Perspectives on Blended Cementitious Systems with Calcined Clay–Limestone Combination for Sustainable Low Carbon Cement Transition

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PERSPECTIVES ON BLENDED CEMENTITIOUS SYSTEMS WITH CALCINED CLAY-LIMESTONE COMBINATION FOR SUSTAINABLE LOW CARBON CEMENT TRANSITION

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Abstract

This paper presents a summary of the major findings from the studies conducted at Indian Institute of Technology (IIT), Madras on Limestone Calcined Clay Cement (LC3), in comparison with plain portland cement and fly ash-based binder. The study attempts to delineate the chemical and physical effects of binder components in LC3 on hydration and hardening, property development, binder chemistry and durability indicators to evolve fundamental understanding on the performance of such low clinker binders. Such an assessment can drive the practical adoption and extend the applicability of such binders in various domains of cement-based materials. The experimental strategy involved the assessment of the pore structure evolution and electrical properties on cementitious pastes, along with measurement of the durability parameters on concrete for resistance to ingress of moisture by absorption, and chloride ions by migration and diffusion mechanisms. The synergistic interactions of the blend of calcined clay and limestone impact the physical structure positively at early ages as opposed to fly ash systems, which require prolonged curing to realise their potential. The study reveals a combination of calcined clay and limestone can be a potential combination for producing high-performance concrete, more specifically in a chloride laden environment, along with the beneficial alternative resource utilisation and sustainability prospects.

Keywords: Calcined clay, Formation factor, Limestone, Microstructure, Ternary Blends.

1. INTRODUCTION

Cement consumption is projected to quadruple in the next few decades in India to meet the growing infrastructure, economic and social advances. Many strategies have been suggested for reducing the CO_2 emission in cement production including – improving the energy efficiency of kilns and pre-calciners, alternative fuels, alternative raw materials, new alternative clinkers, improving grinding efficiency, carbon capture and storage, and substituting clinker with supplementary cementitious materials (denoted as SCM hereafter) [1,2]. In a technology roadmap by World Business Council for Sustainable Development (WBCSD) and International Energy Agency (IEA), clinker substitution was identified as one of the major solutions for a sustainable transition to a controlled 2°C rise in temperature scenario in cement industry [3]. The production of clinker, which is the essence of cement, has a severe impact on the raw material reserves. It is widely accepted that the path forward for the production of sustainable concrete involves the reduction of the clinker factor in the binder, which is made possible by the use of suitable alternative binding materials or SCMs [2,4]. Availability of potential substitute materials and environmental concerns related to clinker production have powered the use of SCM over the last few decades. With the low availability of good quality fly ash and slag and the uncertainty of tapping into the natural pozzolan sources, calcined clay has emerged as the most promising alternative for the extender in blended cement [5,6]. Another development over the last two decades has been the increased use of ground limestone as an additive in the binder, either up to 5% as a performance improver or up to 15% in Portland Limestone Cement (PLC) formulations [7,8]. More recent literature has indicated the synergistic effects of using limestone in combination with other SCMs a part of a ternary binder system with portland cement [9–13].

2. BACKGROUND ON TERNARY CEMENT COMPOSITE WITH LIMESTONE AND CALCINED CLAY

The requirement for SCMs is expected to reach 500 million tons as per estimates presented in [5] to meet the demand

for cement substitutes. This increase in demand can be leveraged by combined substitution of SCMs, which are likely to accommodate a wide range of SCMs with various levels of quality and reactivity potential. The cement sustainability initiative (CSI) predicts that the contribution of limestone would increase from 8% in 2014 to nearly 18% by 2050 as supplementary binding material, as shown in Figure 1. Additionally, calcined clay is expected to compensate availability of fly ash and slag as a pozzolanic cement substitute.
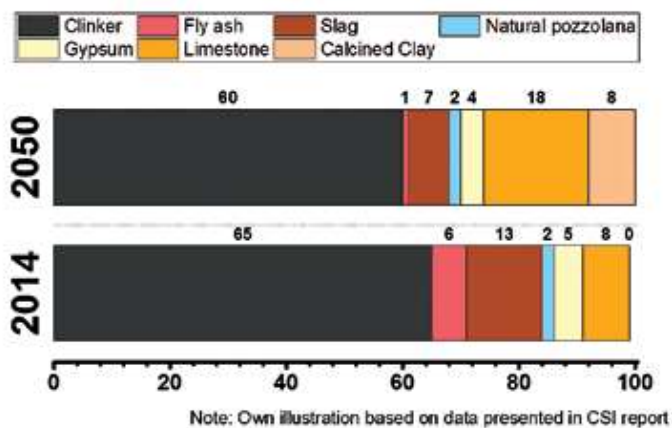

Figure 1: Contribution of different cementitious and pozzolanic materials to constituent binding materials as suggested in the CSI report [14].

2.1 Addition of Finely Ground Limestone Powder

Ground limestone is drawing interest as an additive in cement worldwide. A locally available resource for cement plants and the low emission factor of limestone (See Table 1) makes it a viable choice to reduce emission potential in cementitious materials by moderately and judiciously increasing filler substitution level [14,15]. In addition to the curb on emissions, the energy demand of the binder and concretes for calcined clay-limestone combination were found to be reduced by about 20% and 10% respectively with respect to OPC [16,17]. In current practice, most international standards allow only 5% limestone as performance enhancers in ordinary portland cement (OPC). Interaction from slow dissolution of calcite brings in a whole range of new opportunities for utilization of limestone, which requires only grinding, without any energy-intensive calcination process. Limestone is a readily available resource near clinkerization units. Hence, it does not require extensive transportation as slag and fly ash to supplement cement production houses. However, the slow uptake in Indian standards and industry acts as a barrier to limestone as a binder component. This necessitates extensive research studies to develop the state of art knowledge on the subject of such composite cementitious systems, which can elucidate the areas of benefits and address the concerns for suitable adoption.

Table 1: Summary of the emission factor of different binding materials

OPTIONS FOR BINDING MATERIALS	EMISSION FACTOR (kg-CO_2 PER kg-MATERIAL)	SOURCES
Clinker + Gypsum	0.77-0.93	[16–19]
Calcined clay	0.2-0.35	[18]
Limestone	0.008	[18]
Belite Ye'elimite Ferrite clinker	0.6-0.66	[18]
Carbonated calcium silicate clinkers	0.54	[18]
GGBS	0.070	[17]
LC3 binder	0.46-0.61	[16,17,19]

Limestone powder was traditionally considered as an inert filler. A more rational understanding of the physio-chemical contribution of limestone in a hydrating cementitious matrix has been emphasised in literature [20,21]. The chemical interaction of carbonate species has created avenues for judicious limestone additions [22,23]. The aluminate-carbonate interaction can alter physical structure development because of the difference in space-filling characteristics of the additional hydrate phases [24]. The extent of benefit that could be availed from such interaction needs to be elucidated with scientific research studies.

2.2 Calcined clay as a pozzolanic admixture

Calcined clay is an acknowledged pozzolanic admixture in the Indian standard; it is an ingredient of Portland Pozzolan Cement as per IS 1489 Part 2 [25]. However, the potential utilization of calcined clay has been undermined due to surplus availability of fly ash from thermal power plants in the last few decades and lack of knowledge on the quality of clay to be used for such applications. Studies have shown that 1:1 kaolinite clays possess excellent pozzolanic behaviour after dehydroxylation by thermal activation [6]. Calcined clay with only 40% kaolinite content was found sufficient to produce strengths similar to plain portland cement by 7 days of curing [26]. The presence of reactive aluminates in calcined clay makes it an ideal constituent for co-substitution with calcite-rich materials such as limestone/ dolomite/ marble stone [27,28].

