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Effect of the Carbonate Source on the Carbonation Performance of Blended Binders Containing Calcined Clays

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Abstract. There is a burgeoning interest in determining the feasibility of using different clay types as potential supplementary cementitious materials (SCMs), for the production of more sustainable concretes. Given the connection between sustainability and longevity of construction materials, attention needs to be paid to the potential threats new SCM-containing cements might undergo. This will enable the design of materials accounting for environmental savings during production and improved resilience and longevity.

This research is part of the collaborative USA-UK project ‘RENACEM’ aiming to understand the response to CO₂ exposure of sustainable cements containing calcined clays as SCMs. The present study reports the outcomes of the carbonation performance studied in selected Portland blended specimens exposed to accelerated or natural carbonation evaluating the influence of limestone or dolomite addition. Compressive strength development, carbonation depth and microstructural changes induced by CO₂ exposure were determined. Clinker content governs the carbonation rate of both binary and ternary formulations in accelerated carbonation. Natural carbonation samples exhibited similar carbonation depths independently of the carbonate type used, conversely to those exposed to accelerated carbonation testing.

Keywords: Calcined clay · limestone · dolomite · ternary binders · carbonation front

1 Introduction

Carbonation is a major durability concern for reinforced concrete structures, especially when concrete is produced with cements with low clinker content [1, 2]. Low-clinker cements are considered a promising solution for reducing the high CO₂ emissions associated with Portland cement production [3]. Clinker production is an energy-intensive operation involving decomposition of limestone, the primary source of CO₂ emissions in the Portland cement industry. Therefore, reducing the clinker content in cements

by using supplementary cementitious materials, without compromising on the performance achievable by those materials, is an efficient solution for lowering CO₂ emissions associated with cement manufacturing. This transition towards sustainable low-clinker cements has led to the development of ternary Portland cements, in which high levels of clinker substitution are possible using a combination of two or more SCMs [4–6]. Mainstream application of such low-carbon cement solutions necessitates a sufficient understanding of the long-term durability performance particularly when exposed to CO₂, a process known as carbonation. Although the use of SCMs can lead to significant environmental savings and advantageous performance enhancements, the carbonation resistance of binders with high contents of SCMs is relatively low.

Studies have shown that the clinker content can be reduced to 50 wt.% or less in blended cements using metakaolin and limestone [7]. Recently, there has been a growing interest in shifting from high-purity metakaolin to lower-grade calcined natural clays for partially replacing clinker due to the abundance and economic benefits that might be associated with using such clays [8]. Metakaolin is a high-value product with niche applications such as ceramic, paint, and paper industries. The low-grade clays, however, may contain associated minerals such as quartz and hematite in addition to kaolinite, reducing their value to the above-mentioned industries [9].

Many studies have described the pozzolanic reactivity of calcined clay as a function of its mineralogical composition [10, 11]. It has been identified that the clay kaolinite content is the primary parameter that determines its reaction potential in a cementitious system. This is associated with the fact that the amorphous alumino-silicate fraction in calcined clays reacts with calcium hydroxide to produce additional calcium alumino-silicate hydrate gel, the main binder in blended Portland cement systems. Adding a carbonate source such as limestone (dominantly CaCO₃) or dolomite (CaMg(CO₃)₂) further modifies the hydrated phase assemblage of these systems, resulting in the formation of carbonate-containing AFm phases [12, 13]. Their formation prevents the conversion of ettringite to monosulphate, leading to a densified microstructure and improvement in compressive strength development [14, 15]. However, dolomite was observed to react at a slower rate compared to limestone in these systems. There is potential for hydrotalcite formation, which is known to influence the carbonation performance of composite cements [16]. Additionally, carbonates form volume-filling hydrate phases that could influence the carbonation performance by pore refinement and acting as CO₂ sink in hemi-carbonate [13, 17].

In this study, a series of binary and ternary blends containing limestone and dolomite as carbonate sources are investigated to elucidate their carbonation performance.

2 Materials and Methods

Commercial ordinary Portland Cement (OPC) (CEM I 52.5R, Heidelberg cements) was used. A flash calcined clay (CCF) supplied by Argeco (France) Ltd. With an estimated kaolinite content of ~ 45 wt.% was sourced. The chemical composition of the materials used in the study is given in Table 1. The specific surface area of the calcined clay was 13.85 m²/g and the R³-reactivity evolved heat [18] of the calcined clay was 460 J/g of SCM, which corresponds to a moderately reactive clay as per [19]. Lime-stone was sourced from Heidelberg cement and dolomite was sourced from SIBELCO,

UK. Laboratory-grade gypsum (calcium sulfate dihydrate, 99%) was used as the sulfate source for preparing the blends.

