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Durability performance of binary and ternary blended cementitious systems with calcined clay – A RILEM TC 282 CCL review

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Abstract

The durability performance of blended cementitious systems with calcined clays is reviewed in this paper by the RILEM TC 282-CCL on calcined clays as supplementary cementititous materials (SCMs) (working group on durability). The impact of metakaolin and other calcined clays on the porosity and pore structure of cementitious systems is discussed, followed by its impact on transport properties such as moisture ingress. The durability performance of binary and ternary cementitious systems with calcined clay is then reported with respect to chloride ingress, carbonation, sulphate attack, freeze-thaw and alkali-silica reaction. The role of unique microstructural alterations in concretes with calcined clay-limestone combinations due to the formation of CO_3-AFm and their impact on different durability exposures is emphasised. While a large majority of studies agree that the chloride resistance of concretes with calcined clays is significantly improved, such concretes seem to be more susceptible to carbonation than those produced with plain Portland cement or other SCMs used at lower replacement levels. Also, several studies are focused on metakaolin and lower grade kaolinite clay, while there are limited studies on calcined smectite/ illite or mixed clays, which could also play a crucial role to the improved adoption of large reserves of clay sources to produce sustainable binders.

Table of Contents

Keywords: Blended cement; calcined clay; durability; ternary blended systems; carbonation; sulphate resistance; alkali silica reaction

1. Introduction

Calcined clays belong to the aluminosilicate group of mineral additives for concrete [1]. The rapid pozzolanic reaction of calcined clays contributes to early microstructural development and improves mechanical performance from an early age [2]. Pure forms of calcined clay, commonly referred to as metakaolin (MK), are used at lower substitution levels in high-performance concrete to enhance concrete performance [1, 3–8]. Calcined clay is an acknowledged pozzolanic admixture in several international cement standards [9–14]. Lower-grade kaolinitic calcined clays with a range of kaolinite content (as low as 20% kaolinite content) have been widely explored in recent years, due to their availability and potential to increase substitution levels in blended cement [5, 15–20]. Several clay forms such as kaolinite, illite, montmorillonite, bentonite and smectite are available in pure and mixed forms [15, 16, 21]. There is another white paper prepared by working group-1 of TC-CCL on the different clay mineralogy for cement and concrete adoption. The information on the calcination conditions and the quality of clay have been addressed over the last two decades to optimise the calcined clay's reactivity potential for Portland cement substitution [1, 5, 22]. Studies have shown that 1:1 kaolinite clays possess excellent pozzolanic behaviour after dehydroxylation by thermal activation [15]. Calcined clay with only 40% kaolinite content was found sufficient to produce strengths similar to plain portland cement by 7 days in the presence of limestone [23, 24]. The presence of reactive aluminates in calcined clay makes it an ideal constituent for co-substitution with limestone. Increasingly, ternary formulations of calcined clay-limestone systems, widely known as Limestone Calcined Clay Cement (LC3) binder systems, are being explored due to synergistic interaction of aluminates in calcined clay with carbonates from limestone [23–25].

The addition of calcined clays to Portland cement is expected to alter the hydration products and directly influence the durability of concrete prepared with such cements [26–30]. During the reaction of the calcined clays, a significant amount of portlandite is consumed [2, 15], and additional calcium aluminosilicate hydrate (C-A-S-H) is formed. The additional availability of aluminates in the clays increases alumina uptake in C-A-S-H type gels [31] and the formation of aluminate hydration products such as ettringite and AFm (Al_2O_3–Fe_2O_3-mono) phases [23, 32–34]. The simultaneous addition of carbonates and calcined clays prevents the conversion of ettringite to monosulphoaluminate and leads to the formation of monocarboaluminate and hemicarboaluminate phases [25, 35]. Often, the synergetic effect in compressive strength is reported to occur with several forms of carbonate sources such as limestone, dolomite, and marble stone [36–38]. Whether the synergistic performance in mechanical properties translates into synergistic performance in transport properties and durability performance is still an open debate [39]. Long term durability performance is complex, with several conflicting factors involved depending on the different exposure environments.

Both kaolinitic and non-kaolinitic clays have been used to produce binary blends [40] and ternary blends with limestone [41]. While the pozzolanic reaction, controlled by clay type and calcination, improves the pore structure and transport properties, the reduction in the portlandite content reduces the capacity of the concrete to react with CO_2 [42]. This leads to a higher carbonation rate in concretes prepared with calcined clay. In addition to the portlandite content, there is a significant difference in the amount of C-A-S-H phase formed, with the Ca/Si ratio also decreasing with an increasing amount of calcined clay added [34]. Ternary systems with calcined clay-limestone combinations are expected to form a higher amount of ettringite and CO_3-AFm [25]. These phases are known to be water-rich with a low density, reducing the porosity and pore-connectivity in the microstructure [35, 43]. The formation of the carboaluminate phases also leads to a consumption of portlandite content, which could interfere with carbonation resistance [25]. Also, carboaluminates themselves are prone to conversion under chloride and CO_2 exposure [42, 44]. The conversion of CO_3-AFm to Cl-AFm could be beneficial in binding chloride in marine exposure. Hemicarboaluminate could act as CO_2 sink, as reported in [45], which could modify the carbonation resistance of the calcined clay-limestone binders. On the other hand, sulphate exposure is expected to lead to a conversion of the carboaluminate phases to ettringite; unlike mono-sulphate conversion, this is not expected to lead to a significant increase in solid volume. However, these phases are also known to be vulnerable to carbonation, resulting in a significant porosity increase [45].

The combination of chemical alterations between pozzolanic reaction and carboaluminate formation and the resulting microstructural alteration produces interesting performance characteristics in concrete containing calcined clay, either as a single substitution or in combination with limestone. This paper presents an overview on the durability performance of calcined clay systems in different exposure environments. More focus is laid on the calcined kaolinite clays while alternative clays are also discussed based on the available resources. The paper describes the pore structure features in calcined clay binder and its impact on transport properties such as resistivity and capillary absorption, and further explores the durability performance when exposed to different environmental threats such as chlorides, carbonation, sulphate, alkalis silica and freeze-thaw. It must be noted that the coverage on chloride exposure is only brief here, as the RILEM TC-CCL intends to explore chloride-induced corrosion as a separate subject. This paper also attempts to capture the role of binary and ternary formulations with calcined clay-limestone combinations.

2. Porosity and pore structure of calcined clay systems

Pores are generally classified as air voids (~few mm - 100 µm), capillary pores (~10 µm - 10 nm), gel pores (~10 nm – 2.5 nm) and interlayer spaces (< ~1 nm) [46]. Porosity and pore structure plays a crucial role in hardened concrete characteristics, including mechanical and durability properties. Several studies have proven that the change in pore size parameters correlates with the macroscopic performance parameters such as water accessible porosity and water absorption rate [4, 47–49]. The most widely used pore size parameters in cementitious materials are the critical pore size and threshold pore size that can be obtained from mercury intrusion porosimetry (MIP) technique. The technique provides information on the total pore volume, threshold pore size, and critical pore size (typically in 10-100 nanometer range in cementitious materials). The differential pore volume curve indicates the size corresponding to the maximum volume intrusion, which is the critical pore entry size of the system. In some instances, the minimum continuous pore size for the sample obtained from the cumulative volume intrusion curve is represented as the threshold pore size or breakthrough pore size to draw comparisons of the pore refinement. The ingress of an external agent, including moisture and ions, is expected to be governed by the distribution of the different size fractions in the capillary pore space and its connectivity which is expected to be modified significantly with calcined clay (both with metakaolin and lower grade calcined clays) and calcined clay-limestone combinations.

2.1. Analysis of alterations in porosity

The effect of calcined clay on the "measured" porosity varies in the literature, consistent with the differences in techniques used for their determination, concrete mix design and intrinsic properties of raw materials used. Figure 1 shows the relative porosity (porosity/porosity of reference Portland cement) at different replacement levels measured using mercury intrusion porosimetry (MIP), vacuum saturation and ^{1}H NMR. The data was compiled from [15, 23, 24, 32, 40, 45, 50–63]. The figure distinguishes binary blends with calcined clay (triangles) and ternary blends with calcined clay-limestone combination (shaded squares).

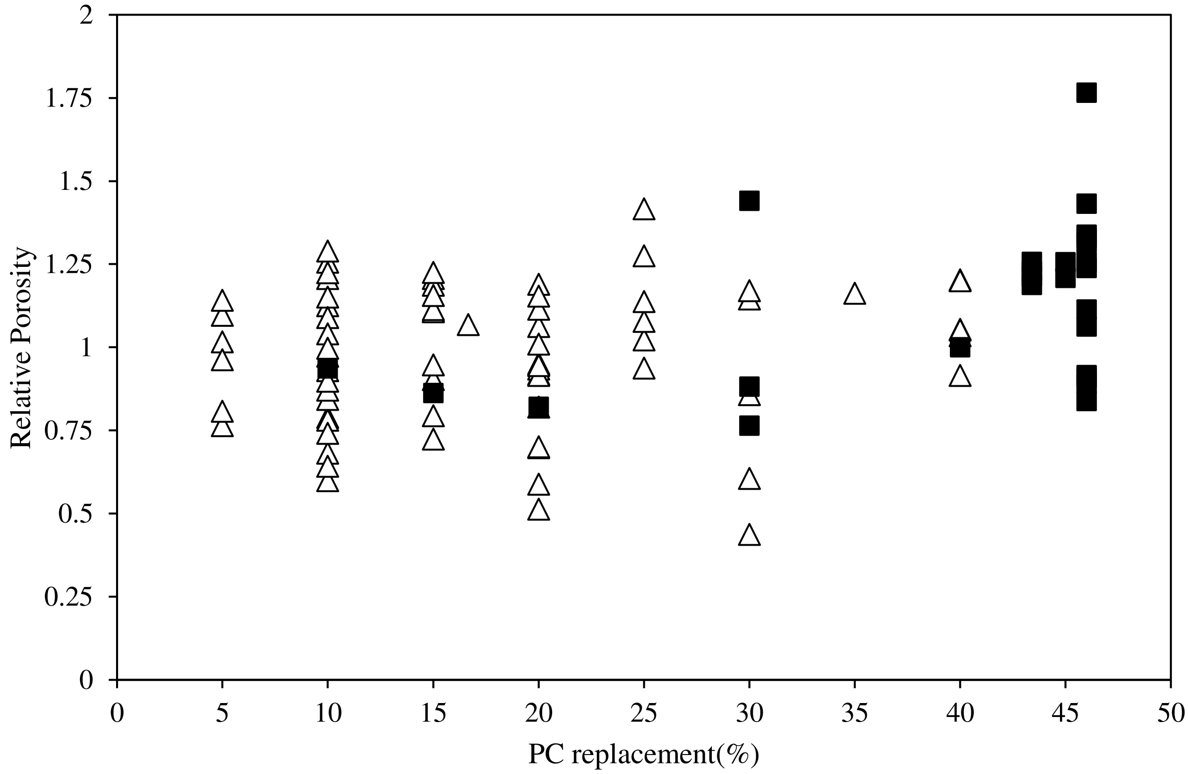


Figure 1: Relative porosity of cementitious systems for varying levels of calcined clay + limestone. Triangles are binary systems with PC and calcined clay, and squares are ternary systems with PC, calcined clay and limestone.

