particles within a cubic volume with the reducing diameter of C3S and increasing inner and outer C-S-H predicted as hydration continued over time [5]. The model also determined the number of new CH particles and placed them in the pore space. The overlapping of particles, and how the hydration and microstructure is affected, was also simulated. Due to the limited computational power at the time,

¹ Cement chemistry notation: C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃, H=H₂O

the model was not developed further but it did provide a methodology for future programmes using this approach. Figure 1 shows an image from their model, which consists of 1,000 C3S and 1,000 CH crystals after 50% hydration.

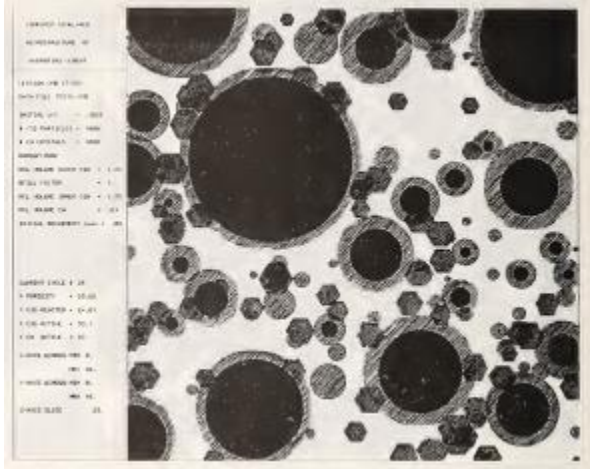


Figure 2: Jennings and Johnston model at 50% hydration [5]

2.2 Navi and Pignat Model

In 1990s, the integrated particle kinetics model was developed by Navi and Pignat [3, 6-8]. This model simulated the hydration of spherical C3S particles using a similar vector approach as the Jennings and Johnson model [5]. This model used kinetic laws and relationships that simulated every particle. Hydration was simulated in three phases. Initially an Avrami-type equation was used, followed by a phase-boundary analysis which depended on the particles surface area and finally a diffusion-type where the rate of C3S consumption was inversely proportional to the thickness of hydrates deposited on the surface of cement particles. This approach was found to be very computationally expensive and as a result, the number of particles had to be limited to ~ 10,000. An example of their models output is shown in Figure 2.

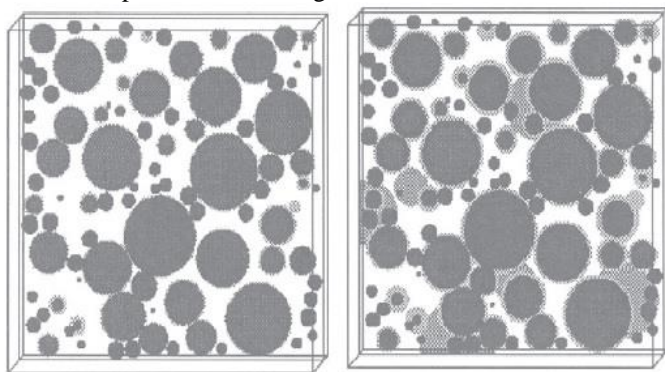


Figure 2: [3] output at 6-hours (left) and 1-day (right).

2.3 HYMOSTRUCT model

The Hydration, Morphology, and Structural (HYMOSTRUC) model was developed by van Breugel [2] and simulates the 3D hydration of spherical particles. Reacting particles form concentric hydrating layers around the original cement grains, which grow and intersect with each other (see Figure 3). It employs various mass and volume balance rules to accommodate microstructural changes from the dissolution and precipitation of various phases. HYMOSTRUCT, however,

does not accurately predict the evolution of the cement microstructure nor does it account for the changing chemistry or transport properties. Recent developments include for random packing of particles and the calculation of autogenous shrinkage. Also, not every individual particle is allowed to hydrate as the authors feel the computation time would be too large. Therefore, a statistical approach to reaction rates is used that assumes the reaction rate of each particle depends only on its size. As the particle interactions or overlaps are not analysed, the microstructure information is not available.

