

Elucidating the carbonation front in blended calcined kaolinite clays binders using analytical techniques

Y. Dhandapani¹, L. Black², M. C. G. Junger³ and S. A. Bernal⁴

Email: Y.Dhandapani@leeds.ac.uk

¹School of Civil Engineering, University of Leeds, Leeds, United Kingdom

Email: L.Black@leeds.ac.uk

² School of Civil Engineering, University of Leeds, Leeds, United Kingdom

Email: mjuenger@mail.utexas.edu

³Architectural and Environmental Engineering, University of Texas at Austin, USA

Email: S.A.BernalLopez@leeds.ac.uk

⁴School of Civil Engineering, University of Leeds, Leeds, United Kingdom

ABSTRACT

Low-purity calcined clays are gaining traction as new sources of supplementary cementitious materials (SCMs) to produce sustainable low-clinker cements. Sustainable use of binders must also be linked with ensuring the durability of concrete structures. It is then crucial to develop a fundamental understanding of mechanisms governing long-term durability of new SCM cement formulations. Carbonation performance is commonly determined using a pH indicator, which gives a speculative indication of the affected region. However, numerous physicochemical changes occur in the microstructure that govern the progression of the carbonation front, which cannot be traced and explained using carbonation depth measurement per se. This study characterised the carbonation front of calcined clay-blended binders using conventional pH indicators, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDX). The microstructural variation at the carbonation front could be used to explain the reaction mechanism. While OPC showed densification along the carbonation front, calcined clay cements showed a visible increase in porosity during carbonation. The progression of the carbonation-affected depth shows densification along the reacted front, a layer enriched in sulfate ahead of the front (diffusing inwards due to the decomposition of ettringite in the carbonated region) and a higher concentration of alkalis within the carbonated region. While the conventional pH indicator did not show any signs of carbonation in reference Portland cement paste, the microstructural investigation does reveal the underlying carbonation process and presents a more rational approach to assess and benchmark the carbonation performance of low clinker cements. This combined approach gives unique insights to explain the carbonation performance of new sustainable cements.

KEYWORDS: *Carbonation; Calcined clays; sulfate front; alkalis; microstructure*

1. Introduction

Low-clinker cements containing calcined clays are a promising solution for reducing carbon emissions associated with Portland cement production (Scrivener, John and Gartner, 2018). Application of such low-carbon cements requires a sufficient understanding of their long-term durability performance, particularly when exposed to CO₂, a process known as carbonation. Carbonation is a major durability concern for reinforced concrete structures that could lead to reinforcement corrosion, especially when concrete is produced with cements containing high-volume replacement of Portland clinker (von Greve-Dierfeld *et al.*, 2020; Saillio *et al.*, 2021). Although using SCMs can lead to significant environmental benefits and advantageous performance enhancements for numerous durability-related conditions, the carbonation resistance of binders with high contents of SCMs is not well understood yet, and it has been

identified to be relatively low based on accelerated test methods. The testing conditions adopted when applying such methods do not resemble natural environmental conditions, and therefore it is unclear how accurately accelerated testing can help understand the performance of sustainable cements. This study focuses on characterising the carbonation process in cement paste exposed to atmospheric CO₂ conditions to develop insights into the underlying carbonation interaction with the hydrated cementitious matrix formed in calcined clay-containing cements.

2. Materials and Methods

A 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 ~50 wt.% was used as a calcined clay source at 30 wt.% cement replacement to produce blended cements (denoted as CCF30 hereafter). The chemical compositions of the materials used in the study are given in Table 1.

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 CCF	0.81	22.60	69.30	0.27	0.08	0.28	0.06	2.89	0.37	1.90	1.50

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

Cylindrical specimens of 33 mm diameter and 50 mm were prepared using cement paste mixed using a high shear mixer at 1600 rpm for 2 min. Specimens were sealed and cured for 28 days before exposure to atmospheric CO₂ in a standard conditioning chamber with a controlled temperature of 20 °C and RH of 57%, simulating sheltered carbonation conditions. Carbonation depth was monitored by spraying a fresh mist of 1% phenolphthalein indicator and thymolphthalein indicator (prepared in 100 ml isopropyl alcohol) on fresh slices (4-5 mm thickness) of cement paste cut using Struers Secotom Precision Cutting Machine. Discs were immersed in isopropyl alcohol for a period of about 20 min to remove free water from cutting before using pH indicator. Slices of cement paste containing carbonation edge were impregnated using low viscosity epoxy to characterise the physical and chemical changes along with the carbonation front using a Zeiss Evo 15 scanning electron microscope (SEM) at 20KV at a working distance of 8.50 mm with a backscattered electron (BSE) detector coupled with an Oxford Energy dispersive X-ray spectrometer.