Table 1. Oxide composition in wt.% of the materials used determined by X-ray fluorescence

	CaO	Al ₂ O ₃	SiO ₂	MgO	SO ₃	K ₂ O	MnO	Fe ₂ O ₃	Na ₂ O	LOI*	Traces
OPC	64.80	3.90	21.80	0.76	3.57	0.67	0.05	1.33	0.30	2.20	0.73
Calcined clay	0.81	22.60	69.30	0.27	0.08	0.28	0.06	2.89	0.37	1.90	1.50
Limestone	52.70	0.98	3.51	0.53	0.11	0.11	0.05	0.43	-	41.50	0.12
Dolomite	31.60	0.26	0.57	20.2	0.05	0.02		0.21	-	46.9	0.12

* LOI stands for loss on ignition at 900 °C determined using a muffle furnace

The OPC was blended with calcined clay (CCF) along with limestone (L) or dolomite (D), and the mix designs of the binders evaluated are shown in Table 2. Addition of gypsum was carried out to account for the dilution of sulfate, the additional gypsum demand due to increased alumina content in the system, and the higher surface area of the cement substitutes, as this has implications in the degree of reaction of the clinker. A 3% gypsum addition was determined as optimal based on calorimetry trials carried out on these blends.

Table 2. Mix design of binary and ternary blends adopted for the study

Mixes ID	OPC (wt.%)	CCF (wt.%)	Limestone (wt.%)	Dolomite (wt.%)	Gypsum (wt.%)
OPC	100	-	-	-	-
L15	82	-	15	-	3
L30	67	-	30	-	3
D15	82	-	-	15	3
D30	67	-	-	30	3
CCF30	67	30	-	-	3
CCF15L15	67	15	15	-	3
CCF15D15	67	15	-	15	3
CCF30L15	52	30	15	-	3
CCF30D15	52	30	-	15	3

Standardised sand (CEN Reference sand, EN 196-1) was used for producing mortars (1:3, binder:sand with water to binder (w/b) 0.5) using a Hobart mixer as per EN 196-1 [20]. Mortar cubes of 25 mm were manufactured for compressive strength testing for the standard mortar mixes. Prismatic specimens (40 × 40 × 160 mm) were produced

for carbonation exposure. Accelerated carbonation was carried out at 1% CO₂, 20 °C and 57% relative humidity (RH) for a period of 180 days using a TFB Carbonator C5. The specimens were cured for 28 days followed by 14 days of preconditioning at 57% RH as per BS EN 12390-1:2021 [21]. Natural carbonation was carried out in a standard conditioning chamber with a controlled temperature of 20 °C and RH of 57%. This was done with the aim to simulate sheltered carbonation conditions with temperature and humidity conditions similar to those used in an accelerated carbonation chamber. Carbonation depth was monitored by spraying a fresh mist of 1% phenolphthalein indicator (prepared in 100 ml isopropyl alcohol) on the freshly broken (using hammer and chisel) surface of the mortar specimens.

In addition, cylindrical cement pastes (w/b: 0.5) of 40 mm diameter and 55 mm height were exposed to natural carbonation with sealed ends to ensure unidirectional carbonation from the circumferential surface. Slices of 4–5 mm were cut from the carbonated specimens to characterise the physical and chemical change along with the carbonation front using scanning electron microscopy in a Zeiss Evo 15 at 20 kV on a polished section in Backscattered electron (BSE) mode. BSE imaging and Oxford Energy dispersive X-ray spectroscopy were used to map spatial variations in the elemental composition.

