A Review on Durability Performance of Calcined Clay Binders for Adoption in the Construction Industry

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Abstract. Calcined clays are considered one of the most promising sources of supplementary cementitious materials (SCMs) for substituting Portland clinker in the production of concrete. Natural clays have been extensively studied for optimizing pre-conditioning treatments to increase their reactivity, and consequently the hydration, and mechanical properties of low energy binders produced with them. Studies on durability performance are essential for providing the confidence required for the widespread adoption of calcined clays as SCMs. This paper analyse the suitability of calcined clay containing binders in different exposure environments to facilitate its adoption, and presents a brief overview of durability performance of cementitious materials produced with kaolinitic or non-kaolinitic calcined clays. Also, the research needs that will facilitate the adoption of calcined clays in construction projects, as well as the physico-chemical alterations introduced by calcined clays in the hydrated cement matrix is discussed.

Keywords: Calcined clays · Durability · Carbonation · Chlorides · Performance

1 Introduction

Activated clays are a widely available resource and have been extensively used as Portland cement substitutes in the production of concretes. Typically, the reactivity of the clays is increased after activation by thermal (calcination) [1] or mechanical (grinding) [2] treatments. Several sources of clays are available globally with variations in mineralogy and purity [3–5]. These differences make treated clays highly versatile materials to produce SCMs that enables the production of cementitious systems with bespoke performance. Kaolinitic clays have been reported to be more reactive than 2:1 clays, such as illite, montmorillonite, when thermally activated [1]; however, it is well known that optimized reactivity can be achieved if appropriate calcination conditions are selected considering the clay mineralogy [6, 7]. Kaolinite clay has been studied extensively in the context of construction materials [4]. Several other alternative clays sources have also been identified, such as marine dredges [8, 9], clay waste from the paper manufacturing industry [5], and mixed clays or clayed excavated soils [10]. The present overview will only centre on durability aspects of materials containing calcined natural clays.

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The aluminosilicates reactive phases in different clays induces distinct variations in the reaction chemistry and microstructure evolution when blended with Portland cements [11]. Upon hydration, aluminates from the calcined clay sources react with carbonate added to the cementitious system such as limestone, dolomite or marble dust to produce additional reaction products such as carboaluminates [12–14]. The reaction from aluminates in calcined clay and calcite present in limestone sources leads to the formation of mono- and hemi- carboaluminates, i.e., CO_3-AFm (Alumino Ferrite- mono) phases. These hydration products have better space-filling characteristics due to lower density states compared to calcium silicates hydrate (C-S-H) and portlandite (CH) [15]. The combination of calcined clay with limestone induces a significantly improved strength development at an early age than the results observed when using calcined clays alone [11, 16–18]. When using lower grade clay seems to enable higher replacement levels of Portland clinker to those achievable with pure metakaolin (below 20%) [19].

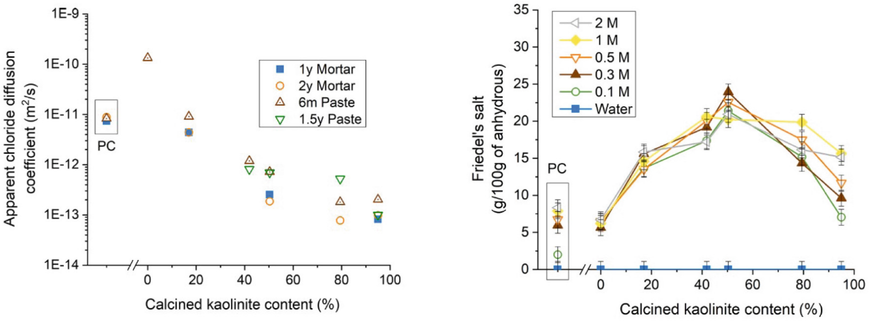
The physicochemical characteristics of the blended calcined clay-Portland cement binders are governed by several factors, including (but not limited to) the clay types and activation treatment, purity, mineralogy, substitution level, among others. Such a wide range of factors consequently induces differences in the durability performance of concrete produced with calcined clay containing binders. Depending on the exposure environment, such as those rich in chlorides, sulphates or CO_2, the performance of blended concretes varies compared to concretes produced with plain Portland cement (PC). Based on the environmental exposure, the response of the material is also altered in terms of chloride/CO_2 binding and/ or chemical interaction with aggressive solutions, which can impact the long-term performance of concretes produced with calcined clays.