From Figure 1, no clear trend can be deduced for replacement levels of calcined clay and limestone. It is evident that there are conflicting results in the literature since articles have reported lower porosity (Relative porosity <1) while many others have reported higher porosity (Relative porosity >1) with the addition of calcined clays compared to reference PC. Therefore, the significant impact of calcined clay on the microstructure related to transport properties and durability performance of the hydrated cement matrix cannot be captured from the total porosity alone. A more dominant impact of the calcined clay is found to be on the alteration of the pore structure, in terms of pore refinement, of the cementitious matrix, which is explored in detail below section.

2.2. Pore structure refinement

The absolute value of the porosity assessed using porosimetry should be carefully used to infer durability performance since concrete is a complex material containing pores and voids at several length scales. The technique selected has a strong influence on the quantitative value of porosity, including voids, interface porosity, capillary and gel pores captured in the measurement. Techniques such as MIP and nitrogen sorption cannot resolve the entire pore structure, which spans sizes over 6 orders of magnitude. While ^{1}H NMR relaxometry can provide a broader picture, only limited studies are reported with calcined clay inclusion [32]. For calcined clay binder systems, the total pore volume measured on cement paste was higher with equivalent volume of gel pores with respect to the reference portland cement [32]. Several studies using MIP have consistently shown a significant pore refinement with the addition of calcined kaolinitic clays, which is also indicated by a lower threshold and critical pore entry radius. Studies reported significantly finer pore structure for the MK systems compared to reference portland cement for MK replacement from 0 to 15% in [64], and 10 to 25% in [65]. Pore refinement was found to occur despite different water to binder (w/b) ratios of 0.35 and 0.55 in [63] for 10% and 20% MK, respectively. A study evaluating pore structure in samples extracted from cement mortar containing three different kaolinite content (31, 36 and 41%) found pore refinement irrespective of MK content, even at 40% PC replacement [51]. This was further affirmed in [23], where all calcined clay paste (w/b = 0.45) systems with >30% kaolinite showed similar critical pore size at 28 days (see Figure 2).

Compared to MK in binary systems at lower replacement levels, the use of MK and limestone combinations at higher replacement levels up to 45% could produce similar refinement of pore structure. A combination of calcined clay and limestone showed similar pore structure refinement as 30% calcined clay systems [25, 66]. The high reactivity of calcined clay could contribute to the refinement of the pore structure even with calcined clay containing 50% kaolinite content [23], as shown in Figure 2. Pore structure assessment of concrete prepared with MK/calcined clay was also found to show that critical entry pore sizes were reduced to the 10-30 nm range [24, 67–69]. Porosimetry studies on several small pieces (total mass <1 gram) containing cementitious paste extracted from concrete were also found to have similar refined pore sizes to those identified in cement paste made of calcined clay [27, 70]. There aren’t any detailed studies that assess the porosity of calcined clay systems in mortar and concrete and evaluate the role of calcined clay in interfacial transition zone (ITZ) densification in concrete systems.

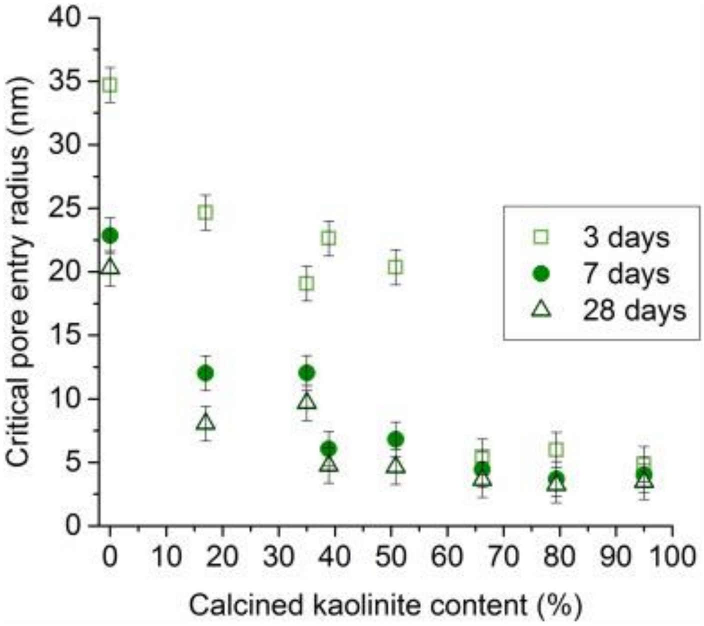


Figure 2: Influence of kaolinite content on the pore structure of cement paste (w/b = 0.45) [23] measured as a funcation of curing time using MIP (contact angle of 120°)

Pore structure features using two illite based calcined shales (about 50-56% amorphous content) were studied in [71]. The results showed a limited difference in pore size refinement in calcined shale systems with respect to OPC. Additionally, an increase in pore volume was also found due to the lower reactivity of these clays compared with kaolinite clays and dilution effect caused due to reduced reactive content in the binder. Fernandez et al. [15] studied the effect of kaolinite, illite and montmorillonite clays and quartz on the capillary porosity of cement mortar after calcining clays at 600 °C with 30% replacement of OPC. They found that compared to reference OPC and calcined kaolinite, there was a significant increase in the capillary porosity for both calcined illite and montmorillonite, and they had similar porosity as the system with quartz. In [15], calcination temperature of 800 °C was also attempted for the clays but capillary porosity was not reported for this case. A study on the pore structure of binder containing kaolinite (calcined at 750 °C) and illite clay (calcined at 950 °C) at 25 wt. % replacement level showed that only the kaolinite clay systems were found to show significantly refined pore size at 28 and 90 days, despite having similar total pore volume to illite systems [40]. Illite clay systems could not reach the refined pore structure state of 28 days cured kaolinite clay systems despite extended curing up to 90 days. This work showcases that kaolinite clay has a dominant impact on pore refinement compared to other forms of calcined clay. However, it is important to explore all forms of clay for potential substitution. A more useful approach would be to produce a combination of more reactive kaolinite clay with other forms of clay (calcined illite and montmorillonite) and explore low-grade mixed clay. Studies on such combined use of clay could be explored to facilitate the adoption of a range of lower grade clay for substitution in cement production.

2.3. Implications of pore structure development on durability performance

Porosity and pore structure play a crucial role in hardened concrete characteristics such as mechanical and durability properties. It was found that the change in pore entry diameter correlated well to the macroscopic performance parameter such as water accessible porosity in calcined clay systems [48] and water absorption rate in MK systems [4]. The presence of calcined clay is shown to significantly reduce the pores > 100 nm by 3 days compared to OPC and fly ash systems – this explains the significant reduction in the concrete pore connectivity factor (typically estimated using electrical conductivity approach [27, 49, 72]) at an early age [48]. In calcined clay-limestone combination, the volume of pores corresponding to 50 nm to 15 µm had the strongest correlation with compressive strength across all ages [66]. Similarly, the ingress of external agents, including moisture and ions, is expected to be governed by the distribution of the different pore size fractions in the capillary pore space, and its connectivity. Studies have shown that several factors, such as porosity, pore size, pore solution, and chloride binding capacity will influence the chloride ingress in calcined clay systems [27, 73, 74].

One of the most significant impacts of early pore refinement of calcined clay systems is the early rise in concrete resistivity in saturated concrete, which is often directly linked to pore refinement [27, 48, 75]. A significantly higher resistivity of concrete prepared with calcined clay and the calcined clay-limestone combination compared to OPC concretes was reported in several works [24, 75, 76]. The resistivity of concretes prepared with calcined clay was found to show a consistent rise between 3-7 days as shown in [48, 77]. Thus, the early resistivity development in several concrete mixtures was found to clearly demonstrated the impact of early pore refinement of the paste matrix.

3. Moisture ingress

Ingress of moisture plays a crucial role in the transport of deleterious ions in concrete, which governs durability performance. The major transport mechanisms associated with moisture movement in concrete are absorption, permeability and diffusion [78, 79]. Absorption is the dominant transport mechanism in a concrete structure whose surfaces are saturated infrequently during exposure. The positive impact on the pore structure with calcined clays is expected to lower the absorption rate in concrete. Resistance to moisture uptake improved with MK dosage from 0 to 20% for concretes cured at different ages such as 1, 7, 14, 28 and 90 days [4]. At initial curing ages up to 14 days, there was a significant reduction in absorption rate with the increase in MK dosage. There was a limited difference by 90 days of curing due to MK dosage on moisture absorption rate [4]. The influence of concrete mixture proportioning on MK concrete's water sorptivity index was studied at three w/b (0.4, 0.5 and 0.6) and MK dosage was varied as 0, 10, 15, 20% [80]. The sorptivity index (a measure of resistance to moisture uptake as per [81]) reduced with an increase in MK dosage even for concrete prepared at a higher w/b of 0.6 [80], in line with pore refinement across w/b observed in [63]. Similarly improved performance was found for ternary mixture with lower grade calcined clay-limestone in [24].

The pore refinement due to the high reactivity of calcined clay could reduce the curing requirement to produce the required transport indices to meet performance specifications. The effect of curing conditions (i.e., water and air curing) on moisture ingress rate for concrete prepared with MK showed that sorptivity rate reduced with MK dosage (10% and 20%) in both air and water curing [82]. Any increase in water cured duration further improves the performance of calcined clay systems. Even concretes with calcined clay with 50% kaolinite content showed improved performance water-related transport indicators [77]. Gonçalves et al. (2009) [83] studied the effect of the sorptivity on commercial and lab calcined MK. The commercial MK1 had lower surface area, Al_2O_3 content and amorphous fraction compared to lab calcined MK2. The study found that the high grade MK2 was more effective in reducing the sorptivity at low replacement levels (up to 20%), while the opposite was true for higher replacement levels (30-40%) for MK1. The use of purer forms of MK with higher fineness showed poorer performance at high volume substitution, possibly due to lack of microstructural evolution once portlandite deficit condition is attained in the concrete with fine MK.

