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# The meta-kaolinite content of the calcined clay source impacts the mechanical and durability performance of blended Portland concrete

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#### ABSTRACT

This study evaluated the mechanical and durability performance of CEM I and CEM I plus limestone blended concrete produced with calcined clays (CC) with a varying meta-kaolinite content (70, 50 or 20 wt%). Results revealed that concrete with >45 MPa can be produced with a CC with only 20 wt% meta-kaolinite. Increased compressive and flexural strengths were obtained using higher meta-kaolinite content CC. Limestone addition did not significantly change the concretes' transport or durability properties when compared to binary mixes, despite the reduced clinker factor. CC-containing concretes exhibited excellent chloride resistance, but reduced carbonation performance compared with CEM I. Using a CC with higher meta-kaolinite content enhanced the concrete's carbonation resistance, when evaluated for 650 days of natural exposure. This suggests that generalising the impact of CC addition on concrete performance can be misleading, as bespoke concrete, compliant with specific exposure class requirements, can be produced by appropriate clay selection.

## 1. Introduction

The climate emergency and the need to mitigate its progress are driving the adoption of low-carbon technology across the construction industry at a rapid pace. There are readily implementable strategies, such as reducing clinker content by using a cement replacement or supplementary cementitious material (SCM), and optimising mix design during concrete production, with the potential to reduce annual CO2 emissions associated with concrete by over 20 % from the current levels [1,2]. SCMs such as pulverised fuel ash, silica fume, granulated blast furnace slag, powdered limestone and metakaolin (MK), have been extensively used to reduce Portland cement contents in concrete production [3,4]. These SCMs are industrial by-products or naturally occurring materials (limestone) with a reduced environmental impact compared to Portland cement clinker production [5,6]. The availability of conventional SCMs is expected to decline in the coming decades due to changes in some industries [7], creating a renewed interest in exploring widely available natural sources, such as low purity clays, as alternative SCM sources.

Naturally occurring clays/soil can be activated through different thermal or mechanical processes to produce reactive SCMs [8-11]. Thermal treatments or calcination between 500 and 800 °C are widely applied to induce structural disorder to enhance the reactivity of clays to make them pozzolanic, which in the case of kaolinitic clays is can be associated with its de-hydroxylation and consequent amorphization [12-14]. The production of calcined clay is less energy- and emissionintensive than clinker production due to lower firing temperatures and the absence of a limestone decomposition reaction [15,16]. Upon calcination, 1:1 kaolinitic clay minerals are more reactive than 2:1 clay minerals like smectite, illite or chlorite [17–21]. For kaolinitic clavs, it is known that the total calcined kaolinite content (i.e., meta-kaolinite content of the calcined clay) controls the reactivity and mechanical properties of materials produced with them [22,23]. A wide range of clays with varying clay mineralogy and chemical compositions [24-26], other associated minerals and impurities [9,27,28], as well as particle sizes have been evaluated for developing SCMs. Additionally, secondary clay sources such as excavation soil spoils are being used to produce SCMs to increase their circularity in construction, while reducing the

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amount of materials landfilled that affects biodiversity [29–31]. The suitability of a given clay source as a potential SCM is determined by its pozzolanic reactivity, once the clay has been treated (e.g., calcined), which changes with variations in mineralogy, purity, surface area, and clay composition [22,32] as well as processing routes [33,34]. Clays with >40 % kaolinite content are widely recognised as suitable for producing reactive SCMs (once calcined) [22]. However, the global distribution of clays varies significantly, and clays with desired purity, i. e., >40 % kaolinite content, are not always available in different locations [35,36]. For instance, the kaolinite content of clay deposits in the UK and in many parts of Europe is known to be typically below 40 wt% and rich in other clay minerals [36], have not widely studied, particularly when used to produce concrete.

With the growing demand for cementitious materials for concrete construction in many parts of the world, there is an urgent need to widen the envelope of resources that can be used. Low-purity clays are expected to become a prominent source for SCMs to develop sustainable concrete, while reducing costs and improving resource efficiency. However, while reducing the clinker factor in cement formulations is essential to achieve the ambitious decarbonisation targets of the concrete industry, it is also essential to ensure the durability and long-term performance of concretes produced with these novel cementitious materials to ensure transition towards a green construction economy [37].

In addition to the intrinsic properties of a calcined clay, its reactivity in cementitious systems will vary based on the clinker replacement level, blend composition (including sulfate and alkali addition), as this influences the portlandite content in the system and consequently the extent of the pozzolanic reaction. This, in turn, controls the hydrates phase assemblage (type and amount of hydration products forming) and pore structure [38-40]. Hence, the choice of calcined clay used can produce varying levels of performance against chloride, sulfate and/or carbonation exposures depending on the blend composition. The use of calcined clays along with finely ground limestone can also enable higher Portland cement replacement [41-45]. Limestone addition as such introduces numerous physical and chemical changes in a cementitious system, modifying the hydration mechanisms and subsequent performance of materials produced with a combination of CC plus limestone, as discussed in [45]. The amount of carboaluminate-based AFm (monoaluminate ferrite) phases formed changes with the kaolinite content in the clays in calcined clay-limestone combinations, with maximum carboaluminate forming while using calcined clays with a min of 50 wt% kaolinite content and carboaluminate phases start decreasing thereafter [22,46]. Similarly, it has been reported that pore refinement and chloride binding vary with kaolinite content in cementitious matrix, based on studies on cement paste systems [22,46,47]. The combined use of limestone and calcined clay usually leads to higher amounts of carbonate-rich AFm type phases, compared to binary binders with calcined clay, which can induce to early ages pore refinement [48,49]. Moreover, limestone addition also leads to preservation of the ettringite formed during initial hydration, which further contributes to space filling [45,50]. Studies comparing different SCMs i.e., fly ashes, blast furnace slags and calcined clays, with limestone addition have consistently demonstrated that the benefit of limestone addition in terms of pore refinement is less pronounced when compared to that of SCM type [51]. These composite, multi-component systems are currently being adopted in different standards [52-54], but there is limited information on long-term concrete durability performance, which needs to be understood for the confident adoption of low-carbon cements in critical infrastructure.

Durability of concrete is dependent on the intrinsic properties of the material and its interactions with the surrounding environment. From the material perspective, it is well known that durability performance is influenced by mix design parameters, including water-to-binder ratio (w/b), and cement type (including different SCMs), as these parameters affect microstructure development and consequently water and gas permeability, as a function of the curing age [55,56]. The in-service

environment poses different threats, mainly identified as chloride ingress and carbonation as the most harmful for reinforced concrete structures. Chloride-induced corrosion is one of the major concerns for reinforced concrete structures, especially in aggressive marine exposure conditions or parts of highway structures with frequent de-icing salt exposure. The transport of chloride ions is governed by the pore size distribution and connectivity of the pore structure [57-60]. It is well accepted that the partial replacement of Portland cement by calcined clays increases the total porosity of the cement paste while resulting in pore refinement [48,61,62]. Pore network tortuosity in calcined clay concrete can be 3-4 times higher than in Portland cement concrete [58]. Hence, the transport of external ions can be retarded [63,64]. Although calcined clays are known to refine the pore structure, being beneficial for durability [8,48,65,66], the extent of pore refinement varies depending on the clay purity and reactivity which is largely lacking. Therefore, the durability performance of concrete containing low-purity clays needs to be assessed before accepting such clays as SCMs for concrete used in aggressive environments, as highlighted by Dhandapani et al. [67].

Previous studies on concrete containing limestone-calcined clay combinations were primarily limited to a single source of calcined clay with purity >50 % [58,66,68]. In [22], it was identified that using clays with increasing kaolinite contents above 50 wt% had a negligible effect on performance due to maximum pore refinement, reduced degree of clinker reaction and limited formation of carboaluminate phases. However, there are no systematic studies showing how the effect of varying kaolinite content and clay mineralogy of low-purity clays may affect concrete performance related to various durability mechanism. Such studies could facilitate the uptake of calcined clay cements and/or accelerate the adoption of calcined clay-limestone combinations as performance-enhancing mineral additions. Furthermore, depending on the chemical composition of the binder, it is possible to reduce chloride ingress by chemical interactions, i.e., Friedel's salt formation (chemical binding) or by adsorption into the hydrated phases of the cement (physical binding) [63,69,70]. While chloride resistance is typically improved by the use of SCMs, reducing clinker content leads to lower pH, which leads to reduced carbonation resistance and lower chloride binding [71,72].