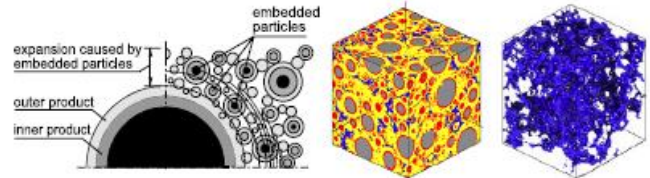


Figure 3: Typical HYMOSTRUCT hydration simulations [2]

2.4 The HydratiCA simulation model

The HydratiCA model has been developed by Bullard at NIST [10] and is based on more fundamental principles of hydration kinetics. HydratiCA directly simulates the (1) dissolution and growth of mineral phases, (2) diffusion of mobile species in solution, (3) complexation reactions among species in solution or at solid surfaces and (4) nucleation of new phases. The principles of detailed balances and mass action are used to unify these disparate kinetic processes.

HydratiCA makes more detailed predictions of the kinetics of phase changes and microstructure development as a function of solution chemistry and temperature than other microstructure-based models of hydration. However, it is very computationally intensive with simulations requiring small time steps of about 0.2 milliseconds to ensure numerical stability. As a result, approximately 18 million steps are required to simulate just 1 hour of hydration. HydratiCA has been used to investigate various mechanisms of hydration of C3S and tricalcium aluminate (C3A).

2.5 The μ ic microstructure model

The μ ic (pronounced “mike”) microstructural modelling platform [11] is a continuation of the work done by Navi and Pignat [3, 6-8], which was, in turn, based on the original Jennings and Johnson model [5] discussed above. μ ic has been written using object-oriented programming in Java and simulates the growth of spherical particles to mimic hydration. As such, it makes significant advances on the limitations of previous methods due to inadequate computational power at the time. The support libraries within μ ic allow for the hydration modelling of millions of cement particles (see Figure 4), which more realistically represent real PSD’s.

The main advantage of μ ic is the fully customizable nature of the simulations by the user including the initial PSD, defining the phases and their composition and the stoichiometry of the reactions to be simulated. While the large number of customizable elements to be set up can be tedious, its flexibility makes μ ic a valuable hydration study tool.

2.6 CEMHYD3D hydration model

While not specifically employing the vector approach, no review of cement hydration models is complete without

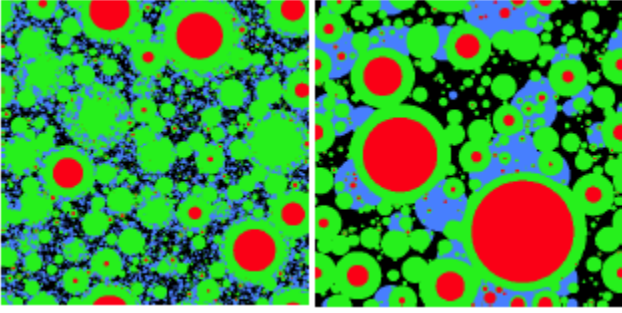


Figure 4: Typical μic microstructure simulations [11]

including the CEMHYD3D model [12]. CEMHYD3D is one of the most widely used and well known hydration and microstructure models and employs the discrete or pixel approach and the cellular-automata (CA) method. The microstructure is presented as a grid of discrete three dimensional cubic elements (Figure 5), called volume-pixels, each representing an anhydrous or hydrate phase or pore.

In CEMHYD3D, CA is used to simulate the diffusion of species through the pore-water leading to reactions and precipitations which either dissolves or reacts and forms a product of hydration. However, due to the maximum pixel size of $1\mu\text{m}$, particles below that are not included.

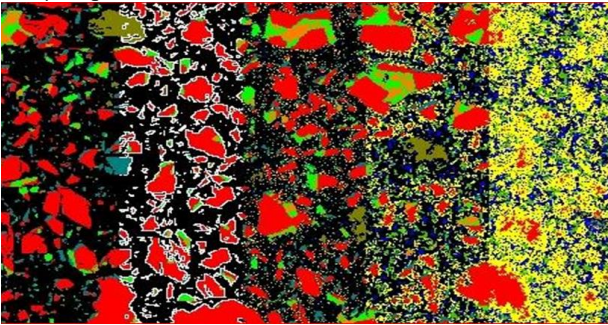


Figure 5: Sample output from CEMHYD3D model [10]

