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Modelling the addition of limestone in cement using HYDCEM

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ABSTRACT

Hydration models can aid in the prediction, understanding and description of hydration behaviour over time as the move towards more sustainable cements continues.

HYDCEM is a new model to predict the phase assemblage, degree of hydration and heat release over time for cements undergoing hydration for any w/c ratio and curing temperatures up to 45°C. HYDCEM, written in MATLAB, complements more sophisticated thermodynamic models by predicting these properties over time using user-friendly inputs within one code. A number of functions and methods based on up to date cement hydration behaviour from the literature are hard-wired into the code along with user-changeable inputs including w/c ratio, curing temperature, chemical compositions, densities and enthalpies. Predictions of hydration product volumes from the silicate, aluminate and ferrite phases can be determined, including C-S-H, calcium hydroxide, hydrogarnet (if applicable) ettringite and monosulfate. A number of comparisons have been made with published phase assemblages using thermodynamic models and HYDCEM predictions to assess its accuracy and usefulness.

This paper presents simulations of cement hydration and microstructure development with and without the additional of ground limestone using the HYDCEM model, both in terms of monocarbonate growth at the expense of monosulfate and ettringite. Comparisons with published phase assemblages show good agreement in terms of volumetric growth and behaviour.

1. INTRODUCTION

The use of cements with added limestone has been increasing in Europe and across the world over the past decade. Within the European cement standard, EN-197, limestone-cements are classed as CEM II/A-L and CEM II/B-L where up to 20 and 35% limestone is allowed respectively (BS EN 197-1, 2000). The addition of limestone is also permitted in the United States (ASTM C150, 2018) and many other countries throughout the world. Indeed, Bonavetti *et al* (2003) states that the addition of limestone filler in low w/c concrete is a rational option to reduce energy consumption, emissions and costs.

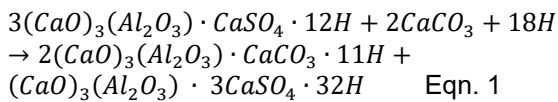
While the use of Supplementary Cementitious Materials (SCM's) in concrete is increasing, their local and worldwide availability compared to limestone is much less. The literature (Lothenbach *et al*, 2008; Matschei *et al*, 2007; Matschei and Glasser, 2006; Antoni *et al*, 2012; Zajac *et al*, 2014; Ingram and Daugherty, 1991) suggests that limestone or calcite additions up to 5% can enhance performance while reducing ettringite dissolution when gypsum/sulfate is depleted. AFm phases like monocarbonate and hemicarbonate are formed in place of monosulfate with reduced consumption of ettringite. Without limestone additions, ettringite becomes unstable and monosulfate is formed over time. With limestone, monocarbonate is formed which stabilises ettringite. As a result, there is an increased volume of hydrates, decreased porosity and improved strength.

The effects of limestone addition were shown to increase the effective w/c of the cementitious material and accelerate hydration, while only mildly reactive. This is due to the fine filler effect where the ground limestone provides additional surfaces to develop nucleation sites for the precipitation of C-S-H (Stark, 2004; Pera *et al*, 1999).

2. MODELLING LIMESTONE ADDITIONS DURING CEMENT HYDRATION

A review of the literature around cement hydration modelling including limestone additions suggests that, outside of thermodynamic analysis, only CEMHYD3D (Bentz, 2000) has been used. The μic microstructure platform (Bishnoi & Scrivener, 2009) allows for the inclusion of limestone with the filler C-S-H can be modelled on the surface of the particle.

The influence of limestone, both for chemical reactivity and 'fine filler effects' was included in the CEMHYD3D V. 2.0 model (Bentz, 2006) by modifying the CEMHYD3D code and including the reaction in Equation 1, based on experimental observations in the literature (Hawkins *et al*, 2003; Klemm & Adams, 1990; Kuzel & Pollmann, 1991; Bonavetti *et al*, 2001; Kakali *et al*, 2000). Monocarbonate is formed in preference to monosulfate and only becomes active in CEMHYD3D when the initial calcium sulfate (gypsum) is depleted and the previously formed ettringite converts to the Afm phase by reaction with more of the cement clinker aluminate phases.