Limestone Calcined Clay Cement (LC³) binder makes use of these two widely available resources and their interaction with clinker compounds and between calcined clay-limestone. A typical limestone calcined clay cement is composed of portland clinker, calcined clay (>40%), limestone and gypsum, as shown in Figure 2.
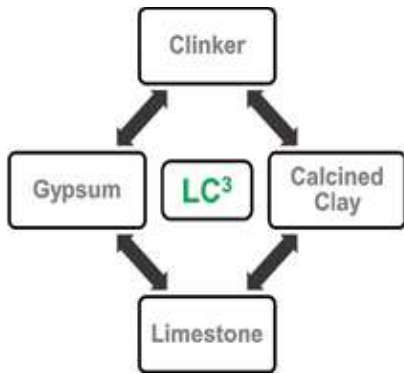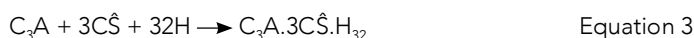
Figure 2: Components of Limestone Calcined Clay Cement (LC³). - more details can be found in www.lc3.ch.

A widely adopted LC³ composition is 50:30:15:5 (clinker: calcined clay: limestone: gypsum) with limestone-calcined clay ratio of 1:2. It is important to note that the composition of the ingredients can be optimised based on the requirement. All four ingredients collectively contribute to multiple interactions. Additionally, there is ample opportunity to explore Limestone-Calcined Clay (LC²) mixture as a pozzolanic admixture for high performance concreting applications [29]. This attracts significant interest in the research community to understand, validate and evolve such technology for large scale commercialization and field adoption.
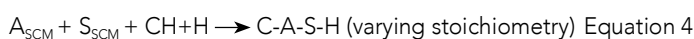
2.3 Chemistry of limestone calcined clay cement

The combination of finely ground limestone and calcined clay has emerged as a global solution for large volume cement replacement, catering to the increasing demand for cementing materials and supplement clinker production. Studies of such ternary blended systems in paste and concrete reveal interesting physicochemical effects on the structure development, strength and durability performance. The chemical interactions in LC³ binder include the clinker reaction, pozzolanic reaction, limestone interaction with clinker hydration and hydration products, and limestone-calcined clay interaction. Initially, the Bogues' compounds react to produce C-S-H, CH and Ettringite as given in Equation 1-3. In the presence of excess aluminates in clinker, ettringite converts to monosulphate (Ms). The addition of an aluminosilicate based pozzolanic admixture leads to the formation of pozzolanic C-A-S-H with variable levels of silica and alumina in the pozzolanic C-A-S-H as given in Equation 4. This reaction leads to a significantly improved pore filling and produces major benefits on transport properties [30, 31].

Clinker reactions:

$C_3S + 5.3H \longrightarrow C_{1.7}SH_4 + 1.3CH$ Equation 1

$C_2S + 4.3H \longrightarrow C_{1.7}SH_4 + 0.3CH$ Equation 2

$C_3A + 3C\hat{S} + 32H \longrightarrow C_3A.3C\hat{S}.H_{32}$ Equation 3

Pozzolanic reaction:

$A_{SCM} + S_{SCM} + CH + H \longrightarrow$ C-A-S-H (varying stoichiometry)   Equation 4

In the presence of fine limestone particles in the hydrating cementing matrix, the ettringite precipitated initially is stabilised as suggested in [32], and the aluminates react with limestone to produce carboaluminates as given in Equation 5 and Equation 6 with varying levels of carbonate ions (i.e., Hemi- or Mono) [24]. Calcined kaolinitic clay catalyses this interaction further due to the presence of reactive aluminate. Aluminates in calcined clay could also increase the additional demand of gypsum to ensure that calcite interaction proceeds after the consumption of gypsum, which needs to be controlled to occur after the primary silicate reaction [33].

Limestone interaction with clinker phases

$C_3A + CaCO_3 + CH + H \longrightarrow C_3A.CaCO_3.H_{12}$ Equation 5

Limestone interaction with calcined clay/SCM

$A_{SCM} + xCaCO_3 + 3CH + H \longrightarrow C_3A.xCaCO_3.H_{12-11}$ Equation 6

A major international collaborative project between leading universities such as EPFL (Switzerland), UCLV (Cuba), IITs Delhi, Bombay and Madras (India) in partnership with an Indian non-governmental organization called Development Alternatives has resulted in a systematic scientific study on Limestone Calcined Clay Cement (LC³), which has contributed vastly to the development of such low clinker binders [34]. So far, two major pilot-scale industrial productions have been made in the project in India; details of the same can be found in [35,36]. The current paper aims to throw light on the major outcomes of the research on ternary binder systems involving limestone and calcined clay. The studies on hydration, microstructure and concrete performance with LC³ binder systems has led to significant insights into the structure-property relationships. This paper mainly relies on the results already published in [37], [38] and [39], in conjunction with some new studies carried out in the project. An overview of the research and development made in the last six years is summarized in this paper with emphasis on the potential uptake of LC³ technology for standardization and field applications.

3. MATERIALS AND MIXTURES

Ordinary Portland cement of 53 Grade conforming to IS 269 [40], Type F fly ash from North Chennai, and Limestone Calcined Clay Cement (LC³) from an industrial production (reported in [35,36]) were used as the binders in this study in Phase 1. The fly ash and cement were blended in the ratio of 30:70 to produce the binder termed as FA30. The complete description of material characteristics is provided in Dhandapani and Santhanam (2017) [37]. In an extension to Phase-1, some investigations are presented from the on-going studies at IIT Madras (i.e., Phase 2). Calcined clay from Bhuj, Gujarat (with around 60% kaolinite content) and limestone from a cement plant in Ariyalur (with CaO content of 42%) were used to produce the ternary blended systems, with the formulations indicated in Table 2.

Table 2: Binder systems investigated in the study

	TYPE	MIX ID:	OPC (**CLINKER) %	SCM %	LIMESTONE* %	GYPSUM %
Phase-1	OPC	OPC	100	-	-	-
	FA30	FA30	70	30	-	-
	LC³	LC³	50 **	31	15	4
Phase-2	OPC	OPC	100	-	-	-
		FAF30	66	30	3.5	0.5
		FAF42	54.5	42	3	0.5
	Class F	FAFL10	54.5	34	11	0.5
		FAFL15	54.5	30	15	0.5
		FAFL20	54.5	25	20	0.5
		CC30	65.0	30	3.5	1.5
		CC42	53.5	42	3	1.
	Calcined Clay	CCL10	53.5	34	11	1.5
		CCL15	53.5	30	15	1.5
		CCL20	53.5	25	20	1.5

Note: *inclusive of limestone contributed from 5% calcite present in OPC

Gypsum amount was adjusted for the calcined clay - admixed binder to ensure that the aluminate peak is pushed beyond the main silicate hydration peak based on isothermal calorimetry profiles. This ensures proper early hydration of tricalcium silicates as recommended in the literature [11,41]. Figure 3 shows the impact of proper gypsum dosage on the silicate hydration peaks with (w-G) and without (w/o-G) gypsum correction. The additional aluminates from calcined clay and acceleration in clinker reaction due to fine substitutes increase the demand for gypsum marginally for LC³ binder composition. The additional gypsum (1.5% in this case) delays the appearance of the aluminate peak outside the silicate peak and ensures proper silicate reaction. A detailed investigation on the influence of gypsum dosage on the hydrate phase assemblage of LC³ binder can be found in Krishnan et al. (2019) [33].
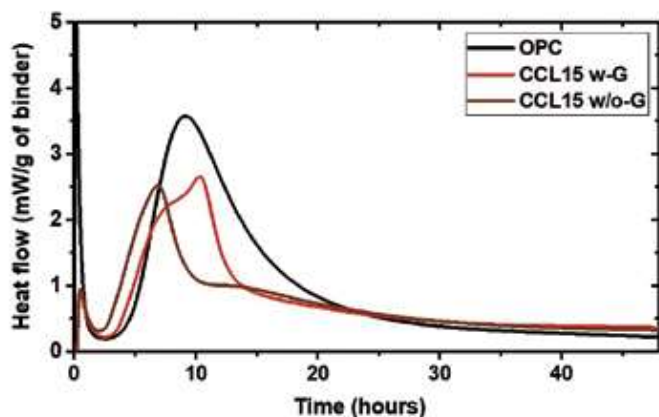

Figure 3: Effect of gypsum addition on the hydration profiles of LC3 binder.