3 MODEL DESIGN

The model was created to employ the problem solving speed of MATLAB utilising the full suite of inbuilt functions and the inherent stability of the programme to set-up and simulate the hydration of tens of thousands of cement particles within a $100\mu\text{m}$ volume. The model is also setup to be as user friendly as possible with key properties changeable before starting hydration. Unlike μic , this model is designed to undertake the analysis with minimal user input values. Two *.txt files are loaded into the programme which are described in detail below. Many different formats are possible to input for MATLAB with *.txt chosen as a personal preference. Furthermore, MATLAB is a reasonably easy language to learn and apply as it's based on matrix mathematics. The use of comments throughout improve the readability of the code.

3.1 User customisable input

As mentioned above, users have flexibility on input via two *.txt files. The first describes the CWD, which the model uses to determine the PSD and number of particles. The CWD input is read into the model via two row vectors with no limit on the number of input columns. The second input file allows the user to customise the cement properties including w/c ratio, volume

size, C3S and CH density (Mg/m^3), time step size (hours) and duration of analysis (days). This file also contains hydration kinetic, reaction stoichiometry, CH growth constants and C3S enthalpy values. Examples of the input data will be discussed in more detail in the next section by means of a worked example.

3.2 Materials

The model, using user defined kinetic and stoichiometries, will output the volume of reaction products from the original C3S particles, namely C-S-H and CH. Each material has its density, reaction stoichiometry defined. For instance, what proportion of C-S-H should be defined as inner C-S-H and outer C-S-H and subsequently deposited on the C3S particle with their particular density defined and volume determined. Four types of materials are defined and simulated (Figure 6).

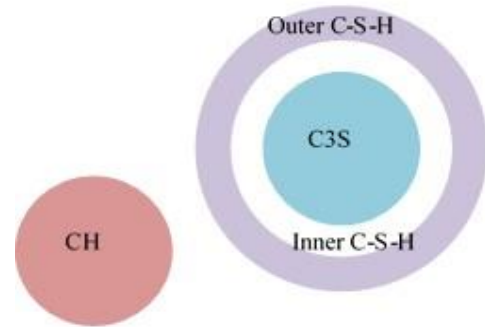
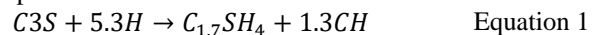


Figure 6: Materials and particle types simulated

3.3 Reactions

The reactions are defined in the model using the input parameters described above. The volumes, using the different stoichiometries and densities, are calculated. The reducing water volume is also calculated and is related to the continued reactivity of the C3S particles. Equation 1 shows the governing hydration of C3S upon reaction with 5.3 molar of water (H) which produces C-S-H and 1.3 molar of CH.