In terms of the ‘filler effect’, the early time dissolution probabilities in CEMHYD3D were altered so to be proportional to the ratio of the initial total (cement clinker and limestone) surface area divided by the initial cement clinker surface area raised to the second power (Bentz, 2000). This methodology implies that hydration during the induction period is ‘accelerated’ where a thinner C–S–H¹ layer is formed over a larger surface area. It was concluded that the revised model provided good agreement with experimental results.

The effect of limestone on the hydration of cementitious systems has also been undertaken using thermodynamic modelling using the Gibbs free energy minimization (GEMS) programme. GEMS (Kulik, 2007) is a broad-purpose geochemical modelling code that has been used to compute phase assemblage from the systems total bulk elemental composition (Lothenbach et al, 2008). Chemical solid interactions, solid solutions and aqueous electrolyte are considered simultaneously along with the speciation of the dissolved species including the kind and amount of solids precipitated.

Thermodynamic modelling was undertaken using a w/c ratio of 0.4 at a curing temperature of 20°C with the cementitious systems in (Lothenbach et al, 2008). Figure 1 shows the thermodynamically modelled phase assemblages for the cements with limestone. As may be seen, monocarbonate forms in place of monosulfate in the limestone cement. Also shown is the stability of ettringite through the hydration in the limestone cements which is unstable in the Portland cements as it is converted to monosulfate over time. Furthermore, monosulfate begins to form at approximately 3 days where monocarbonate is formed after approximately 1 day. Finally, the total volume of the limestone cement is slightly higher than the Portland cement, which confirms the higher compressive strengths seen in the literature.

Figure 2 presents comparisons between modelled and experimentally measured (using XRD & TGA) amounts of ettringite, monosulfate and monocarbonate over time (Lothenbach et al, 2008). The authors noted that the differences between measured and modelled is due to the underestimation of AFm phases deduced by XRD was due to its low crystallinity and variations in composition. It was also concluded that thermodynamic modelling is capable to reasonably accurately predicting the formulation of C-S-H, portlandite, ettringite, monosulfate and traces of hydrotalcite and hemicarbonate, as shown in Figure 2. However, the XRD measurements show more ettringite than predicted by the model.

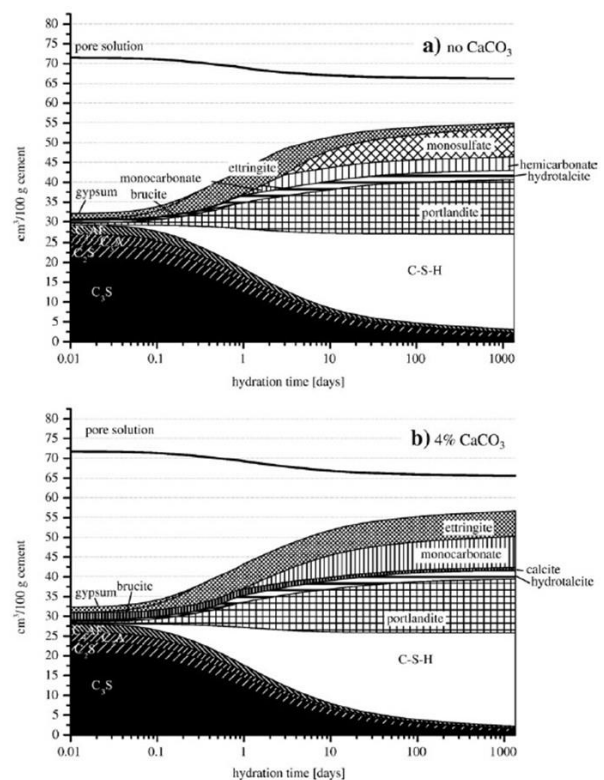


Figure 1: Results from Thermodynamic modelled changes during the hydration of a Portland cement (a) without and (b) with 4 wt.% limestone (Lothenbach et al, 2008)