This paper presents a brief overview of the performance of calcined clay binders in different durability exposure environments. The need for more systematic studies, particularly on the carbonation of calcined clay containing binders is emphasized.

2 Durability Performance of Calcined Clay Containing Binders

2.1 Chloride Ingress

Ingress of chlorides is one of the primary causes for deterioration of steel reinforced concretes. There is a good consensus that concrete chloride resistance is improved significantly with the addition of calcined kaolinite clay due to the combined effect of refined pore structure [20, 21], and improved chloride binding capacity due to the reactive aluminates from calcined clays [21, 22] which favors the formation of Friedel's salt. The apparent chloride diffusion (and migration) coefficient was found to be reduced by nearly an order of magnitude in mortar or concrete containing calcined clay [16, 20, 21, 23, 24]. Chloride ingress is strongly influenced by the kaolinite content of the clay, i.e., the higher the kaolinite content, the lower the apparent chloride diffusion coefficient [21], as shown in Fig. 1a. However, this trend was evident only at lower kaolinite content (10 to 50%). At high kaolinite content (above 50%), the enhancement in chloride resistance was minimal due to limited pore refinement for calcined clay with kaolinite content above 60% [11]. A comparison of binary cementitious systems with calcined kaolinite clay and ternary combination with calcined clay-limestone have shown a minimal variation in chloride ingress rate in concretes produced with them [17].



(a) (b)

Fig. 1. Influence of kaolinite content on (a) chloride diffusion coefficient and (b) chloride binding, from [21].

Although chloride binding has been demonstrated to increase with the blending of calcined clays with Portland cement [21, 22], it seems that a higher binding capacity is achievable when using calcined clay with 40–50% kaolinite clay than what could be obtained with high purity clays. Specifically, in calcined clay-limestone, more carboaluminate form with lower grade calcined clays which facilitate more chloride binding, as shown in Fig. 1b. Furthermore, it has been reported that there is an impact on the chloride binding capacity identified in these materials can be impacted by the pH of the chloride rich solution. A reduction in pH of the chloride exposure is likely to increase the chloride binding capacity of calcined clay containing cements [25, 26]. On the contrary, internal pH reduction associated with CH consumption due to the pozzolanic reaction of calcined clay, has been shown to reduce the chloride threshold value [24]. Herein, the reduced alkalinity could affect the corrosion resistance of reinforced concrete structures containing calcined clays, which needs to be assessed in field exposure studies.

The role of calcined kaolinite clays regarding chloride ingress in concrete are well understood. However, studies on calcined clays with varying clay mineralogy are spare. In addition, it remains largely unclear what is the role of microstructure, in terms of pore structure, tortuosity and pore solution conductivity in the chloride resistance of calcined clay containing binders. In [20], the improved chloride ingress in calcined clay containing concretes was attributed to the highly tortuous pore network formed in these materials (see Fig. 2); while other studies have attributed the chloride ingress to be a function of the pore solution conductivity [23, 27]. Nevertheless, the use of calcined clays in the production of concrete seems to be beneficial to produce durable concrete exposed to chloride rich environments [24].

2.2 Carbonation Resistance

Replacement of Portland cement with SCMs reduces the calcium buffering capacity of the binder, and makes the cementitious systems more prone to carbonation [28]. However, the refined and more tortuous pore structure typically identified in blended Portland cement, compared with plain systems, could offset the lower Ca^{2+} buffering

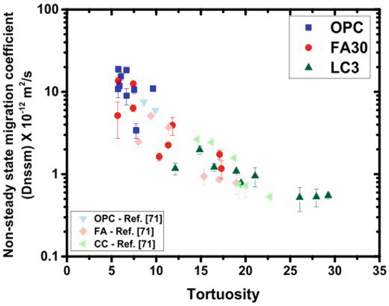


Fig. 2. Improved chloride resistance in calcined clay and calcined clay-limestone concrete systems as a function of (electrical) tortuosity from [20]. *Note* FA – fly ash, CC- calcined clay, and LC3 is limestone calcined clay systems

capacity to some extent. This being strongly influenced by the SCM replacement level, its reactivity, the water-binder ratio, among other factors [28].