A major part of this paper reports the results of three types of concrete produced with the three binder systems: (i) Concrete of grade M30 (i.e. characteristic compressive strength of 30 MPa), (ii) Concrete of grade M50 (i.e. characteristic compressive strength of 50 MPa), and (iii) Concrete with binder content of 360 kg/m³ and w/b of 0.45 (designated as C mix). A second investigation reports the results of binary and ternary blended mixtures with fly ash/ calcined clay and limestone, as indicated in Table 2. In all the mixes in Phase-2, the binder content and w/b were maintained at 360 kg/m³ and 0.45 respectively.

For all concrete mixes, the coarse aggregate was crushed granite with a maximum size of 20 mm, and the fine aggregate was well-graded river sand. The coarse to fine aggregate ratio was maintained at 60:40 by weight and a polycarboxylic ether (PCE) based superplasticizer was used to obtain a slump of 80 – 120 mm. The actual composition of cement paste used in the study is mentioned in the different sections.

4. RESULTS

4.1 Hydration, Hardening and Compressive strength

Figure 4 presents hydration heat and setting characteristics of the cement paste (w/b: 0.4) for all binder compositions investigated in Phase-2. The cumulative heat release in these binder systems reflects the kinetics of hydration reaction in binary and ternary combinations. It is clear that an increase in the amount of SCM, i.e., fly ash or calcined clay from 30% to 45%, reduces the total heat release by 7 days. The reduction
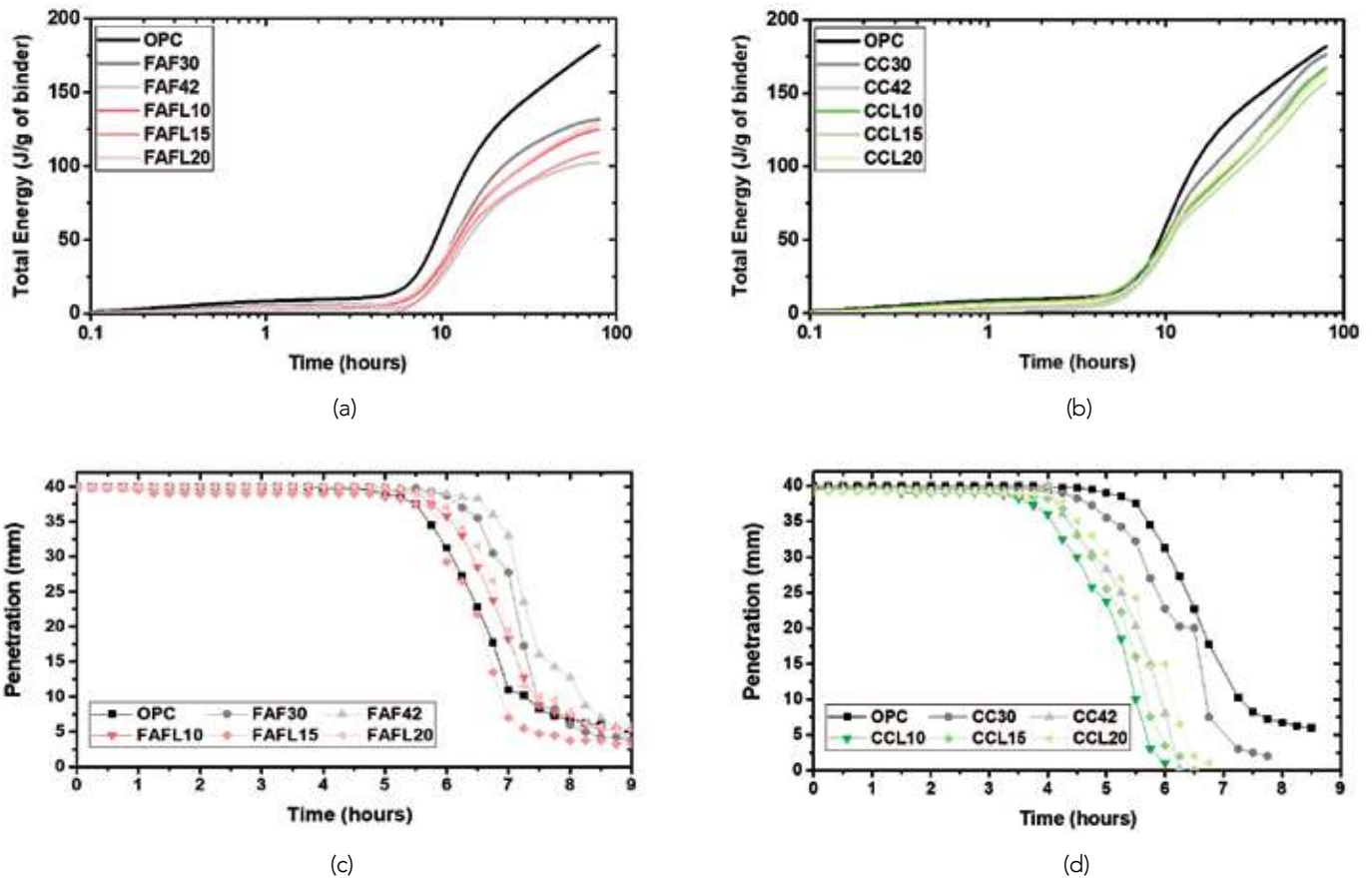
(a)

(b)

(c)

(d)

Figure 4: Hydration heat of fly ash (a) and calcined clay (b) mixes and Setting characteristics of fly ash (c) and calcined clay (d) mixes as presented in [42].

was significantly higher for increasing dosage of fly ash than calcined clay, as noticed in Figure 4(a) and Figure 4(b). The early interaction of calcined clay and the consequent acceleration in the hydration process contribute to the heat release in calcined clay binder combinations as opposed to fly ash binders. A combination of limestone-fly ash showed higher heat release than FAF42, which is characteristic of the positive influence of limestone on early hydration characteristics. Figure 4(b) shows that the change in heat release was not significant between CC30 and CC42, and only a marginal variation was observed in the cumulative heat release due to limestone addition in calcined clay binders. High reactivity potential of the calcined clay starts dominating hydration from the early stages itself. The onset of energy rise for calcined clay binder is similar to OPC in Figure 4(b).

Setting characteristics of all binder compositions with fly ash and calcined clay is presented in Figure 4 (c) and (d), respectively. The penetration resistance reduces with increasing dosage of fly ash (See FAF30 and FAF42 in Figure 4 (c)). Increase of dosage of fly ash from 30% to 42% shifts the time taken to develop resistance from nearly 6 hours to 7 hours. Addition of limestone manages to delay and shift the time taken between 5-6 hours in all ternary binders with limestone-fly ash combination. This shift signifies the acceleration in hydration characteristics due

to the presence of limestone addition, to compensate for the delay in setting characteristics of fly ash binders and bring it close to plain portland cement. Similar results were previously reported for high volume fly ash concretes with a minor dosage of limestone in literature [43].

