Understanding the Carbonation Performance of Cements Containing Calcined Clay

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Abstract. Low-purity calcined clays are becoming increasingly popular as supplementary cementitious materials (SCMs) due to their wide availability, and potential ability to reduce the carbon footprint associated with concrete production. To ensure the longevity of concrete structures, it is crucial to understand the mechanisms governing long-term durability when using new SCM-containing cement formulations. Understanding of the carbonation resistance of cements containing calcined clay is limited, and this remains a concern. This research is part of the collaborative USA-UK project "Response to CO_2 exposure of concrete with natural supplementary cementitious materials" (RENACEM), aiming to understand the connections among the properties of natural clays, activation treatments to enhance their chemical reactivity, and the response to CO_2 exposure of cements, mortars and concretes produced with them. The current study presents the carbonation resistance results of binary and ternary materials containing calcined clays upon exposure to natural CO_2 concentrations under controlled relative humidity (57% RH), resembling in-service conditions. Four cement compositions were studied, including a CEM I (OPC), CEM I with 30% limestone substitution (L30), CEM I with 30% calcined clay substitution (CCF30) and CEM I with 30% calcined clay + 15% limestone (CCF30L15). The carbonation performance of these binders was monitored using pH indicators on cement paste and mortar specimens. Scanning electron microscopy coupled with EDX was used to identify the carbonation front. The results demonstrate that chemical alterations identified using analytical techniques can be used to characterise the reaction front of these materials, offering more insights into the effect of carbonation beyond potential changes in alkalinity of these systems.

Keywords: Carbonation · Calcined clays · microstructure · carbonation front

1 Introduction

High-volume replacements of Portland clinker using supplementary cementitious materials (SCM) is a major route to producing low carbon cements. Thermally-activated low-purity clays are gaining prominence as SCMs instead of conventional SCMs, such as fly ashes and slags. In general, using SCMs leads to significant environmental benefits

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and durability performance enhancements, including chloride ingress, sulphate attack and alkali silica reaction [1]. However, these low clinker cements containing calcined clays are more prone to carbonation, which is a durability concern for reinforced concrete structures [2, 3]. Since carbonation leads to pH reduction in cementitious materials, reinforced concrete made with low clinker cements is susceptible corrosion of steel reinforcement [4]. Many studies use conventional accelerated test methods to assess the performance of new cementitious materials. Some of the standard approaches, such as pH indicators, offer limited insights into the chemical alterations, specifically when faced with differences in phase assemblages in the composite cements. Long-term durability performance upon exposure to CO_2 is one of the major considerations that hinder the adoption of low-clinker cement in concrete construction, particularly in infrastructure projects. In this study, cement pastes and mortars were prepared from four cement blends: Ordinary Portland cement (OPC), binary blends containing 30% limestone or 30% calcined clay, and a ternary blend containing 30% calcined clay and 15% limestone. Carbonation performance was assessed using conventional pH indicator and scanning electron microscopy to probe physicochemical alterations due to carbonation.

2 Materials and Methods

Commercial ordinary Portland cement (CEM I 52.5R, Heidelberg Cement) was used. A flash calcined clay (CCF) was supplied by Argeco (France) Ltd., with an estimated kaolinite content of ~ 50 wt.%. The chemical compositions of the materials used in the study are given in Table 1. Limestone was sourced from Heidelberg Cement. The OPC was blended with calcined clay (CCF) along with limestone (L), and the mix designs of the binders evaluated are shown in Table 2. Sulphate contents were optimised based on calorimetry experiments. About 3% laboratory-grade gypsum (calcium sulphate dihydrate, 99%) was used as the sulphate source.

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

	CaO	Al_2O_3	SiO_2	MgO	SO_3	K_2O	MnO	Fe_2O_3	Na_2O	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

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

Prismatic specimens (40 × 40 × 160 mm) were produced for carbonation exposure using standard mortar as per EN 196 -1 [5]. Cement pastes (w/b: 0.5) were cast as cylindrical specimens of about 35 mm diameter and 55 mm height and cured for 28 days in sealed conditions. The specimens were exposed to natural carbonation with ends sealed to ensure unidirectional, circumferential carbonation. Natural carbonation was carried out in a standard conditioning chamber with a controlled temperature of