In a recent review of Bakera et al. [29], it is reported an improved carbonation performance with metakaolin (MK) addition at lower replacement levels <20%, as shown in Fig. 3 (A). However, high volume replacement of calcined clay and calcined clay-limestone significantly affect carbonation performance [30, 31] (see Fig. 3 B to E). It is worth noting that the majority of the studies evaluating carbonation performance of metakaolin containing concretes have been conducted inducing accelerated carbonation by exposing specimens to high CO_2 concentration for example, from 50% CO_{2eq} [32] to 5% CO_{2eq} [33]. These CO_2 concentrations values are far above what is recommended in the EN 12390-12:2020 (3% CO_{2eq}) [34], which suggest that historical accelerated carbonation results might not be very representative of what could be expected in terms of carbonation of these material under in-service conditions.

Natural carbonation depths of MK blends with 15, 20 and 25% replacement with CEM I and CEM II were compared with commercial CEM I, CEM II (limestone filler), CEM III (Slag) and CEM V (fly ash + Slag) in [35]. Carbonation depth after 365 days and 730 days were used for assessing performance. MK blended with CEM II exhibited reduced carbonation compared to commercial cements, while MK blended with CEM I was found to have average carbonation depths marginally above the upper limits of commercial binders. The natural carbonation coefficient of ternary cements combining calcined clays, limestone and PC was reported for concrete with varying water-to-binder (w/b) ratios in [36]. The carbonation coefficient were found to be 0.42, 0.37, 0.34 mm/d$^{0.5}$ (recalculated from [36]) for concretes produced with 0.50, 0.45 and 0.40 w/b, respectively. Higher carbonation coefficients, determined via accelerated carbonation testing, have been reported for calcined clay-limestone combinations in numerous studies [30, 37, 38], compared with systems produced without limestone addition as show in Fig. 3, and when compared to the values determined after natural carbonation exposure mentioned above.

From the consulted literature, the significant differences in carbonation coefficients are expected considering the differences in the type of samples studied (concrete vs mortars whose pore structure is different), varying accelerated carbonation exposure conditions adopted (temperature, relative humidity and CO_2 concentration) and curing/preconditioning duration as well as environment conditions (See Fig. 3, C, D and E).

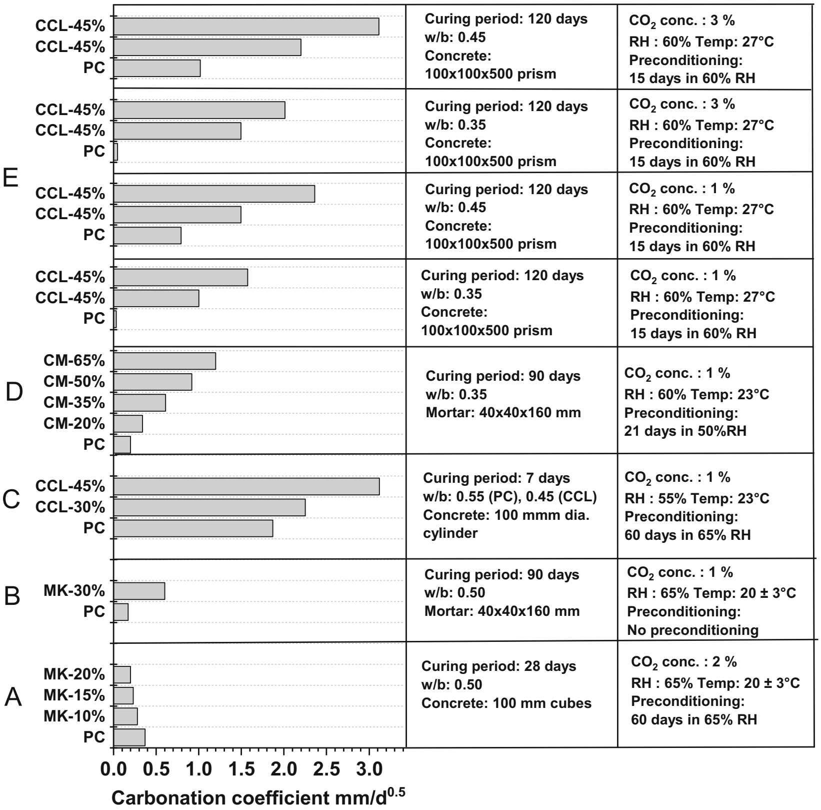
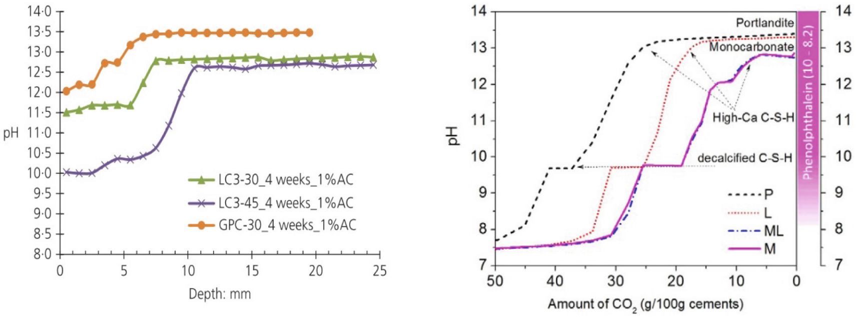


