Synthesis and Use of Different $CaCO_3$ in Portland Cement

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Abstract

Calcite has been extensively used in blended cement, whereas the effects of other $CaCO_3$ forms remain underexplored. Due to their distinct thermodynamic properties, different forms of $CaCO_3$ may influence the reaction mechanisms and hydration behaviour in blended cement systems. This study synthesised various forms of calcium carbonate ($CaCO_3$), including calcite, aragonite, vaterite, and amorphous calcium carbonate (ACC), and investigated their dispersion behaviour in Portland cement (PC) pastes, as well as their effects on cement hydration. The drying method was found to critically influence the phase stability of the synthesised $CaCO_3$: oven drying at 50 °C preserved calcite and aragonite, whereas solvent exchange with acetone was required to retain vaterite and ACC. Dry $CaCO_3$ powders exhibited a tendency to agglomerate during mixing, resulting in visible deposits in hardened pastes. To address this, a wet-mixing method using the freshly synthesised $CaCO_3$ slurry was developed, significantly improving homogeneity. Isothermal calorimetry revealed that all crystalline forms of $CaCO_3$ accelerated early-stage cement hydration, while ACC induced a retardation effect. Moreover, the use of fresh calcite slurry led to enhanced hydration compared to dried powders, likely due to increased calcium ion availability. These findings highlight the importance of $CaCO_3$ form, processing conditions, and incorporation method in optimising the performance and sustainability of blended cement systems.

Keywords: Cement hydration, Calcium carbonate polymorphs, Drying method

1. Introduction

Portland cement (PC) remains the most widely used binder in construction. However, due to its high carbon footprint, there is a growing need to explore strategies for reducing its environmental impact. One widely adopted approach is to partially replace PC clinker with mineral additives without compromising the engineering performance of concrete. Among various options, limestone powder (with calcite as the primary component) has been extensively used as a mineral additive in blended cements. Calcite, one of the most stable phases of calcium carbonate under ambient conditions, has been recognised for accelerating the hydration of alite and stabilising the formation of ettringite, both of which can ultimately contribute to strength development in cement paste, particularly at early ages [1].

In addition to calcite, there are different polymorphs of calcium carbonate ($CaCO_3$) such as aragonite and vaterite and amorphous calcium carbonate (ACC). Recent advances in carbon capture technologies, combined with growing interest in the mineralisation of alkaline wastes, have highlighted the potential to deliberately control the formation of specific $CaCO_3$ polymorphs, including metastable and unstable phases [2, 3]. These techniques offer the possibility of maximising the benefits of calcium carbonate in sustainable cement production. Nevertheless, the effects of these alternative $CaCO_3$ forms on cement hydration remain underexplored [4, 5], representing a critical knowledge gap for the future implementation of such techniques within the construction industry. To address this gap, the study aimed to: (i) synthesise different forms of $CaCO_3$ for use, (ii) investigate the phase stability of these forms under different drying methods, (iii) evaluate their dispersion behaviour in cement pastes, and (iv) assess the influence on early-age cement hydration. The findings advance scientific understanding of how specific $CaCO_3$ forms affect cement hydration mechanisms, while also offering practical strategies for stabilising and incorporating synthetic or waste-derived $CaCO_3$ into cement systems, which can support the development of more consistent and sustainable blended cements.

2. Materials and methods

2.1. Materials

$CaCl_2{\cdot}2H_2O$, Na_2CO_3, NH_4Cl, and $MgCl_2{\cdot}6H_2O$ (all ≥99% purity) were used to synthesise different forms of $CaCO_3$, namely calcite, aragonite, vaterite, and ACC. Additionally, CEM I 52.5 N was used for cement paste preparation and isothermal calorimetry measurements. Deionised water was employed for all synthesis processes and as the mixing water for cement pastes.