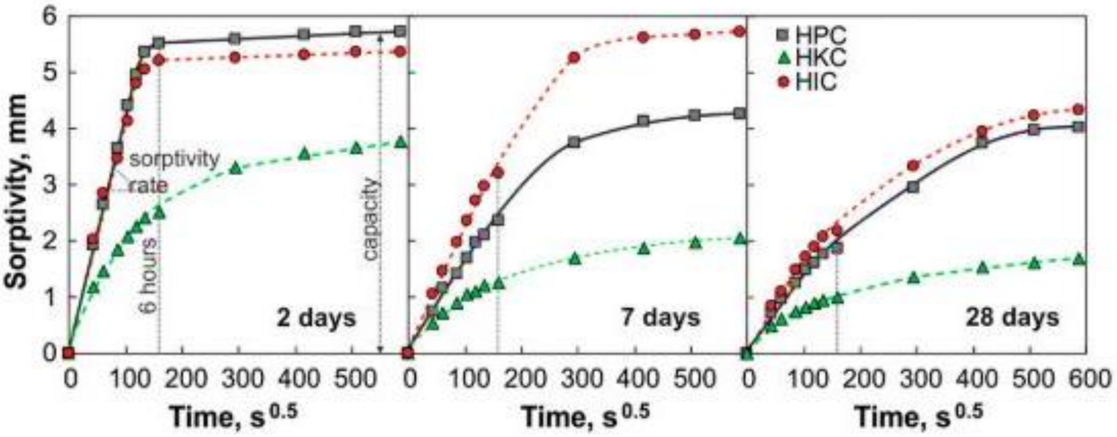


Figure 3: Influence of clay mineralogy and curing duration on the performance of calcined clay concrete [40].

Note: HPC corresponds to- plain cement concrete and HKC and HIC are concretes containing 25% kaolinite and illitic shale, respectively. All concretes were prepared with 350 kg/m^3 and w/b = 0.5.

The role of clay mineralogy on the water sorptivity of mortar and concrete was reported in [15] and [40], respectively. In both instances, calcined kaolinite clays were found to be more effective in reducing the water sorptivity than calcined illite or montmorillonite clay (see Figure 3). Both studies show that the performance of concrete with illite and montmorillonite clays was poorer, with respect to moisture uptake rate, than OPC concrete by 28 days due to dilution of hydrated phases. The role of kaolinite content was studied in four calcined clays with 38 – 54 % kaolinite content in comparison with a pure MK. The results showed a consistent reduction in water sorptivity with higher replacement level and limited difference was observed when varying the calcined clay's kaolinite content [21]. Limestone calcined clay combinations were found to reduce the water absorption rate by 40% compared to OPC in [77]. An increase in the replacement level of limestone-calcined clay mixture as pozzolan was studied at 10, 15 and 20% [55]. The sorption rate was consistently reduced with an increased replacement level due to improved microstructure. Similarly, the moisture ingress variation was studied at different calcined clay-limestone ratios for a ternary mixture containing up to 20% limestone

[84]. The results showed that limestone addition as filler does not further increase the absorption rate like in PLC systems, as the refined pore structure formed due to the presence of calcined clay positively improves the performance of calcined clay-limestone combination.

Figure 4 compiles the relative sorptivity (sorptivity rate normalized with respect to OPC value as reference) of MK, calcined clays binary blends and ternary blends with limestone in mortar and concrete. Differentiation between MK and CC was made based on Al_2O_3/SiO_2 ratio calculated from published data. Purer form of MK was assumed for $Al_2O_3/SiO_2 > 0.7$. The data seems to be scattered a lot, as one would expect, due to the differences in clay mineralogies, w/b ratios used, reference cement type, clay calcination procedures etc. However, the trend suggests a reduction in relative sorptivity until 30% replacement in binary systems, although scatter is higher. All MK, calcined clay and calcined clay-limestone systems were found to have between 30-50% reduction in absorption rate compared to the reference concrete in most studies.

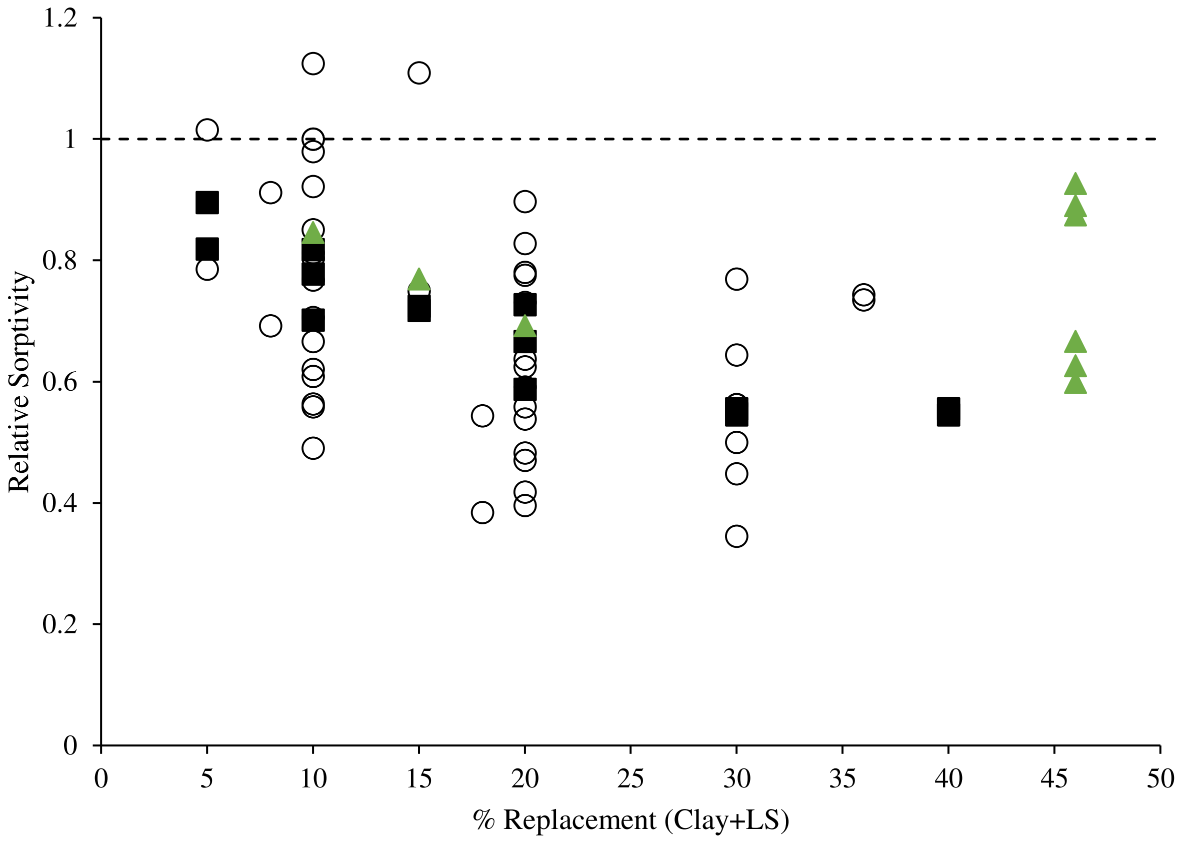


Figure 4: Influence of calcined clay replacement level on the absorption rate [15, 24, 55, 60, 82, 85–89], where Circles: metakaolin, squares: calcined clays ($Al_2O_3/SiO_2 > 0.7$) and triangles: PC-limestone calcined clay systems

4. Durability characteristics

4.1. Chloride ingress

Resistance to ingress of chlorides is governed by both pore structure and chloride binding. The ingress of an external agent, including moisture and ions, is expected to be governed by the distribution of the different pore size fractions in the capillary pore space and its connectivity. Studies have shown that several factors, such as porosity, pore size, pore solution, and chloride binding, influence the chloride ingress in calcined clay systems [27, 73]. Chloride binding was also reported to be increased due to higher reactive alumina in metakaolin/calcined clay [26, 44, 74, 90]. The early refinement of pore structure in calcined clays systems is expected to induce a significantly lower chloride penetrability rate in concrete at an early curing period [21, 91–93]. Attempts to study the role of calcined kaolinite content on chloride transport in cement based systems showed that the chloride diffusion coefficient in calcined clay systems varies consistently with alterations in the critical pore sizes rather than the chloride binding capacity [74]. Another study on chloride transport using non-steady-state migration coefficient for concrete prepared with calcined clay-limestone systems also found a similar reduction in chloride ingress rate with critical pore size [27]. However, in the study, chloride penetrability in calcined clay systems was rationalised with an increase in pore tortuosity, which was found to occur along with pore structure refinement. Such an observation has been reported for MK systems in [67] and calcined clay-limestone systems [27]. The lower chloride penetrability rate was found to enhance the predicted corrosion initiation time in calcined clay concrete despite lower pH and lower chloride threshold value [94]. Chloride-induced corrosion is one of the major durability concerns in reinforced concrete structures. The performance of calcined clay concretes in a chloride environment will be discussed in a separate white paper with focus on the physicochemical aspect of chloride transport and corrosion of reinforced concrete systems.

4.2 Carbonation

Carbonation of cementitious systems with SCMs is one of the most relevant topics when evaluating durability of these materials, as concentrations of CO_2 in the air are higher currently than at any point in human history. It has been extensively reported that concretes with SCMs are more susceptible to carbonation compared with those produced with plain OPC [95]. The mechanism of carbonation in these systems can be quite complex due to the differences in phase assemblage and pore water evolution when using different SCMs; hence, many open questions remain regarding what are the key factors controlling performance of concretes with SCMs when exposed to CO_2 [95].

There is a significant number of studies reporting carbonation of blended cementitious systems (including systems with calcined clays) determined by applying accelerated test methods [42, 54, 96]. In contrast, there is very limited data on long term natural carbonation of calcined clays contining concretes, and even more limited data and understanding of the process of carbonation-induced corrosion in reinforced concrete. A detailed review on the carbonation performance of blended cements as covered by RILEM TC 281-CCC can be found in [95]. For the purpose of this study, only reported results of the carbonation performance of MK and calcined clay systems will be discussed.

In concrete, the extent of carbonation is measured as the depth until which the reaction of dissolved CO_2 with alkalis has led to a reduction in pH, which is often measured by colorimetry method using pH indicator. At the same time, the measurement serves to identify the visual depth of pH change based on the choice of the indicator. The carbonation extent is far from ideal to explain the complex chemical alteration during the carbonation process [97] and variation in the chemical interaction for binary and ternary formulations with calcined clay [42]. The carbonation rate depends on several factors, including the reserve alkalinity, permeability, relative humidity, temperature, among others. It has been reported that mixes with calcined clay have a higher tendency to carbonate due to the lower portlandite content and a higher content of aluminate products [42, 98].

Carbonation under atmospheric conditions can be an extremely slow process, which takes decades to progress through the concrete cover. Accelerated tests have been established to characterize the carbonation resistance of concrete in a laboratory setting where the concentration of CO_2 is significantly higher (~25 to 2500 times) compared to natural concentration [99]. A common depiction of the carbonation performance is through the use of carbonation rate/coefficient (mm/ √time) which is the slope of the plot between carbonation depth (mm) and the square root of time (day or year). Despite the fact that accelerated carbonation testing, and particularly the sample pre-conditioning, can induce drying and microcracking, as well as modify the phase assemblages and porosity [100, 101], in the case of MK containing cementitious systems there seems to be a good correlation between natural and accelerated carbonation rates (Figure 5) considering the existing data available in the literature. Note that accelerated carbonation rate was corrected considering the CO_2 concentration as described in [102].