Fig. 3. Summary of carbonation coefficient from literature with metakaolin (MK), calcined clay-limestone (CCL) and calcined marl (CM). Data in A from [29], B from [31], C from [30], D from [37], E from [38]. *Note* carbonation coefficients were calculated from carbonation depth data or converted to similar units for comparison.

Unlike chloride ingress, it remains unclear what is the role of kaolinite content or varying clay types, as well as the impact of exposure conditions in the carbonation resistance of concretes containing calcined clays. Consequently, there is an urgent need to determine what are the major differences in microstructure and CO_2 interaction mechanism within calcined clay cementitious systems, compared to other SCMs containing materials. For practical adoption, provision of higher cover depth seems to be required for metakaolin concrete to produce similar service life to those expected in plain PC concretes, due to the higher carbonation coefficient [35].

Figure 4a shows the pH profile after carbonation of limestone calcined kaolinitic clay cement with 30% and 45% PC replacement by clay, based on the results reported in [30]. At higher the replacement levels of limestone-calcined clay, the pH profile after accelerated carbonation was lower, with a more significant difference between non-carbonation and carbonation pH identified in the carbonation zone. In [31], it was reported that a lower amount of reacted CO_2 could lead to decalcification of the low Ca/Si (C/S) ratio aluminium substituted calcium silicate hydrate (C-A-S-H) typically formed in metakaolin systems compared with plain PC (Fig. 4b).



(a) (b)

Fig. 4. Carbonation performance in terms of (a) pH profile in calcined clay limestone systems from [30], and pH changes linked to simulated phase assemblage alterations as a function of CO_2 exposure concentration [31]

To the best of the authors' knowledge, there are no studies reporting on the specific role of clay mineralogical or kaolinite content on carbonation performance of blended Portland cement systems, from a mechanistic perspective. There is a lack of understanding about any potential differences in the carbonation mechanism of impure calcined clay containing cement, particularly on the microstructure changes that the exposure to CO_2 might induce.

A systematic study on the carbonation mechanism in terms of decalcification of low C/S C-A-S-H type gel and carbonation of carboaluminate phase was not found, with a very limited number of studies on carbonation of C-A-S-H type gels [39–41]. This has been highlighted in a recent review by the RILEM TC-281 CCC [28] as one of the main research gaps for understanding the carbonation mechanism of SCMs containing concretes.

Thermodynamic predictions of phase assemblage have shown the potential carbonation sequence of different hydrate phases formed in calcined clay-limestone (see Fig. 4b). However, the difference in phase assemblage in natural and accelerated conditions for the AFm rich phase assemblage formed in ternary binders with calcined clay is not well established.

Two promising strategies to control carbonation and carbonation induced corrosion in calcined clay containing systems are the provision of increased curing duration and higher cover depth, as presented in [35]. More studies have to focus on tailoring the performance of calcined clay systems for carbonation exposure from a fundamental perspective by considering microstructure-performance relationships. It is essential to revisit the existing carbonation relationship with respect to exposure relative humidity and temperature on calcined clay and calcined clay-limestone systems due to the complex microstructure formed in these systems, which might be susceptible to alterations under standardized accelerated carbonation conditions.

