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HYDCEM: A new cement hydration model

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Abstract - Hydration models are useful to predict, understand and describe the behaviour of different cementitious-based systems. They are indispensable for undertaking long-term performance and service life predictions for existing and new products for generating quantitative data in the move towards more sustainable cements while optimising natural resources. One such application is the development of cement-based thermoelectric applications.

HYDCEM is a new model to predict the phase assemblage, degree of hydration, heat release and changes in pore solution chemistry over time for cements undergoing hydration for any w/c ratio and curing temperatures up to 45°C. HYDCEM, written in MATLAB, is aimed at complementing more sophisticated thermodynamic models to predict these properties over time using user-customisable inputs. A number of functions based on up to date cement hydration behaviour from the literature are hard-wired into the code along with user-changeable inputs such as the cement chemical (oxide) composition, cement phase densities, element molar mass, phase and product densities and heat of hydration enthalpies. HYDCEM uses this input to predict the cement phase and gypsum proportions, volume stoichiometries and dissolution and growth of hydration products from the silicates, aluminates and ferrites, including C-S-H, calcium hydroxide, hydrogarnet (if applicable) ettringite and monosulphate. A number of comparisons are made with published experimental and thermodynamic model results and HYDCEM predictions to assess its accuracy and usefulness.

The results show that HYDCEM can reasonably accurately predict phase assemblages in terms of volume change and behaviour for a range of cements and curing temperatures. It is proposed that HYCEM can complement more sophisticated thermodynamic models to give users a reasonable prediction of cement behaviour over time.

Keywords: Cement; Hydration; microstructure; model; 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. A comprehensive review of other cement hydration and microstructure models over the past 45 years including single particle models, mathematical nucleation and growth models and vector and lattice-based approaches to simulating microstructure development can be found at [1]. 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 and other sustainable materials [2]. Model outputs here are based on the cements chemical (oxide) composition and element molar masses to calculate phase proportions (based on modified Bogue equations [3]) and volume stoichiometries to improve the accuracy of the predictions. Previous work to compare simulation and measured properties have been presented [3-6] but, in order to accelerate the acceptance of prediction models, direct comparisons are best [8].

Cement particles at the micro-scale are made up of four main phases, namely tri-calcium silicate (C_3S)¹, di-calcium silicate (C_2S), tri-calcium aluminate (C_3A) and tetra-calcium aluminate ferrite (C_4AF) with particle size distributions ranging from 60-100µm to less than 1µm. Of the four phases above, C_3S is by far the most influential in terms of chemical reactivity and contribution to long term strength gain making up

¹ Conventional cement chemistry notation: C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃, and H=H₂O.

approximately 65-70% of overall cement content. It is no surprise therefore that the hydration of C_3S alone has been the focus of several numerical models [1,9] due to its influence and relative straightforward reaction and product development. Upon reaction with water, C_3S produces calcium silicate hydrate (written as C-S-H) and calcium hydroxide $(CH)^2$. However, in order for a full prediction of the hydration of a cement, it is important that all cement phases are included in any analysis.

One way of predicting the performance of a hydrating cement is by thermodynamic modelling which provides, amongst others, phase assemblage and pore concentration predictions. Such hydration predictions allow cement scientists assess the performance, troubleshoot short and long-term problems and even help design new cement-based materials. Despite significant effort and progress, the ability to perform such a complete simulation has not been developed, mainly because cement hydration is one of the more complex phenomena in engineering science.

This paper presents a new model, HYDCEM, written in MATLAB to undertake cement hydration analysis to predict phase assemblage, degree of hydration, heat release and pore solution chemistry over time for any w/c ratio and curing temperatures up to 45°C. HYDCEM is aimed to complement the more sophisticated thermodynamic models giving users an accurate prediction of how their Portland cement will perform by demonstrating cement phase and gypsum dissolution and the development of hydration products over time.