In contrast to the fly ash mixes, an increase in calcined clay dosage from CC30 to CC42 resulted in early hardening, and the Vicat resistance was further accelerated in the presence of limestone-calcined clay combination. The combined early contribution of both calcined clay and limestone can also be noticed in the energy pattern in Figure 4(b), which collectively accelerates the setting characteristics of calcined clay-limestone binders. The penetration resistance was found to rise between 3-4 hours, which indicates that LC³ formulations have regular setting characteristics and could adequately meet the requirements of blended and masonry cement applications. In fly ash mixes, limestone addition was found to be beneficial in improving the kinetics of heat release rate, and correspondingly reduced the delay in setting characteristics that are typical in higher dosage of fly ash additions as a cement substitute.

Figure 5 presents the evolution of compressive strength for the concrete mixes. Figure 5(a) and 5(b) shows the results from Phase 1 [38], while Figure 5(c) and (d) shows the results from

Phase 2. It is evident from Figure 5(a) that the rates of strength development of LC³ concrete are similar to OPC concrete and significantly higher than FA30 concrete, which needs extended curing to achieve similar ultimate strengths. LC³ was able to produce comparable strength development despite lower clinker content than FA30. On the other hand, the Phase 2 results in Figure 5 (d) indicate that it is possible to produce concrete strengths with calcined clay-limestone combinations on par with OPC strengths when the calcined clay is at 30-35% replacement level, and limestone is used up to 15% replacement level.

The compressive strength development (up to 180 days) in concretes reaffirmed the influence of limestone on the early age mechanical properties (See Figure 5(c) and (d)). This can be identified from the comparable strength development of ternary mixes with limestone to binary mixes. The early increase in hydration and strength were possible despite the fact that limestone is replaced at the expense of a more reactive component such as clinker and pozzolan. For both fly ash and calcined clay, compressive strengths at 7 days and 28 days were marginally higher for ternary mixes than binary mixes with 42% SCMs. Even in CCL20 with limestone substitution of 20%, there is a steady development of strength up to 180 days. In CC42 with 42% binary substitution of calcined clay, there was a stagnation in the strength development beyond 28 days at higher substitution levels of calcined clay due to a probable portlandite-deficient state. The compressive strength results from ongoing Phase-2 studies indicate the compositional robustness of calcined clay-limestone combination to produce comparable early and later age mechanical strengths to plain portland cement and accommodate varying levels of limestone-calcined clay ratio. In fly ash-limestone combination, early age strength of ternary mixes was found to be comparable to binary fly ash binders. However, a consistent difference in strengths was visible at later ages with increasing dosage of limestone as shown in Figure 5c.
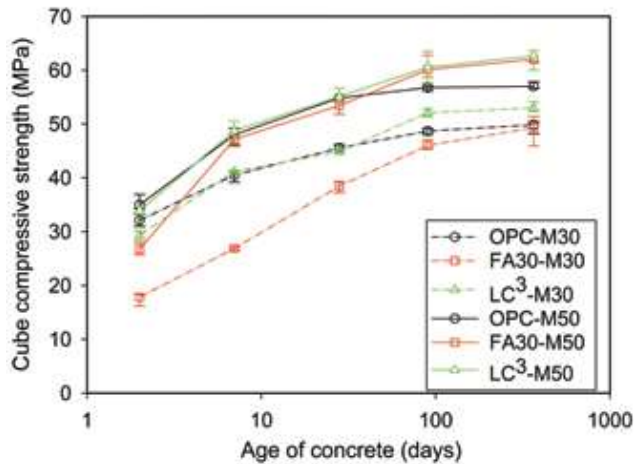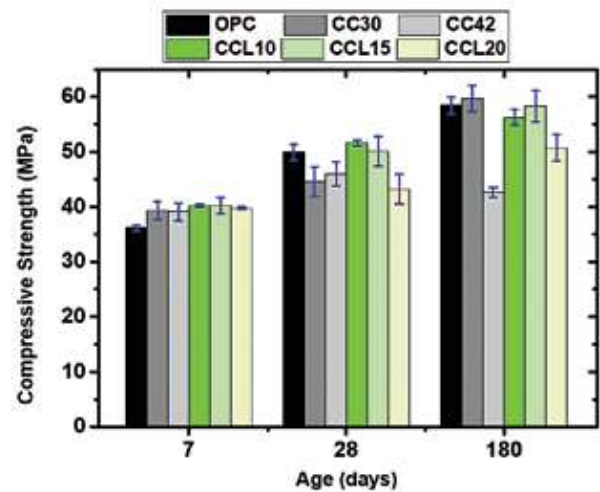

(a)
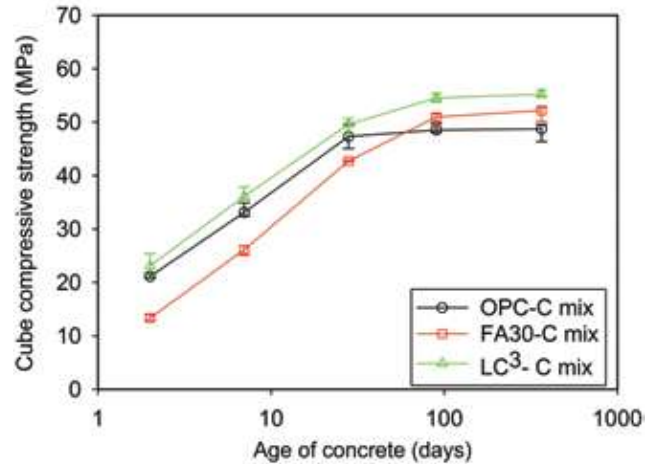
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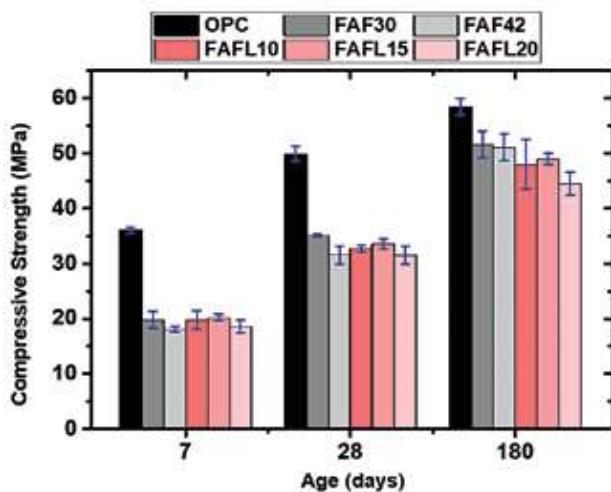
(c)

(d)

Figure 5: Results for compressive strength evolution a) comparison of strength evolution from phase-1 concrete made with OPC, FA30 and LC³ (reproduced from [38]) and Influence of fly ash/calcined clay-limestone ratio on strength development of LC³ concrete from Phase-2 studies (c) fly ash and (d) calcined clay [44].

4.2 Durability characteristics

The detailed results of durability tests on concretes from the Phase 1 study are presented in Dhandapani et al. [38,45]. The concept of formation factor has been extensively explored in [46-48]. In simple terms, the formation factor is the ratio of the conductivity of the pore solution (σ_o) to the effective conductivity of the bulk concrete (σ_b) as given in Equation 7 which is related to porosity (φ), pore connectivity (β) and cementation exponent (m). The use of formation factor helps in understanding the influence of pore structure i.e., pore volume (φ) and connectivity on durability, without the concomitant effects of the pore solution conductivity.

$$F = \frac{\sigma_o}{\sigma_p} = \frac{1}{\varphi^m} = \frac{1}{\varphi.\beta} \qquad \text{Equation 7}$$

The variation of formation factor with age for the cement paste studied in Phase 1 is presented in Figure 6 (a), based on Dhandapani and Santhanam [37]. The result clearly shows that pore tortuosity (or disconnectedness), as represented by the formation factor, rapidly increases for LC³ concretes. In the case of FA30, extended curing is essential to get the same level of increase in formation factor. The OPC paste, on the other hand, does not show much increase in formation factor beyond 7 days. From the same literature, the results of the relationship between formaton factor and the water-filled porosity (as determined by vacuum saturation process on thin slices of cement paste) are presented in Figure 6 (b) reaffirming Archie's law for cementitious porous systems. The plot in Figure 6 (b) clearly indicates that the formation factor can be a unifying approach to compare the capillary pore space, structure development and durability characteristics across cementitious systems with different binder chemistry.