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	–	–	–	–
L30	67	–	30	–	3
CCF30	67	30	–	–	3
CCF30L15	52	30	15	–	3

20 °C and 57% RH, simulating sheltered carbonation conditions with temperature and humidity conditions similar to those commonly used in accelerated carbonation studies. Carbonation depths were monitored by spraying fresh mists of 1% phenolphthalein and 1% thymolphthalein indicator (each prepared in 100 ml isopropyl alcohol) on freshly broken surfaces of mortar specimens. For cement pastes, sliced discs were immersed in isopropyl alcohol for 10 min after cutting before testing with pH indicators. A small portion of the cement paste discs from the carbonated edge was dried and impregnated with low viscous epoxy resin under vacuum and polished for observation using scanning electron microscopy in a Zeiss Evo 15 at 20kV and working distance of 8.5mm in backscattered electron (BSE) mode.

3 Results and Discussion

3.1 Carbonation Assessment in Cement Mortars

Figure 1 shows the carbonation depths for the four cements after 365 days. These were 1.27 mm (±0.41), 1.72 mm (±0.45), 1.60 mm (±0.34) and 2.35 mm (±0.58) for OPC, L30, CCF30 and CCF30L15, respectively. No significant differences were found between the carbonation depths of OPC, L30 and CCF30. Although CCF30 would be expected to have less portlandite reserves due to the pozzolanic reaction from calcined clay addition, the difference in carbonation depth after 1 year was limited, due to pore refinement. Noticeably higher carbonation depths were observed in mixes with 45 wt.% replacement i.e., CCF30L15. As seen in Fig. 1, measurement using pH indicator didn't offer much insight on the difference between the cements, despite undoubted differences in pore structure and phase assemblage. Even though 1 year is a short time span in terms of carbonation under natural conditions, the carbonation reaction occurs from this early period, and identifying differences in carbonation mechanisms from early age may offer in-depth insights on the progression of the carbonation front, to model and predict long-term carbonation in reinforced concrete structures.

3.2 Carbonation Assessment in Cement Paste

Cement pastes exposed to the same conditions as mortars i.e., atmospheric CO_2 and 57% RH, were used to characterise the carbonation front. Figure 2 shows images of carbonation depth measurements carried out using pH indicator after 240 days of exposure. Carbonation depths were 0 (no visible region for measurement), 0.75 mm (±0.06), 0.36 mm

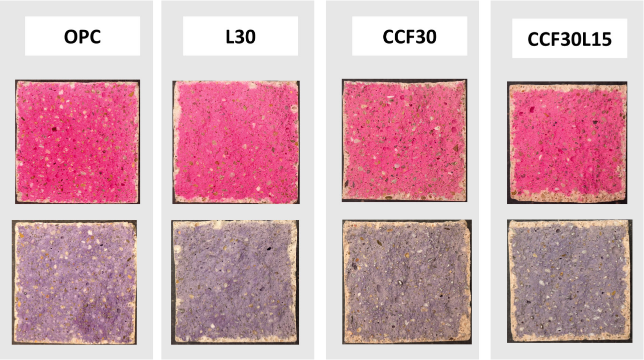

Fig. 1. Carbonation measurement in cement mortar after 1 year of carbonation exposure (Atmospheric CO_2 and RH 57%) using 1% phenolphthalein and 1% thymolphthalein indicator

(±0.14) and 0.77 mm (±0.05) for OPC, L30, CCF30 and CCF30L15, respectively. L30 and CCF30L15 showed higher and more noticeable carbonation depths compared to OPC. Interestingly, CCF30, with 30% calcined clay replacement, showed a lower carbonation depth; likely due to pore refinement [6]. Similar to the observation on cement mortar, CCF30L15 showed a higher carbonation depth.

In order to gain more insights on the carbonation progress, the exposure surface was observed using a SEM. Figure 3 shows a typical microscope image of a carbonation front in OPC (OPC Natural carbonation) compared to a cement paste cured (OPC cured) under sealed conditions. EDX mapping was performed to study the difference in elemental distributions along the carbonation front. As seen in Fig. 3, carbonated regions showed sulfate depletion due to ettringite carbonation, which is consistent with observations in previous studies [7, 8]. Also, 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 formed due to decalcification [9].