3. Results and Discussion

2.1 Carbonation depth determined using a pH indicator

Fig 1 shows the carbonation depth of OPC and calcined clay binder revealed using different pH indicators – the most widely used and standardised method to determine carbonation depths in cementitious systems. The OPC paste did not show signs of carbonation after 240 days' exposure when evaluated using either indicator. CCF30 showed a visible carbonation depth, i.e., change to colourless, indicating that carbonation reaction had occurred, lowering pH in that region. About 8 points along the disc were measured using a digital calliper, and images obtained using handheld digital microscope. The average carbonation depth was 0.36 ± 0.14 mm after 240 days of carbonation.

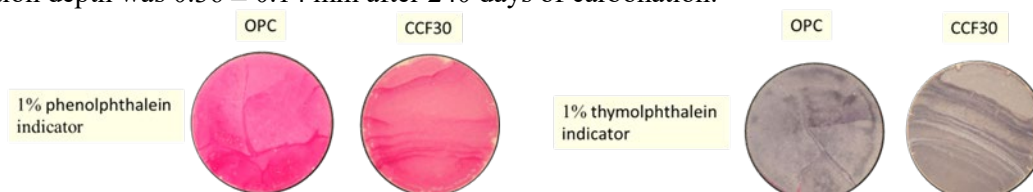


Figure 1 Photograph of cement paste slices after sprayed with two different pH indicator

2.2 SEM analysis of the carbonated regions

SEM micrographs were obtained at 250X to observe a large area near the carbonation front (Fig 2). A specimen sealed and cured for 240 days was used to compare and identify the microstructure changes due to carbonation. While the cement paste kept in sealed conditions showed a homogenous microstructure with no signs of physical alterations along the exposure surface for both OPC (Fig 2A) and CCF30 (Fig 2C), specimens subjected to carbonation showed variations in the microstructure along the carbonation surface. In the case of OPC (Fig 2B), a denser microstructure along the carbonation front, i.e., initial 100-200 micrometers was observed upon carbonation. This could be attributed to the precipitation of carbonation reaction products along the exposed front, consistent with observation of carbonation in OPC systems (Shah *et al.*, 2018). In the case of CCF30 (Fig 2D), there was a more prominent change in the microstructure upon carbonation showing an increased porosity in the carbonated region, similar to the observations by Shah *et al.* (Shah *et al.*, 2018). Additionally, the depth of the affected region, showing an increase in porosity, was higher in the case of the calcined clay binder.

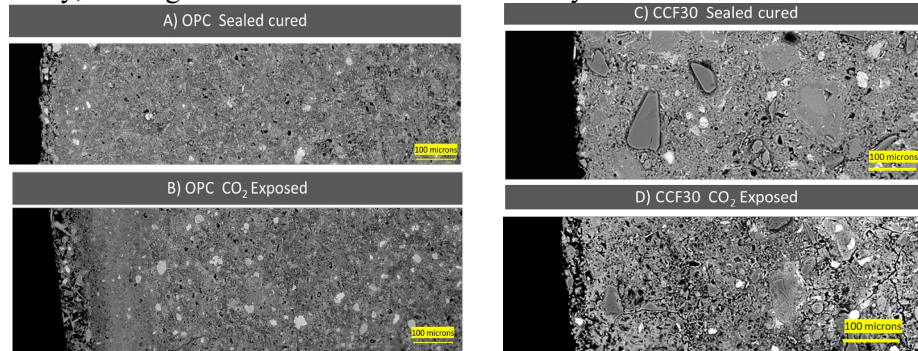


Figure 2 Micrographs showing carbonation front in OPC and CCF30

2.3 Chemical analysis of the carbonated regions

Figure 3 presents the EDX maps of OPC after 120 days (Fig. 3A) and 240 days (Fig. 3B) of carbonation. It can be seen that sulfate was depleted in the carbonated region, and the depth of this sulfate depletion increases as carbonation progresses, consistent with observations in previous studies (Collier *et al.*, 2019; Georget, Soja and Scrivener, 2020). The sulfate depletion is most likely associated with the decomposition of ettringite, leading to the formation of gypsum. Gypsum formation could lead to a concentration gradient of sulfate, enabling inwards movement of sulfate, as observed from the EDX maps. Additionally, ettringite carbonation is often reported to occur when pH reaches about 9.7 at high levels of reacted CO_2 (Shi *et al.*, 2016). This demonstrates that EDX maps could be used as an alternative method to measure the region affected by carbonation by tracing the carbonation of the ettringite phase formed in the low clinker cements. Alkalis were concentrated in the carbonated region (showed in Figures 3A and 3B by potassium) due to the leaching upon carbonation of both anhydrous clinker or reaction products, or potential binding of a higher amount of alkalis in the low Ca/Si calcium aluminium silicate hydrate (C-A-S-H). Further investigation to explain the increased concentration of alkalis in the carbonated region is required.