The promising trends of formation factor to reflect the structure development in capillary pore space were extended to understand the durability performance of concrete made with different binder systems. The results of the charge passed in

RCPT (as determined from the ASTM C1202 [49]), plotted against formation factor, are presented in Figure 7 (a) and (b). The charge passed in RCPT and formation factor was measured over different curing ages up to 1 year as shown in Figure 7 (a). The influence of the binder type is evident, with the results from the LC³ concretes showing a much lower charge passed and higher formation factor as compared to FA30, which in turn shows higher resistance to ionic ingress than OPC concretes. The combined reduction of porosity and pore connectivity, which leads to higher formation factor, can explain the role of pore structure development on durability parameter. In Santhanam et al. [44], the influence of formation factor to represent chloride transport was validated with migration coefficient based on NT BUILD 492 test [50], which is a reliable test for chloride penetrability and also gives an acceptable parameter for performance-based design approaches and service life estimates as per FIB Model Code 34 [51]. This relationship confirms the generic adoption of formation factor as a representative microstructure-based factor which relates to durability characteristics of a range of concretes across different binder chemistry by deconvoluting the impact of pore structure and pore solution from the bulk electrical response.

The results for the secondary rate of water absorption as per ASTM C1585 [52] also indicate a superior performance for the LC³ concretes (results in Figure 8 presented here are for the C-mix). In simple terms, the superlative benefit of early rise in formation factor is prudent not just in migration-based experiments, but also in unidirectional water absorption by a measure of moisture transport in LC³ on an unsaturated concrete system. This difference in performance draws attention to the fundamental difference in the characteristics of capillary pore space of the binder phase. It is clearly shown by the published works of Avet and Scrivener [26] and Dhandapani and Santhanam [37] that this edge in performance can be related to the rapid development of a pore structure i.e., early disconnection in capillary pore space in the LC³ binding phase. Evidence of this phenomenon is
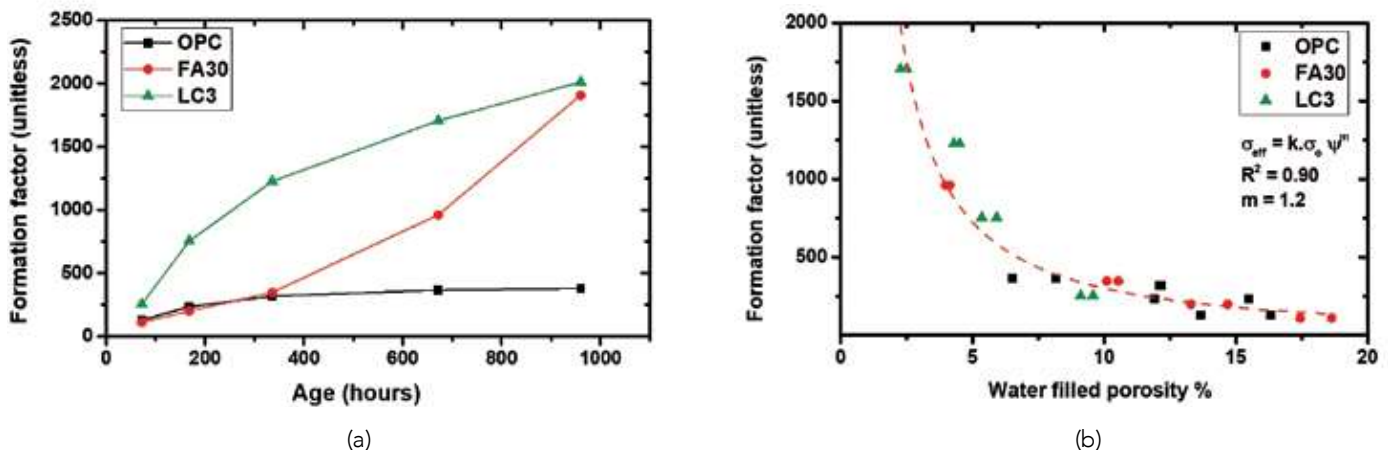

(a)

(b)

Figure 6: (a) Change in formation factor with curing age for the Phase 1 for cement paste, (b) Exploring relationships between formation factor and durability (in terms of water-filled porosity) for all Phase 1 binder compositions – from [37].
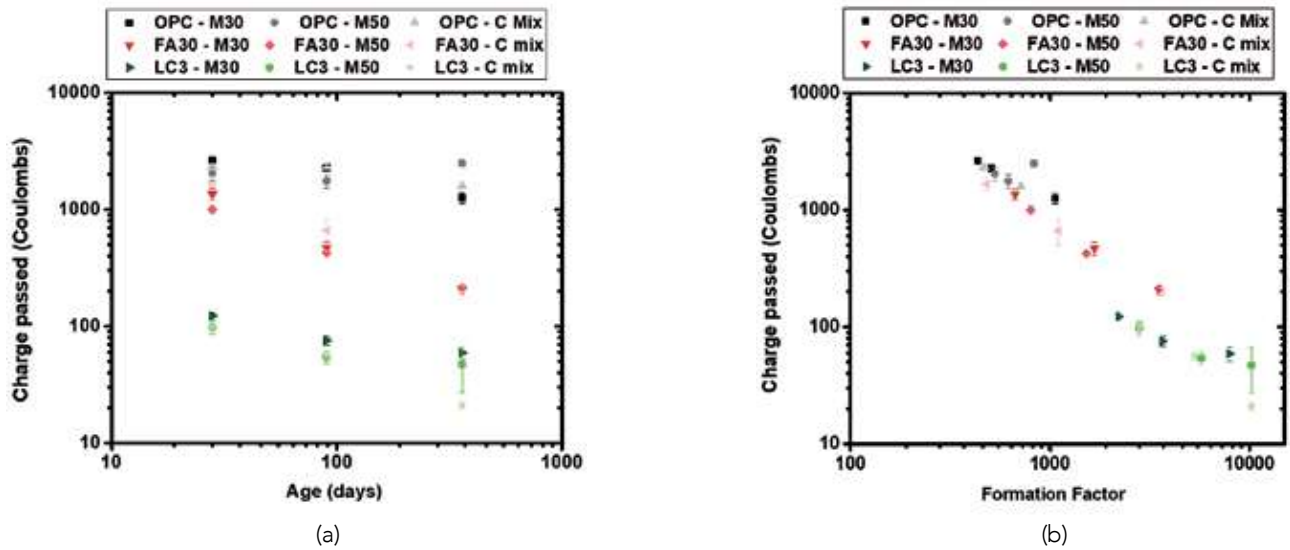
(a)

(b)