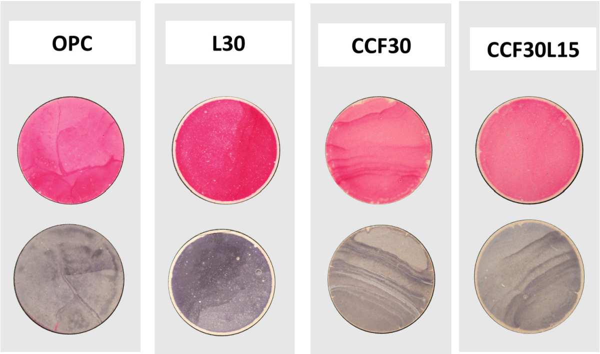

Fig. 2. Carbonation measurement on cement after 240 days of carbonation exposure (Atmospheric CO_2 and RH 57%) using 1% phenolphthalein and 1% thymolphthalein indicator

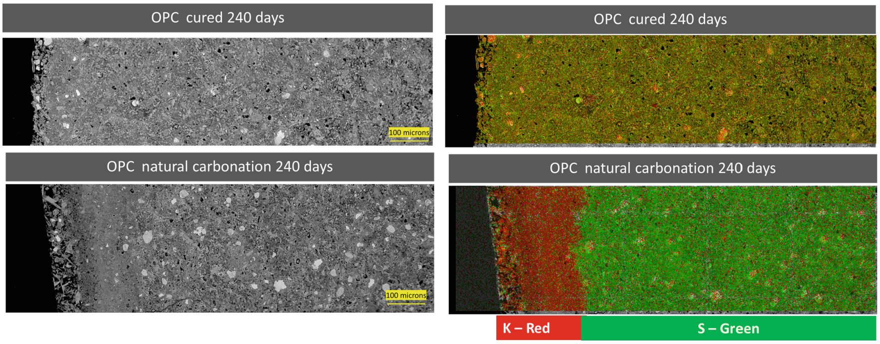

Fig. 3. Microscopic image and elemental distribution of OPC sealed cured and carbonated for 240 days.

Line scans were taken from the exposure surface to approximately 2 mm depth. About 5 line scans were chosen on the SEM image, and each line was scanned for 5 frames to improve reliability of the data acquisition and analysis. Figure 4 presents the line scans for each cement with the distribution of sulphate and potassium. The sulphate-depleted and potassium-enriched regions overlap quite clearly each scan, which confirms the elemental distribution in the EDX maps, Fig. 3, and reflects the carbonation process in these microstructures. L30 showed highest carbonation affected depth, of about 800 micrometer (0.8 mm), which matched with the carbonation depth obtained using pH indicator (about 0.75 mm).

Based on Fig. 4, early carbonation of OPC to a depth of about 200 mm, was captured using elemental distribution, unlike pH indicators. Cements containing calcined clays i.e., CCF30 and CCF30L15, showed similar carbonation reaction depths, to about 200–300 micrometer, and L30 showed a carbonated region of 800 micrometer due to higher porosity. Absolute wt% of K was lower in CCF30L15 due to high volume replacement of clinker causing dilution of alkalis. Another noticeable difference was the more gradual change in sulphate content in L30, spanning from 400 to 800 micrometer from the exposed surface, reflecting the partially carbonated region within the matrix. This transition zone was much sharper for OPC and may be due to pore blocking effect along the carbonation front due to calcite formation from the remnant of CH reserves present in the partially carbonated zone in OPC (as shown in Fig. 3). Pore refinement limiting CO_2 diffusion is the major reason for lower carbonation depth observed by 240 days in the case of calcined clay binders.