Carbonation resistance is increasingly identified as a concern for new low-clinker cements [60,73-77], this is often related to the reduced portlandite content in such systems, due to the both the lower clinker content along with the ongoing pozzolanic reaction [78]. Changes in the key binding phases - e.g. formation of an aluminium substituted calcium silicate hydrate (C-A-S-H) with reduced Ca/Si ratios than C-S-H -along with carbonation of secondary phases such as AFt (Tri-aluminate ferrite) and hemi- or mono-carboaluminate phases, which form in larger amounts in the presence of some SCMs, can significantly change the chemical interaction of CO<sub>2</sub> with hydrated cement paste [79,80]. Since calcined clay-limestone combinations are effectively produced with high clinker replacement levels (up to 45 wt%), these could also lower the CO<sub>2</sub> binding capacity in ternary formulations [79], and the beneficial effects of pore refinement observed in calcined clay-based systems may not be sufficient to mitigate the chemical reactions taking place upon CO<sub>2</sub> exposure [81]. The pore refinement observed in calcined claylimestone cement can contributes to enhance the carbonation resistance by reducing the permeability of CO<sub>2</sub> into concrete, however, carbonation in Portland cements containing SCMs is known to coarsen the pore structure [82] which may eventually counteract the benefits of pore refinement achieved as hydration progress [81]. Studies have also shown that accelerated carbonation testing using high CO2 and controlled relative humidities can modify the carbonation mechanism compared to that observed in specimens exposed to ambient conditions [84]. This means that for modern blended cements materials selection, or performance prediction cannot be relied on accelerated testing alone. Therefore, for the adoption of newer low carbon cements, natural exposure studies to evaluate the long-term performance in service

conditions are required. The critical role of the clay's kaolinite content on the performance of concretes containing calcined clays is not well understood, despite its critical importance for clay resources selection. In response to this knowledge gap, the present study conducted an extensive evaluation of the mechanical (e.g. compressive, flexural and splitting tensile strength, among others), transport properties (e.g. water absorption) and durability performance (e.g. chlorides and carbonation), at various curing ages and exposure durations, of two sets of concrete: binary mixes of CEM I blended with 30 wt% calcined clay, and ternary mixes of CEM I, 30 % calcined clay and 15 wt% limestone. Concrete was produced with three calcined clays, each with a different meta-kaolinite content. Recommendations for materials selection based on specific desired performance (depending on the potential in-service condition of a given concrete) are provided.

## 2. Experimental programme

## 2.1. Raw material characterisation

In this study a commercial plain Portland cement, type CEM I 52.5 R, complying with EN 197–1 [85], and three clays with various kaolinite contents were used. The nomenclature used here is K70, K50, and K20 to indicate the clay's kaolinite contents of 70, 50, and 20 wt%, respectively. K70 and K50 have quartz and muscovite as the major associated minerals, while K20 is an excavated London clay containing about 20 wt % kaolinite plus other clay minerals and carbonate impurities. Detailed characterisation of the London clay can be found in [30]. The K70 clays were calcined at a laboratory scale using a Carbolite CWF muffle furnace at about 800 °C for 1 h using porcelain crucibles in multiple batches (about 500 g each). Both K50 and K20 were industrially calcined, and details are available in [86] and [30], respectively. Ground limestone, supplied by Heidelberg Materials, Germany, and gypsum (calcium sulfate dihydrate, Alfa Aesar 98 % pure) were also used to formulate binder combinations.

The chemical compositions of the materials used were determined by X-ray fluorescence (XRF) using a fused bead preparation method in a Rigaku ZSX Primus II, as shown in Table 1. Non-negligible LOI value (Table 1) can be noticed for both calcined clay source (i.e. K50 and K20) which could be from trace of carbonate impurities present or decomposition of any other minerals. All calcined clays were characterised using X-ray diffraction (XRD) and thermogravimetric analysis which confirmed that there is no uncalcined kaolinite phase remaining in both K50 and K20. The quantitative mineralogical composition of the three calcined clays was calculated via quantitative XRD applying the Rietveld refinement method using external standard method, and the quantities of major minerals phases (quartz, muscovite and amorphous content), are included in Table 1. Particle size distribution (PSD) measurements were conducted using a Malvern Mastersizer 3000. An in-situ ultrasonication treatment of 5 min was carried out before each measurement. For clays, a dispersal medium of deionised water was used, using a pinch of sodium hexametaphosphate as a dispersal agent. The optical parameters used were refractive index = 1.56, and absorption coefficient = 0.01 [87]. For the cement powder, isopropanol was used as the dispersing medium, and measurements were collected using a refractive index = 1.7, and absorption coefficient = 0.1 [87]. The PSD curves for the three clays are provided in Fig. A1 in supplementary information. Specific surface area was obtained using the BET method using Micromeritics Tristar Flowprep 060 unit (testing methodology as detailed in [30]) and the values are reported in Table 1. Specific surface area of the three clays were found vary in the order K50 > K20 > K70 (Table 1) which shows the contribution of other mineral phase on physical properties; not directly linked to the meta-kaolinite content of calcined clay source used. The specific gravities of CEM I, calcined clay, limestone and gypsum were determined by helium pycnometry, and shown in Table 1.

The chemical reactivity of the calcined clays was evaluated

## Table 1

Oxide composition,	mineralogical	composition,	physical	properties	of	CEM I,
clays <sup>a</sup> and limestone	2.					

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Oxides	CEM I	Limestone	K70 <sup>a</sup>	K50	K20
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
CaO	64.78	52.7	0.05	0.81	3.41
Al <sub>2</sub> O <sub>3</sub>	3.89	0.98	34.8	22.59	18.55
SiO <sub>2</sub>	21.82	3.51	49.05	69.34	57.97
Fe <sub>2</sub> O <sub>3</sub>	1.33	0.43	1.12	2.89	8.05
K <sub>2</sub> O	0.67	0.11	3.25	0.28	3.80
MgO	0.76	0.53	0.32	0.27	3.44
Na <sub>2</sub> O	0.30	0	0.21	0.37	0.77
SO <sub>3</sub>	3.57	0.11	0.03	0.08	0.80
TiO <sub>2</sub>	0.17	0	0	1.24	1.06
LOI-900 °C 1 h	2.20	41.5	10.92	1.9	1.20
Other traces	0.65	0.17	0.23	0.26	0.97
Major mineralogical phases	of CEMI a	nd calcined clav	s (wt%)		
Ouartz	-	_	3.08	33.01	23.4
Muscovite	_	_	6.66	2.04	35.3
Amorphous content	_	_	86.97	56.83	29.6
C <sub>3</sub> S	56.97	_	_	_	_
C <sub>2</sub> S	20.36	_	_	_	_
C <sub>3</sub> A	7.78	_	_	_	_
C₄AF	2.04	_	_	_	_
Anhydrite+Gypsum	6.38	_	_	_	_
+Bassanite					
Calcite	2.97	_	_	_	_
Other minor phases	3.50	_	3.29	8.12	11.7
Ĩ					
Physical properties of ceme	nt calcined	l clays and lime	stone		
Specific gravity	3.11	2.63	2.66	2.62	2.56
Particle size distribution	1.2/	15/81/	3.4/	4.0/	0.5/
(um) d10/d50/d90	8.0/56	42.7	8.6/	24.27	121/
(µ) a10, a00, a90	0.0,00		21	80.5	86.6
BET Specific surface area			5.86	13.85	9.45
m <sup>2</sup> /g			2.00	- 5100	

<sup>a</sup> XRF of K70 is for raw clay, and K50 and K20 are for the calcined clays.

according to the ASTM C1897-20 [79] using a TAM air calorimeter. The 7-day cumulative heat of the three calcined clays were 810, 460 and 310 J/g of SCM for K70, K50 and K20, respectively. All three calcined clays had R3 cumulative heat release > 190 J/g of SCM that meets the 90 % confidence threshold to classify as "moderately reactive calcined clay" [88]. The higher the kaolinite content in the uncalcined clay, the higher the reactivity of the calcined clay. The calorimetry cumulative heat release curves are available in Fig. A2 in supplementary information.

## 2.2. Characterisation of aggregates

Physical properties of the fine and coarse aggregates, such as specific gravity and water absorption, were determined as per BS EN 1097-6-2022 [89]. Specific gravity of gypsum was 2.32. The specific gravity and water absorption of fine aggregates were 2.64 and 0.81 %, respectively. The coarse aggregates were 10 mm and 20 mm crushed aggregates with specific gravities of 2.59 and 2.58 and water absorption of 0.85 % and 0.86 %, respectively.

## 2.3. Mix design of the blended cement and concrete

Binary and ternary blends were prepared with three calcined clays and calcined clay-limestone combinations. The binary blends replaced 30 wt% of the CEM I with calcined clay, while the ternary blends contained 30 wt% calcined clay and 15 wt% powdered limestone, as per the mix design summarised in Table 2. Additional gypsum was included in the mix for sulfate balance based on a hydration kinetics assessment of each calcined clay. For K20, 1 wt% gypsum was found to be suitable (details discussed elsewhere [30]) and for K50 and K70, about 3 wt% gypsum addition was required. No further adjustments in terms of intergrinding were carried to the cement blends. The blends are denoted

#### Table 2

Blended cement mix design (wt%).