Figure 7: (a) Charge passed as a function of age from [38] and (b) Influence of formation factor on durability indices.
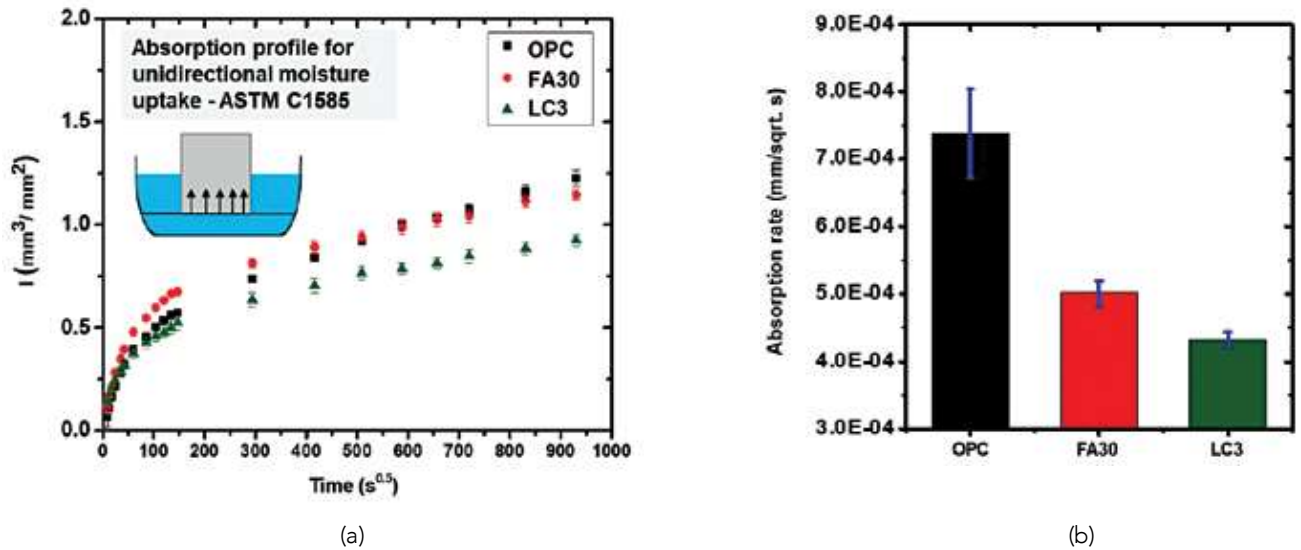

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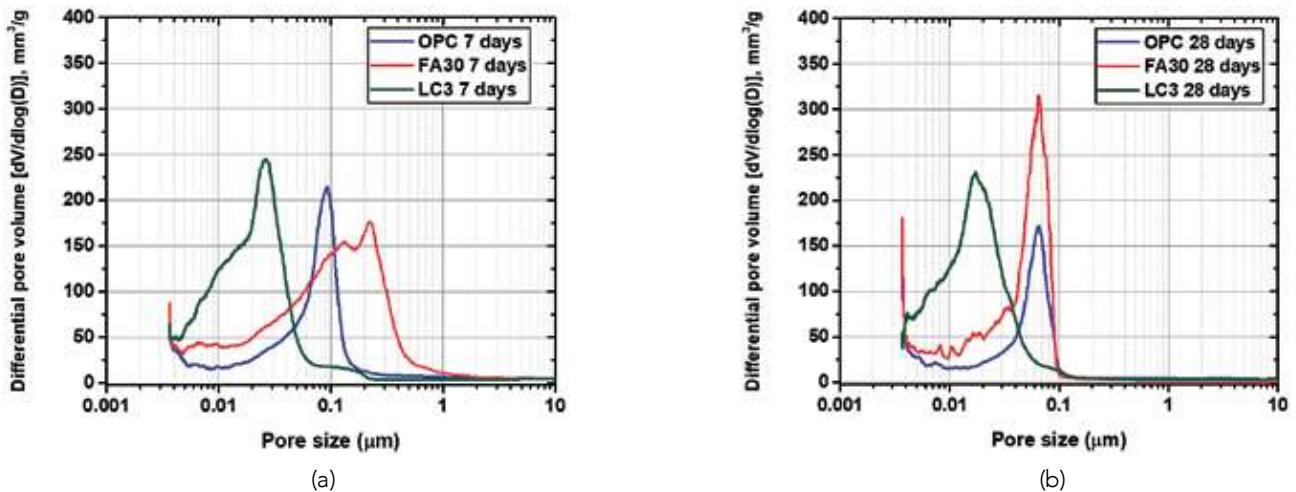Figure 8: Results of the sorptivity test as per ASTM C1585.

(a)

(b)

Figure 9: Pore size distribution from mercury intrusion porosimetry, as presented in Dhandapani and Santhanam [37].
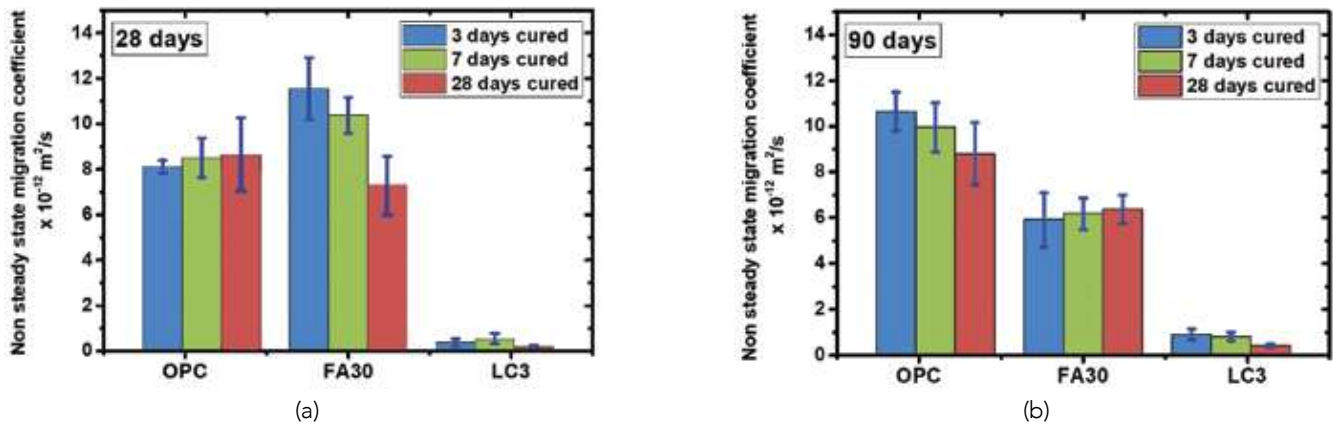
Figure 10: Influence of curing age on durability properties.

presented in Figure 9 from [37], where the results clearly indicate the shift in pores towards finer sizes as early as 7 days for the LC³ systems for cement pastes with 0.35 w/b. A similar reduction in pore sizes was also noticed in the porosimetry assessment made on LC³ concretes [38] and paste with varying water-binder ratio [29]. These trends seem to indicate that LC³ systems would not be significantly affected by the curing duration with respect to the development of the durability characteristics.

In order to validate the potential benefits of early refinement of pore structure, the effects of curing duration on OPC, FA30 and LC³ concrete were studied. Concretes in the C-mix category were subjected to different moist curing regime (i.e., 3 days, 7 days and 28 days) after which the concretes were placed in a controlled environment (25°C and 65% RH) till the age of testing. Non-steady state migration experiment was used to evaluate the chloride resistance at 28 days and 90 days after the initial moist curing. The results from the study are presented in Figure 10, which shows that LC³ concretes attain significantly higher resistance to ingress of chloride ions irrespective of the moist curing duration (varied between 3 and 28 days). The OPC and FA30 concretes show a significant dependence on curing

duration. For instance, the impact of extended moist curing duration can be noticed in Figure 10 reporting the transport performance of OPC concretes at 90 days. The concretes cured for 28-days show lower D_{nssm} than concretes cured for 3 days and 7 days, as seen in Figure 10 (b). At 28 days, the difference was insignificant to capture the influence of curing in OPC concretes. For fly ash concrete, there was a consistent reduction in transport parameter for extended curing from 3 days to 28 days, which was visible by 28 days (See Figure 10a). Fly ash concretes managed to attain similar resistance to chloride transport by 90 days after the initial moist curing regime due to steady interaction of fly ash on the microstructure (See Figure 10b). The LC³ concrete showed lower D_{nssm} irrespective of curing duration, and the 28 days cured LC³ concrete showed lower D_{nssm} at both 28 days and 90 days (See Figure 10b). The results reiterate the fact that the early development of pore structure noticed from microstructural assessment firmly controls the performance characteristics in concrete systems.