All input parameters required by the model are fully defined by the user including the cement chemical (oxide) composition, element molar mass, cement phase densities, phase and product densities and heat of hydration enthalpies. It uses this information to calculate the unhydrated cement proportions, gypsum content and magnesium and volume stoichiometries, which in turn determines the volumes of silicates, aluminates and ferrites hydration products namely, C-S-H, calcium hydroxide, hydrogarnet, ettringite, monosulphate and hydrotalcite. The model employs the empirical-based Parrot and Killoh [10] approach for the degree of hydration for the cement phases with an input file read in that includes the Blaine surface area of the cement, temperature, phases activation energies and the constants developed by Lothenbach [11,12] for the three reaction regimes, namely nucleation and growth, shell formation and diffusion.

The initial design of the model is presented along with worked examples to compare HYDCEM phase assemblage predictions with results from the literature. Phase assemblage predictions provide a much better insight how the microstructure is developing. MATLAB is particularly well suited to this type of analysis due to its 'engineering-like' architecture both in terms of coding language and background calculations. Also, the significant amount of help available for MATLAB programmers online make writing and understanding the code very straightforward.

2 Model Design

2.1 Input files

HYDCEM was developed with the user in mind by providing clearly laid out and easy to change flat text input files. The analysis/calculation flow for HYDCEM is shown in Figure 1. As may be seen, when the input data files are read into the model, the analysis follows a well-structured methodology by using multiple functions within the main HYDCEM script along with pre-allocation of single precision outputs for quicker analysis. The data is stored within predefined single column vectors with the number of rows equal to the number of hourly time steps. There is an expected increase in analysis time with the duration of hydration (Figure 2) with 10,000 hourly time steps analysed in less than ½ second.

2.2 Chemical Properties

Using four customisable input files (oxide_proportions.txt, densities.txt, molar_mass.txt & molar_mass_reaction.txt) as shown in Figure 1, the four cement phase and gypsum proportions are determined using the Bogue equations [3] shown in Equations 1-5 below. The volume stoichiometries are calculated based on the molar mass reaction of the cement phase, the molar mass of the phase (C_3S , etc.)

² H = water; CH = Calcium Hydroxide; CAH = Hydrogarnet; GYP = Gypsum; ETTR = Ettringite; MONO = Monosulphate; FH = Iron Oxide