2.2. Methods

The synthesis parameters for different $CaCO_3$ were based on previous studies [4-6] and shown in Table 1. The precipitates were washed with deionised water and centrifuged at least three times. XRD was applied to identify the mineralogical composition of synthesised products. Subsequently, they were either oven-dried at 50 °C or subjected to solvent exchange with acetone (performed more than twice). Residual acetone was removed by air-drying the samples under a fan at room temperature. A detailed discussion on the phase stability of $CaCO_3$ during the drying process is presented in Section 3.1. Isothermal calorimetry was conducted to evaluate the effects of the different $CaCO_3$ samples on cement hydration. In this study, 30 wt.% of the cement was replaced with $CaCO_3$, and the water-to-binder (w/b) ratio was maintained at 0.5.

Table 1: Synthesis parameters for different forms of $CaCO_3$ (RT refers to room temperature)

Sample	Synthesis parameters							Targeted $CaCO_3$ form
	$CaCl_2{\cdot}2H_2O$	Na_2CO_3	NH_4Cl	$MgCl_2{\cdot}6H_2O$	H_2O	Temperature	Time	
C	111 g	106 g	-	-	2 kg	RT	10 min	Calcite
A	111 g	106 g	-	-	2 kg	80 °C	10 min	Aragonite
V	111 g	212 g	53.5 g	-	2 kg	RT	10 min	Vaterite
ACC	111 g	106 g	-	570 g	3 kg	RT	20 min	ACC

3. Results and discussions

3.1. Synthesised products and their stability upon drying

Figure 1(a) presents the XRD patterns of the synthesised $CaCO_3$ samples prior to drying. The diffraction peaks confirm the successful formation of various crystalline polymorphs, while the broad hump associated with ACC reflects its poorly crystalline nature.

The effect of the two drying methods on the phase stability of the metastable or unstable $CaCO_3$ samples are shown in Figure 1(b)-(d). The results indicate that vaterite (Figure 1(c)) and ACC (Figure 1(d)) underwent phase transformations to calcite and monohydrocalcite, respectively, following oven drying at 50 °C. In contrast, aragonite (Figure 1(b)) remained stable under the same conditions. Notably, the solvent exchange method using acetone successfully preserved all $CaCO_3$ phases. These findings suggest that cautions must be taken when using vaterite and ACC as cement additives in the dry powder form, as the drying process may induce undesired phase transformations prior to incorporation into cement.