4.3 Microstructure

The variation in the microstructure characteristics was studied in order to understand the cause of early development of physical
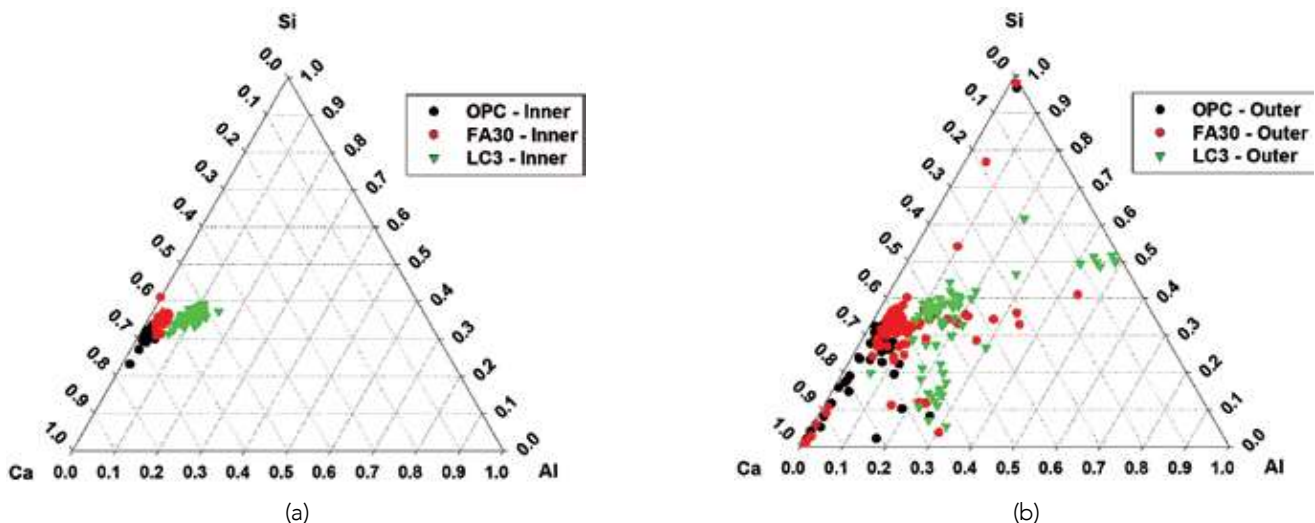

Figure 11: Composition of CASH in the OPC, FA30, and LC3 cementitious systems at 150 days (reproduced from [38]).

structure and durability properties. The significant change in durability properties in LC³ systems can be explained by the characteristics of the C-A-S-H phase produced in the calcined clay-limestone systems. Energy-dispersive X-ray analysis was carried out on nearly 200 points for each cement paste made of three binder. The variation in chemistry of C-A-S-H produced in the three binders were assessed. Microstructural composition of LC³ presented in [38] is reproduced in Figure 11. The high reactivity of calcined clay lowered the Ca/(Si+Al) to 1.21 in the LC³ system. In OPC and FA30, the ratio of Ca/(Si+Al) was nearly 1.95 and 1.60, respectively. The chemical composition inherently alters the molar volume of the bulk C-A-S-H and thus, space-filling characteristics of the microstructure. A significant reduction in Ca/Si ratio indicates that the low packing density C-A-S-H (further reaffirmed in [53]) formed in LC³ is the cause for dominant refinement of the capillary porosity, contribute to densification and discontinuation of the capillary pores. The early rise in resistivity and formation factor confirms the primary implication of the SCM's reactivity on concrete properties. This difference in C-A-S-H chemistry and resulted development of macroscopic properties places emphasis on the fact that the durability indices can be adjusted to a target value by a suitable mixture proportioning scheme. However, the kinetics of property development is directly governed by the reactivity of SCM constituents in binder phase [54].

5. DISCUSSION – IMPACT ON CHLORIDE INDUCED CORROSION

The results in the preceding section indicate that transport parameters of LC³ concretes are expected to be superior in chloride environments. However, the performance of concrete structures is also affected to some extent by steel-binder characteristics. Literature indicates that the chloride threshold is lowered in blended binder systems [55]. Indeed, results from the study conducted in the IIT Madras (reported in Pillai et al. [39]) also found a reduction in chloride threshold value. The determination of the chloride threshold was as per the method suggested by Rengaraju et al. [56]. The chloride threshold in FA30 and LC³ were 0.32% and 0.17% (by weight of binder), respectively, which was lower than 0.44% found in OPC binder [39]. Pillai et al. [39] used the chloride threshold data along with the transport characteristics (chloride diffusion coefficient) shown in Figure 12 – to predict the service life with respect to chloride-induced corrosion as per the probabilistic modelling approach suggested by LIFE 365. The results of the analysis, shown in Figure 13, indicate that despite the lower chloride threshold, the service life of LC³ concretes is on par with FA30, and much superior to OPC systems in a chloride environment. The ingress rate was found to be lower by an order of magnitude for LC³ concrete and the evolution of chloride transport was also was found to be higher than OPC concrete [39]. Both these factors dominantly influenced the service life estimates in the case of LC³ concrete systems to produce longer time for corrosion initiation.
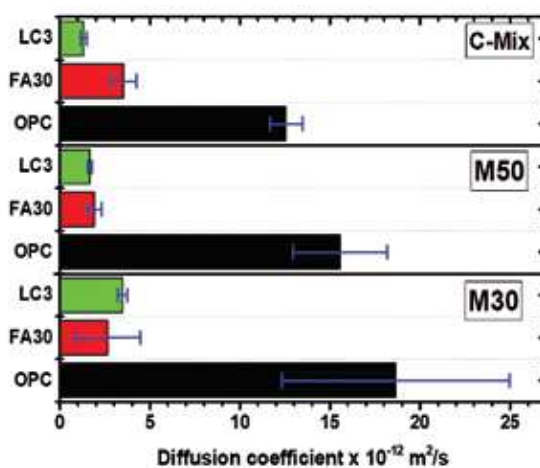

Figure 12: Comparison of chloride diffusion coefficients for all mixes from Phase 1 from [39].
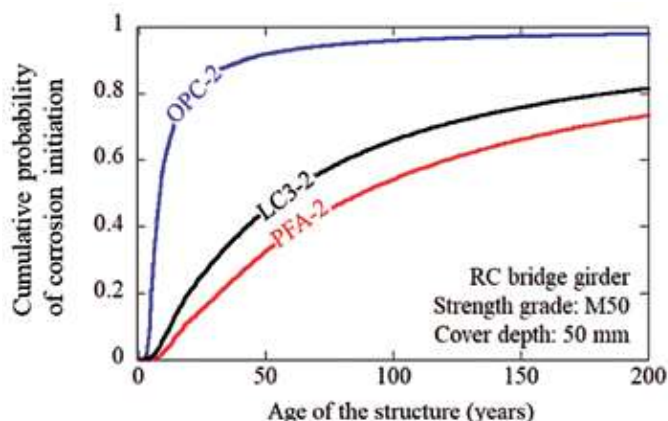

Figure 13: Comparison of service life calculations for the concretes with the three binder systems as presented in [39].