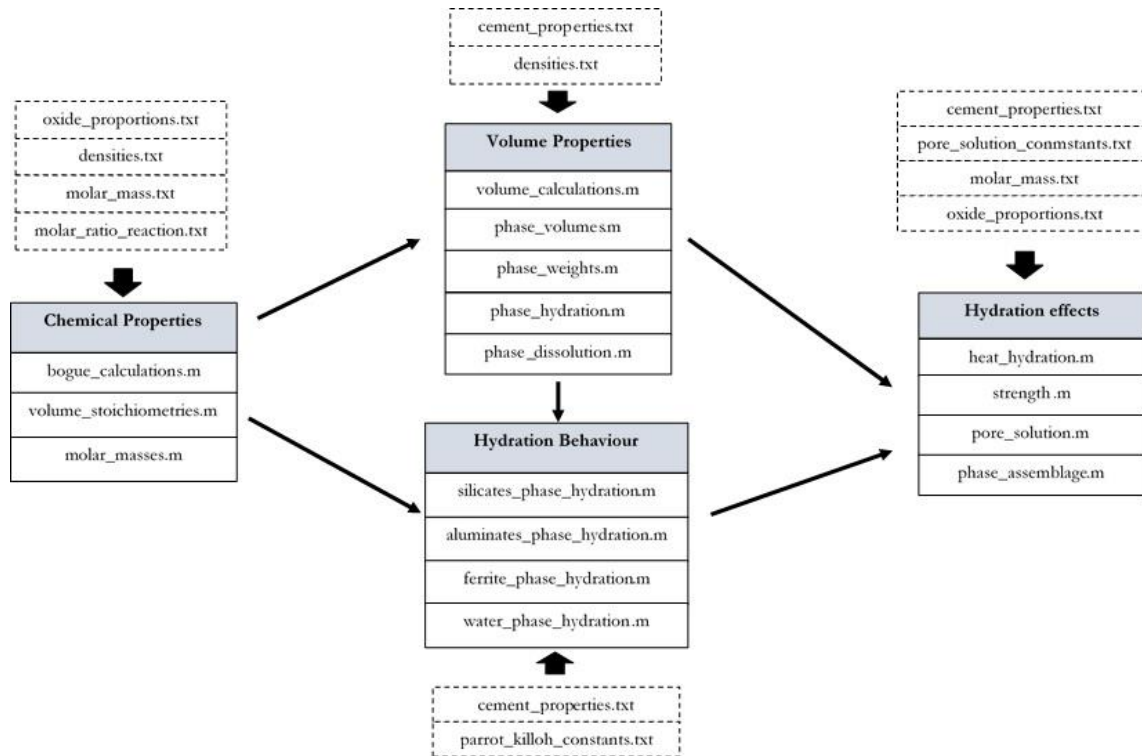


Figure 1: Diagram of HYDCEM's Matlab functions (*.m) and customisable input text files (*.txt)

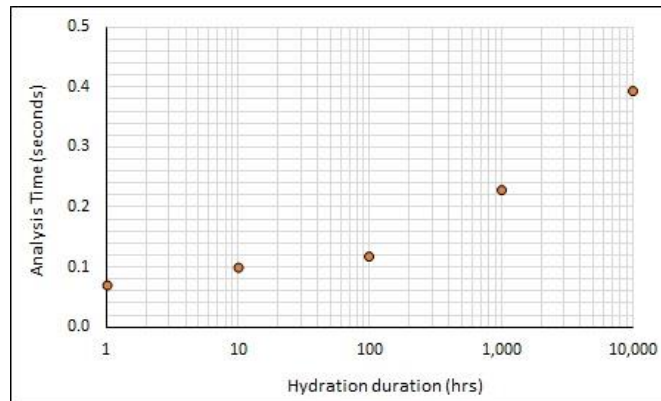


Figure 2: Analysis time for increasing hydration durations

$$C_3S = (4.071C_aO) - (7.600S_iO_2) - (6.718Al_2O_3) - (1.430Fe_2O_3) - (2.852SO_3) \quad (1)$$

$$C_2S = (2.867S_iO_2) - (0.7544C_3S) \quad (2)$$

$$C_3A = (2.65Al_2O_3) - (1.692Fe_2O_3) \quad (3)$$

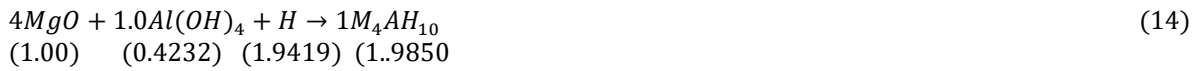
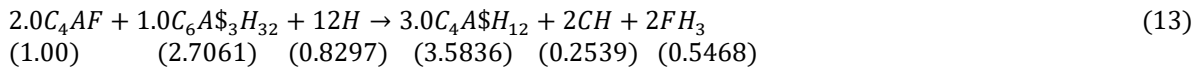
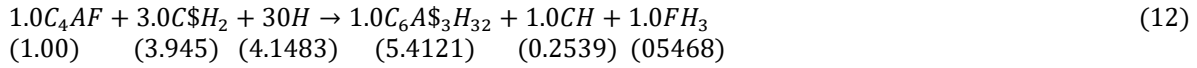
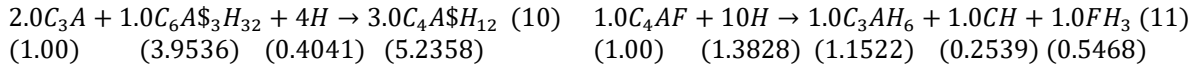
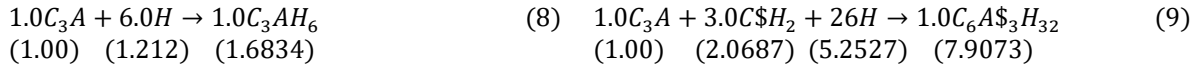
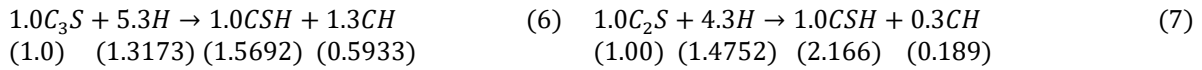
$$C_4AF = (3.043Fe_2O_3) \quad (4)$$