3 Results and Discussion

3.1 Mechanical Performance of Calcined Clay-Based Blended Portland Binders

Figure 1 presents the compressive strength of all the mortar formulations after 7 and 28 days of curing. The replacement of OPC by 15 wt.% limestone or dolomite promoted a similar compressive strength development at 7 days of curing and a marginal reduction in strength at 28 days. An increase in the replacement level of limestone or dolomite in binary systems reduces the strength at both 7 to 28 days (i.e. L30 < L15 and D30 < D15). However, the addition of calcined clay had a pronounced effect on increasing the compressive strength at 7 days, compared to what was observed in L30 and D30 mixes, due to the high reactivity of the calcined clay. The mixes formulated with 15 wt.% calcined clay and 15 wt.% limestone or dolomite i.e., CCF15L15 and CCF15D15, reported a similar compressive strength at 28 days to that identified in CCF30. This demonstrates the synergistic interaction of calcined clay with carbonates, independently of its source, favouring the development of a strength comparable to that reported for binary binders containing moderately reactive calcined clay. More interestingly, mixes formulated with calcined clay and limestone with a replacement of 45 wt.% OPC (CCF30L15) developed similar strengths to those observed for OPC/dolomite binders (D15) with comparable improvements in early-age compressive strengths values. Limestone addition showed marginal improvement in later age strength compared to dolomite, perhaps due to the higher dissolution of calcite present in limestone than dolomite.

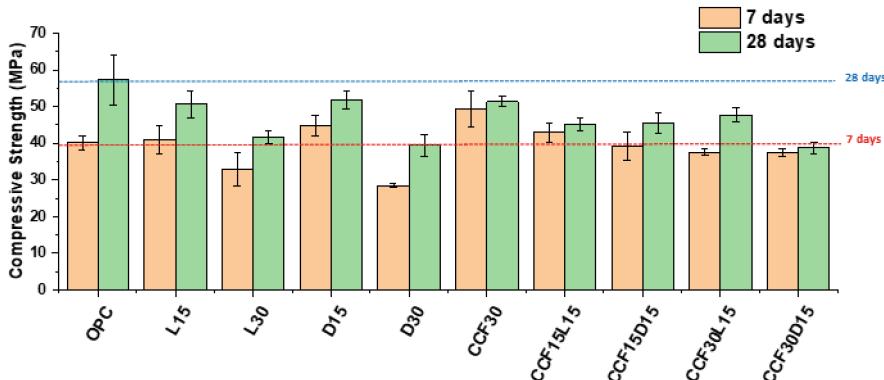


Fig. 1. Compressive strength of binary and ternary mortars containing limestone (L), dolomite (D) and/or calcined clay (CCF) as a function of curing time. Dashed lines indicate the compressive strength of OPC (reference) at 7d and 28d of curing

3.2 Carbonation Performance of Binary and Ternary Systems

Figure 2 presents the carbonation depth data of the 10 blends evaluated in this study. Carbonation depths up to 15 mm were considered to be the maximum carbonation depth measurable on the tested specimens.

The carbonation depth of OPC was minimal at the exposure conditions studied. An increase in the exposure duration beyond the standard recommendation of 70 days in accelerated conditions, induced a slow carbonation progression in OPC (Fig. 2a). An increase in the replacement level of limestone/dolomite from 15 wt.% to 30 wt.% increased the carbonation rate of the blends, with D30 showing a marginal increase in average carbonation depth compared to L30 systems.

Figure 2b shows the carbonation depth for binders containing calcined clays. No significant difference was found between the carbonation depth of CCF30 with L30 or D30 despite the higher portlandite consumption that can be expected from pozzolanic reaction with the calcined clay addition. This could be related to better pore refinement, which might also explain the higher compressive strength of CCF30 compared with L30 and D30 blends [11]. The carbonation depth of CCF30L15 and CCF30D15 with 45 wt.% replacement levels were the highest among all binders evaluated. Notably, the carbonation depth of the 45 wt.% replacement binders by 28 days of exposure was similar to that identified after 100 days of carbonation depth in mixes with 30 wt.% replacement. This indicates that there is not a linear correlation between the level of replacement and the reduction in carbonation resistance of ternary binders.

Early results from natural carbonation after 180 days (Fig. 3) show that the carbonation depth of most binders was similar to OPC. Unlike accelerated carbonation, no significant difference can be observed in natural carbonation for 15 wt.% and 30 wt.% replacement levels. Noticeable higher carbonation depths can be observed in mixes with 45 wt.% replacement for both dolomite or limestone addition i.e., CCF30L15 and CCF30D15.