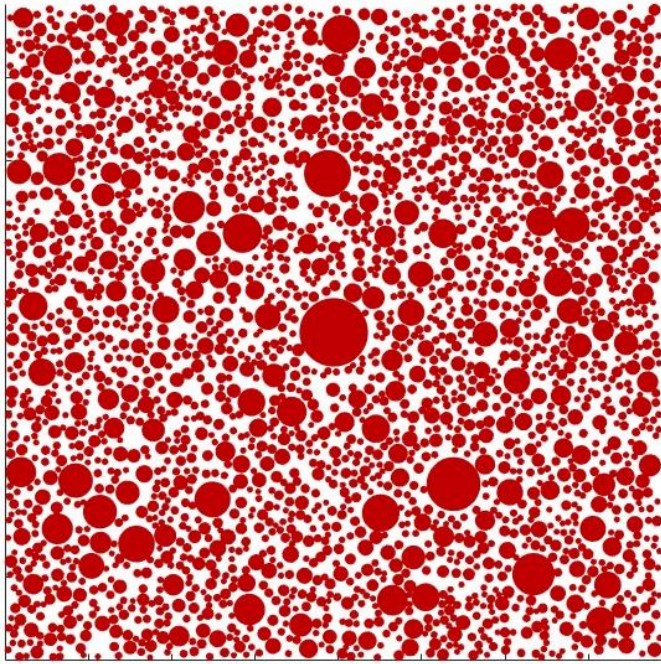


4 WORKED EXAMPLES

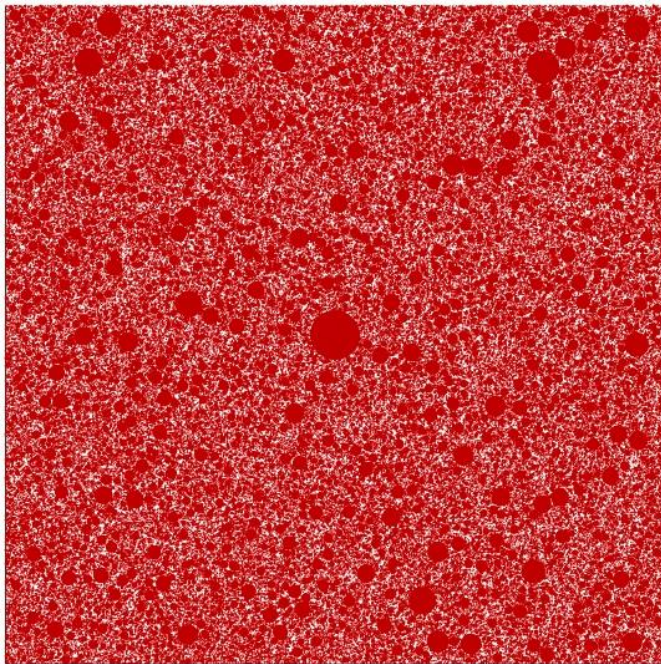
The following section describes examples of analysis undertaken on C3S particles with different CWD based on rules for hydration described by Pignat et al. [3, 6-8] including hydration and microstructure kinetic rates. These rules are fully customisable in the model by the user before the analysis begins. The results demonstrate the ease of use of the model and speed of calculations. The following sections provide an overview of the steps undertaken during the analysis with input and output shown in figures and tables.

4.1 Particle size distribution

Two CWD's shown in Table 1 were used for this example for a 0.4 w/c cement within a $100 \times 100 \times 100\mu\text{m}$ volume. The two CWD's produces 2,628 and 96,579 C3S particles (Figure 7). The model places the largest diameter particle ($40.4\mu\text{m}$ here) first and determines the next particle diameter using the CWD above. This repeats until no volume is remaining. The model then places each particle within the volume ensuring there are no overlaps.



(a) 2,628 particles



(b) 96,579 particles

Figure 7: 2D particle distributions for C_1 & C_2 in Table 1

4.2 Hydration and microstructure calculations

The input data for the second *.txt file is shown in Table 2. The value for the density of C3S varies amongst researchers so the value used (3.15 g/cm³) is based on the published value given by [11]. A time step of 1-hour was chosen for the analysis for 100 days, giving 2400 steps in total.

4.3 Particle Kinetics

The hydration of cement has been described by previous modellers [3, 6-8, 11] as three mechanisms over different time scales. The first is nucleation and growth which is the subject

Table 1: Particle diameter (μm) and CWD.

Particle diameter (μm)	CWD	Particle diameter (μm)	CWD
Cement 1		Cement 2	
40.4	1	40.4	1
23.0	0.845	23.0	0.90
17.4	0.706	17.0	0.80
13.2	0.547	13.0	0.65
9.94	0.395	9.0	0.50
7.51	0.263	7.0	0.40
5.17	0.123	4.0	0.20
2.95	0	0.5	0
# particles = 2,628		# particles = 96,579	

Table 2: Cement properties input into the model

Property	Input
w/c ratio	0.4
Box size (μm)	100
C3S phase density (g/cm ³)	3.15
Duration of hydration (days)	100
Hydration rate (K_1 , $\mu\text{m/hr}$)	0.012
Hydration rate (K_2 , $\mu\text{m}^2/\text{hr}$)	0.006
root - rin (μm)	4
Volume of C3S converted to inner C-S-H	1.00
Volume of C3S converted to outer C-S-H	0.57
CH constant 1	0.2
CH constant 2	0.213
Volume of C3S converted to CH	0.593
CH phase density (g/cm ³)	2.24
Volume water used during C3S reactions	1.318
C3S enthalpy (J/g)	500

of much discussion amongst researchers in this area. There is widespread disagreement between the precise cause of very rapid heat production and reduction within 1-2 hours. Some believe this is due to the formation of a meta-stable layer of hydrates around the reacting particles [13,14]. Others [15] believe it is based on a geochemical approach where, during cement hydration, dissolution is initially dominated by the formation of etch pits on surfaces and later becomes limited to step retreat from such pits