$$Gypsum = (1.7SO_3) \quad (5)$$

or hydration product (C-S-H, etc.) and the density, all of which are customisable by the user. The molar mass reaction for the four cement phases and magnesium (Mg) are shown in Equations 6-14 with their calculated volume stoichiometries shown in brackets below.

2.3 Dissolution of cement phases

The dissolution of the four cement phases are calculated in HYDCEM using the approach presented by Parrot and Killoh [10] that uses a set of empirical expressions to estimate the degree of hydration of each phase as a function of time. The dissolution of each phase is determined using Equations 15 to 17 where the lowest hydration rate R_t is taken as the rate-controlling value.



The degree of hydration (α) is expressed as $\alpha_t = \alpha_{\infty} - 1 + \Delta t \cdot R_{t-1}$. The K, N and H values used for the three phases are those proposed by Lothenbach *et al* [11,12]. The influence of the surface area on the initial hydration are included as well as the influence of w/c ($= (1 + 3.333 (H * w/c - \alpha_t))^4$; for $\alpha_t > H * w/c$).

$$R_t = \frac{K}{N} (1 - \alpha_t) (-\ln(1 - \alpha_t))^{(1-N)} \quad (15)$$

$$R_t = \frac{K(1 - \alpha_t)^{\frac{2}{3}}}{1 - (1 - \alpha_t)^{\frac{1}{3}}} \quad (16)$$

$$R_t = K(1 - \alpha_t)^N \quad (17)$$

2.4 Hydration Behaviour

The change in volume of cement phases, gypsum, hydration products and water are calculated using the volume stoichiometries calculated from the molar ratios in reactions (Equations 6-14) within using a series of programming operations. HYDCEM has implemented well accepted cement hydration behaviour found in the literature as shown Figure 3, for example where the growth in monosulfate (for limestone free cements) begins after gypsum has been depleted [12,13] with increased ettringite volume until all gypsum is depleted [11,13]. The following section presents a worked example to show HYDCEM predictions of hydration behaviour over time.

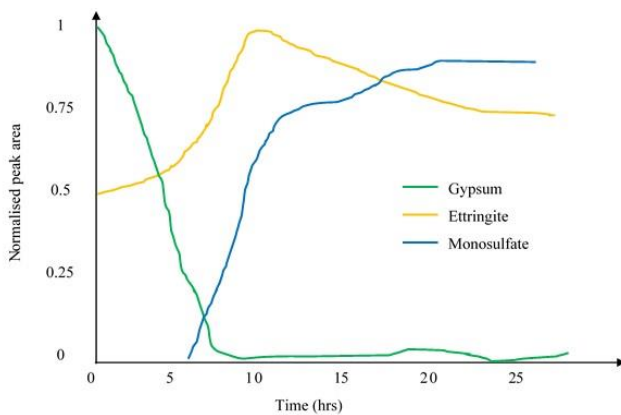


Figure 3: Kinetics of aluminate hydration for limestone-free cements (after Scrivener, 1984 [13])

3 Worked Example

The worked example is based on work by Lothenbach *et al* [11] with the cement properties shown in Table 1. The published phase assemblages or thermodynamic modelling shown here to compare the HYDCEM output with were carried out using the Gibbs free energy minimization program GEMS [14,15]. GEMS is a broad-purpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. A detailed description of GEMS can be found elsewhere in the literature [14-17].

