Reaction Kinetics of Blended Cements Incorporating Wet and Dry Calcite

Yaowen Xu[1], Guan Feng Chua[2], Mingshan Zhao[2], Liwu Mo[3, 4], Fei Jin*[1]

[1] School of Engineering, Cardiff University, UK.
(E-mail: XuY123@cardiff.ac.uk, JinF2@cardiff.ac.uk (Corresponding Author))
[2] Singapore Institute of Technology, SINGAPORE.
(E-mail: guanfeng.chua@singaporetech.edu.sg,
mingshan.zhao@singaporetech.edu.sg)
[3] College of Materials Science and Engineering, Nanjing Tech University, CHINA.
(E-mail: andymoliwu@njtech.edu.cn)
[4] State Key Laboratory of Material-Oriented Chemical Engineering, Nanjing Tech University, CHINA.

Keywords: Calcite, Dissolution test, Hydration kinetics, Isothermal calorimetry, Low-carbon cement

ABSTRACT

Valorising alkaline wastes in cementitious systems can cut CO_2 intensity while enabling carbon capture and utilisation in construction materials. Building on our previous work on regulating calcium carbonate polymorphs as cement additives, this research further investigates how incorporation form of calcite - fresh slurry (Wet-C) versus dried powder (C) - affects hydration kinetics in blended cement.

Analytical grade of $CaCl_2{\cdot}2H_2O$ and Na_2CO_3 were used to synthesise calcite following the method in [1]. The precipitates were washed with deionised water and centrifuged at least three times. Both the wet calcite slurry and 50 °C-dried calcite powder were used to replace 30% of cement, denoted as CEM70Wet-C30 and CEM70C30, respectively. The control sample, consisting of plain cement, was labelled as CEM100. CEM I 52.5N was used in the isothermal calorimetry tests, with a water-to-binder (w/b) ratio of 0.5 (by accounting for the water in the slurry). CEM II/A-L 32.5R (with 6-20% limestone in its composition) was used in the dissolution test, with a w/b ratio of 50 according to [2] to simulate the cement hydration process while minimising precipitation. Deionised water was used throughout all experimental procedures. Based on our previous findings, the incorporation of Wet-C effectively prevents agglomeration of calcite particles that commonly occurs when dry calcite powder is used. Isothermal calorimetry and dissolution experiments were performed to evaluate the impact of these two forms of calcite on cement hydration kinetics. Inductively coupled plasma - optical emission spectroscopy (ICP-OES) analysis was conducted to determine the concentrations of different elements in the dissolution test solutions.

The results of isothermal calorimetry are shown in Figure 1. It can be found that the incorporation of either C or Wet-C into cement pastes shows earlier and sharper occurrence of the main peaks, as well as a higher normalised total heat at 7 days, compared to the control sample. These findings indicate that both C and Wet-C accelerate the early-stage hydration of cement. Furthermore, cement paste with

Wet-C show a more pronounced acceleration effect than that with C, attributed to its better dispersion within the cement matrix.

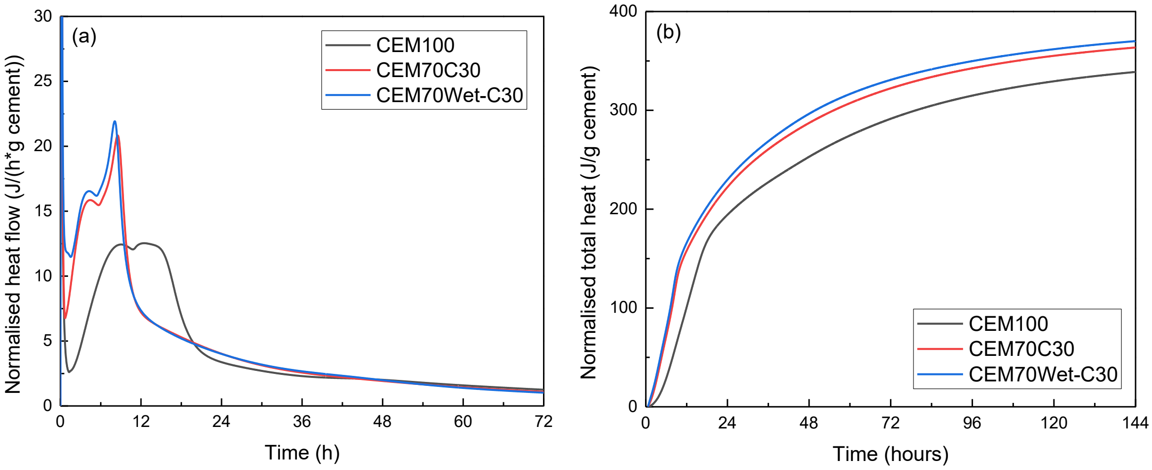

Figure 1. (a) Heat flow and (b) cumulative heat of cement pastes blended with C and Wet-C.