As this period of hydration is quite short (1-2 hours) and contributes little to the final strength, it has been left out of the analysis here. The second mechanism is commonly referred to as 'the phase-boundary controlled reaction' [11]. Here, the hydration products of C-S-H inner and outer are formed around the C3S particle and CH is formed in the pore space. The growth of the thickness of the inner product is given by Equation 2 [3, 6-8, 11] where K_1 is in units of $\mu\text{m/hr}$. The degree of hydration $\alpha(t)$ (for a spherical particle with an original radius R) is given by Equation 3 [3, 6-8, 11] where r_{in} is the changing C3S radius over time.

$$dr_{in}(t) = K_1 dt \quad \text{Equation 2}$$

$$\alpha(t) = 1 - \left(\frac{r_{in}}{R}\right)^3 \quad \text{Equation 3}$$

The third mechanism is controlled by diffusion which begins when the radius of the outer C-S-H ($r_{out} - r_{in}$) reaches a critical value, typically $4\mu\text{m}$. The rate of hydration is then given by Equation 4 [3, 6-8, 11] where r_{out} is the outer C-S-H radius

$$dr_{in}(t) = \frac{K_2 dt}{r_{out} - r_{in}} \quad \text{Equation 4}$$

As shown in Table 2, the values for K_1 , K_2 and $r_{out} - r_{in}$ are $0.012\mu\text{m/h}$, $0.006\mu\text{m}^2/\text{hr}$ and $4\mu\text{m}$ respectively. The above hydration rates determine the C-S-H growth on the C3S particles, either growing inwards (inner C-S-H) or outwards (outer C-S-H). As shown in Equation 5, for every 1.0 volume units of C3S reacting with 1.318 volume units of water, 1.57 volume units of C-S-H and 0.593 volume units of CH are produced. The model, which can be changed by the user, allocates 1.00 volume units to inner C-S-H (thereby replacing the original volume of C3S at each time-step with inner C-S-H) and 0.57 volume units to outer C-S-H units.

$$1.0V_{C3S} + 1.318V_{H_2O} \rightarrow 1.57V_{C-S-H} + 0.593V_{CH} \quad \text{Equation 5}$$

The CH is allowed to form in the free pore space using a random number generator that defines a location after checking for the availability of a free space. The number of CH particles generated ($n(t)$) is given by Equation 6 where n_{max} is the maximum number of CH particles and assumed to be 20% of the total number of C3S particles [3, 6-8, 11] but is changeable by the user. α is another constant which has been reported to be 0.213 but also changeable by the user. The volume of C3S converted to CH as shown in Equation 5 and the density of CH are 0.593 and 2.24 g/cm^3 respectively, and are both adjustable by the user.

$$n(t) = n_{max}(1 - e^{-\alpha t}) \quad \text{Equation 6}$$

As shown in Equation 5, the volume of the hydration products is less than the volume of the reactants. This follows Le Chatelier's contraction [16] and leads to chemical shrinkage, which is also calculated by the model together with the change in water volume, porosity and the heat release during hydration using an enthalpy value of 500 J/g (Table 2).

4.4 The simulations

The model was run for the two cements (C1 & C2) in Table 1 with a w/c ratio of 0.4. The pre-processor time required to run a complete analysis for a range of particle distributions (Figure 8) is quite short and approximately linear in n , compared with the processing time required of n^2 and $n \cdot \log(n)$ (where n = number of particles) reported by Navi and Pignat [3, 6-8] and Bishnoi [11] respectively.

Figure 9 shows the 2D microstructure development at $t = 0$, 7, 28 and 91 days (0, 60.3, 91.7 & 99% hydration) for the 2,628 particle distribution in Figure 6(a). The lesser number of particles were chosen for clarity. The red, green and dotted black lines circles represents the decreasing C3S, the outer C-S-H and the original C3S radius respectively. At each step in the analysis (1 hour here), the degree of hydration, heat release during hydration, chemical shrinkage and porosity are calculated and shown in Figure 10. Figure 11 presents a phase assemblage diagram for the C3S, C-S-H and CH.