Table 1: Sample of input for worked example

Cement composition [11]		Enthalpy (J/g) [2]		Parameters for degree of hydration analysis [11]				
CaO	63.9	C3S	517	Parameter	C3S	C2S	C3A	C4AF
SiO ₂	20.2	C2S	262	K1	1.5	0.5	1.0	0.37
Al ₂ O ₃	4.9	C3A	1144	N1	0.7	1.0	0.85	0.7
Fe ₂ O ₃	3.2	C4AF	725	K2	0.05	0.02	0.04	0.015
CaO(free)	0.93			K3	1.1	0.7	1.0	0.4
MgO	1.8			N3	3.3	5.0	3.2	3.7
K ₂ O	0.78			H	1.8	1.35	1.6	1.45
Na ₂ O	0.42							
CO ₂	0.26			Blaine surface area (m ² /kg)			413	
SO ₃	2.29			w/c ratio	0.4			
K ₂ O (soluble)	0.72			Temperature (°C)		20		
Na ₂ O (soluble)	0.09							

The (a) HYDCEM predicted and (b) published cement dissolution of the four phases are shown in Figure 4. As may be seen, there is close agreement between the measured and predicted phase dissolution values. Figure 5 shows (a) the HYDCEM and (b) published phase assemblage diagrams [11] for the cement described in Table 1. Figure 5(b) shows small quantities of monocarbonate, brucite and hemiacarbonate that are not included in the HYDCEM model. Despite this, the HYDCEM predictions are very close to the measured phase assemblage with the products of hydration forming at a similar rate over time. Also, the dissolution of gypsum is very similar with both predictions showing it completely depleted within 10 hours. As expected, both show similar reductions in the volume of ettringite with increasing monosulphate volume over time. Figure 6 shows the modelled aluminates products of hydration over time. Again, there is a reasonably close agreement between both.

Figure 7 shows a suite of HYDCEM predictions of the (a) degrees of hydration and (b) heat release over time for curing temperatures of 5, 20 and 40°C. Lower curing temperatures cause hydration to start very slowly allowing the dissolved ions more time to diffuse prior to precipitation of hydrates along with the slower dissolution of gypsum [18]. This leads to a less dense C-S-H, a more even distribution of hydration products and a less coarse porosity [18-22]. The effect of the higher temperature can be observed with an initially fast dissolution of the four cement phases and a more rapid precipitation of hydration products early on. This is responsible for the early strength development observed at higher temperatures along with a more heterogeneous distribution of hydration products in and around the clinker particles [20]. The effect of the higher temperature demonstrates a much more rapid rate of hydration, as discussed above. The predicted degree of hydration (Figure 7(a)) at the three temperatures are as expected. At 5°C, the degree of hydration is slower whereas at 40°C, it is more rapid early on quickly slowing down over time. For instance, after 10 hours of hydration, the overall degree of hydration at 5°C, 20°C and 40°C is 7, 18 and 36% respectively. However, after 100 hours of hydration, the overall degree of hydration at the three temperatures is 47, 61 and 71% respectively, which clearly shows the effect of curing temperature as discussed above.

4 Conclusions

The HYDCEM model has been found to simulate the hydration and microstructure development of