	6			
Mix ID	CEM I	Calcined clay	Limestone	Gypsum
CEM I	100	-	-	-
CC30-K20	69	30	-	1
CC30-K50	67	30	-	3
CC30-K70	67	30	-	3
CCL45-K20	54	30	15	1
CCL45-K50	52	30	15	3
CCL45-K70	52	30	15	3

as CC for binary calcined clay, and CCL for calcined clay-limestone, and the following number indicates the total replacement levels of the Portland cement, i.e., 30 or 45 wt% in each case. For example, CC30-K20 denotes a binary blend containing 30 wt% calcined clay with 20 wt% meta-kaolinite content. Binary blended cements with 30 % clinker replacement are widely used by the construction industry, when using the conventional SCMs such as fly ashes, natural pozzolan, blast furnace slags [90]. In this study, the performance of binary blended cements was compared with those with a 45 % replacement of clinker for calcined clay + limestone to assess the potential variation in performance at an increased clinker substitution in composite cements. All experiments were conducted on the seven blends listed in Table 2.

Table 3 provides details of the mix designs and measured initial slumps of each concrete mix evaluated in this study. The mix designs were based on a minimum binder content of 360 kg/m<sup>3</sup> and 0.50 (w/b) for 50 years' service life concrete in XS3 conditions, as per Table A.4 in BS 8500-1 [91] for a cover depth of 55 mm. The ratio of coarse aggregate and fine aggregate was 55:45, and within the coarse aggregate fractions, a mixture of 10 mm and 20 mm sized crushed aggregate in a 45:55 ratio was used. Initial superplasticiser (SP -ViscoCrete 600 MK from SIKA Ltd.) content was obtained from mortar mixes with similar w/b ratios, with further adjustment of SP contents in the concretes to produce an initial slump in the range of S2 class.

## 2.4. Experimental methods

Table 3

## 2.4.1. Evaluation of hardened concrete properties

Compressive, flexural and splitting tensile strength were tested, as per BS EN 12390-3 [92], BS EN 12390-5 [93] and BS EN 12390-6 [94], respectively. Compressive strength was measured on 100 mm cubes, cured in a moist room (>95 % relative humidity) continuously after demoulding and tested in triplicate at 3, 7, 28, 90 and 180 days of curing. Prismatic specimens of size  $500 \times 100 \times 100$  mm were tested for flexural strength at 28 days, and  $100 \times 200$  mm cylinders were tested for splitting tensile strength at 28 days.

Ultrasonic pulse velocity (UPV) of hardened concrete cubes was recorded in triplicate, as per BS EN 12504-4 [54] at 3, 7, 28, 90 and 180 days of curing.

## 2.4.2. Evaluation of transport properties and durability performance Surface resistivity test was used to evaluate the resistivity of water-

saturated concrete, which provides a rapid indication of the resistance to the flow of ions within concrete. Test was carried out on  $100 \times 200$  mm cylindrical specimen in accordance with AASHTO-T358: 2015 [95] and BS EN 12390-19: 2023 [96]. A four-point Wenner probe with 1.5-in. spacing was used on specimens placed in a moist room for the entire duration of the study. The average surface resistivity of ten measurements was taken on 3 specimens each at 3, 7, 28, 90 and 180 days of curing.

Water Sorptivity was carried out by estimating the water absorption (sorptivity) as a function of time with one of the cross-sectional surfaces being exposed to water. The test was carried out on a 50 mm cylindrical disc obtained from 100  $\times$  200 mm cylindrical specimens as per BS 1881-208 [97]. Cylindrical specimens of 100 mm diameter were sliced to 50 mm, and the peripheral surface was coated with epoxy to ensure unidirectional absorption. The specimens were conditioned at 105 °C for 7 days and later cooled to room temperature before testing. It is widely known that preconditioning used for the specimens, such as drying temperature and relative humidity, can significantly influence the moisture uptake profiles [98]. Hence, similar conditioning was adopted for all mixes to ensure comparability between different binder compositions. The water level was maintained at 2-3 mm above the specimens' base during the entire duration of testing, and the mass of the specimen was recorded at various time intervals over 14 days. The specimens were covered on top, and the vessel was covered to avoid moisture uptake or loss. Water-accessible porosity was determined by the vacuum saturation process after sorptivity testing, and this is reported as concrete porosity. During the vacuum saturation process, the entrapped air porosity and a portion of the cement paste's water-accessible porosity are filled with water. Hence, this measurement gives a measure of wateraccessible porosity [99]. The mass of the dried and saturated specimen measured up to an accuracy of 0.01 g can be used to compute porosity in the concrete. Porosity is calculated as per the formula below:

Porosity (%) = 
$$\frac{(24 \text{ hr saturation mass} - Intial dried mass)}{(Exposed area \times Thickness of sample) \times 10^{-3}} \times 100$$
 (1)

Bulk conductivity and chloride migration test was carried out on 50 mm thick, 100 mm diameter cylindrical sections extracted from 100  $\times$  200 mm cylinders, as per NT BUILD 492 [100]. The test was conducted after 28, 90 and 180 days of curing. The bulk conductivity and chloride migration test was conducted using the 8-channel PROOVE'it system, capable of testing from 5 to 60 Volts, as per NT Built 492 [100]. Before chloride migration testing, bulk conductivity was measured on the same specimen using an in-built bulk conductivity module available in PROOVE It®, by applying a potential of 60 V for 1 min to assess the current. For the chloride migration test, the procedures used 10 % NaCl solution and 3 M NaOH on two cells after applying a potential difference (usually 30-60 V, depending on the initial current measured after applying 30 V). The test can last from 24 h to 96 h depending on initial current values, and the duration was based on the NT build standard. Finally, the depth of chloride ingress was measured using a colorimetric indicator (0.1 M AgNO<sub>3</sub> spray) on specimens split after testing. The calculated chloride migration coefficient based on the final chloride

3inary and ternary concrete mix designs (kg/m <sup>3</sup> of fresh concrete).												
Mix ID	CEM I	CEM I Calcined Clay		LP Gypsum	Water	Water Sand	Coarse aggregate		SP	Slump <sup>a</sup> (mm)		
		CC20	CC50	CC70					10 mm	20 mm		
CEM I	360.0	0	0	0	0	0	180.0	814.0	437.0	534.0	0.72	70
CC30-K20	248.0	108.0	0	0	0	4.0	180.0	807.0	433.0	529.0	1.08	80
CC30-K50	241.2	0	108.0	0	0	10.8	180.0	805.0	432.0	528.0	1.08	75
CC30-K70	241.2	0	0	108.0	0	10.8	180.0	804.0	431.0	527.0	1.80	80
CCL45-K20	194.4	108.0	0	0	54	3.6	180.0	803.0	431.0	527.0	1.08	80
CCL45-K50	187.2	0	108.0	0	54	10.8	180.0	805.0	430.0	526.0	1.08	70
CCL45-K70	187.2	0	0	108.0	54	10.8	180.0	800.0	424.0	525.0	1.80	60

<sup>a</sup> Slump cone test was carried out while casting the specimens following BS EN 12350-2 [80].

penetration depth for the testing parameter (voltage and duration) can be used as a quantitative parameter to compare the performance of concrete mixes with different mix design and blend compositions. To calculate the non-steady state chloride ion migration coefficient, Eq. (2) was used, according to NT BUILD 492 [100].

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t} \left( x_d - 0.0238 \sqrt{\frac{(273+T)Lx_d}{U-2}} \right)$$
(2)

where  $D_{nssm}$  is the non-steady state migration coefficient in  $10^{-12}$  m<sup>2</sup>/s, U is the applied voltage in V, T is the average temperature in °C, L is the thickness of the specimen in mm,  $X_d$  is the average penetration depth in mm, t is the duration of the test in hours.

Accelerated and natural carbonation. Split rectangular prisms after flexural strength testing were used for carbonation studies. The prismatic specimens were wrapped in aluminium foil on both ends and preconditioned in a humidity chamber at 20 °C, 57 % relative humidity (RH) for 14 days. Subsequently, specimens were moved to a carbonation chamber maintained at 3.0 % CO\_2, 20  $^\circ\text{C}$  and 57  $\pm$  3 % RH. Carbonation depths were measured after 14, 28, 70, 100, and 140 days of accelerated CO<sub>2</sub> exposure. The testing duration was extended beyond the 70 days as recommended in EN 12390-12, to determine the potential deviation in performance of the composite cement concretes evaluated here, with longer carbonation exposure times, accounting for differences in the pore structure [22]. Additionally, two specimens were placed in the controlled humidity chamber (atmospheric CO2, 20  $^\circ C$  and 57  $\pm$  3 % RH) to evaluate the natural carbonation (sheltered condition) after an exposure time of 300, 500, and 650 days under ambient conditions. At each testing time, accelerated or naturally carbonated specimens were broken using a splitter and tested with a spray of 1 % phenolphthalein solution in isopropyl alcohol (IPA) on the freshly broken surfaces, as per EN 12390-12 [101]. A total of 16 measurements, 4 measurements on each side, were taken on each broken section of the prism. Fig. A3 in the supplementary file shows photographs after spraying with phenolphthalein indicator prepared with (i) 1 % phenolphthalein prepared in 100 % IPA, and (ii) 70 % IPA + 30 % water (as per existing standard) on CEM I and calcined clay concrete specimens. There is a distinct difference in visible carbonation affected region based on the solution used for testing, which could influence the carbonation depth measurement. Hence, 1 % phenolphthalein prepared in 100 % IPA was used for determining carbonation depths in this study.