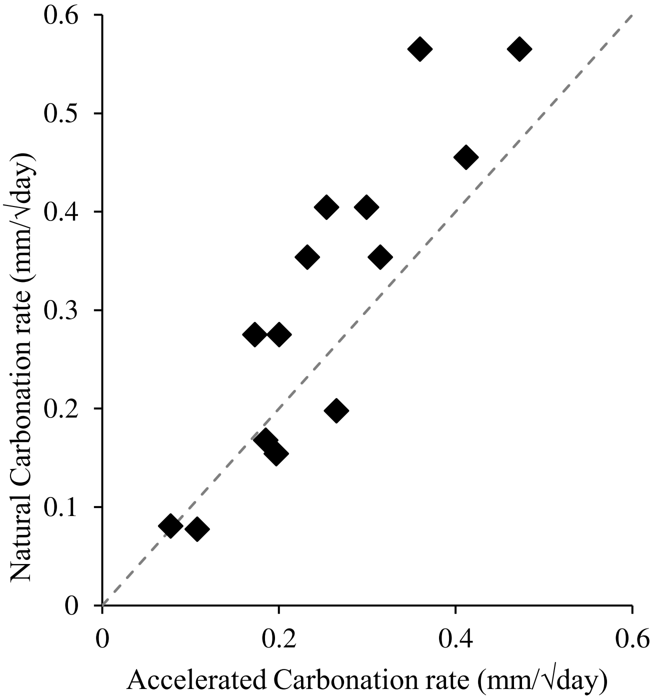


Figure 5: Comparison of carbonation rate from natural and accelerated tests for calcined clays [45, 96, 98, 103]; accelerated carbonation rate was corrected considering the CO_2 concentration as described in [102]

Note: Line marked on the figure is mainly to show linearity and is not modelled relationship

4.2.1 Influence of clay mineralogy and replacement level on carbonation potential

Figure 6 summarizes the carbonation coefficient of calcined clay concretes in binary and ternary systems from literature along with the reference OPC system. In ternary systems, the clay: limestone ratio was 2:1, in most instances. The carbonation coefficient plotted is determined from both natural and accelerated carbonation tests, and further corrections for CO_2 concentration were applied based on [102]. If carbonation depths at different ages reported in the literature, carbonation coefficient were calculated based on the carbonation depth values. The increase in carbonation coefficient with increasing calcined clay replacement level is visible.

Increasing the replacement level of calcined clay has been found to increase carbonation rate compared to reference Portland cement in both binary and ternary systems [42, 45, 96, 98, 103–106]. However, lower carbonation rates were reported with an increase in MK replacement up to 20% in [80]. This improved performance was attributed to lower permeability due to pore refinement. Apart from the replacement level, the reactivity of the clay could also influence the carbonation rate as this is directly linked to the degree of hydration achieved in the system. Calcined clays with higher kaolinite content are also reported to have higher carbonation due to the higher calcium hydroxide consumption compared with calcined clays with reduced kaolinite content [96, 103].

From Figure 6, it can be seen that there is a trend of increasing carbonation coefficient with increasing cement replacement with calcined clay and limestone. Several alternative forms of clays sources are identified in several research programs across the world. More specifically, co-substitution of calcined clay with other substitute materials, including limestone, marble dust and fly ashes is gaining interest. There are not many detailed studies on the carbonation of systems with different clay mineralogy apart from metakaolin and calcined kaolinite clays. These trends warrant more focus on carbonation performance of such systems.

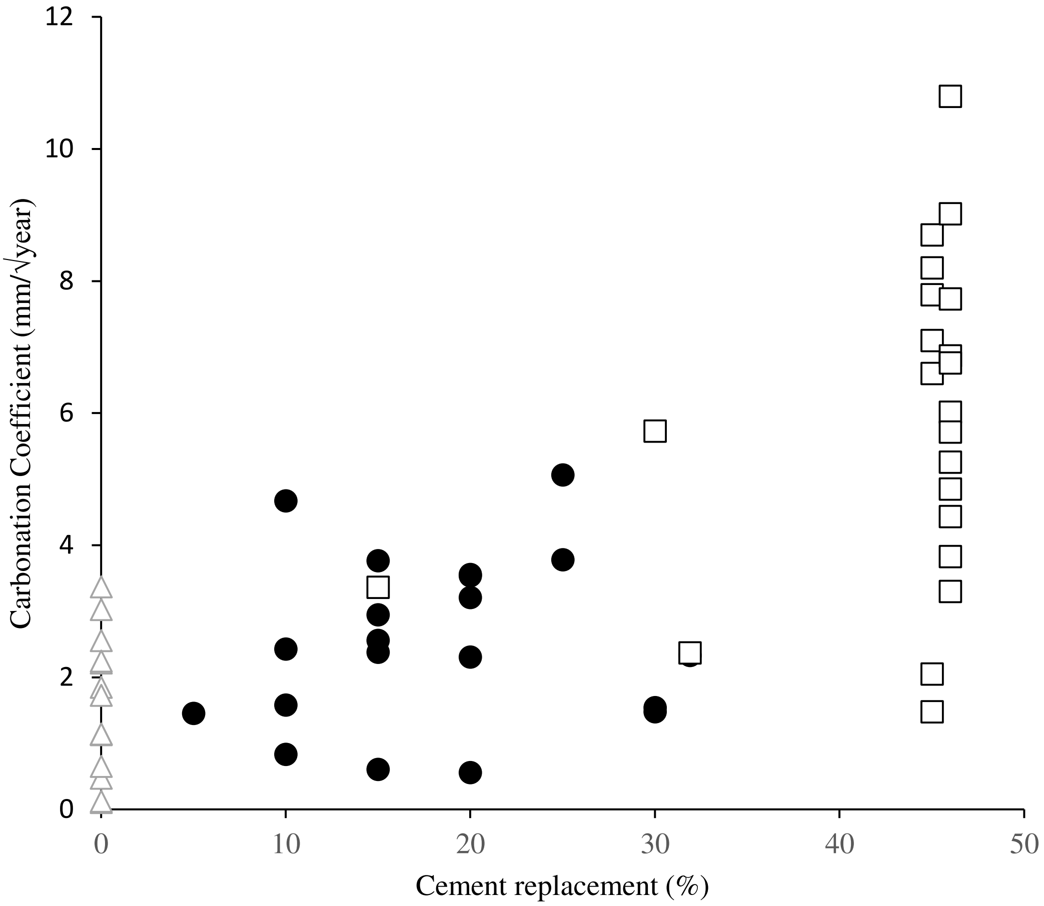


Figure 6: Carbonation coefficient – effect of replacement level [42, 45, 96, 98, 103–106] Triangles: PC, circle: binary systems with PC and calcined clay, square: ternary systems with calcined clay and limestone.

4.2.2 Microstructural alteration due to carbonation

Carbonation modifies the microstructure of cements, which has a notable effect on the macroscopic properties of concretes. The increase in porosity as a result of carbonation in blended cementious systems, which is unlike the reduction in porosity in OPC systems, is further reported to increase carbonation depths [107]. Shah et al. [54] reported the presence of aragonite and vaterite along with calcite upon the accelerated carbonation of calcined clay-limestone system in accelerated conditions at 3% CO_2 and 60% RH. Shi et al. [42] studied the effect of accelerated carbonation (1% CO_2) on a binary system (31.9% MK replacement) and ternary cement (25.5% MK and 6.4% limestone) replacement, and PLC (Portland Limestone Cement with 31.9% limestone) and compared it with reference OPC. They reported a considerable increase in pore threshold radius, attributing to coarsening of pore structure upon carbonation for all systems. No particular change was seen in the overall porosity [54] in the OPC system. It was reported [96] that, upon both natural and accelerated carbonation, the overall porosity measured from MIP increased for LC3, while it reduced for reference OPC. On the other hand, with respect to the pore structure, carbonation consistently contributed to the coarsening of pore structure for all samples. Upon longer exposure to carbonation, a significant increase in the water absorption rate was also reported for LC3 systems compared to marginal increase in OPC systems [108]. It has been speculated that a portion of the pore structure coarsening in carbonation exposure occurs due to drying along with carbonation at lower RH (<70%) during carbonation studies [107]. It is not clear whether calcined clay binders have a varied potential for desiccation and microcracking upon carbonation, specifically in accelerated conditions.

Based on thermodynamic modelling, it has been predicted that for binary or ternary blends with calcined clay, there is an increase in the porosity at a lower carbonation extent compared to OPC systems [42, 54]. This has been explained by the lower portlandite content in blended systems, which is rapidly consumed by the hydration reaction of calcined clay and MK in particular. In plain OPC systems the presence of calcium hydroxide during carbonation leads to a reduction in porosity due to the volume difference between portlandite and calcium carbonate. With lower portlandite content, there would be increased C-(A)-S-H carbonation, leading to decalcification and transformation to silica gel [109], which increases the porosity and may lead to carbonation shrinkage [110]. Shah et al. [54] reported higher decalcification of C-(A)-S-H based on EDX analysis upon carbonation for LC3 compared to reference OPC at the same exposure condition.

In addition to decalcification, the reduction in calcium hydroxide content of blended cements dominates over the pore refinement. The rate of carbonation is inversely proportional to the alkalinity of the system as identified in [96] for different blended binders containing slag, fly ash and calcined clays. Ternary systems containing 15% limestone and 31% calcined clay were studied at two water to cement ratios (0.35 and 0.45) and two different clays were tested [96]. The reserve alkalinity of cement paste cast at the same water to cement ratio as of concrete was measured by titrating the suspension of cement paste in the water against sulfuric acid. The pH of the uncarbonated cement paste samples was measured by a suspension method on the powdered cement paste sample. A linear relation was seen between the accelerated carbonation rate (at 3% CO_2) and reserve alkalinity, which is governed by the Ca^{2+} buffer present in the system. The correlation between carbonation rate and pH of the system which is primarily governed by the Na^+ and K^+ is less clear [96].

An increase in w/b ratio leads to an increased rate of carbonation owing to increased porosity [80, 96, 111]. Independent of the duration of wet curing (28 days or 365 days), increasing the substitution rate of calcined clay increases the carbonation rate compared with plain OPC systems. A more extended period of curing was found to be beneficial to the calcined clay concretes with an optimum OPC replacement of up to 20% to limit carbonation [80]. An increase in the carbonation coefficient with an increased exposure temperature from 27 °C to 45 °C has been reported [96]. This is possibly due to faster evaporation of pore water, including the water formed due to carbonation reaction.