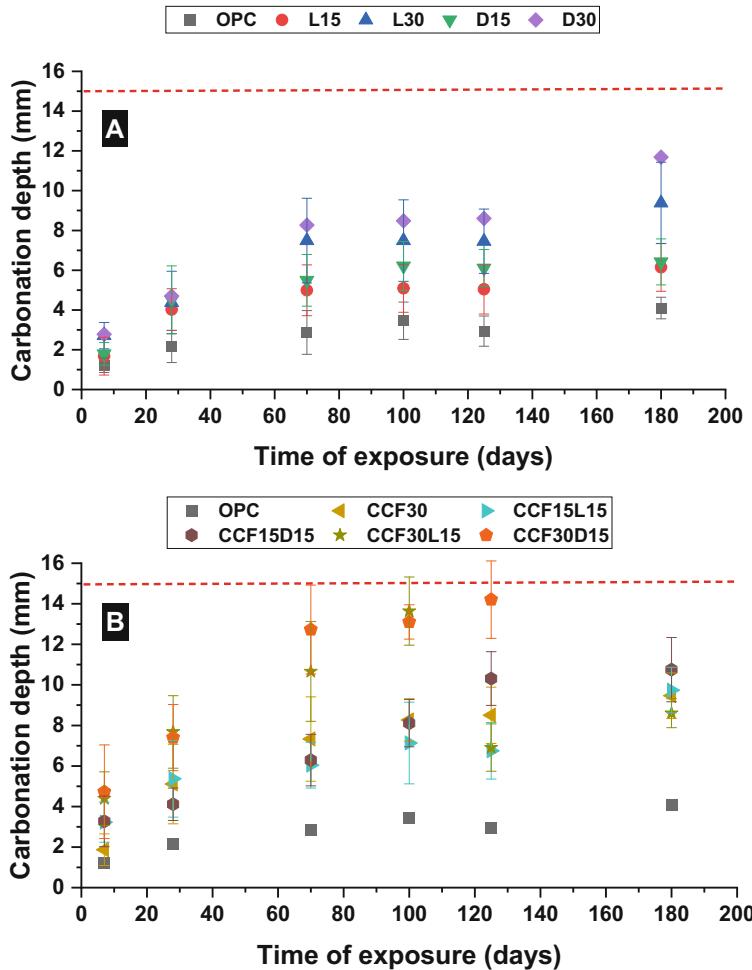


Fig. 2. Accelerated carbonation depths of (A) binary mortars with limestone (L), or dolomite (D) addition; and (B) mortars containing calcined clay (CCF), L and/or D as a function of accelerated carbonation exposure time. The red line indicates the maximum measurable carbonatable depth of the samples assessed

3.3 Microscopy Analysis of the Carbonation Front

Although carbonation depths are useful for the comparison of the potential performance of different blend formulations, values determined using a pH indicator offer limited insight into the carbonation mechanism, specifically the chemical or physical changes occurring in the samples at the carbonation front. In this study, preliminary analysis of OPC and CCF30 pastes exposed to atmospheric CO₂ for 120 days in controlled conditions (57% RH and 20 °C) were analysed by SEM. Figure 4 presents the carbonation front of the OPC and the blended mix with 30 wt.% replacement by calcined clay (CCF30). In Fig. 4A and 4D three distinctive regions can be identified: (i) an highly porous and

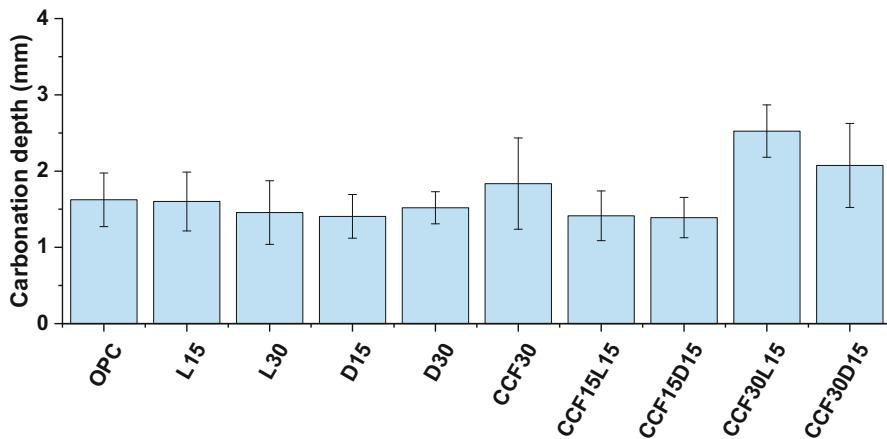


Fig. 3. Natural carbonation depths of binary and ternary mortars containing limestone (L), dolomite (D) and/or calcined clay (CCF) after 180 days of exposure