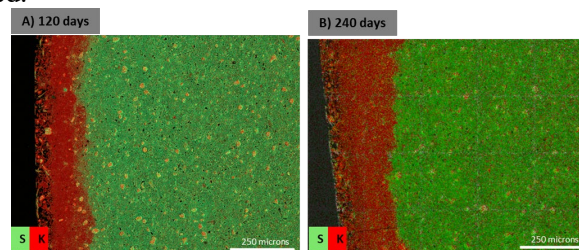


Figure 3 EDX maps of carbonated OPC for (A) 120 days and (B) 240 days

The carbonation-affected depth from EDX data was obtained using the built-in Aztec software tool, analysing maps obtained in two different locations. Four depth measurements were taken in each map. Figure 4 summarises the depth (average of 8 depth measurements) of sulfate depletion in the region considered to be carbonation-affected region. Although OPC specimens showed no signs of carbonation using the pH indicators, EDX maps show a possible carbonation affected region of 110 and 275 μm after 120 and 240 days of carbonation, respectively. CCF30 showed a carbonation affected depth of about 265

and 386 μm after 120 and 240 days, respectively. Additionally, the carbonation depth of CCF30 at 240 days compares well with the depth measurement obtained when using a pH indicator, i.e., 0.36 mm, indicating that there is likely underestimation of the carbonated region in OPC, when using standardised testing methods based on pH indicators, as those only capture depletion of portlandite rather than carbonation of other binding phases, which could lead to bias in the interpretation of the carbonation performance of low clinker cement.

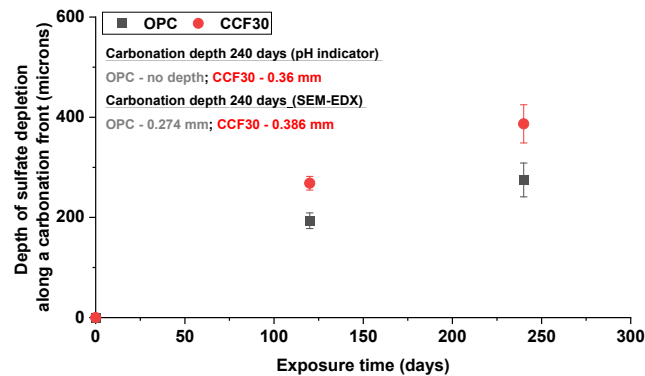


Figure 4 Carbonation depth obtained from EDX elemental maps for OPC and CCF30

4. Conclusions

Characterisation of carbonated specimens using electron microscopy reveals that pH indicators can underestimate the carbonation occurring in the OPC system. There is visible densification due to carbonation in OPC, while cements containing calcined clay may tend to show increased porosity. Estimation of the carbonation-affected zone, obtained using EDX maps, reveals a similar progression of carbonation front in OPC and calcined clay binders over time, unlike the phenolphthalein indicator measurement. The sulfate front formed along the carbonation exposure surface should be investigated further to explain the role of other reaction products during carbonation in low clinker cements.

Acknowledgements

This study was sponsored by the National Science Foundation (NSF) through award 1903457 and the UK Engineering and Physical Sciences Research Council (EPSRC) through grant EP/T008407/1.

References

- Collier, N. C. *et al.* (2019) 'Gaseous carbonation of cementitious backfill for geological disposal of radioactive waste: Nirex Reference Vault Backfill', *Applied Geochemistry*, 106, p. 120–133.
- Georget, F., Soja, W. and Scrivener, K. L. (2020) 'Characteristic lengths of the carbonation front in naturally carbonated cement pastes: Implications for reactive transport models', *Cement and Concrete Research*, 134, p. 106080.
- von Greve-Dierfeld, S. *et al.* (2020) 'Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC', *Materials and Structures/Materiaux et Constructions*, 53(6).
- L'Hôpital, E. *et al.* (2016) 'Alkali uptake in calcium alumina silicate hydrate (C-A-S-H)', *Cement and Concrete Research*, 85, p. 122–136.
- Saillio, M. *et al.* (2021) 'Effect of supplementary cementitious materials on carbonation of cement pastes', *Cement and Concrete Research*, 142, p. 106358
- Scrivener, K. L. *et al.* (2018) 'Eco-efficient cements: Potential economically viable solutions for a low- CO_2 cement-based materials industry', *Cement and Concrete Research*, 114, p.p. 2–26.
- Shah, V. *et al.* (2018) 'Changes in microstructure characteristics of cement paste on carbonation', *Cement and Concrete Research*, 109, pp. 184–197.
- Shi, Z. *et al.* (2016) 'Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars', *Cement and Concrete Research*, 88, pp. 60–72.