To understand transport properties in carbonated concrete, a sliced cylindrical specimen ( $\sim$ 50 mm thickness) was obtained from a 100  $\times$  200 mm cylindrical specimen. The sliced disc was sealed using epoxy

coating and low permeability aluminium tape to ensure unidirectionally exposure to accelerated and ambient  $CO_2$  (57 % RH) for a period of 100 days and then tested for water sorptivity (as discussed earlier) on a carbonated surface. A sacrificial specimen was kept in a similar sealed condition to assess carbonation depth in the companion specimens used for sorptivity testing.

## 2.5. Results and discussion

#### 2.5.1. Mechanical properties

2.5.1.1. Compressive strength development. Fig. 1A and B depict the compressive strength up to 180 days of binary and ternary concrete mixes. In both mix types, concrete containing calcined clays with higher meta-kaolinite content (K70) attained higher strength than K50 and K20 concrete mixes at both early ages (i.e., up to 7 days) and longer-term (i. e., beyond 28 days) assessed. Similar observations have been found for cement mortars containing calcined clays [22,102]. While binary mixes containing K70 (CC30-K70) achieved higher strength than K50 and K20, and also reached similar strength to CEM I concrete at a later age, i.e., beyond 28 days, CC30-K20 and CC30-K50 still developed strengths >50 MPa and achieved about 95 % of PC's strength by 180 days. All ternary concrete mixes showed marginally lower strengths than PC concrete at all curing ages evaluated. Both binary and ternary concrete mixes attained about 20 MPa by 2 days, irrespective of the original kaolinite content in the uncalcined clay, and despite the higher clinker replacement in ternary mixes. Ternary blends showed comparable strength till 7 days for all three clays, and only CCL45-K70 showed higher strength, whereas K50 and K20 showed similar strength irrespective of metakaolinite content till 180 days. This is contrary to results reported for mortar, where compressive strength was found to consistently vary with meta-kaolinite content from 3 days [22]. By 180 days, all ternary concrete mixes achieved about > 85 % of CEM I strength despite 50 % Portland clinker content in the concrete mixes.

The development of compressive strength of ternary blend mixes was more prevalent at later stages, indicating prolonged microstructural development. The results suggest that the meta-kaolinite content of the calcined clays used to produce composite calcined clay-limestone cements controls the performance of concrete. While all concretes produced with low purity clays (K20 and K50) showed continuous evolution of compressive strength, concrete produced with K70 exhibited comparable to CEM I reference. Other lower purity kaolinite clays (K20 and K50) showed a continued strength development up to 180 days attaining >50 MPa in all binary mixes, and >45 MPa in ternary mixes. For a



Fig. 1. Compressive strength of binary and ternary calcined clay concretes as a function of curing time.

similar mix design, a reduction of 5-10 MPa can be expected by 28 days due to the additional replacement of clinker with 15 wt% powdered limestone. This, however, can be compensated by optimising mix design (in terms of binder content and w/b), if similar strength is desired, as shown in [66], as continuous strength development is visible till 180 days. All calcined clay concretes achieved >15 % increase in later-age strength between 28 days and 180 days, unlike CEM I concrete. Most importantly, concretes produced with K20, developed a good compressive strength (>20 MPa in binary or ternary mixes) despite its low metakaolinite content. The strength development of both CC30 and CCL45 are similar for K20 and K50. Although previous studies have shown that strength varied consistently with kaolinite content [22], the calcined London clay used in this study (K20) is known to have some nonnegligible reactivity contribution from the other clay minerals, as reported in [30].

2.5.1.2. Ultrasonic pulse velocity (UPV) testing. Fig. 2 illustrates the UPV results of all the concrete mixes tested as a function of the curing age. Binary concrete mixes showed similar UPV to CEM I from 7 days onwards, while ternary mixes gave much lower UPV values, with considerable dependence on the meta-kaolinite content in the calcined clay. Ye et al., [103] reported that the UPV depends on the content of solid products and the assemblage of solid phases in the microstructure. Thus, the lower UPV values are consistent with the lower compressive strength values recorded for the ternary blended concrete (Fig. 1B). Ternary mixes only attained similar UPV to CEM I by 180 days, independently of the meta-kaolinite content in the calcined clay used, despite the significant differences in the 180d compressive strength recorded among CEM I and concrete produced with K20 and K50 clays.

Fig. 3 depicts the relationship between UPV and compressive strength. Although a clear positive trend can be observed across all the curing ages and concrete mixes evaluated, there is significant dispersion in the data, suggesting that for a given compressive strength value, different UPV values can be recorded. This is consistent with the fact that different binder types will develop different microstructure features, which compressive strength alone cannot capture. Nevertheless, UPV seems to be suitable in this case to provide an indication of continuous development of properties in blended calcined clay concrete.

2.5.1.3. Spitting tensile and flexural strength. Table 4 presents the splitting tensile- and flexural strengths of 28 days cured concretes. The splitting tensile strength of CC30-K70 was similar to that of CEM I, while CC30-K20 and CC30-K50 concrete mixes developed slightly lower strengths, consistent with their reduced compressive strength at 28d (Fig. 1A). All ternary CCL45 mixes achieved split tensile strengths



Fig. 3. Correlation of UPV with compressive strength for different concrete mixes evaluated.

Table 4
Splitting tensile strength and flexural strength of binary and ternary concrete a
28 days of curing.

Mix ID	Splitting tensile strength (MPa)	Flexural strength (MPa)
CEM I	$3.81\pm0.22$	$6.00\pm0.15$
CC30-K20	$3.26\pm0.04$	$5.10\pm0.26$
CC30-K50	$3.49\pm0.16$	$5.48\pm0.10$
CC30-K70	$3.84\pm0.12$	$6.30\pm0.27$
CCL45-K20	$3.24\pm0.01$	$4.68\pm0.11$
CCL45-K50	$3.50\pm0.30$	$5.22\pm0.56$
CCL45-K70	$3.41\pm0.04$	$5.62\pm0.17$

between 80 and 85 % of the strength reported by the CEM I reference mix. Flexural strength values were comparable in the binary mixes produced with the K20 and K50 clays, with slightly higher values recorded when using K70 clay. The lowest flexural strength was recorded for the ternary concrete made with the K20 clay, while concrete with K50 or K70 clays reported comparable flexural strength.

Fig. 4A and B depict the relationship between compressive strength ( $F_c$ ) and splitting tensile ( $F_{c,t}$ ) or flexural strength ( $F_{c,f}$ ) of all concrete mixes. Results indicate that the existing relationship (as per various



Fig. 2. UPV values for the concrete mixes as a function of the curing time.



Fig. 4. Correlation between compressive strength and the (a) flexural and (b) splitting tensile strengths of 28 day-cured binary or ternary calcined clay containing concrete mixes.

Note: splitting tensile strength formulation in ACI and *fib* MC are based on cylinder compressive strength. Values reported here were converted to equivalent cube compressive strength for the analysis.

international building codes, including the AS 3600 ( $F_{of} = 0.6*(F_{c})^{0.5}$  [104]), and ACI-318 ( $F_{of} = 0.62*(F_{c})^{0.5}$  [105]), and IS 456 ( $F_{c,f} = 0.7*(F_{c})^{0.5}$  [106]) used for conventional concrete can possibly be adopted for the conversion of flexural strength for calcined clay concrete. Similar observations were reported for metakaolin concretes in a recent review summarising flexural and splitting tensile strength data [102]. While flexural strength results were consistently higher compared to predicted values using models recommended in the standards, the experimental splitting tensile strength swere quite close to the strength predicted values from ACI 318 ( $F_{ot} = 0.56*F_{c,Cy}^{0.5}$  [105]) and *fib* model code 2020 ( $F_{ot} = 0.3*F_{c,Cy}^{0.67}$  [107]), independent of the clay type used. Additional results are required to further support the development of a robust

relationship between compressive, splitting tensile and flexural strength of binary and ternary calcined clay concretes.