heterogeneous region near the edge of the sample, followed this by (ii) a highly dense region where only small white particles that can be assigned to unreacted OPC can be observed, followed this by (iii) a more porous and heterogeneous region where small pores, unreacted OPC and a binding phase is identified, consistent with the microstructure of the uncarbonated material. EDX map showed that sulfate is found to be depleted in this region. The sulfate depletion is most likely associated with the decomposition of ettringite leading to the formation of gypsum, consistent with observations in previous studies [22, 23]. Since gypsum formation creates a concentration gradient of sulfate, the soluble sulfate in gypsum tends to move inwards from the exposed surface creating a sulfate front, as seen in the EDX maps. Additionally, alkalis are concentrated in the carbonated region, which might be due to the leaching or binding of a higher amount of alkalis in the low Ca/Si C-A-S-H, as shown in [24]. The release of alkalis could be potentially associated with the decalcification of C-(N)-A-S-H during carbonation. The depth of this decalcification region in OPC and CCF30 was found to be 110 μm and 250 μm , respectively, after 120 days of CO_2 exposure. Such local microstructural features indicate that there are significant differences in the formation of a carbonation front in composite lower clinker cements compared with OPC systems.

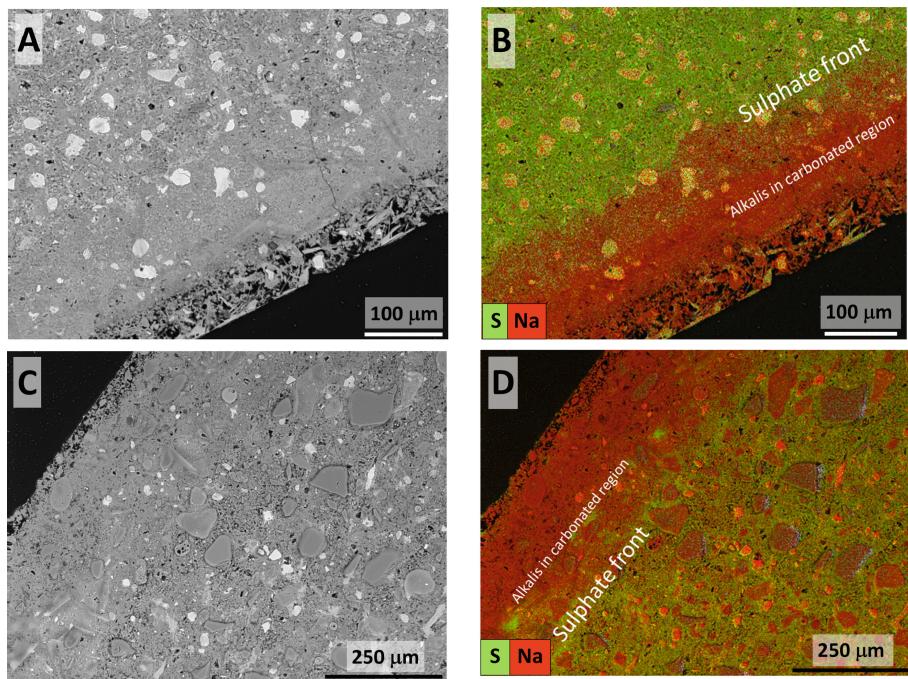


Fig. 4. BSE micrographs of (A) OPC and (C) CCF30, along with (B, D) BSE with sulfur (S) and sodium (Na) EDX maps overlaid respectively, after 120 days in natural carbonation

4 Conclusions

Ternary cements containing limestone or dolomite develop compressive strengths of more than 30 MPa after 7 days of curing even at 30 and 45 wt.% replacement levels, which indicates that it is feasible to produce materials of high compressive strength at such high replacement levels.

The replacement of OPC by either calcined clay or calcined clay and a carbonate source, reduces the carbonation resistance of such binders. Binary and ternary blends with 30 wt.% replacement have similar carbonation performance, demonstrating that limestone or dolomite addition do not increase the carbonation susceptibility of composite binders.

The carbonation depth of calcined clay-limestone and calcined clay-dolomite with a 45 wt.% replacement was fourfold that of OPC, indicating that there is not a linear correlation between the level of replacement and increase in carbonation rate.

Scanning electron microscopy reveals formation of three distinctive regions in the carbonation front of both OPC and CCF30 mixes with significant changes in density and chemical composition. More studies focused on the characterization of the carbonation front are necessary to elucidate how carbonation proceeds in these samples.

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