2.3 Sulphate Ingress

Sulphate resistance has been shown to improve with the addition of metakaolin. Shi et al. 2019 [42] studied expansion for metakaolin and metakaolin-limestone combination studied at 20 and 5 °C in sulphate exposure for 700 days. They reported no mass change and expansion at both 5 and 20 °C for both binary and ternary systems containing metakaolin. Lower-grade kaolinite clay has similarly improved performance in sulphate resistance with no expansion up to 90 weeks of exposure to sulphate solution in [43]. The addition of metakaolin was found to reduce the tendency for thaumasite attack caused in limestone systems at low temperatures [44, 45]. Rossetti et al. [46] studied two different illite calcined clay (calcined at 950 °C) with limestone addition. The study reported expansion and mass loss up to 720 days and showed that illite clay with higher amorphous showed no expansion at 30% replacement level. The study also found that an increase in replacement level from 15 to 30% calcined illite improved sulphate resistance.

3 Discussion

Based on the recent studies, the major observation on durability performance of calcined clays containing cementitious materials are summarized in Table 1. The role of physical change, in terms of pore structure, and chemical interactions with the aggressive environment, on the durability performance in different exposure conditions is summarized. In general, there is a good understanding on the performance of calcined clay containing concrete when exposed to a chloride rich environment. However, there is limited understanding of their potential carbonation performance. The reaction of calcined clay and calcined clay-limestone is expected to consume most of CH at an early age, and this could facilitate faster carbonation in concretes produced with these binders. This behavior is typically reported in SCMs containing concretes, so it is not exclusive to calcined clays; however, the limited number of studies available on accelerated carbonation of concretes under varying exposure conditions, makes it really difficult to draw any reliable conclusions about their potential performance. Thus, carbonation of calcined clays containing concretes needs to be studied in more detail and more extensively to provide the evidence needed for the confident use of these promising binders in structural concrete applications. Another research gap identified in this overview is the need to focus on assessment of the different clay mineralogy and its potential impact on various durability performances. This should be attempted with the aim to elucidate what potential sources of clay deposits will be more effective SCMs from a durability viewpoint.

4 Conclusion and Perspectives

This paper presents a brief overview of the durability performance of cementitious systems containing calcined clay when exposed to different environments. Chloride resistance and sulphate resistance are expected to be improved with the addition of calcined

Table 1. Summary of factors controlling durability performance of calcined clay containing systems

Durability exposure	Physical	Chemical	Role on durability performance
Chloride resistance	+	+	• Improved pore structure increase chloride resistance • Aluminate from calcined clay promotes chloride binding • CO_3-AFm phase promotes chloride binding
Carbonation resistance	+	–	• Significant reduction in CH due to high reactivity of calcined clay reduce carbonation resistance • Low Ca/Si ratio C-A-S-H formed to become more prone to decalcification • The difference in carbonation tendencies of calcined clay with dominant CASH phase and calcined clay-limestone with CO_3-AFm phase is not clear
Sulphate resistance	+	+	• Lower ingress due to improved pore structure • Limited gypsum formation due to lower CH • Lesser tendency for CO_3-AFm to Ettringite conversion compared to monosulphate

Note: '+' and '–' implies positive and negative impact on performance respectively

kaolinitic clay, and the mechanism taking place when these materials are exposed to those environments have been widely studied, and relatively well understood. However, there are limited studies on durability performance of systems containing low content kaolinite, or non-kaolinitic clay sources. Given the increasing interest in utilizing calcined clays as SCMs from different regions, it is then important that durability studies of concretes produced with this new generation of SCMs are conducted.

Carbonation performance of calcined clays containing systems, determined by accelerated carbonation, varies significantly from study to study. This is attributed to differences in testing condition, curing, and exposure conditions (relative humidity, CO_2 concentration or temperature), among other factors. The carbonation coefficient reported for these materials also varies significantly at different replacement levels of calcined clay. More systematic studies on carbonation focusing on establishing mechanism leading to microstructure alterations, so that performance of these concretes can be tailored as needed. This will facilitate the adoption of calcined clay systems in carbonation prone exposure environments.

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