From what is reported in the literature, the understanding of carbonation of cementitious systems with calcined clays is scattered with several inconsistencies. More studies are required to understand the carbonation performance which will enable identifying the best mitigation strategies. Some key factors identified for future studies are alkali enrichment in high volume calcined clay replacement mixes to account for the significant alkali binding in calcined clay systems, as a potential measure to alter carbonation performance. Due consideration to curing duration, replacement level, alkali content and w/b should be accounted for to effectively control the carbonation rate in calcined clay systems from a holistic perspective.

4.2.4 Carbonation induced corrosion

While there is a clear understanding that the reactive SCMs such as calcined clay would lead to an increased carbonation rate, the resultant implication on corrosion has not been studied extensively. There is an interplay of the carbonation depth and the moisture availability for corrosion, making the simulation of the actual scenario very difficult. As shown in Figure 7, for different ratios of calcined clay/limestone, the corrosion rate is very similar; however, corrosion rate increases with the increase in w/b ratio [112]. These corrosion rates are still on the lower side compared to the widely reported range of corrosion rates for chloride attacked concretes, which are as high as 10 µA/cm^2 [113].

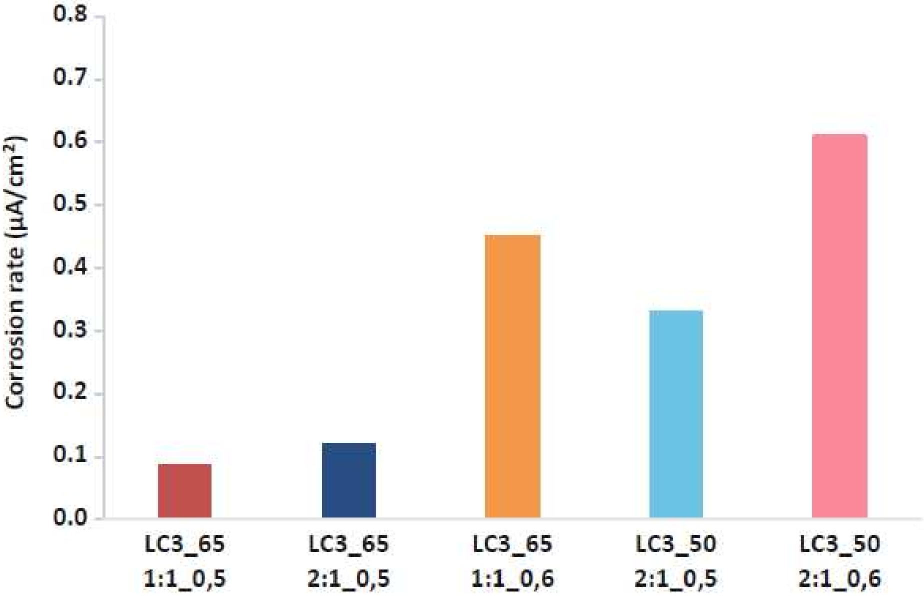


Figure 7: Corrosion rates of LC3 mortar with different calcined clay/limestone and w/b ratios measured by Linear Polarization Resistance (LPR) technique [112]

Note: LC3_65 and 50% denotes 35% and 50% replacement respectively. 1:1 and 2:1 is the ratio of calcined clay:limestone in the blends and 0,5 and 0,6 are w/b of the concrete mixture used in the study

A more recent study showed that corrosion rate should be carefully assessed due to the high resistivity in the calcined clay binder systems. As per the recent investigations of [114], the performance of reinforced LC3 concrete specimens was comparable to traditional OPC concrete in corrosion propagation phase, despite the higher resistivity. The evolution of both E_{corr} and polarization resistance of OPC and LC3 concretes exhibited a similar decreasing trend over the entire testing period of 500 days. However, there was significant dissimilarity in Tafel constants from the results obtained on LC3 concrete and suggested values for OPC corroded systems. Tafel “B” constants are used to calculate corrosion rates from polarization resistance. For LC3 concrete corrosion active samples, insignificant fluctuation of parameter B was recorded with an average value of 47 mV, which is noticeably higher than the suggested B of 26 mV in Portland cement concrete. A good agreement between gravimetric and electrochemical mass loss was observed when considering a B value of 47 mV in the electrochemical mass loss calculation.

Due to the combined effects of lower ionic concentration in the pore solution and a refined porosity in LC3 concrete, the bulk resistivity measured was about 3 times higher than that of reference concrete, which could reduce the ionic current. Moreover, the refined porosity of LC3 concrete may delay oxygen renewal at the steel-concrete interface leading to further reduction of cathodic reactions and ionic currents. This can explain the reduction of the Tafel slopes observed, justifying the higher "B" constant for LC3 concrete. However, carbonation induced corrosion in calcined clay systems is still a subject of debate, and more studies should focus on the interplay between concrete microstructure in carbonated concrete, resistivity and corrosion potential.

4.2.5 Service life and role of the concrete cover requirement for calcined clay binder in carbonation exposure

The carbonation rates are expected to be higher in calcined clay systems due to combinations of factors (discussed earlier in Figure 6). The rates could increase in ternary systems due to lower lime reserve from the high replacement level in ternary systems such as LC3. A more conventional option to improve service life in such cases would be to provide an additional cover depth. Attempts have been made to model carbonation depth and identify the excess depth required for calcined clay/MK binders. Figure 8 shows that an addition of 10-15 mm cover depth could ensure a service life of 50 years for MK systems [45]. In order to identify the excess cover depth requirement, it is necessary to predict the natural carbonation rate using accelerated data. A study found that the inclusion of reserve alkali content in the pore solution could improve the prediction of carbonation for concretes containing calcined clay at three different RH (40, 60 and 80%) conditions [96]. However, there is a critical need to develop and validate carbonation performance using long term data of natural carbonation for calcined clay systems. More studies on modelling approach for predicting natural carbonation rates and necessary modification for probabilistic assessment of service life as per model code [109] are necessary to facilitate the adoption of calcined clay in carbonation governing environments.

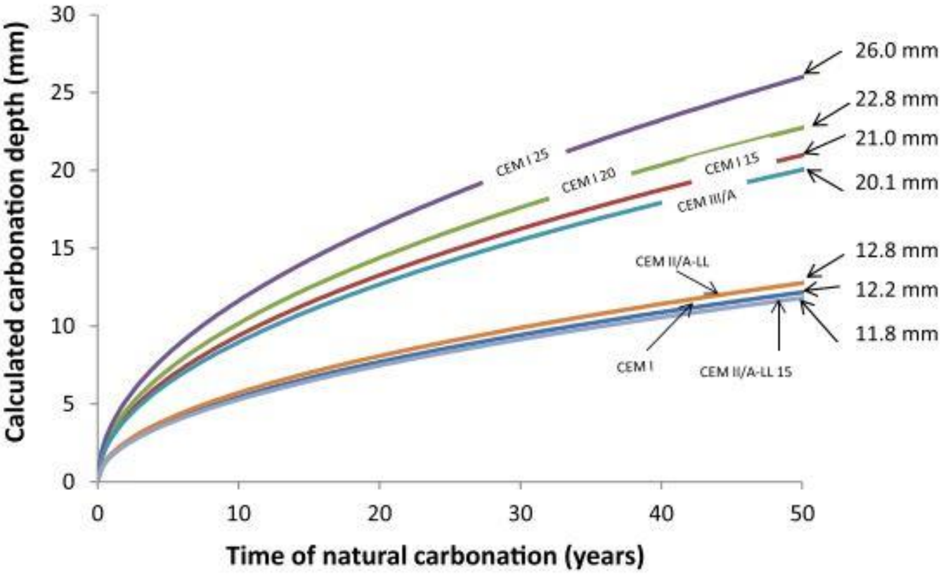


Figure 8: A comparison of predicted carbonation depth for MK systems vs commercial CEM I, CEM II/A-LL and CEM III, as presented in [45]. The MK systems are denoted with the MK replacement levels; for instance, CEM I 15 contains 15% MK.

4.2.6 Case of study on carbonation exposure

While the previous sections focused on accelerated carbonation, this section presents a 24-month assessment of concrete specimens subjected to carbonation under natural conditions in three exposure classes according to Cuban Standards. The limestone calcined clay cement (LC3) formulation with 50:30:15:5: clinker:calcined clay:limestone:gypsum was used for the study. A reference concrete was cast using a Type I Portland Cement (i.e., CEM I) , with 90 wt.% clinker, 5 wt.% limestone and 5 wt.% gypsum. Three series were cast with cement content and water to cement ratio established following the prescriptive specifications of the Cuban standard NC 120:2014 [115]: (i) H1, less than 500 m from the seashore (high relative humidity and high chloride concentration), (ii) H2, between 500 m and 1500 m from the seashore (high relative humidity and mid chloride concentration), and (iii) H4, more than 20 km from the seashore (mid relative humidity and low chloride concentration). The binder content and aggregate proportion were the same for all concretes in the study. Table 1 presents the mix design.

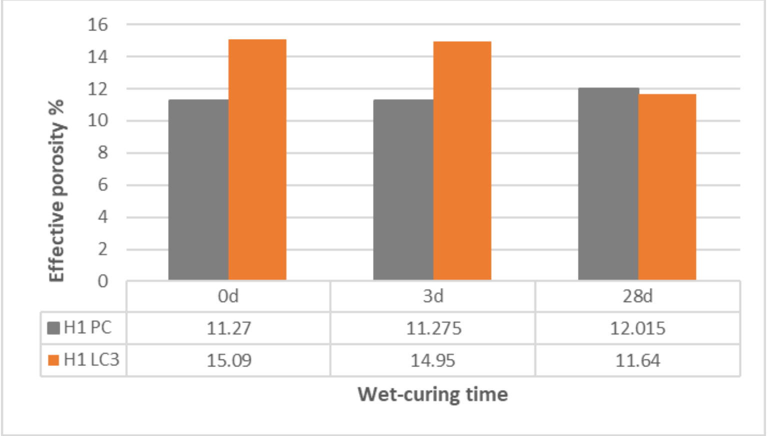
Table 1: Mix design for concrete specimens produced for carbonation studies

Mix type	Exposure class NC 120: 2014	Strength (MPa)	w/b	Cement (kg/m^3)	SP (kg/m^3)	Sand (kg/m^3)	Medium aggr. (kg/m^3)	Coarse aggr. (kg/m^3)	Water (kg/m^3)
H1	Very high	35.0	0.40	430	3.87	634	352	775	172
H2	High	30.0	0.45	405	3.65	651	362	796	182
H4	Low	20.0	0.55	345	3.10	690	384	844	190

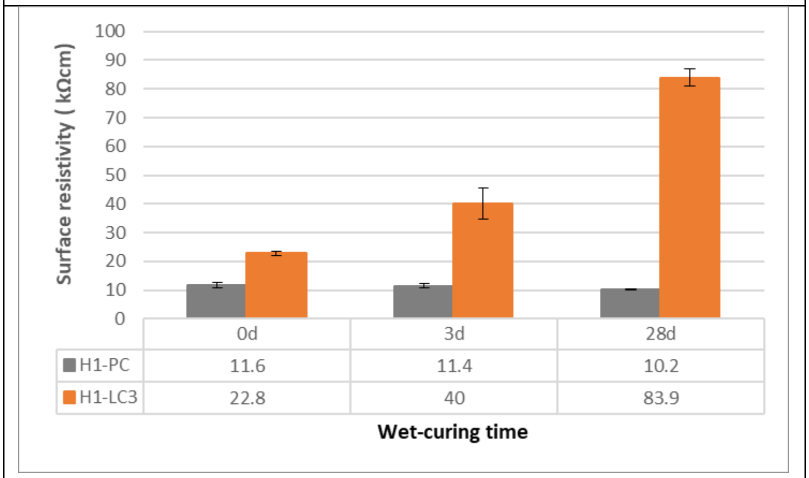
Note: Cement refer to cementitious materials that is OPC and LC3 (55% OPC + 30% Calcined clay + 15% Limestone)

The study was carried out in a condition that is expected to generate poor carbonation performance (60-70% RH and sheltered conditions). Initial properties of concrete (H1 series), carbonation performance of concrete (in realistic condition for 24 months) and integrity (in terms of strength and resistivity) of concrete after 24 months carbonation are presented.