## 2.5.2. Water absorption, porosity and resistivity

2.5.2.1. Water sorptivity and porosity. Fig. 5A-F show the sorptivity curves for concrete mixes at different curing ages. Sorptivity is a direct measure of transport property denoting the moisture ingress in the concrete matrix by capillary absorption through the concrete's interconnected pore network [108]. It can be observed that the water sorptivity decreases with curing time, this being more noticeable in concrete produced with calcined clays with higher meta-kaolinite content. This



Fig. 5. Sorptivity curves of the binary (A,B,C) and ternary (D,E,F) concrete mixes as a function of curing time.

indicates that the use of higher purity calcined clays (i.e., K70 here) induced better resistance to moisture ingress likely due to a more marked pore refinement as the kaolinite content in the clay increases. It is worth noting that the reduction in water sorptivity was more significant with changes in meta-kaolinite content in the calcined clay than with advanced curing time. This emphasises the importance of the meta-kaolinite content of the calcined clay source on the transport properties of concrete produced with them.

The initial water sorptivity coefficient results, determined as the slope of water absorbed vs square root time (in sec) curve at 3 h, are summarised in Table 5. A systematic decrease in the sorptivity coefficient can be seen with an increase in the curing duration (except for CC30-K50 at 90 days, which is likely an experimental anomaly) and with increasing meta-kaolinite content of the calcined clay (K70 < K50 <K20). Previous studies observed that the sorptivity of concrete is mainly governed by the pore network (total porosity, pore size and connectivity), which provides the pathways for moisture [66,109], and the initial sorptivity coefficient is mainly associated with the total porosity of the concrete. Therefore, it can be expected that in the concretes evaluated in this study, densification of the paste microstructure occurs at longer curing times and with an increased meta-kaolinite content of the calcined clay used, limiting the ingress of water. Across all curing ages, CEM I concrete had the highest sorptivity coefficient, and concretes produced with K70, in both CC30 and CCL45 mixes, had the lowest. The ternary mixes CCL45-K50 and CCL45-K70 exhibited lower sorptivity coefficients than CEM I, indicating that the blended K50 and K70 calcined clay along with finely ground limestone induced the development of comparable porosities to those of binary calcined clays systems, even with 45 wt% clinker replacement. The CCL45-K20 presents a similar sorptivity coefficient to CEM I at all curing age.

Following the sorptivity test, the cylindrical specimens were used for porosity determination using the vacuum/water saturation method, and the results are reported in Table 5. A continuous reduction in wateraccessible porosity can be observed with extended curing durations in all concrete mixes. By 180 days of curing, no noticeable effect of limestone addition on concrete porosity was identified in the CCL45 mixes.

2.5.2.2. Bulk conductivity and surface resistivity. Concrete resistivity is commonly used in practice as a rapid indicator of resistance to ionic transfer within concrete microstructure [48]. Surface resistivity and bulk conductivity/resistivity depend on a range of physicochemical factors, such as pore structure parameters and pore solution composition [110–112]. Fig. 6A and B depict the surface resistivity of binary and ternary blended concrete, respectively. Although the CEM I concrete showed higher resistivity at early curing ages, i.e., 3 and 7 days, binary and ternary concrete mixes produced with K50 or K70 exhibited higher resistivity values at longer curing times. Conversely binary or ternary concrete mixes evaluated up to 90 days of curing. A significant increase in the resistivity is observed at 180d, when concrete with K20 clay compared to those obtained for CEM I.

Although limestone addition to calcined clays containing cements is known to induce synergistic reactions through carboaluminate formation from the aluminate-calcite reaction, which is often considered beneficial for pore refinement and strength development, there seems to be a negligible effect of limestone addition on resistivity development for the clays used in this study. This is consistent with the previous findings reported in [107,108], which showed that the reactivity of SCMs dominated resistivity development in paste and concrete more than limestone dosage in composite cements. Among all the mixes studied, CCL45-K70 showed the highest resistivity beyond 28 days, indicating potential better pore refinement due to the higher meta-kaolinite content. By 180 days, concrete containing K70 reached about 50 % higher resistivity than CEM I. The results also indicate that low meta-kaolinitic calcined clays can still exhibit adequate performance, particularly at longer curing ages.

The bulk conductivity results of the concrete mixes evaluated are summarised in Table 6. Similar trends to those observed for surface resistivity are identified in the results, albeit inversed due to values being presented as conductivities). In binary and ternary concrete mixes, conductivity reduced with curing duration and meta-kaolinite content, so that CCL45-K70 at 180 days showed the lowest conductivity. Irrespective of the meta-kaolinite content in the calcined clay used, the conductivity of the calcined clay mixes was lower than the CEM I mix, consistent with the pore refinement and modifying pore solution composition that is typically reported in calcined clay blended cements [48].

Although there were noticeable differences in resistivity measurements, both K20 and K50 containing concrete showed comparable porosity values (Table 5). This could be due to the fact that calcined clay additions have been known to refine the pore structure by changing the sizes [113], and also reduce the pore solution conductivity [114] rather than lowering the total pore volume, which could cause significant improvements in resistivity despite similar total porosity of the concrete mixes.

A correlation between water-accessible porosity, resistivity, and water sorptivity across curing ages was attempted to evaluate the interdependencies between different transport properties and the results are presented in supplementary information in Fig. A3. There is considerable scatter indicating that the porosity measurements of concrete bulk alone cannot truly capture the potential water uptake or bulk conductivity of the concrete mixes evaluated. Similarly, bulk conductivity measurements do not show a better correlation with water sorptivity exhibiting significant variations to draw any clear conclusion.

## 2.5.3. Durability performance

2.5.3.1. Chlorides ingress. The non-steady chloride migration coefficients ( $D_{nssm}$ ) measured as per NT Build 492 [100] for all mixes at different curing ages are shown in Fig. 7. All concretes showed a reduction in  $D_{nssm}$  with increasing curing age. For CEM I, this reduction was modest, falling by about 20 % from 28 days to 180 days. Conversely, the binary and ternary blends showed substantially reduced chloride migration coefficients with curing time beyond 28 days. Furthermore, the blended calcined clay concrete also showed better resistance to chloride ingress even by 28 days, with  $D_{nssm}$  values below 5 × 10<sup>-12</sup> m<sup>2</sup>/

Table !	5
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Summary of initia	l sorptivity	coefficient and	porosity	v measurement as a	function of age.
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Mix ID	Initial sorptivity coeffic	ient (mm/s <sup>0.5</sup> )	Porosity (%)			
	28 days	90 days	180 days	28 days	90 days	180 days
CEM I	$0.0231 \pm 0.0029$	$0.0210 \pm 0.0012$	$0.0192 \pm 0.0021$	$5.09 \pm 0.45$	$4.28\pm0.15$	$3.93\pm0.18$
CC30-K20	$0.0180 \pm 0.0008$	$0.0162 \pm 0.0011$	$0.0159 \pm 0.0015$	$4.86\pm0.33$	$4.38\pm0.35$	$3.28\pm0.05$
CC30-K50	$0.0152 \pm 0.0024$	$0.0243 \pm 0.0012$	$0.0166 \pm 0.0004$	$4.76\pm0.75$	$4.05\pm0.83$	$3.23\pm0.11$
CC30-K70	$0.0154 \pm 0.0003$	$0.0117 \pm 0.0022$	$0.0102 \pm 0.0010$	$4.61\pm0.24$	$3.86\pm0.25$	$2.45\pm0.20$
CCL45-K20	$0.0226 \pm 0.0010$	$0.0191 \pm 0.0007$	$0.0173 \pm 0.0014$	$5.15\pm0.49$	$4.59\pm0.54$	$3.18\pm0.26$
CCL45-K50	$0.0182 \pm 0.0016$	$0.0190 \pm 0.0030$	$0.0169 \pm 0.0022$	$4.74\pm0.35$	$4.07\pm0.20$	$3.08\pm0.17$
CCL45-K70	$0.0147 \pm 0.0045$	$0.0104 \pm 0.0001$	$0.0106 \pm 0.0003$	$\textbf{4.46} \pm \textbf{0.20}$	$3.85\pm0.38$	$2.34\pm0.10$



Fig. 6. Surface resistivity of (A) binary or (B) ternary concrete mixes as a function of curing time.

 Table 6

 Bulk conductivity of concrete mixes evaluation as a function of the curing time.

Mix ID	(mS/m)		
	28 days	90 days	180 days
CEM I	$15.11\pm1.17$	$10.67\pm0.58$	$\textbf{9.84} \pm \textbf{0.38}$
CC30-K20	$\textbf{2.64} \pm \textbf{0.86}$	$3.26\pm0.15$	$2.66\pm0.13$
CC30-K50	$3.14\pm0.60$	$3.10\pm0.01$	$2.83\pm0.07$
CC30-K70	$1.29\pm0.13$	$1.10\pm0.03$	$\textbf{0.89} \pm \textbf{0.02}$
CCL45-K20	$4.53\pm0.53$	$3.98\pm0.28$	$2.62\pm0.08$
CCL45-K50	$3.17\pm0.34$	$2.31\pm0.07$	$1.7\pm0.10$
CCL45-K70	$\textbf{0.68} \pm \textbf{0.06}$	$0.52\pm0.02$	$0.34\pm0.02$



Fig. 7. Chloride transport coefficient of binary and ternary concrete mixes.

s, irrespective of clay used. The chloride resistance value,  $D_{nssm}$ , improved with when using a calcined clay with higher meta-kaolinite content, for both binary and ternary mixes. This indicates the key role of clay mineralogy on the chloride resistance performance of the concrete mixes evaluated. Limestone addition had a negligible effect on the  $D_{nssm}$  values so, ternary blends exhibited comparable performance to that of the binary system despite the reduced clinker content.