5 DISCUSSION AND CONCLUSION

A new model has been developed to simulate cement hydration and microstructure development over time. The simulations of several thousand particles in a short period of time above give reasonable predictions. Future work includes calibrating against experimental analysis and comparing with other hydration models in the area.

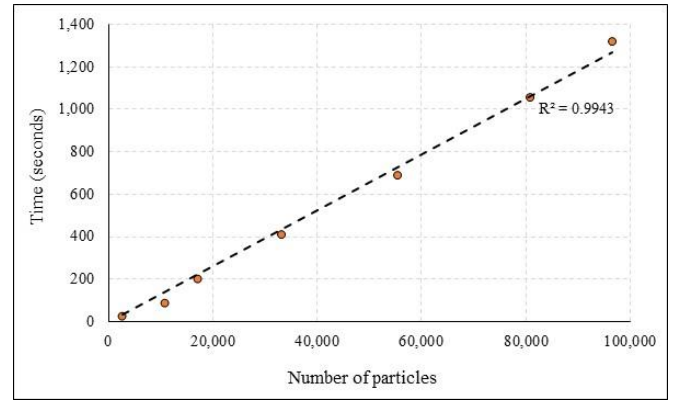


Figure 8: Analysis time for increasing number of particles

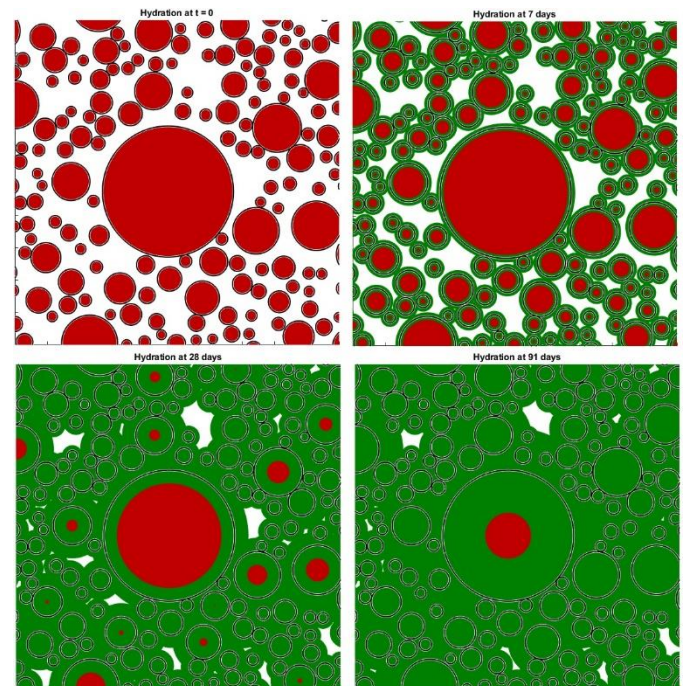


Figure 9: Hydration at 0, 7, 28 and 91 days (red = C3S; green = C-S-H; black line = original C3S boundary)

The model is currently focussed on C3S hydration. However, work is ongoing to include the other cement phases, namely C2S, C3A and C4AF.

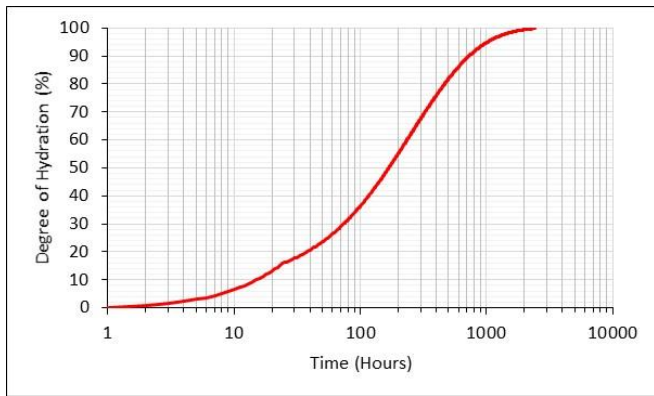
The model has been developed with customisable user input in mind and has the potential to be a useful tool for the simulation of cement hydration that can include, in time, supplementary cementitious materials (SCM's) and supplement experimental analysis of new cement products as the industry continues to move towards sustainable cement.