Figure 9 a) presents the effective porosity (vacuum saturation) of the concretes studied for carbonation, which were cured for 1, 3 and 28 days. While in the series produced with OPC, curing does not seem to greatly influence the effective porosity, in the series produced with LC3, curing produces a reduction in effective porosity, even to levels below those of the series with OPC. This fact shows the importance of curing in calcined clay blended cements. Figure 9 b) presents the results of surface resistivity in specimens with 6 months of exposure to carbonation under the conditions in which the specimens were stored. The resistivity values in the LC3 series are higher even in the case of 1 day of curing, and the difference increases as the curing time increases; with only 3 days of curing, the surface resistivity of the LC3 series exceeds 4 times that of the OPC series, indicating that this concrete has a less connected pore system [24, 116]. This means that, despite having a higher porosity produced by the curing deficit, the series produced with LC3 has a less connected pore structure, as discussed in section 2.3, which is a crucial aspect of durability. Such differences in porosity and performance have been identified in slag-limestone combinations in [117]. It is important to note that surface resistivity can be affected by degree of saturation and pore solution compostion, despite the usefulness of the measurement to estimate the quality of the surface concrete.



(a) Porosity



b) Surface resistivity

Figure 9: Influence of wet curing time on (a) porosity and (b) surface resistivity on field concretes

Figure 10 shows the depths of carbonation for the H1, H2 and H4 series at 6, 18 and 24 months. The trend of higher carbonation in the systems produced with LC3 is confirmed, when compared with the values of the series with OPC. As the total cement content decreases and the w/b ratio increases, the carbonation depth increase rapidly over time. However, the values measured at 24 months are not significantly high, especially in the H1 series, because the exposure conditions have an average relative humidity greater than 70%, and the pore system of the concrete are expected to be saturated; hence, the entry and dissolution of CO_2 in the matrix is difficult [118, 119]. These conditions are typical of marine environments, where concretes produced with calcined clay show excellent behaviour against chlorides, the primary source of aggression in these environments [27, 73, 74]. The properties of the pore network of the matrix appear to impact these results [23, 27].

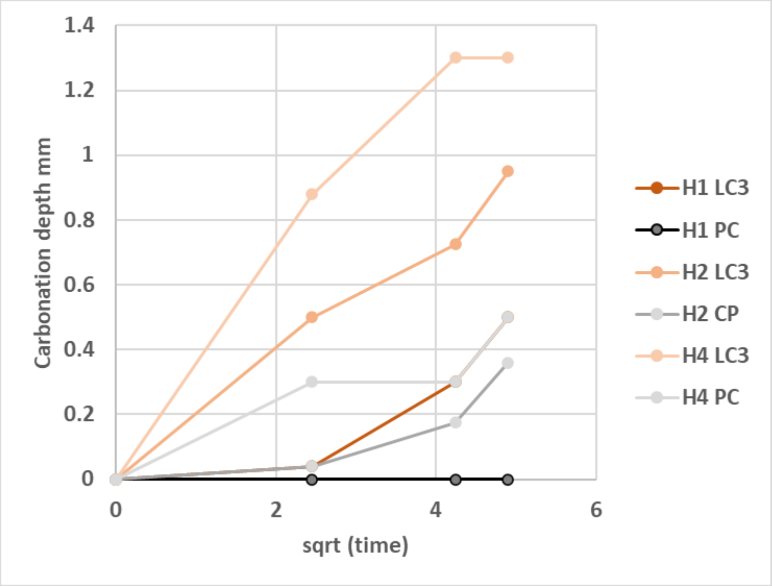


Figure 10: Carbonation vs. time (months$^{0.5}$) for all series studied

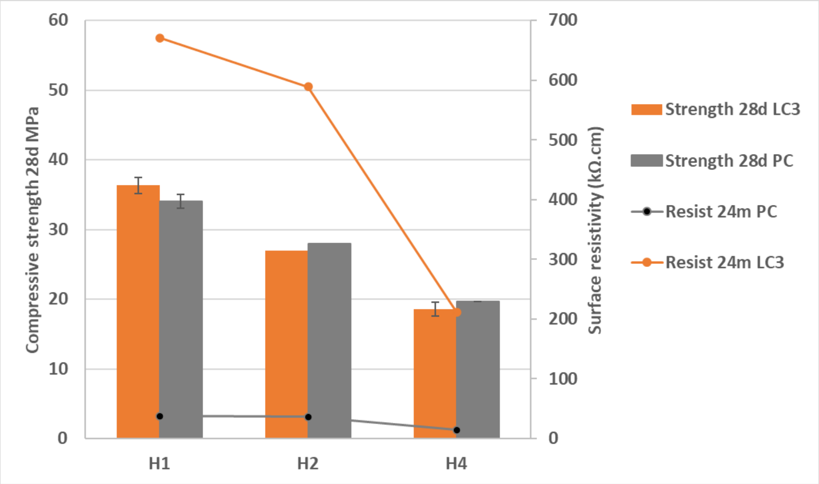


Figure 11: Influence of water-binder ratio and cement content on concrete resistivity

Figure 11 presents the combined effect of reducing water-binder ratio and cement content on the compressive strength and surface resistivity of concrete specimens produced. The reduction of the cement content and the increase of the water-binder ratio in both series have a similar impact on the compressive strength. An increase in surface resistivity is seen in the series produced with LC3 for all water-binder ratios and cement contents, compared to the reference concrete made with OPC. This confirms that under the exposure conditions of this study, the integrity of concretes upon natural carbonation exposure induced negligible changes in strength and surface pore structure after 24 months of carbonation in natural exposure environment.

4.3 Sulphate exposure

External Sulphate Attack (ESA) is caused by the reaction between SO_4^{2-} and AFm phases or portlandite forming secondary ettringite or gypsum, and sometimes thaumasite (when carbonates are present) inducing expansion, cracking, strength loss and spalling of paste, mortar or concrete [120–125]. This results in damage of cementitious binders and may jeopardize the engineering properties.

The extent of ESA depends on the physical (porosity, pore size, connectivity and tortuosity) and chemical (AFm, CH, alkalis) factors of the cementitious matrix. The physical resistance is determined by the pore structure, while the chemical resistance is governed by the availability of calcium and aluminium ions to form ettringite and portlandite to form gypsum. The classical zone-wise degradation profile of Portland cement mortars is confirmed by [120, 124, 126] : a) the outer sulphate deteriorated zone, b) the second zone with high sulphate concentration and generally with the formation of gypsum veins, and c) the gradual decrease in sulphate concentration to the bulk material where the formation of ettringite promotes the cracking of matrix. For sulphate resistant concrete, the use of less permeable concrete is the necessary to resist external sulphate attack [126–128]. In Portland cement systems, sulphate resistance is achieved mainly by reducing the water to cement (w/c) ratio and cement content. Changes in cement minerology can also improve the sulphate resistance by reducing the C_3A content in the OPC, reducing the AFm content and lowering portlandite precipitation by reducing C_3S content or using an active pozzolan.

The replacement of portland cement by SCM generally leads to improved resistance to sulphate attack by:

- the dilution effect that causes reduction of the C_3A content in the cement and reduces the amount of ettringite formation
- the filler effect caused by its relative fineness to the OPC that contributes to accelerating the hydration of OPC and refining the pore structure by the solid packing of the cementing particles
- the reduction of calcium hydroxide content in the cement paste, due to the pozzolanic reaction, preventing the secondary formation of calcium-rich phases such as ettringite while reducing the supersaturation of the pore solution with respect to ettringite and gypsum and thus crystallization pressures [129–131]
- enhancing the uptake of aluminium and thereby increasing the Al/Si ratios in C-(A-)S-H. This aluminium is mostly unavailable for secondary ettringite formation [23, 31, 132]. The presence of limestone along with calcined clay is expected to consume the alumina and produce carboaluminate phases, which otherwise would go C-(A-)S-H [23, 32]

The literature on sulphate attack in relation to cements utilizing calcined clays have the same challenges as discussed previously in this paper. The following sections explore the influence of the use of calcined clay and its combinations with limestone on the resistance to sulphate attack.

4.3.1. Studies using calcined clays

Various researchers have explored the performance of cementitious systems with MK after exposure to sulphate solutions, and a summary of the studies is presented in Table 2. The information presented in the table indicates that in laboratory studies with MK, cementitious mortars with high replacement levels of MK (> 10 – 15%) lead to improved performance in sodium sulphate exposure and more unsatisfactory performance in magnesium sulphate exposure. The reasons in both cases are tied to the higher consumption of CH. A reduction in gypsum and ettringite formation in sodium sulphate, leading to lower expansion in sodium sulphate solution. In $MgSO_4$, CH would be converted to brucite. The lack of buffering capacity of CH due to the pozzolanic reaction of MK causes a direct attack on C-(A-)S-H in the case of magnesium sulphate and favours the conversion of C-(A-)S-H into the M-S-H and gypsum, as is known from other SCM binders such as high slag content cements exposed to $MgSO_4$ [121, 133]. $MgSO_4$ leads to the formation of secondary gypsum and non-cementitious magnesium silicate hydrates (M-S-H) [121, 125, 133]. The formation of these phase are associated with disintegration of the cementitious nature and mass loss of the specimens. It is also seen that there are limited studies with lower grade calcined clay and ternary combination of calcined clay with limestone/dolomite in $MgSO_4$. Specific focus on additional phases formed in calcined clay binders such as CO_3-AFm and stratlingite and their interaction with $MgSO_4$ needs more focus in further studies.