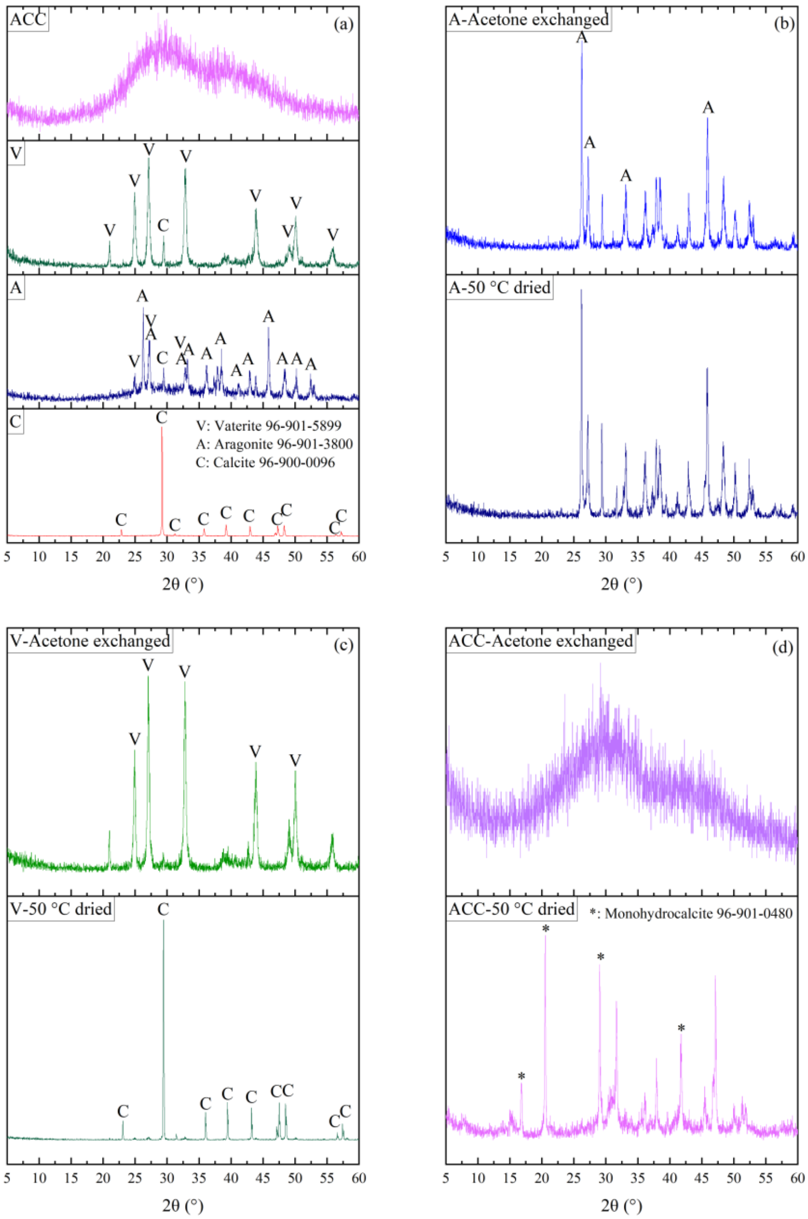

Figure 1: XRD patterns of (a) freshly synthesised samples of different $CaCO_3$, and samples of (b) A, (c) V, and (d) ACC after drying at 50 °C or solvent exchange with acetone

3.2. Dispersion of synthetic $CaCO_3$ in cement paste

Cement pastes were prepared by replacing 30 wt.% of cement with each $CaCO_3$ sample. Despite initially homogeneous slurries, white deposits were observed in the hardened cement pastes due

to agglomeration of $CaCO_3$ particles. Figure 2(a) shows an example of the cement paste incorporated with sample C. Agglomeration likely occurred during the plastic stage after casting, driven by the high surface energy of the synthetic particles, which promoted particle cohesion and cluster formation within the fluid paste.
To mitigate the agglomeration of $CaCO_3$ particles and its detrimental effect on the engineering performance of the cement pastes, a wet-mixing approach was employed. This involved incorporating freshly synthesised $CaCO_3$ slurries without drying, while accounting for the water content in the slurry to maintain a constant w/b ratio of the paste. As shown in Figure 2(b), this method eliminated visible deposits and improved matrix homogeneity.

(a) (b)

Figure 2: Photos of the cement pastes prepared with 30 wt.% replacement of cement using C in (a) dry powder form and (b) slurry form

3.3. Effect of different $CaCO_3$ on the hydration heat of cement pastes

Figure 3 shows the isothermal calorimetry results of cement pastes incorporating difference forms of $CaCO_3$. Note that all forms of $CaCO_3$ were added as dry powders, except in the case of the CEM70Wet-C30 group, where the $CaCO_3$ slurry was used.