Also, with an increase in the meta-kaolinite content from 20 to 70 wt %, the enhanced pozzolanic reaction can compensate for additional clinker replacement with powdered limestone, so ternary systems can develop similar  $D_{nssm}$  performance to binary calcined clay concretes. Similar observations of minor differences between binary (i.e., calcined clay) and ternary (i.e., calcined clay-limestone) concretes have been reported in other studies carried out with a single calcined clay source

[64,113]. However, it is important to highlight that while studies on pastes reported no major improvement in pore structure for calcined clays above 50 % meta-kaolinite content beyond 7 days [22], this study suggests that differences in concrete performance, in terms of chloride and water ingress, are strongly influenced by meta-kaolinite contents above 50 %. K50 and K70 in the CCL45 series achieved near comparable chloride migration coefficients only by 180 days of curing, suggesting that observations on cement pastes [22] may not directly translate to concrete performance. It is also important to note that all CC30 and CCL45 concrete mixes showed a reduction in the chloride migration coefficient from 90 days to 180 days, indicating microstructure development even up to 180 days, unlike observation made in cement paste showing limited pore structure development with calcined clay beyond 7 days [22,48,115]. Unlike water sorptivity, limestone additions with calcined clay (i.e., CCL45 mixes) improved chloride resistance compared to CC30 mixes.

Time-dependant changes in the chloride migration coefficient can be used to obtain the ageing coefficient used in service life modelling in marine exposure as per fib Model Code [116]. The ageing coefficient can be obtained as the slope of the log-log plot of the chloride migration coefficient over time. The ageing coefficient values are summarised in Table 7. A higher value in the ageing coefficient indicates a more rapid reduction in the chloride diffusion coefficient during the service life. The results suggest that the microstructure of calcined clay concrete studied here continues developing, inducing changes in the pore structure as well as phase assemblages beyond 28 days of curing. Concrete produced with K70 presents a lower coefficient in both binary and ternary concrete, compared with the cases where calcined clays with lower metakaolinite content were used. This may be due to limitations on the pore structure change or due to lack of space with increasing kaolinite content [22], which could slow down further microstructural development [49,58]. K50 has moderate reactivity, inducing a better improvement in durability performance (by lower D<sub>nssm</sub> value) over time in both binary and ternary concrete mixes, consistent with a higher ageing coefficient, while K20 has lower reactivity and, hence, the D<sub>nssm</sub> value does not improve as much as in K50-containing concretes and hence exhibiting a lower ageing coefficient than K50; but still higher than CEM I.

Resistance to chloride ingress is usually related to reduced pore connectivity from microstructural refinement, and chloride binding of the cementitious matrix [37,63]. Several studies have reported that the ability of hardened cement paste to bind chlorides, either physically (adsorption in the AFm phases or C-S-H) or chemically (Friedel's salt formation) influences the chlorides ingress [58,117]. However, recent studies have shown limited differences in chloride binding between CEM I and calcined clay blends, and that chloride resistance in calcined clay concretes can be explained by changes in pore structure and pore

#### Table 7

Ageing	coefficient	of	the	concrete	studied
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Ageing coefficient value	CEM I	CC30-K20	CC30-K50	CC30-K70	CCL45-K20	CCL45-K50	CCL45-K70
m	0.12	0.29	0.39	0.19	0.39	0.83	0.39

solution composition [58,118,119]. Fig. 8A and B show the chloride migration coefficient as a function of water-accessible porosity and bulk conductivity, respectively. The correlation between  $D_{nssm}$  and porosity values changes significantly for a given diffusion coefficient, indicating that other factors in addition to porosity are influencing the chloride ingress.

A good correlation between  $D_{nssm}$  and bulk conductivity was identified in this study, consistent with the fact that both measurements account for ionic mobility in the materials evaluated. A similar relationship between bulk conductivity and chloride diffusion coefficient resistance was reported for calcined clays cement along with other SCMs for cement paste in [64,119] and in concrete [58].

2.5.3.2. Carbonation resistance upon accelerated and natural  $CO_2$  exposure. Fig. 9A and B show the carbonation depths for the binary and ternary concrete mixes, respectively. As expected, extended exposure times lead to a higher carbonation depth, and carbonation depths being the lowest for CEM I concrete and highest for ternary blends with higher clinker replacement levels. Carbonation depths reduced with increasing meta-kaolinite content of the calcined clay used for both binary and ternary concrete mixes.

It has been reported [22,46] for pastes produced with different calcined clay with meta-kaolinite content that the CH content at 28 days reduced from 20 % (g/100 g of clinker) to about 5 % (g/100 g of clinker) for 50 wt% meta-kaolinite content, and it remains similar thereafter for calcined clays with 100 wt% meta-kaolinite due to the limitation of hydration in a highly dense and refined pore structure. Upon carbonation, it could be expected that a higher content of meta-kaolinite in the calcined clay might reduce the buffering from CH, due to its higher reactivity, and potentially reducing the carbonation resistance. However, in this study, concrete produced with K70 clay (with or without limestone addition) exhibited the lowest carbonation depths, high-lighting the benefit of microstructure densification.

Carbonation is often evaluated as a function of the  $w/CaO_{reactive}$  (water-cement ratio to reactive CaO content) of a given cementitious system [74,120]. In this study, the CC30 and CCL45 concrete mixes contains a similar clinker content, respectively, and therefore comparable  $w/CaO_{reactive}$  ratios. This means that the only variable influencing

carbonation is the meta-kaolinite content of the clay type used for producing such specimens. The improved carbonation resistance of concrete mixes produced with the K70 clay are, therefore, attributed to pore refinement and a dense microstructure, consistent with the low sorptivity coefficient (Table 5), low bulk conductivity (Table 6), and reduced chloride migration coefficient (Fig. 8) identified in these mixes. The higher carbonation depths recorded when using the K20 clay is consistent with a reduced reactivity, and consequently, less mature microstructure at early curing ages, as identified in [22]. These results indicate that the carbonation resistance of CC-containing concretes can be controlled by the selecting a given calcined clay sources, i.e., calcined clays with 70 wt% meta-kaolinite will be more suitable for applications where higher carbonation resistance is required.

The addition of limestone powder to increase replacement level to 45 % clinker substitution diminished the carbonation resistance of the concrete mixes evaluated. Modest differences in the carbonation depths are identified between binary or ternary concrete mixes at early exposure times (< 28 days). For example, by 140 days of CO<sub>2</sub> exposure, CC30-K20 and CC30-K50 concrete exhibited a carbonation depth of 20 mm. Conversely, the concrete CCL45-K50 reported a maximum carbonation depth of 30 mm after 140 days of exposure, which is significantly higher than the reported carbonation depth ( $\sim$ 23 mm) in CCL45-K20. In the case of CCL45-K70 by 140 days of CO2 exposure, a carbonation depth of about 20 mm is reported, similar to the maximum carbonation identified in the CC30 concrete series. Thus, indicating that a comparable carbonation performance can be achieved with greater clinker replacement levels when using calcined clays with a higher meta-kaolinite content. For ternary concrete mixes with limestone and low meta-kaolinite containing clays additional concrete mix design optimisation strategies (lowering w/b and increasing binder content) will need to be implemented to ensure their suitability for carbonation exposure conditions (XC3, XC4 and XC5).

Table 8 summarises the carbonation coefficient (or carbonation rate in mm/d<sup>0.5</sup>) determined by two fitting approaches: (i) fitting through the origin, and (ii) fitting with an intercept. Comparable carbonation coefficient values were calculated independently of the fitting method, except for the CEM I concrete mix, where a significantly lower coefficient was obtained when adopting the fitting method (ii). For the



Fig. 8. Relationship between chloride migration coefficient with (a) porosity, (b) bulk conductivity in concrete mixes.

Table 8



Fig. 9. Carbonation depth of accelerated carbonated (3 % CO<sub>2</sub>, 57 % RH) concretes produced (a) without, and (b) with limestone addition, as a function of exposure time. Each data point is an average of about 16 measurements, with the scatter bar indicating one standard deviation.

Table o		
Summary of accelerated carbonation coefficient 'k' (mm/d <sup>0.5</sup> ) of concrete mixes obtaining	g by two f	fitting methods.