ACKNOWLEDGMENTS

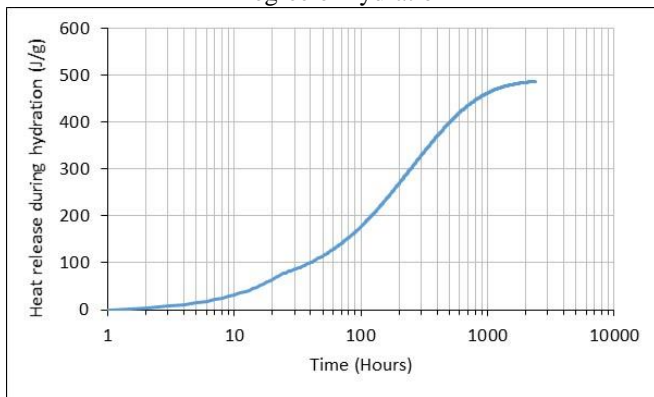
The authors acknowledge the advice received from Mr. Dale Bentz and Dr. Shashank Bisnoi.

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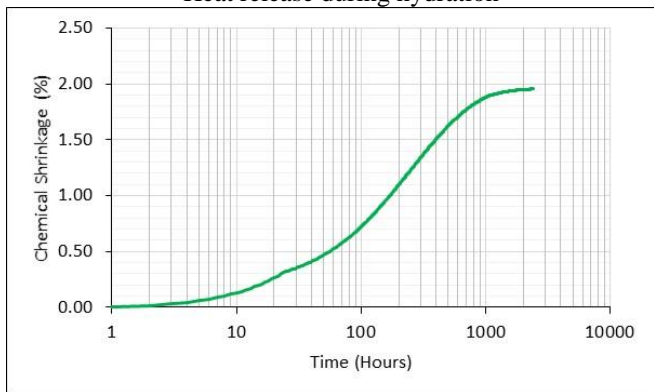
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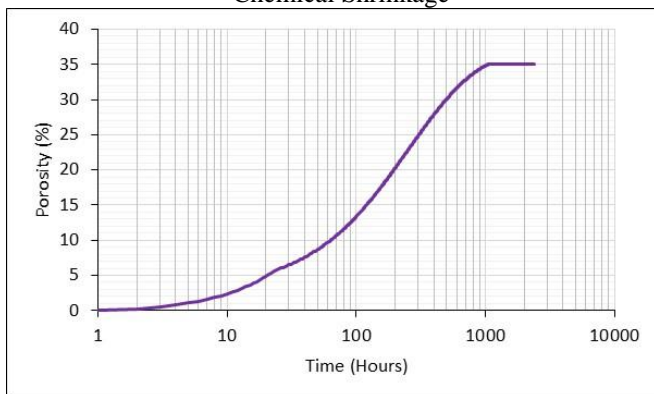
Degree of hydration



Heat release during hydration



Chemical Shrinkage



Porosity

Figure 10: Degree of hydration, Heat release during hydration, chemical shrinkage & porosity for C_1 .

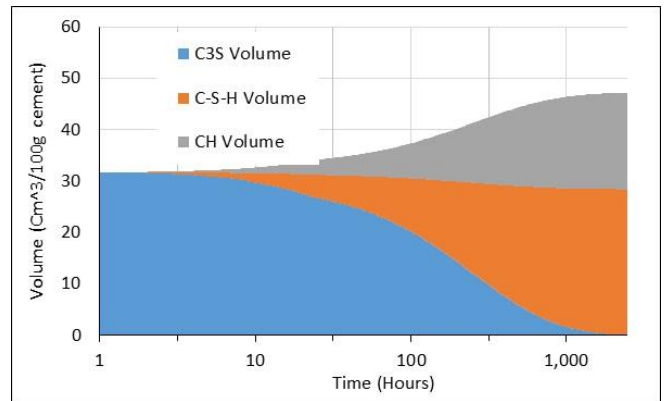


Figure 11: Phase assemblage diagram for C3S, C-S-H and CH over time for cement C_1 .

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