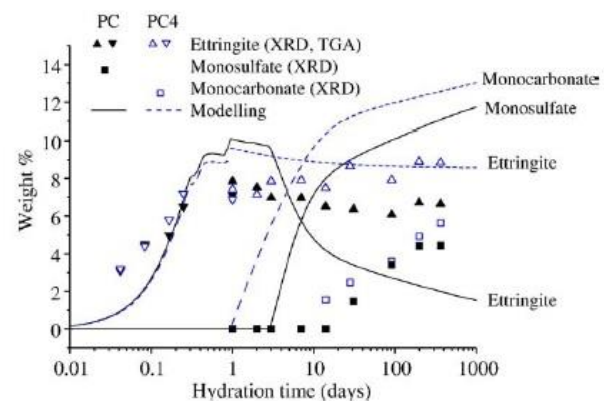


Figure 2: Measured and predicted (thermodynamic modelling) hydrated crystalline products as a function of hydration time (Lothenbach et al, 2008).

The above review suggests that any hydration model simulating the effect of limestone inclusion must be capable of predicting the development of monocarbonate in place of monosulfate after the depletion of sulfates/gypsum while maintaining the stability of ettringite using appropriate chemical relationships. The following presents how the HYDCEM cement and hydration microstructure model (Holmes et al, 2019) can simulate the hydration of limestone cements.

3. HYDCEM HYDRATION MODEL

HYDCEM was developed with the user in mind by

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

providing clearly laid out and easy to change input flat (*.txt) files. The analysis/calculation flow for HYDCEM is shown in

Figure 3. 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 without a loss of accuracy. The data is stored within predefined single column vectors with the number of rows equal to the number of hourly time steps.

Using the four input text (*.txt) files, the cement phase and gypsum proportions are determined using modified Bogue equations (ASTM C150, 2018). The volume stoichiometries are calculated based on the molar mass reaction of the cement phase, the molar mass of the phase (C₃S, etc.) or hydration product (C-S-H, etc.) and the density, all of which are customisable by the user.

The dissolution of the four cement phases are calculated using the approach presented by Parrot and Killoh (1984) that uses a set of empirical expressions to estimate the degree of hydration of each phase as a function of time. Previous work has shown that the approach gave good comparisons with experimental results for any temperature shown in Figure 3 (Lothenbach et al, 2007).

The change in volume of hydration products, water and gypsum are calculated using the volume stoichiometries calculated from the molar ratios in reactions within using a series of programming operations. HYDCEM has implemented accepted cement hydration behaviour found in the literature.

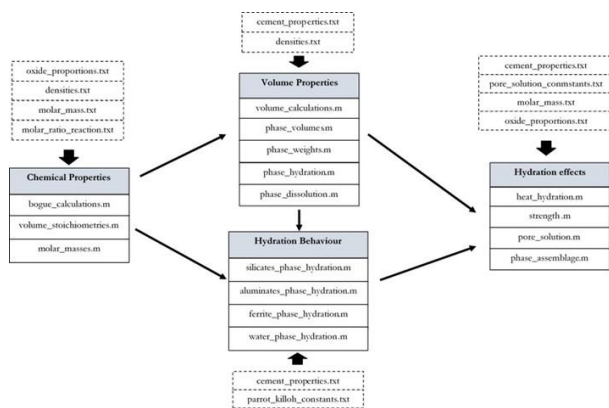


Figure 3: Diagram of HYDCEM's Matlab functions (*.m) and customisable input text files (*.txt)

3. HYDCEM SIMULATIONS

To assess the accuracy of HYDCEM simulations, comparison were made against the published experimentally determined and modelled behaviour in Figure 1 and Figure 2 above. Table 1 shows the cement properties used as input for the HYDCEM model based on work by Lothenbach *et al* (2008). Table 2 shows the Parrot and Killoh (1984) parameters used to calculate the hydration of the four cement phases.