•				•	• •			
Fitting Method	Fitting results	CEM I	CC30-K20	CC30-K50	CC30-K70	CCL45-K20	CCL45-K50	CCL45-K70
Through origin	k	0.92	1.53	1.67	1.14	2.10	2.49	1.63
	R <sup>2</sup>	0.93	0.98	0.99	0.99	0.99	0.99	0.98
With Intercept (a)	k	0.67	1.60	1.64	1.14	2.02	2.45	1.71
	а	2.26	-0.70	0.24	0.02	0.74	0.32	-0.77
	$R^2$	0.74	0.96	0.98	0.97	0.99	0.99	0.96

reference concrete, an anomalous result at 14 days of exposure was recorded, as the carbonation depth was much higher at this time, compared with extended exposure times. This is likely related to a potential issue with the skin carbonation or with the samples evaluated, rather than an indication of the material performance. A clear trend on the carbonation coefficient could not be identified as a function of the meta-kaolinite content in the calcined clay. Nevertheless, concretes containing K70 reported a lower carbonation coefficient, with or without limestone addition, compared with concretes made with K20 or K50. Concrete made with K20 presented slightly lower carbonation coefficients compared with K50-containing concretes. This is likely associated with the contribution to the microstructure development of the *sec*ondary minerals present in this clay [30]. In all cases, the addition of limestone lead to an increase in the carbonation coefficient, consistent with the reduced clinker content in the ternary mixes.

Fig. 10 shows the accelerated carbonation coefficient at a given exposure time to identify the variation with exposure time, compared to the average carbonation coefficient calculated when fitting results at different exposure times, as reported in Table 8. For CEM I concrete, the carbonation rate significantly reduces at increasing exposure time from 14 to 100 days, and remains roughly constant thereafter up to 180 days of carbonation exposure. The reduction in carbonation rate with exposure time can be linked to porosity reduction during carbonation, leading to the formation of a denser carbonation front [82,121]. In the case of binary and ternary concrete, it is difficult to identify specific trends connecting the mix design parameters of the concretes tested with



Fig. 10. Accelerated carbonated rate (mm/d<sup>0.5</sup>) from accelerated carbonation exposure with CO<sub>2</sub> exposure duration of 70 days, 100 days and 140 days.

their carbonation rates. This is consistent with the fact that carbonation is not only dependent on the chemistry of the matrix, but also on its pore structure. Saying that some observations can be noted, for example: CCL45-K20 and CCL45-K50 present similar trends in the carbonation rate, showing slightly higher coefficients at 14 days of exposure, with negligible changes after 28 days of CO<sub>2</sub> exposure. For concretes produced with similar clays but without limestone addition, there is more variability on the carbonation coefficient at different exposure times. The current European standard for evaluating carbonation performance of concrete, EN 12390-12 [122] recommends an exposure duration of 70 days of exposure for determining carbonation rates. Overall negligible changes in carbonation coefficients are identified in most of the concrete mixes evaluated up to 70 days of exposure, except for CC3-K20 and CC30-K70, exhibiting an increase in the carbonation rate beyond that exposure time and CEM I, whose carbonation rate decreases at extended exposure durations. This indicates that the recommendation from the standard is applicable to binary and ternary concretes containing calcined clays, however carbonation coefficients calculated at early exposure times will be higher than those determined at extended exposure durations in accelerated carbonation testing.

In specimens exposed to ambient conditions, changes in pH were determined as carbonation depth using a phenolphthalein indicator. Photographs of the specimens sprayed with the pH indicator after 300, 500, and 650 days of natural carbonation exposure are reported in the supplementary information file in Fig. A6. Table 9 summarises the carbonation depths and coefficients based on the depth measurements. Concrete prepared with lower-grade calcined clays, i.e., K20 and K50, had higher carbonation rates (determined by dividing the carbonation depth by the square root of exposure duration), in both binary and ternary concrete mixes, than either CEM I or the K70 blended concrete. This is consistent with the observation upon exposure to accelerated carbonation. However, both CC30-K70 and CCL45-K70 showed similar performance to CEM I, which is unlike the accelerated carbonation results.

Natural carbonation results (reported in Table 9) confirm that using a calcined clay with high meta-kaolinite content (K70) leads to a better carbonation resistance of concrete compared to using K50 or K20 in both binary and ternary concretes, consistent with the observation from the accelerated carbonation results (Fig. 9). It is important to note that the natural carbonation coefficient, in both binary and ternary concrete produced with the K70 clay is similar to that of CEM I concrete. It is known that for concrete with SCMs, accelerated carbonation tests, although lead to a similar ranking of concrete in terms of carbonation resistance to that observed under natural carbonation, the carbonation coefficients can be significantly different [123].

Based on the carbonation coefficients obtained at 300, 500 and 650 days of natural carbonation (Table 9), carbonation depths were extrapolated to 50 years of exposure using Fick's square root law i.e.,  $k^*$  (sq.rt.(t) where *k* is the carbonation coefficient in  $mm/d^{0.5}$  and *t* is time in *days* (Table 10). A similar carbonation resistance to that identified in CEM I concrete can be achieved with 30 wt% calcined clay substitution by increasing the concrete cover depth about 5-7 mm (CEM I - 35.9 mm and CC30-K20-42.8 mm). This is similar to the increased cover depth

#### Table 10

Extrapolated carbonation depths for 50 years of exposure of binary and ternary concrete produced with calcined clay, determined using natural carbonation coefficient (k) values determined after 300, 500 and 650 days of carbonation exposure.

Mix ID	Extrapolated carbonation depth (mm)							
	Using 300 days k values	Using 500 days k values	Using 650 days k value					
CEM I	31.4	30.3	35.9					
CC30-K20	37.4	42.6	42.8					
CC30-K50	36.3	35.4	37.1					
CC30-K70	26.0	24.0	30.6					
CCL45- K20	38.8	42.1	48.6					
CCL45- K50	55.1	48.2	56.3					
CCL45- K70	33.4	35.5	40.7					

requirements identified for blast furnace slag and fly ash concrete <30% replacement reported in the literature [76]. For ternary mixes with limestone, a required cover depth increase from 13 mm for K20 to  $\sim$ 20 mm for K50 concrete will be required, this estimated considering the carbonation coefficient obtained from 650 days. Kaolinite content is evidently more critical in the carbonation performance of ternary calcined clay-limestone systems than in binary calcined clay concrete. Also, the extrapolated value of carbonation depth at 50 years with different *k* values based on different exposure times, highlighting the need for long-term data for accurate performance assessment in the newer cementitious materials.

A direct correlation between natural and accelerated carbonation results is generally made according to Eq. (3), which assumes a direct correlation between the carbonation coefficient ( $k_c$ ) and the concentration of CO<sub>2</sub> under natural ( $c_{CO2, nat}$ ) or accelerated ( $c_{CO2,acc}$ ) carbonation exposure conditions [124]. However, this relationship is only valid if the degrees of saturation of the concrete and the maturity of the binding phase (concrete matrix) are comparable at the moment of testing, so the mechanism of carbonation under different exposure conditions is comparable [125].

$$\frac{k_{c-acc}}{k_{c-nat}} = \sqrt{\frac{c_{CO_2,acc}}{c_{CO_2,nat}}}$$
(3)

Fig. 11 presents the relationship between natural and accelerated carbonation coefficients. The theoretical line is determined based on the square root law using ratios of atmospheric  $CO_2$  (0.04 %) and accelerated  $CO_2$  conditions (1 or 3 %). Although there is a reasonable correlation between natural and accelerated carbonation, the results significantly deviate from the theoretical line according to Eq. (3). This suggests that accelerated carbonation coefficient results cannot be directly used to predict natural carbonation coefficients, using Eq. (3), which only accounts for the diffusivity of  $CO_2$  into the material, but cannot capture the chemical interactions of  $CO_2$  with the hydrated phases forming in different systems which might modify the long-term performance. The primary reason for the difference between

Table 9

Ca	bonation (	depth	(mm)	and	carbonation	coefficient	$(mm/d^{0.5})$	) after 300	), 500 and 6	550 da	vs in natural	carbonation exposure.	
									/			1	