Table 2: Studies exploring the performance of MK and calcined clay blended systems upon sulphate exposure

Reference	Experimental variables	Major findings	Implications
Calcined Kaolinite clay			
Khatib and Wild, 1998 [134]	C_3A content of 7.8% and 11.7% MK replacement between 5 and 25% 5% Sodium Sulphate solution	Expansion reduced with increasing MK replacement At least 15% replacement of MK needed to enhance resistance	At higher replacement levels of MK, there is a significant reduction in CH, leading to lesser gypsum and ettringite formation.
Ramlochan and Thomas, 2000 [135]	ASTM C1012 protocol with three cements, having C_3A contents of 0, 6.3, and 10.1% 5 – 25% replacement by MK	Irrespective of replacement level, showed moderate sulphate resistance. For high C_3A content, at least 10% MK substitution required to cause good sulphate resistance.	MK replacement of more than 10 – 15% can lead to improved performance even in high C_3A systems.
Courard et al. 2003 [136]	CEM I MK replacements at 5 – 20% 16.1 g/l sodium sulphate solution 0.5 w/b; 1:3 cement:sand, cured for 28 days initially and then subjected to exposure.	Sulphate expansion inhibited in systems with more than 10% MK replacement. CH consumption attributed to causing the positive effect.	Same as previous
Yazici et al. 2014 [137]	9.8% C_3A content in cement Exposure to sodium sulphate solution	MK replacement of 10 – 20% led to very good resistance to expansion	Same as previous
Vu et al. 2001 [138]	8.8% C_3A, 0.48 – 0.53 w/b, 1:3 cement:sand MK replacement 10 – 30% Exposed to 0.2M $MgSO_4$ solution	When MK replacement was high (30%), a significant reduction in exposed mortars' compressive strength of exposed mortars, when w/b was varied to attain the same flow as reference. When SP was used at same w/b as a reference, the damage was not seen.	At high w/b, systems with the large replacement of MK show significant damage to $MgSO_4$ solutions; this could be due to increased attack of C-S-H, due to the complete consumption of CH because of pozzolanic reaction
Lee et al. 2005 [139]	10.3% C_3A in cement MK replacement 0 – 15% Controlled w/b in all systems using SP $MgSO_4$ solutions of 0.42, 1.27 and 4.24% concentration used for exposure after 7 days of initial curing	No damage at low concentration (0.42%) in the MK systems. But for high concentration solution (4.24%), 15% of replacement systems showed high degree of deterioration – more gypsum seen in XRD	Consumption of CH due to highly pozzolanic MK can lead to direct attack of C-S-H and conversion to M-S-H

Kakali et al. 2003 [140] (then reconfirmed by [141])	Mortar (w/b 0.5 and 1:2.50) of Portland Limestone Cement (C_3A of clinker = 6.3%, 15% LF) with and without MK (10%) exposed to 1.8% $MgSO_4$ solution at 5 and 25°C during 12 months	Combination of PLC and MK was able to inhibit thaumasite form of sulphate attack	Thaumasite formation inhibited due to the altered chemistry brought about by the use of reactive MK and finely ground limestone
Hossack & Thomas (2015) [142]		Sulphate resistance of mortar bars with MK appears to increase at lower temperatures.	Attributed to early hydration caused by fine MK particles and the better hydration progress at low temperature for the mortars containing MK.
Calcined Non-Kaolinite clay			
Trumer and Ludwig (2018), Trumer et al. (2019) [143, 144]	Used calcined illite, montmorillonite and kaolinite – 30% replacement. German mortar flat prims (10 mm thick) 0.44% Na_2SO_4 solution at 5 and 20 °C	At 20 °C, OPC and blends with illitic (I) and montmorillonite (M) clays exceeded 0.1% expansion by 42 days, but overall expansion at 180 days lower for blended systems – these combinations had a practically same performance at 5 °C; Calcined kaolin (K) suppressed attack at both temperatures. M based systems better than control	Illitic clays may not show sufficient resistance to sulphates in the early stages; but long term performance may be better than OPC
Cordoba et al. 2018 [145]	ASTM C1012 tests on blends with white OPC (11% C_3A) and sulphate resistant OPC (3.5% C_3A) – 20 and 40% mass replacement by illite clays calcined to 950 °C and ground	High C_3A cement – expansion less than 0.1% even at 365 days; low C_3A – expansion less than 0.05%	Reduction in gypsum and ettringite formation in the mortar

Both increase in replacement level [146] and the reduction in water-binder ratio [147] has been shown to have a remarkable effect to improve the sulphate resistance of concrete containing MK . For calcined clays, results of blended sulphate solutions (different cations, or blends with chlorides or carbonates) have not been published so far, but based on the experiences with other SCMs, one would expect that expansion and deterioration would be less compared to pure sodium or magnesium sulphate solutions of high concentrations [130, 133]. Also, the role of sulphate in the natural environment like seawater and the impact of physical damage like salt crystallization due to fine pore structure in calcined clay systems and its role on sulphate ingress is not explored and warrants more studies.

Several studies have also worked with calcined clays based on illitic or montmorillonite clays (both 2:1 clays) or other clayey formations that may also include shale. The observations from these studies are also included in Table 2. As the reactivity of illlitic or montmorillonite clays is typically lower than the kaolinitic ones, the calcination conditions of these alternative clay types affect the concrete microstructure, phase assemblage and engineering properties. One example of this is illustrated for a lower Oxford clay calcined at different temperatures (600-1100°C) [148]. The OPC ($C_3A = 7.7\%$) was replaced by 10 and 20% by mass of calcined clay and the expansion of mortar (w/b= 0.485; 1:2.5) bars (25x25x285 mm) was measured in an exposure to 5% Na_2SO_4 up to 720 days. Results show that mortars containing clay calcined at a temperature higher than 900 °C show superior sulphate resistance to those containing clay calcined at temperatures below 900 °C – this is attributed to the correct proper thermal activation temperature this type of clay. Hence, proper calcination of clay could improve the sulphate resistance of the binders.

4.3.2. Influence of blends of calcined clay with limestone

In blended systems with calcined clay, additional ettringite is formed until complete depletion of gypsum, sourcing alumina from MK and calcium from portlandite after depletion of C_3A [35, 149]. Even though cements containing limestone alone have been shown to be prone to thaumasite formation [141, 150–152], MK has been reported to have a beneficial effect on thaumasite formation (reduced) [140, 141, 153]. MK was also seen to reduce the thaumasite form of sulphate attack in concretes made with PLC or containing calcareous aggregate [150]. Hence, the calcined clay-limestone combination is not expected to have expansion due to thaumasite formation at low temperature like PLC systems. This was confirmed in [154], where PLC showed higher expansion at 5 ºC than 20 ºC while MK-limestone combination did not show any significant expansion up to 400 days.

Shi et al. [154] studied a white cement ($C_3A = 9\%$) against sulphate attack with 35% replacement of SCM (limestone and MK). The results showed that mortars containing MK or calcined montmorillonite and limestone (35 % w/w replacement) with $CC/(CC + L) \geq 0.5$ exhibit excellent sulphate resistance. Rossetti et al. [155] showed results on sulphate performance of blended cement with limestone filler (LF) and lower grade illitic calcined clay ($C_3A> 8\%$; 15%LF; 15%CC) that were exposed immediately to the aggressive environment. The study showed that monocarboaluminates in the OPC+LF systems were unstable in a sulphate environment. They rapidly formed ettringite causing cracking and massive penetration of sulphate ions promoting the gypsum formation, expansion and compressive strength reduction. On the contrary, the pozzolanic reaction of illitic calcined clay in mortars consumed the CH and blocked the sulphate ingress due to pore size refinement. Although CO_3-AFm phases formed during hydration were converted to ettringite in exposed pastes, the mortar showed no expansion and retained the compressive strength at 6 months in these ternary systems. Finally, the studies identified that calcined clay to limestone ratios of more than 1:1 lead to a suitable performance.

The severity of damage could increase for alternate soaking and drying exposure due to the salt crystallization phenomenon, which could cause harmful effect due to physical damage. However, there are only limited studies in this regard. While there are several examples of standard laboratory tests with paste or mortar exposed to sulphate solution, concrete performance results are not available aplenty as concrete studies are typically inconclusive for the short periods of laboratory investigations. Since calcined clay and calcined clay-limestone combinations are currently gaining interest in several countries, it is essential to document the field performance of calcined clay concrete in the sulphate rich environment. The initial premise from laboratory assessment suggests that performance of calcined clay systems would be satisfactory in most sulphate exposure.

4.4 Alkali Silica Reaction

Alkali silica reaction is the chemical reaction between reactive silica phases in aggregates and the hydroxyl ions present in the pore solution of concrete. The occurrence of ASR was reported and investigated all around the world in many different types of structures [156–160]. Many types of siliceous aggregates have a potential reactivity of ASR and are thus disregarded, limiting the concrete sustainability in locations where the availability of non-reactive aggregate is limited [160]. Therefore, numerous studies have been conducted to develop effective methods to mitigate ASR in concrete structures, which allow for using the reactive aggregates in concrete structures. Most ASR mitigation methods have focused on preventing and/or reducing the amount of ASR gels formed by modifying the chemical environment in concrete. These include i) usage of the low-alkali cement, ii) usage of SCMs and ii) usage of chemical admixtures such as lithium-based admixtures [161–167].

In a relatively recent review [144], recommendations were given for the use of calcined clays for ASR mitigation. It was identified that the amount of aluminium and amorphous phase in calcined clay should be quantified before using them for ASR mitigation. The amount of aluminium can control reactive silica dissolution and form hydrates with higher alkali-binding ability. Additionally, it was suggested that the quantification of the impurities in calcined clays could also be useful in evaluating the effectiveness of calcined clays towards ASR mitigation, as such impurities in calcined clays are usually not pozzolanic. Concrete prism tests (ASTM C1293 [168]) were performed using the high-reactivity MK (HRM) as a SCM in [6]. This study suggested that 15% HRM concrete can effectively prevent the ASR expansion – the results showing that the ASR expansion was less than 0.04% after 2 years, as shown in Figure 12.