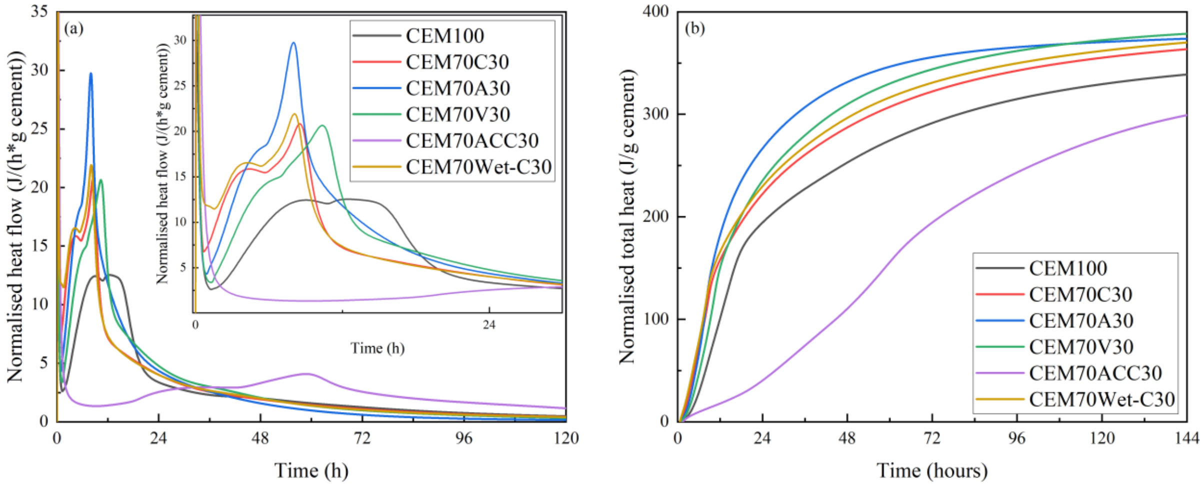

Figure 3: (a) Heat flow and (b) total heat of cement pastes blended with different $CaCO_3$

It can be seen from Figure 3 that the incorporations of crystalline $CaCO_3$ polymorphs, i.e. C, A and V in cement pastes accelerated early-stage hydration, as evidenced by the earlier occurrence of the main reaction peaks compared to the reference paste. Among these, the addition of A resulted in the sharpest main peaks, indicating more intense hydration reactions, while V led to the highest normalised total heat release at seven days, followed by A. This acceleration is likely attributable to their nucleation effects [7]. In contrast, ACC significantly impeded cement hydration, reducing both the intensity of the main hydration peak and the cumulative heat release over seven days, with the overall reaction progressing more slowly than in the reference paste. These results highlight the significance of $CaCO_3$ forms in influencing cement hydration. It is notable that the paste prepared with calcite slurry (CEM70Wet-C30) exhibited a more intense reaction than that made with dried calcite powders, particularly during the induction period. This could be attributed to the higher concentration of free calcium ions in the calcite slurry, which promoted the early precipitation of reaction products. These results suggest that the wet-mixing method not only improved homogeneity of the cement pastes, as discussed in Section 3.2, but also had a significantly greater influence on cement hydration.

4. Conclusions

This study synthesised various forms of $CaCO_3$ and evaluated their effects on cement hydration to explore the potential of employing polymorph control techniques to maximise the benefits of calcium carbonate in sustainable cement production. To preserve the desired $CaCO_3$ phases, appropriate drying methods are essential: solvent exchange with acetone is recommended for stabilising vaterite and amorphous calcium carbonate (ACC), whereas oven drying is suitable for calcite and aragonite. To improve dispersion, freshly synthesised $CaCO_3$ slurries were mixed directly with cement, highlighting the importance of addressing dispersion challenges to ensure matrix homogeneity in blended cement systems. Isothermal calorimetry revealed that crystalline forms of $CaCO_3$ accelerated cement hydration, while ACC exhibited a retarding effect. Compared to cement paste incorporating calcite, that containing aragonite exhibited more intense hydration, and pastes incorporating either vaterite or aragonite demonstrated higher cumulative heat release over seven days. Fresh calcite slurry enhanced hydration more effectively than dried powders, likely due to greater calcium ion availability in the slurry. These findings underscore the importance of $CaCO_3$ form, processing, and incorporation method in optimising hydration kinetics and microstructural development in blended cement systems, offering valuable insights for the use of waste-derived, low-carbon mineral additives.

Acknowledgements

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