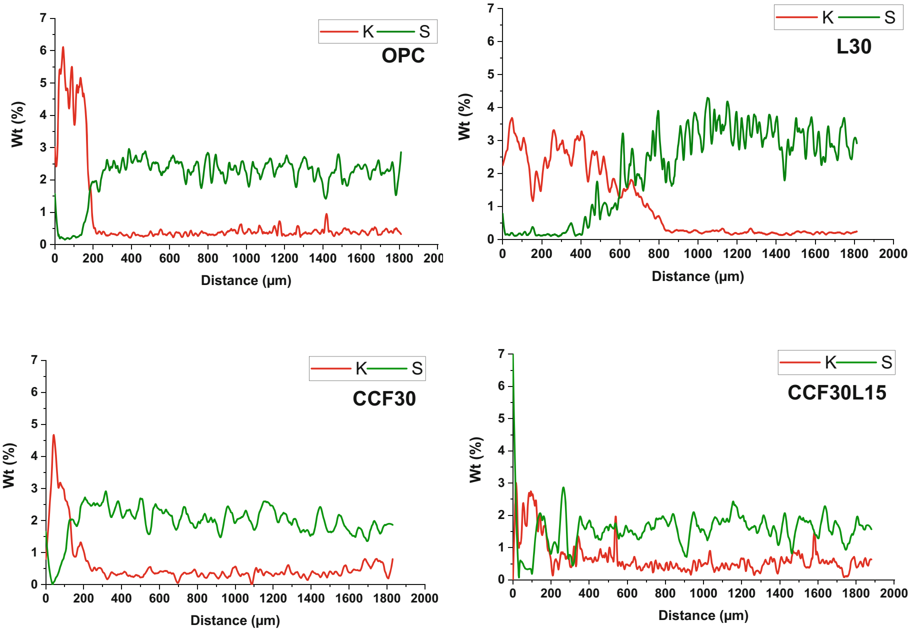

Fig. 4. Line scan using EDX on showing difference in the distribution of sulphates and alkalis along the carbonation front

4 Conclusions

Carbonation of calcined clay binders was studied by scanning electron microscopy to develop insights on carbonation reactions. Assessment of the carbonation-affected zone, obtained using EDX maps, reveals chemical alteration along the carbonated region that can be linked to carbonation of hydration products. Application of this technique reveals differences in the carbonation-affected region between blends containing 30% limestone and 30% calcined clay, despite them showing similar carbonation depths in cement mortars. The elemental distribution also gradually changed in each carbonation affected region, indicative of a partially carbonated region within the microstructure instead of the abrupt carbonation front indicated using pH indicator. Such characterization approaches can be used in future to study the carbonation mechanism with a focus on the understanding the role of chemical additives, including alkalis, on carbonation performance and the role of RH on the partially carbonated region in low clinker cements.

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References

1. Dhandapani, Y., Sakthivel, T., Santhanam, M., et al.: Mechanical properties and durability performance of concretes with Limestone Calcined Clay Cement (LC3). Cem. Concr. Res. **107**, 136–151 (2018). https://doi.org/10.1016/j.cemconres.2018.02.005
2. von Greve-Dierfeld, S., Lothenbach, B., Vollpracht, A., et al.: Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC. Mater Struct Constr **53** (2020). https://doi.org/10.1617/s11527-020-01558-w
3. Saillio, M., Baroghel-Bouny, V., Pradelle, S., et al.: Effect of supplementary cementitious materials on carbonation of cement pastes. Cem. Concr. Res. **142** (2021). https://doi.org/10.1016/j.cemconres.2021.106358
4. Angst, U.M.: Steel corrosion in concrete – Achilles' heel for sustainable concrete? Cem. Concr. Res. **172**, 107239 (2023). https://doi.org/10.1016/j.cemconres.2023.107239
5. 196–1:2016 E (2014) Methods of testing cement Part 1: Determination of strength
6. Dhandapani, Y., Santhanam, M.: Assessment of pore structure evolution in the limestone calcined clay cementitious system and its implications for performance. Cem. Concr. Compos. **84**, 36–47 (2017). https://doi.org/10.1016/j.cemconcomp.2017.08.012
7. Georget, F., Soja, W., Scrivener, K.L.: Characteristic lengths of the carbonation front in naturally carbonated cement pastes: Implications for reactive transport models. Cem. Concr. Res. **134**, 106080 (2020). https://doi.org/10.1016/j.cemconres.2020.106080
8. Collier, N.C., Heyes, D.W., Butcher, E.J., et al.: Gaseous carbonation of cementitious backfill for geological disposal of radioactive waste: nirex reference vault backfill. Appl. Geochem. **106**, 120–133 (2019). https://doi.org/10.1016/j.apgeochem.2019.04.020
9. L'Hôpital, E., Lothenbach, B., Scrivener, K., Kulik, D.A.A.: Alkali uptake in calcium alumina silicate hydrate (C-A-S-H). Cem. Concr. Res. **85**, 122–136 (2016). https://doi.org/10.1016/j.cemconres.2016.03.009