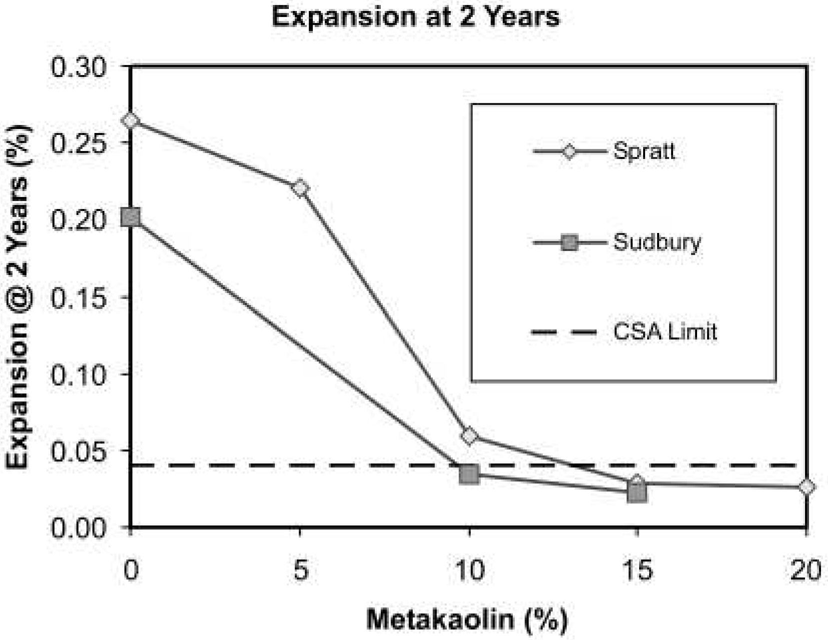


Figure 12: Effect of high-reactivity MK on the ASR expansion of concrete prisms, tested using two highly-reactive aggregates [6]

To date, there are only limited studies available for alkali-silica reaction (ASR) in LC3 concrete [169–171]. In [169], the modified accelerated mortar bar tests for ASR were conducted. In their tests, three types of mortar bars were prepared using the highly reactive Jobe sand: i) 100% Portland cement (OPC), ii) 50 wt.% replacement of PC with limestone and calcined clay, and (iii) 65 wt.% replacement of OPC with limestone and calcined clay. The clay used had a calcined kaolinite content of 50%. The mortar bars prepared in the study were cured for 28 days in a fog room and then immersed in 0.32M NaOH solution. The results clearly showed that the replacement of OPC by the limestone – calcined clay blend significantly reduces the ASR expansion.

Recently, the ASR mitigation potential of by LC3 was reported in [170] using the standard accelerated mortar bar tests (ASTM 1567 that is equivalent to AS 1141.60.1). A low-quality flash-calcined clay composed of 49.1% of quartz and 50.9% of amorphous phases was selected to make the LC3 blends. As shown in Figure 13, both mortar bars had less expansion than the expansion limits specified in AS 1141.60.1 and ASTM C1567. In addition to the LC3 benefits similar to the other SCMs for ASR mitigation, the results showed that, in the initial stage of ASR, the calcium-rich phases such as C-S-H, C-A-S-H, monocarboaluminate and katoite were produced near the ASR reaction sites. These calcium-rich phases delayed the formation of ASR gel, and also the resulting ASR gels had a high Ca/Si ratio that is less expansive [170].

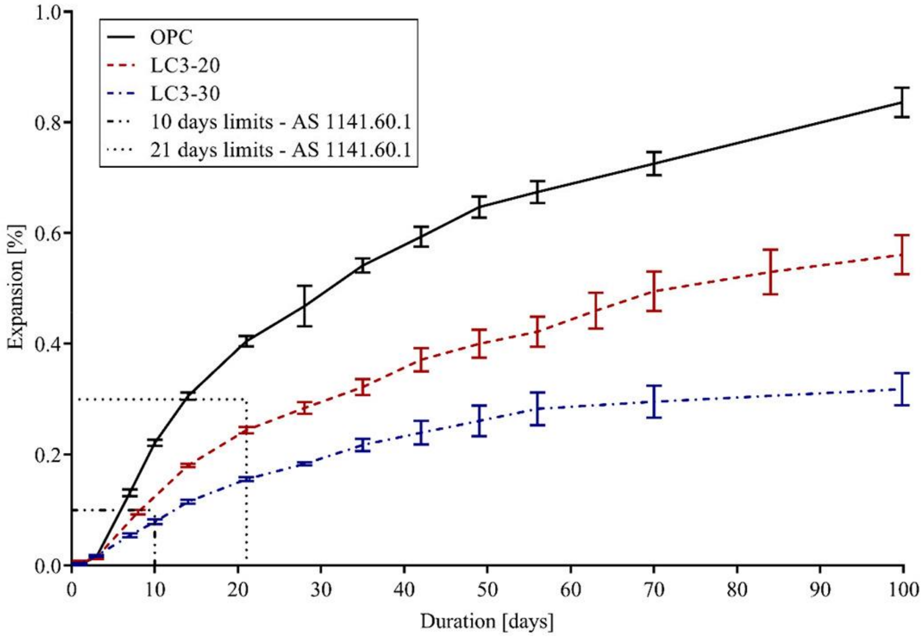


Figure 13: ASR expansion of mortar bars in accelerated mortar bar [170].

Note: Two different mortar bars were prepared, including i) 20 wt.% replacement of OPC with limestone and calcined clay (LC3-20) and ii) 30 wt.% replacement of OPC with limestone and calcined clay (LC3-30).

The exact mechanisms of mitigation of ASR expansion in LC3 systems are not fully understood. However, considering the pozzolanic reaction of calcined kaolinite (MK), one can expect that LC3 would have similar effects to typical SCMs (such as fly ash and slag) on the mitigation of ASR expansion. These include i) reducing the alkali content in the binder due to the dilution effect, ii) reducing the alkali concentrations in the pore solution due to the alkali fixation by supplementary hydration products, iii) producing a denser paste matrix to slow down the diffusion or migration of ions involved in ASR reaction, and iv) limiting the silica dissolution due to the effect of aluminium [145, 161–163, 170, 172–175].

4.5 Durability against acid attack

The resistance of concretes containing calcined kaolinite clays to acids has been investigated on several occasions. In the vast majority of the studies, the addition of MK in concrete proved beneficial in terms of acid resistance. Even a 10% cement replacement with MK improved the acid resistance by 10% compared to a neat Portland cement mix [133], whilst greater replacements, e.g., 20 and 30% did not significantly improve the acid resistance. Similar improvement in acid resistance was found for 10% MK replacement in [177]; the acid resistance was reportedly improved by approximately 30% compared to a pure Portland cement mix. In another study, even better acid resistance was reported where a 15% MK containing mix immersed in sulphuric acid exhibited 38% less reduction in compressive strength compared to a 50E cement (65% Portland cement, 35% slag) mix after 61 days of immersion [178]. Similar results confirming MK addition's beneficial effect in acid resistance have been reported elsewhere [179, 180]. However, the identified literature focused mainly on highly kaolinitic clays (in the form of MK), highlighting the need to investigate the performance of lower grade clays. Additionally, the interaction of carboaluminate phases formed in LC3 like systems in an acidic environment and its impact is not well reported in the existing literature.

4.6. Durability against freeze-thaw cycles

MK addition also increases the resistance of concrete to freeze-thaw related damage. The resistance of MK containing concrete on freeze-thaw exposure was investigated by [106], where it was reported that the MK containing mixes with 5 and 10% MK content exhibited similar or even better freeze-thaw performance compared to neat cement mixes. Another study [68] demonstrated excellent frost performance of MK mixes with no effect on compressive and bending strength after 100 cycles. Such improvement is possibly observed due to the pore refinement resulting from the pozzolanic activity [181]. Similar observations regarding the efficiency of adding MK on the frost resistance of concrete were reported by [182], where mixes containing MK up to 25% were investigated, with 20% being the most efficient replacement level. There are currently limited studies identified with low grade/non-kaolinitic clays and LC3 systems, which can be focused in future research. Since calcined clay addition makes fresh concrete cohesive, the control of air content in calcined clay concrete needs to be studied in detail as it is key to improving the freeze-thaw resistance in concrete systems.

5. Conclusion and perspectives

This paper explores the impact of calcined clays on the durability performance of concrete in binary and ternary blended cementitious systems. The role of the pore structure alteration due to the replacement of cement by calcined clays is explicitly highlighted as the main contributor to the observed transport properties of such systems, which improves the performance of concrete systems in several durability exposure conditions. Major highlights on the role of calcined clay on durability performance of concrete systems are summarized below:

i. Calcined clay modifies the pore structure by the refinement of sizes rather than reducing the total pore volume. Hence, total pore volume, per se, is not a reliable indicator of the durability performance for binary and ternary binders containing calcined clays. Due to pore refinement, durability indices such as resistivity and absorption rate are improved significantly in calcined clay concretes, more specifically in concretes prepared with kaolinite clay. Less information exists on pore structure and transport properties using non-kaolinitc clays. Moisture uptake was consistently lower by 30% for calcined clay replacement >20%. More research should focus on understanding the role of porosity and pore sizes on transport properties in calcined clay systems. When kaolinite content in the raw clay was above 40%, there is no significant difference in pore structure obtained using MIP. The role of clay reactivity on physical structure development, specifically at later ages, is not well reported. While it is believed that the pore structure parameter controls the transport properties, there are limited studies to link the structure-property relationship with respect to transport properties; unlike structure-property relationships established to explain mechanical properties in cementitious systems.

ii. The carbonation rate in calcined clay concrete is expected to increase with clay replacement level. A statistical analysis of existing data showed that the carbonation rate could be 3-4 times higher than plain cement concrete. Due to the limited portlandite reserve, decalcification of C-(A-)S-H and other AFt and AFm phases is the primary interaction with atmospheric CO_2 in calcined clay systems. Incorporation of factors such as reserve alkalis were found to be necessary for calcined clay systems. Carbonation of low Ca/Si ratio C-A-S-H formed in calcined clay systems leads to coarsening of pore structure, which was found to reduce transport indices. Still, there are limited investigations of transport properties of carbonated calcined clay concrete which is close to concrete in realistic conditions. Studies on carbonation induced corrosion in calcined clay are limited and suggest conflicting results, which needs to be investigated further. Detailed investigations exploring service life prediction models are limited to analysing the impact of higher carbonation rate found on calcined clay on the service life of infrastructure systems.

iii. Sulphate resistance improved for calcined clay systems in sodium sulphate exposure for both kaolinite and non-kaolinite clays. The addition of limestone with calcined clay did not lead to any thaumasite attack as in PLC. Limited studies exist on seawater exposure, physical sulphate attack, magnesium sulphate attack for calcined clay systems, which could be explored in further research on leaching and decalcification of alumina rich low Ca/Si ratio C-S-A-H expected to form in calcined clay systems.

iv. The tendencies for ASR were effectively reduced by calcined clay addition with metakaolin (at lower replacement level of 10-15%) and calcined clay-limestone combination. The use of non-kaolinite clay for ASR reduction is not well reported.

While the refined pore structure is seen to have a significant impact on most durability properties, it is seen that certain phenomena such as carbonation and magnesium sulphate attack result in reduced performance compared with plain OPC systems, owing to the lack of the calcium hydroxide buffer that is typically present in plain cement systems. While calcined kaolinite clays have been explored in the recent past, there are very limited studies on durability with marine dredging clays, mixed clays and other clay types. More studies can focus on understanding these alternative clays forms for substituting energy-intensive Portland clinker. The paper highlights the need for additional studies to be carried out in several domains, given the growing interest in calcined clays – both kaolinitic and non-kaolinitic – all over the world.

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Conflict of interest Statement

There are no conflicts of interest in this paper for any of the authors.

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