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# Influence of cement replacement by limestone calcined clay pozzolan on the engineering properties of mortar and concrete

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**This study investigates the effect of a new type of blended pozzolan on the hydration, mechanical and durability performance of cement. A blend of limestone calcined clay pozzolan (LCCP) was produced by grinding calcined clay and limestone in a ratio of 2:1 with 2% gypsum. Blends with cement replacement level of 0, 10, 15, 20, 30 and 50% using LCCP were cast. The effect of LCCP on the hydration of cement was investigated using isothermal calorimetry and X-ray diffraction. Mortar and concrete samples were cast to study the influence of LCCP on mechanical and transport properties. The addition of LCCP was found to have a beneficial effect on the early age hydration of cement. The induction period and initial setting time of cement paste were found to reduce on increased cement replacement level. Higher or similar compressive strength was observed for all the LCCP blends as compared to ordinary Portland cement. The pozzolanic reaction of calcined clay and formation of carboaluminates on the reaction of calcium carbonate with alumina helps to develop a refined pore structure that aids in reducing transport properties of concrete such as porosity, rate of water absorption and permeability.**

## Introduction

The cement industry is one of the major emitters of anthropogenic carbon dioxide into the atmosphere, accounting for approximately 5–8% of the total carbon dioxide emissions (Rehan and Nehdi, 2012; Scrivener, 2014). Rapid and continuous development in the construction and infrastructure sector in the near future will further drive up the collective cement demand. The increased demand will distress the already depleting natural resources required for cement production and environment. Supplementary cementitious materials (SCMs) offer the most promising means to meet the demand by optimising resource utilisation, along with economic and environmental benefits.

SCMs are materials with a pozzolanic or cementitious property that can be used to substitute partially for cement. The utility of an SCM as a clinker replacement depends upon its availability, variability and the properties of the material itself. The SCMs can be classified as natural or man-made based on their origin (Snellings *et al.*, 2012). The products formed on the pozzolanic reaction of SCMs help in the densification and refinement of pore structure, which subsequently helps to enhance the mechanical and durability performance of concrete (Duan *et al.*, 2013; Ghrici *et al.*, 2007; Snellings and Scrivener, 2015). The effect of SCMs on the strength of the concrete depends upon numerous parameters of the SCMs, such as type,

replacement level, curing and physical and chemical properties (El-Diadamony and Amer, 2016; Lothenbach *et al.*, 2011). Major technical barriers in the use of cements containing SCMs are usually related to physical or chemical incompatibilities between the SCMs and the cement. Low reactivity, low early strength, high water demand, variability, volume stability, longer curing period and so on are some of the most common incompatibility issues associated with SCMs. Incorporating SCMs for a certain specific durability performance may lead to the attenuated performance of other durability parameters (Mehta and Monteiro, 2006; Saraya, 2014; Siddique, 2008; Zhang *et al.*, 2014). Moreover, irrespective of the type of SCM used as cement replacement, an increase in compressive strength is observed only until a particular level of replacement. Thereafter, the dilution effect becomes more prominent, resulting in a lower compressive strength (Cyr *et al.*, 2006; Liu, 2010). Also, the majority of the good-quality traditional SCMs that are produced or available are already being optimally used in the cement industry, providing limited scope to further reduce energy consumption and emissions. Therefore, the development of new materials such as coupled SCM blends from sources that are widely available could provide a viable alternative for the cement industry. Using a combination of SCMs can help to compensate for the inadequacies of individual SCMs. The use of a combination of fly ash/silica fume, slag/fly ash, slag/silica fume, limestone/slag, limestone/fly ash

at different replacement levels of ordinary Portland cement (OPC) has been reported (Bagheri *et al.*, 2012; Espion *et al.*, 2013; Meddah *et al.*, 2014; Nehdi *et al.*, 2004; Thomas *et al.*, 1999).

Owing to their easy availability and large quantities, calcined clays have a significant potential in lowering the clinker content and thereby carbon dioxide emissions (Scrivener, 2014). Clay minerals are a combination of numerous aluminium and silicon sheets. Depending on the weathering conditions, different clay minerals are formed based on the stacking arrangement of the sheets (Lopez, 2009). Clay minerals have limited pozzolanic activity due to their highly ordered crystal structure and are usually subjected to thermal treatment to impart them with pozzolanic activity. On calcination, they undergo dehydroxylation process – that is, the process of removal of its structural water, resulting in the formation of a highly reactive amorphous aluminosilicate phase (Tironi *et al.*, 2012; Vizcayno *et al.*, 2010). Kaolinitic clays have the highest potential for pozzolanic activity (Fernandez *et al.*, 2011). The kaolinite content of the clay governs its reactivity, which can be determined by thermogravimetric analysis (Avet and Scrivener, 2018).

Limestone filler in cement provides the extra nucleation sites for hydration products, helps in better packing and improving the workability of concrete. Although limestone does not possess any pozzolanic property, in a high-pH environment it has a tendency to react with the aluminate ions present in the cement or SCMs and form mono-carboaluminate and hemi-carboaluminate (Antoni, 2013; Deschner *et al.*, 2012; Kakali *et al.*, 2000; Matschei *et al.*, 2007). The OPC–limestone reaction is not so prominent owing to limited availability of aluminate in the clinker. A more reactive alumina content in an SCM could favour the formation of carboaluminates in the presence of limestone. The reaction between calcium aluminate and calcium carbonate is of greater importance when both the materials are mixed with each other to form a blend of ternary cement.