The volume stoichiometry used in HYDCEM for the growth of monocarbonate (AFmc) due to the addition of calcite/limestone (CaCO₃) is shown in Equation 2 (Mohamed *et al*, 2015) where H represents water.

$$1.0V_{AFm} + 0.12V_{CaCO_3} + 0.347V_H = 0.6281V_{AFmc} \quad \text{Eqn. 2}$$

Table 1: Details of the PC and limestone cements (Lothenbach et al, 2008)

Composition	PC	Limestone
CaO	63.9	55.0
SiO ₂	20.2	0.8
Al ₂ O ₃	4.9	0.3
Fe ₂ O ₃	3.2	0.3
CaO (free)	0.93	< 0.01
MgO	1.8	1.8
K ₂ O	0.78	<0.01
Na ₂ O	0.42	<0.01
CO ₂	0.26	42.5
SO ₃	2.29	0.05
Blaine (m ² /kg)	413	429

Table 2: Parott & Killoh (1984) parameters to calculate the hydration of the individual clinker phases

Parameter	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
K ₁	1.5	0.5	1.0	0.37
N ₁	0.7	1.0	0.85	0.7
K ₂	0.05	0.02	0.04	0.015
K ₃	1.1	0.7	1.0	0.4
N ₃	3.3	5.0	3.2	3.7
H	1.8	1.35	1.6	1.45

Figure 4 and Figure 5 shows the HYDCEM predicted phase assemblages over a 1,000 day period (24,000 hrs) for the cements with and without limestone using the inputs above. The growth of monocarbonate and monosulfate is programmed to begin 1) after the depletion of gypsum and 2) at one and three days respectively. Comparing the HYDCEM simulations with the thermodynamic predictions, there is good agreement both in terms of volumetric calculations and behaviour. Furthermore, the model accurately simulates the behaviour of the ettringite, monocarbonate and monosulfate with and without limestone.

4. CONCLUSIONS

HYDCEM has been shown to provide reasonably accurate predictions of the phase assemblage with and without limestone for all four cement phases. The phase assemblages produced shown close agreement with published thermodynamic model predictions for silicate, aluminates and ferrite hydrates. HYDCEM therefore provides a very useful tool for the study of cementitious materials currently and into the future as the cement industry continues to seek more environmentally friendly materials to include in its products. HYDCEM is particularly suited to these developments owing to its ease of use both in terms of model structure and customisable input and analysis features.

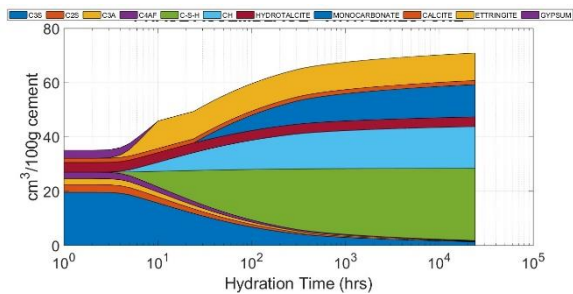


Figure 4: HYDCEM phase assemblage with limestone

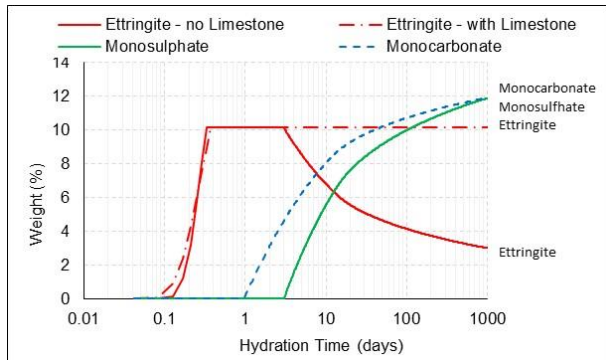


Figure 5: HYDCEM predicted ettringite, monocarbonate and monosulfate growth with and without limestone respectively over a 1,000 day hydration time.

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