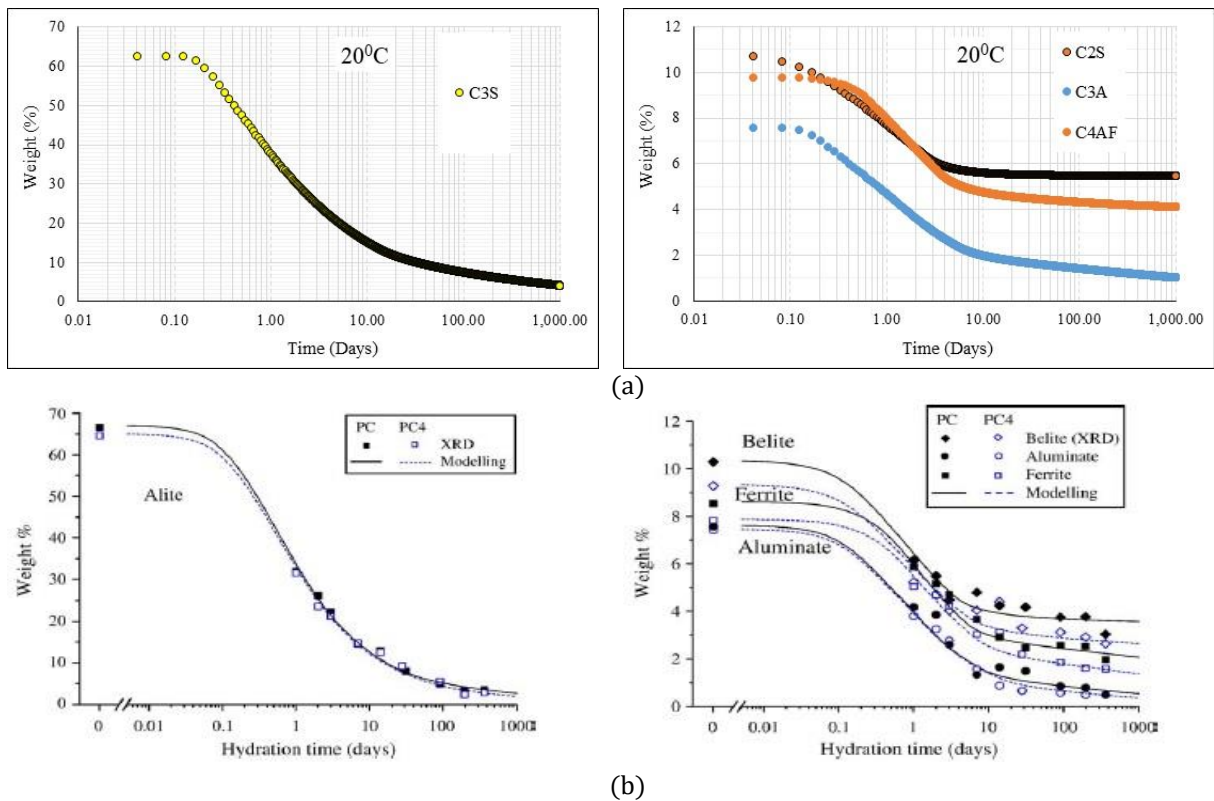


Figure 4: (a) Predicted (HYDCEM) and (b) published [11] cement phase dissolution at 20°C.

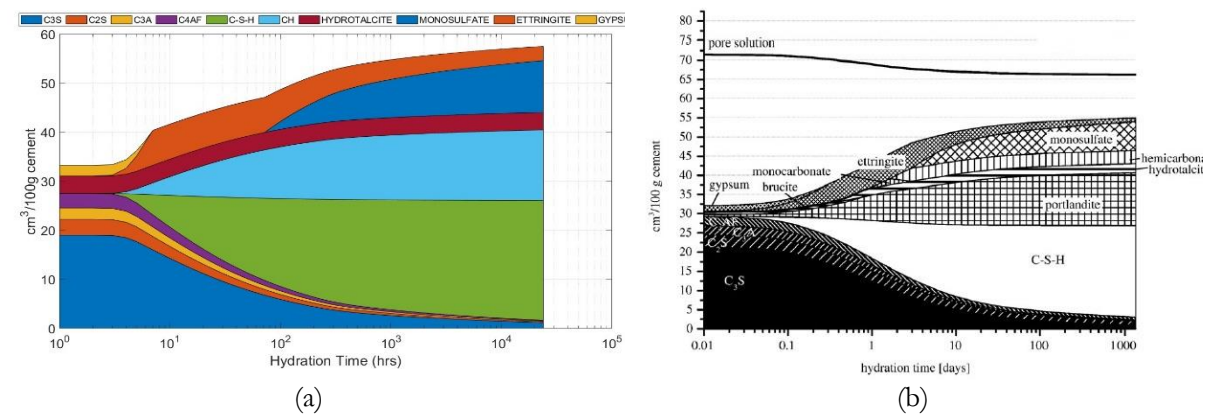


Figure 5: (a) Predicted (HYDCEM) and (b) GEMS modelled phase assemblages [11] at 20°C.