The corrosion propagation current is expected to be lower for LC³ binder as concrete resistivity plays a crucial role in the corrosion current density of steel [57]. This reduction could be partially attributed to the extremely high resistivity of LC³ concretes – an order of magnitude higher than for OPC and significantly higher than FA30 as found in [29,38]. A study on the influence of concrete mixture proportioning on the resistivity development confirmed the higher resistivity potential of LC³ concretes. Figure 14 presents a resistivity range for concretes between M20-M50 strength grades. The resistivity rise was found to occur consistently between 3 to 7 days in LC³ concretes, whereas fly ash concretes showed a major increase only post 28 days. The higher resistivity of LC³ concretes is expected to slow down the corrosion propagation – post-initiation. Current work at IIT Madras looks at the role of the CSH chemistry in addition to the pore structure characteristics with respect to the development of resistivity, resistance to sulphate ingress [58], and influence of corrosion initiation and propagation characteristics in chloride and carbonation environments for LC³ concretes.
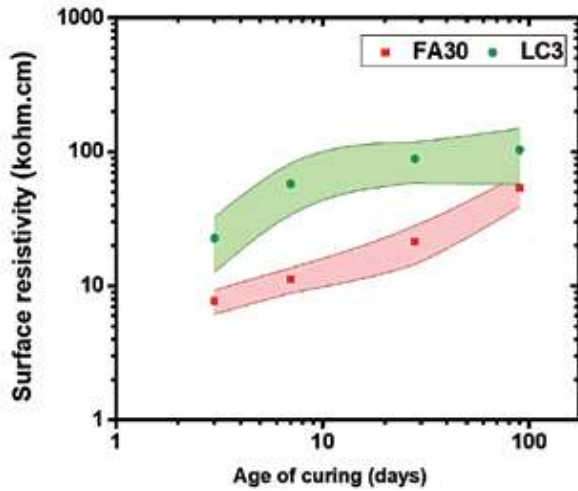
Figure 14: Surface resistivity of concretes measured using Wenner 4-probe test based on 21 sets of LC3 concretes and 18 sets of FA30 concretes reported in [29].

6. DISCUSSION – APPLICATION PROSPECTS IN FRC PAVEMENTS

In this section, the potential of low clinker LC^3 binder for use in fibre-reinforced concretes (FRC) is highlighted based on a small-scale pavement segment constructed for feasibility assessment and demonstration purpose. A segment of concrete pavement with FRC was made with OPC and LC^3 in Feb 2016 (See Figure 15 (a) & (b)) inside IIT Madras campus. The concrete mixture was composed of 310 kg/m^3 binder content and 0.5 water-binder ratio with 15 kg/m3 dosage of hooked end steel fibres (i.e., about 0.2% by volume of concrete). Both FRCs (OPC and LC^3) had a compressive strength of about 32 MPa at 28 days. Figure 15 (c) shows the view of the in-service pavement segments as on Sep 2019. To characterize the behaviour of the LC3-FRC concretes, flexural testing was carried out on concrete used in the pavements as per Nayar et al. (2014) after 28 days of concreting [59]. A typical flexural response of the plain concrete
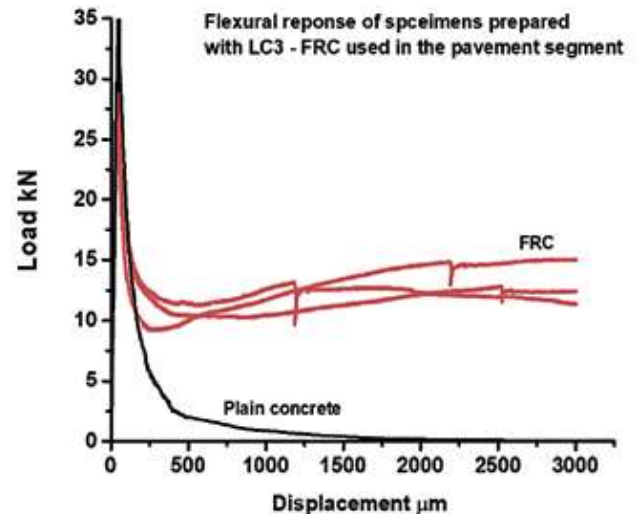

(a) Concrete pour for a pavement segment with FRC made with LC^3 .
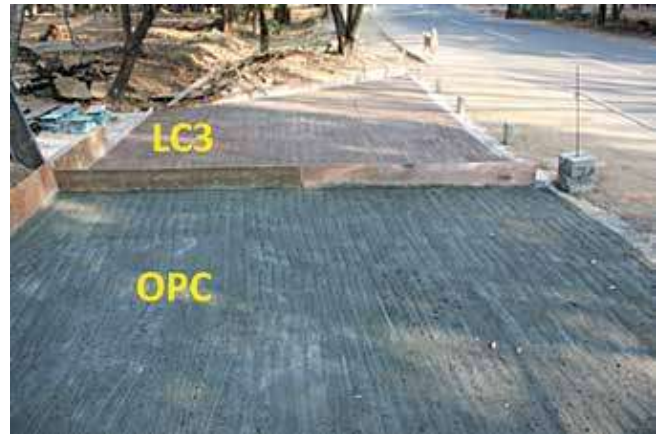
(b) Finished pavement segments with OPC and LC^3 concrete in February 2016.

(c) Integrity of pavement segments in September 2019.

(d) Flexure response of LC3 concrete used in pavement.

Figure 15: Details on FRC pavement segments made with LC^3 concretes.

and FRC made with LC^3 is given in Figure 15 (d). In general, the behaviour is more typical of the FRC which is expected to show toughening characteristics or higher energy absorption capacity in comparison to plain concrete as demonstrated in the numerous previous works from our laboratory [59–61].

7. CONCLUSIONS

Studies conducted over the last six years at IIT Madras evaluating the robustness of LC^3 binder have shown that the new binder is a promising low carbon alternative to meet the growing demand for cement and concrete in the light of dwindling resources of slag and fly ash in certain geographical locations. The knowledge generated can severe as a vital database for standardization of the calcined clay-limestone cement and facilitate industrial uptake of this low carbon technology. More specific conclusions summarising the performance of calcined clay-limestone binder based on the results presented in this paper are:

1. Durability performance concerning chloride ingress, moisture ingress and corrosion resistance was studied. LC^3 systems were found to have better resistance (than OPC and FA30 systems) against chlorides, moisture and chloride-induced corrosion initiation.

2. The ternary system with cement-limestone-calcined clay offers an excellent alternative cement for the future with key benefits for high-performance application in chloride laden environment. More detailed investigation on carbonation and carbonation induced corrosion is necessary due to low clinker content in such binder systems.

3. The LC^3 systems exhibited slightly lower chloride threshold than the OPC and FA30 systems. However, the significantly lower chloride diffusion coefficient results in a delay in the time taken for chlorides to build on the steel surface and in turn is reflected as much longer service life estimates for chloride exposure.

4. The study puts forward the promising use of the calcined clay-limestone mixture in producing various grade of concretes and the compositional robustness to deal with change in calcined-limestone ratio. The impact of early refinement of pore structure due to densification of capillary pore space and a corresponding improvement in macroscopic properties were identified as the fundamental driving force for higher formation factor and durability indices.

5. The positive role of limestone was confirmed based on heat release, setting and early-age strength development with calcined clay and fly ash binder. This alteration in strength development due to limestone addition was obvious at all ages for calcined clay-limestone binders. The extent of benefit in concrete performance was mainly governed by the choice of SCM (i.e., calcined clay or fly ash). The calcined clay-limestone binders could accommodate up to 15%-20% finely ground limestone without any reduction in mechanical and durability characteristics.

Based on the promising results from the LC^3 Phase-1 project, it is believed that many areas of application would benefit from such low carbon cement, considering its high-performance potential against attack from ionic ingress. One such application in a concrete pavement is demonstrated based on field implementation of FRC concretes made with LC^3 binder. Lower carbon footprint and better durability performance with LC^3 are seen as major benefits for the cement in further concrete applications.

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