Dissolution tests (Figure 2) showed that the replacement of 30% cement by C increased the dissolution of Si in the first 2 hours, with the concentration of Si increasing gradually and then decreasing after approximately 30 minutes. Notably, Wet-C showed a much more significant impact, leading to Si concentrations more than 50 times higher than C within the first minute (Figure 2b). Since Si mainly derives from the dissolution of C_3S and C_2S phases in cements, these results indicate that calcite enhances the dissolution of these clinker phases. Ca concentrations decreased with both additives, especially Wet-C (Figure 2a). When considering both Si and Ca data, it can be deduced that calcite promotes the precipitation of C-S-H gels, especially when freshly synthesised calcite is incorporated in the slurry (i.e., Wet-C). Similarly, the formation of Al-bearing phases is also facilitated, as evidenced by lower Al concentration in samples with Wet-C than in control samples (Figure 2c), which is attributed to the faster precipitation of Al-bearing phases such as AFt/AFm. These results are in line with the isothermal calorimetry data, where earlier and sharper main peaks were observed (Figure 1). Lower Al concentrations and higher S concentrations in samples with Wet-C compared to the control (Figure 2d) suggest formation of SO_4-CO_3-AFt, releasing sulfate into the aqueous solution [3]. By contrast, samples blended with C showed higher Al concentration and lower S concentration than the control, likely due to enhanced dissolution of aluminate phases in cement and faster precipitation of sulfate-bearing phases. These findings show that even for the same mineral (i.e., calcite), the change of incorporation form not only affects dispersion, but also significantly influence the hydration kinetics/mechanisms of cements.

In conclusion, the incorporation of freshly synthesised calcite in the slurry form without drying improves dispersion of calcite in cements and accelerates cement hydration via facilitating the precipitations of C-S-H gels and Al-bearing phases. Further investigation on optimising the dosage of calcite and assessing the mechanical performance of the blended cements would provide new insights on the strategy of carbon capture and utilisation and facilitate valorisation of alkaline wastes for the development of low-carbon cementitious materials.

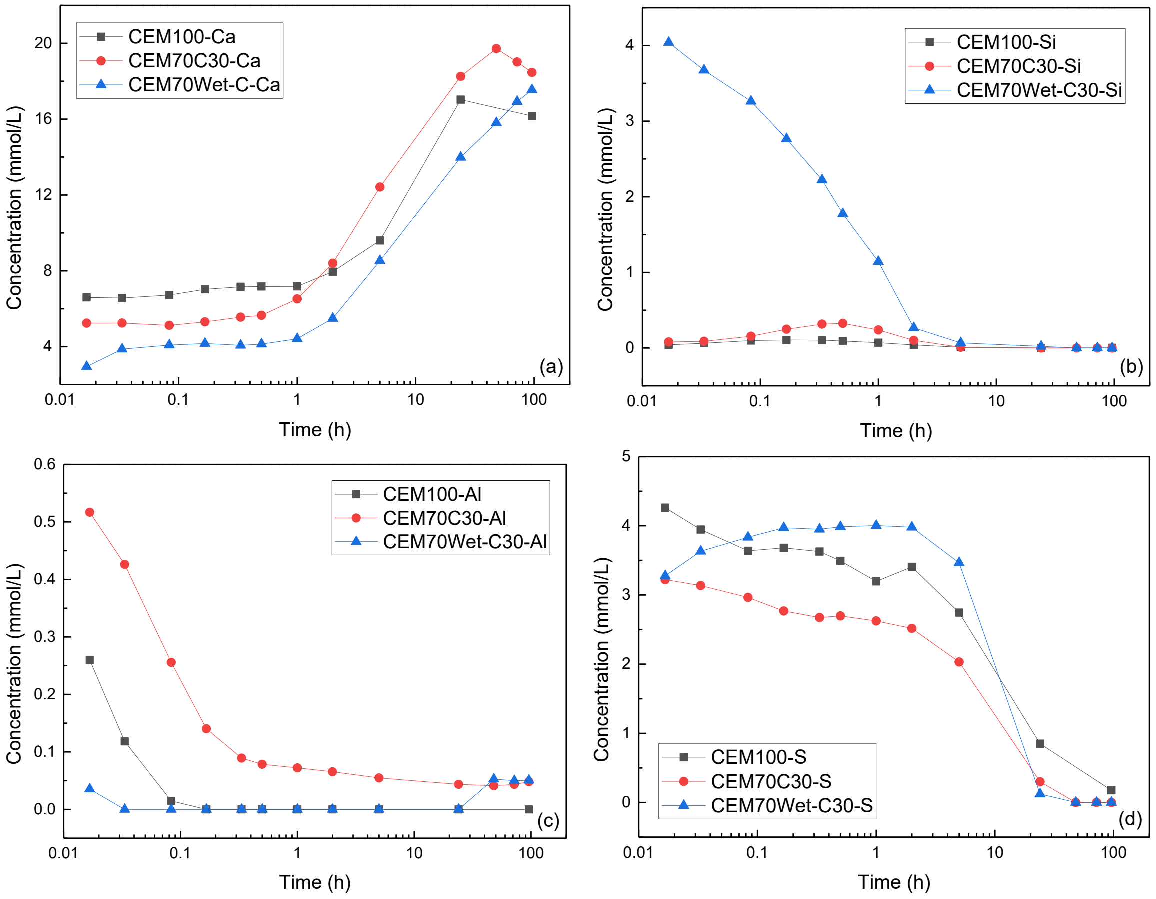

Figure 2. Concentrations of different elements from the blended cement with two forms of calcite (a) Ca; (b) Si; (c) Al; (d) S.

Acknowledgment: The authors would like to acknowledge the financial support from EPSRC (EP/Y001117/1).

References:

[1] Zhao, D., Williams, J. M., Park, A. H. A., et al.. 'Rheology of cement pastes with calcium carbonate polymorphs', *Cem. Concr. Res.*, 2023, 172, pp. 107214

[2] Bellmann, F., Sowoidnich, T., Ludwig, H. M., et al.. 'Dissolution rates during the early hydration of tricalcium silicate', *Cem. Concr. Res.*, 2015, 72, pp. 108-116

[3] Lothenbach, B., Saout, L. G., Gallucci, E., et al.. 'Influence of limestone on the hydration of Portland cements', *Cem. Concr. Res.*, 2008, 38, pp. 848-860