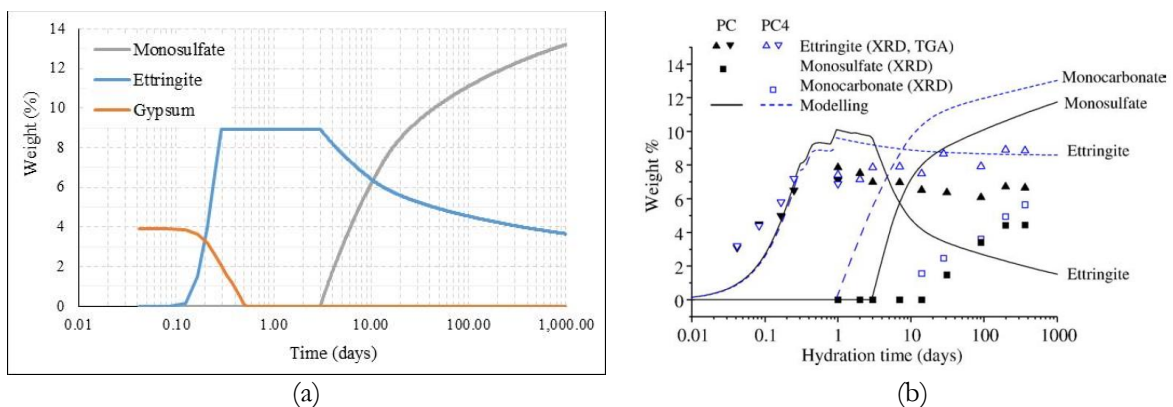


Figure 6: (a) HYDCEM and (b) GEMS predicted [11] products of hydration from the aluminate phase

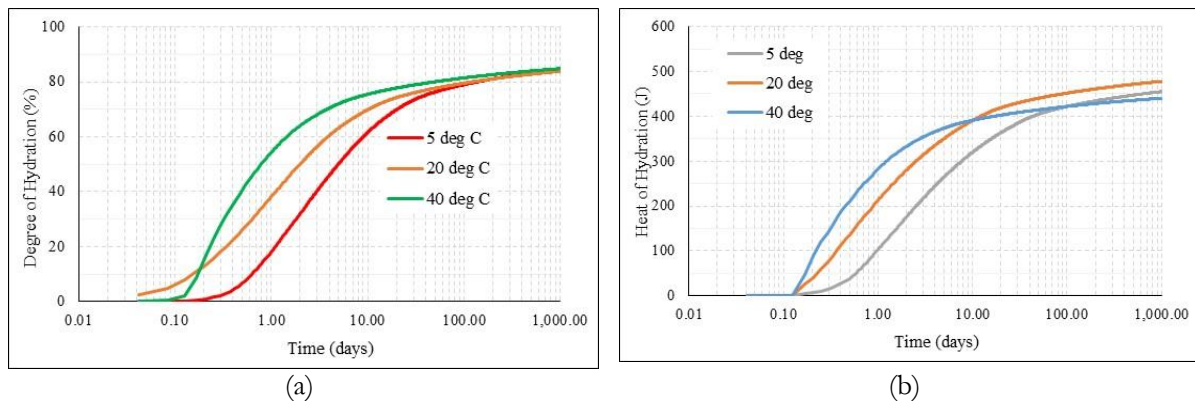


Figure 7: HYDCEM predicted (a) degree of hydration and (b) heat of hydration at (a) 5°C, 20°C and 40°C over time.

Portland cements. Using cement composition and reaction relationships, the cement phase and products of hydration are determined in volumetric terms over time for any w/c ratio and curing temperatures up to 45°C. Results presented here have shown good agreement with published hydration behaviour. HYDCEM can therefore become a useful tool for the initial prediction of cement hydration and microstructure behaviour before the use of more sophisticated thermodynamic models. Development of the model is ongoing with additional features being added to include limestone and predictions of the pore solution chemistry by coupling with the PHREEQC geochemical model [23]. Future developments also include predictions of electrical and thermal conductivities to better understand the potential of cement based thermoelectric materials.

5 Acknowledgement

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