Mix ID	Carbonation depth	(mm)		Carbonation coeffic	Carbonation coefficient (mm/d <sup>0.5</sup> )			
	300 days	500 days 650 days		300 days	500 days	650 days		
CEM I	$4.03\pm1.07$	$5.01 \pm 1.88$	$6.77 \pm 1.46$	$0.23\pm0.06$	$0.23\pm0.08$	$0.26\pm0.06$		
CC30-K20	$\textbf{4.80} \pm \textbf{1.24}$	$\textbf{7.05} \pm \textbf{1.43}$	$8.08 \pm 1.19$	$0.28\pm0.07$	$0.32\pm0.06$	$0.32\pm0.05$		
CC30-K50	$4.65\pm1.01$	$5.87 \pm 1.22$	$\textbf{7.06} \pm \textbf{0.67}$	$0.27\pm0.06$	$0.26\pm0.06$	$0.28\pm0.03$		
CC30-K70	$3.33 \pm 1.61$	$3.96 \pm 1.57$	$5.77 \pm 1.38$	$0.19\pm0.09$	$0.18\pm0.07$	$0.23\pm0.05$		
CCL45-K20	$\textbf{4.97} \pm \textbf{1.51}$	$6.96 \pm 1.14$	$9.26 \pm 1.66$	$0.29\pm0.08$	$0.31\pm0.05$	$0.36\pm0.07$		
CCL45-K50	$\textbf{7.07} \pm \textbf{1.20}$	$\textbf{7.98} \pm \textbf{1.26}$	$10.62 \pm 1.57$	$0.41\pm0.07$	$0.36\pm0.06$	$0.42\pm0.06$		
CCL45-K70	$\textbf{4.28} \pm \textbf{1.97}$	$\textbf{5.88} \pm \textbf{1.36}$	$\textbf{7.68} \pm \textbf{1.85}$	$0.25\pm0.11$	$0.26\pm0.06$	$\textbf{0.30} \pm \textbf{0.07}$		



**Fig. 11.** Relationship between accelerated and natural carbonation coefficient (from 650 days carbonation depth) for calcined clay concrete with and without limestone addition.

accelerated and ambient carbonation, despite exposure at similar RH, could be the variation in carbonation mechanism modifying the microstructure through coarsening of pore structure in blended cements [82], increased gas diffusivity [126], difference in CaCO<sub>3</sub> polymorphs formed [127], and decomposition of reaction products under accelerated conditions [128,129], which is widely reported in alternative and blended cements. Although pore coarsening is reported with accelerated carbonation exposure [82], results from 3 % accelerated carbonation exposure was found to strongly correlated to long-term natural carbonation coefficients with conventional SCMs [130]. More complex empirically determined correlation of natural and accelerated carbonation results exists (e.g. fib code [107], SIA standard [131], and Vollpracht A. et al. [132]), which have been developed for concretes with other SCMs such as fly ash and blast furnace slag. Applicability of such correlations to calcined clay containing concretes needs to be investigated further, which is not conducted in this study due to the limited data points available to draw robust conclusions.

2.5.3.3. Transport properties of carbonated concretes. As identified in the previous section, blended Portland cement containing calcined clays, with or without limestone, presents higher carbonation depths than CEM I concrete. This is consistent with what has been reported for other blended concrete mixes with fly ash and blast furnace slag, where changes in porosity and reduction in mechanical properties are also identified [60]. Several studies have characterised the changes in the porosity and pore structure of calcined clay systems during carbonation [82,133–135]. However, there are limited studies evaluating the transport properties of carbonated concrete.

Fig. 12A presents the initial water sorptivity coefficient on cylindrical specimens, exposed to accelerated or ambient  $CO_2$  (57 % RH) for a period of 100 days. All sorptivity curves are reported in Fig. A7 in the supplementary information file. Before sorptivity testing, one specimen was split open to obtain the carbonation depth (Fig. 12B), and the trends in the results are similar to those shown in Fig. 9 after 100 days of  $CO_2$  exposure and discussed in the previous section. For CEM I, the initial sorptivity coefficient reduced after natural and accelerated carbonation. Natural carbonation of blended cement concretes led to minimal changes in initial sorptivity coefficients, or to slight decreases. However, accelerated carbonation led to a distinct increase in the sorptivity coefficient for both binary and ternary blended concretes, independently of the clay type used.

The results indicate that natural or accelerated carbonation leads to densification of the carbonation front in CEM I concrete, conversely to the observation in concrete containing calcined clay, consistent with what has been reported in other studies [81,82], where an increased permeability has been reported in carbonated systems.

## 3. Conclusions and general remarks

This study demonstrates the significant impact of the kaolinite content in the clay source on the mechanical and durability performance of binary and ternary concrete mixes containing calcined clays. This is of critical importance for the selection of the right clay resources accounting for the in-service requirements of the concretes produced with them, beyond considering compressive strength alone. Specific conclusions from this study include:



Fig. 12. (A) Sorptivity coefficient of 100-day naturally or accelerated carbonated concrete specimens (with the sorptivity coefficients of 28-day cured specimens marked with red points on the bar chart for reference) and (B) Carbonation depth measured on specimens before sorptivity testing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- Concrete's mechanical performance improved with increasing metakaolinite content of the calcined clay source. Continuous strength development up to 180 days was observed in concrete containing calcined clays, even when using lower purity clays with just 20 % kaolinite content obtained from excavation operations. This suggests that lower purity kaolinite clays can be utilised for producing concrete with desirable strength. Clays with higher kaolinitic contents (50 and 70 wt%) can be used to produce concrete with 28-day compressive strengths comparable to CEM I concrete.
- The existing relations for structural concrete design (e.g. *fib*, ACI) correlating compressive, flexural strength and splitting tensile strength are applicable to the calcined clay concrete mixes evaluated in this study, independently of the clay type used or the addition of limestone.
- Calcined clay concrete presents enhanced surface resistivity and bulk conductivity compared to CEM I, with performance improving with increasing kaolinite contents in the clay used, for both binary and ternary concrete. Initial water absorption coefficient, as a measure of resistance to moisture ingress by capillary absorption, also improved at increased kaolinite contents, potentially indicating better pore refinement. In general, limestone addition has only a negligible role in resistivity compared to the difference due to the meta-kaolinite content of the calcined clay source. So, from a durability perspective, no significant gain is identified with the addition of limestone.
- Non-steady state migration coefficients of both binary and ternary calcined clays and calcined clay-limestone concretes were significantly lower than those of CEM I concrete (by about 50 %), irrespective of the meta-kaolinite content. In general, calcined clay concretes are highly suitable materials for chlorides rich environments as they exhibit better resistance to chloride penetration. Chloride resistance improved with increasing meta-kaolinite content (K70 > K50 > K20) in the calcined clay used for both binary and ternary concrete mixes. However, concrete containing very lowpurity calcined clay (i.e., 20 % kaolinite content) exhibited significant improvements only beyond 28 days. Therefore, compliance testing is recommended to be conducted in concretes at extended curing durations for concrete containing low purity clays. These results are of great practical importance for the selection of materials for a marine environment. Additionally, it will be more suitable to use calcined clays with 50 and 70 wt% meta-kaolinite in a highly aggressive exposure condition such as tidal zones in marine environments or highway structures with frequent de-icing salt spray. In contrast, low-purity clays can be preferred for moderate chloride exposure conditions (such as airborne chloride exposure) where limiting values in performance specifications are less demanding.
- Carbonation resistance improved with increasing kaolinite content in both binary and ternary mixes, indicating that the choice of calcined clay is important when considering carbonation resistance. Concrete containing K70 achieves better resistance to carbonation compared with concrete containing K20 and K50 in both binary and ternary concretes. Conversely, concrete containing K50 and K20 exhibited higher carbonation rates than CEM I concrete by 650 days of natural carbonation exposure, particularly in ternary concrete. No direct correlation between natural and accelerated carbonation results was identified when evaluated considering Fick's law of diffusion, indicating that accelerated carbonation results of calcined clay concretes cannot be used for predicting the natural carbonation performance of these materials.
- Carbonation induces changes in concrete's transport properties. While CEM I concrete showed reduced sorptivity upon natural and accelerated carbonation, composite calcined clay concretes did not. Under natural carbonation, calcined clay cement concretes showed similar or reduced sorptivity post-carbonation compared to their respective 28 days cured concrete. However, accelerated carbonation induced significantly increased sorptivity independent of the clay type used, indicating the significant difference in the

microstructure due to exposure conditions which will further modify the carbonation process and how carbonation progresses. Therefore, natural carbonation measurements might be more reliable for potential service life performance predictions.

The addition of limestone reduced the strength in all concrete mixes evaluated, but no significant differences in durability performance were identified with limestone addition, compared with binary concrete. Consequently, from a mechanical performance perspective, the addition of limestone might not be advantageous. However, from a sustainability perspective, when considering the clay source (mined or obtained from other processes) and its mineralogy, the addition of limestone to achieve higher clinker factor reductions needs to be considered as a technically sound option. This study provides new insight for the selection of clay resources and concrete design for a given application, for the continued widespread uptake of calcined clays as promising cement replacements for concrete infrastructure development.

## CRediT authorship contribution statement

Yuvaraj Dhandapani: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Kirthika Kala Subramanian: Writing – original draft, Investigation, Formal analysis, Data curation. Fragkoulis Kanavaris: Writing – review & editing, Formal analysis. Leon Black: Writing – review & editing, Supervision, Funding acquisition. Susan A. Bernal: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconres.2025.107922.

## Data availability

The data associated with this paper are openly available from the University of Leeds Data Repository at https://doi.org/10.5518/1675.

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