Recently, wide interest has been generated in research into calcined clay limestone blend cement. The pozzolanic reaction of calcined clay and the reaction of limestone with alumina create a synergetic effect in the system (Antoni, 2013; Bishnoi *et al.*, 2014; Emmanuel *et al.*, 2016). The cement, comprising a blend of calcined clay and limestone, is reported to provide equivalent strength to OPC even at a 50% clinker factor (Antoni *et al.*, 2012; Avet, 2017; Dhandapani *et al.*, 2018; Emmanuel *et al.*, 2016; Krishnan *et al.*, 2018). In this study, a blend of limestone calcined clay pozzolan (LCCP), a potential SCM for use in the ready-mix concrete and construction industries, was studied. The effect of different replacement levels of cement with LCCP on the rate of hydration and strength development were investigated. The effect of replacement of cement with LCCP on transport properties of concrete was also studied.

## Methodology and experiments

### Materials

The OPC used in the present study was procured from a cement plant based in India. Clay with kaolinite content of around 60% was selected for the study. Kaolinite, quartz and haematite were the major mineral phases present in the clay. Studies have reported that only a small fraction of the total limestone added undergoes chemical reaction to form carboaluminates (Antoni, 2013). Therefore, in this study, a less pure form of limestone that is usually discarded from clinker production was procured from a cement company. Along with calcite, peaks corresponding to quartz, kaolinite and muscovite were detected in the X-ray diffraction (XRD) analysis of the limestone sample. The chemical composition of the raw materials used in the study was measured using X-ray fluorescence and is shown in Table 1. The calcination of clay was carried out in a rotary kiln at a temperature of around 950°C. No peaks corresponding to kaolinite were observed in X-ray diffractograms of the calcined clay, implying proper and complete calcination of clay.

The LCCP was produced at a cement-grinding unit of J. K. Lakshmi in Jajjhar, India by inter-grinding the raw materials in a ball mill. The ratio of calcined clay to limestone was kept as 2:1, based on earlier studies (Antoni, 2013; Bishnoi *et al.*, 2014; Emmanuel *et al.*, 2016). Two per cent of gypsum was added to support the hydration of aluminates in the calcined clay based on laboratory trials. The gypsum added in the LCCP is in addition to the gypsum already present in OPC. Figure 1 shows the particle size distribution of OPC and LCCP measured using laser diffractometry. The Blaine's fineness value of OPC and LCCP was measured to be 300 and 600 m<sup>2</sup>/kg.

### Experiments

#### Cement paste and mortar

The hydration kinetics of cement are altered in the presence of SCMs. Isothermal calorimetry can be used to investigate the changes occurring in the hydration kinetics of cement on replacing part of the cement with SCM. In this study, the effect of replacement of different quantities of cement with LCCP on

**Table 1.** Chemical composition of raw materials (%)

Weight: %	OPC	Clay	Limestone
Calcium oxide (CaO)	55.94	0.06	31.50
Silicon dioxide (SiO <sub>2</sub> )	20.99	54.67	27.01
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	7.16	27.69	9.92
Iron (III) oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.83	4.93	5.27
Magnesium oxide (MgO)	3.06	0.13	0.73
Sodium oxide (Na <sub>2</sub> O)	0.52	0.12	0.20
Potassium oxide (K <sub>2</sub> O)	0.90	0.25	0.68
Sulfur trioxide (SO <sub>3</sub> )	4.39	0.10	0.02
Loss on ignition	2.55	10.28	26.1

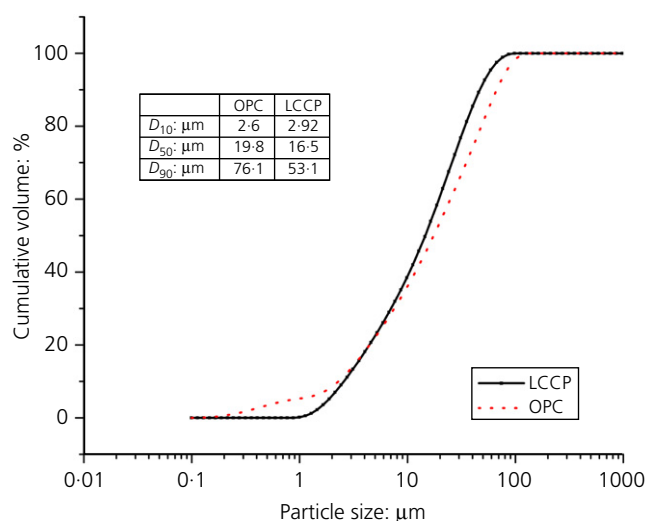


Figure 1. Particle size distribution of OPC and LCCP

the rate of hydration of the cement was measured using a Calmertix ICal 8000 isothermal calorimeter. The calorimeter was maintained at a constant temperature of 27°C while the energy released on hydration was measured. The test was done on cement paste samples prepared at a water-to-binder ratio of 0.45 and 0, 10, 15, 20, 30 and 50 replacement levels of cement with LCCP.

Depending on the physical and chemical properties of the SCMs, an increase or decrease in the initial setting time of the cement paste occurs. The initial setting time of the cement paste at the above-mentioned replacement levels of cement was measured in accordance with the relevant Indian standard (IS 4031, Part 5 (BIS, 1988)) using Vicat apparatus. Cement paste samples were cast at 0.85 times the water required to prepare a paste of standard consistency. The initial setting time was measured by marking the time at which the needle failed to pierce the cement paste sample in a Vicat mould beyond  $5 \pm 0.5$  mm. All the times measured were taken from the instant when water was added to the cement.

The XRD was used to characterise and study the variation occurring in the phase assemblage of hydration products of cement containing LCCP. Cement paste samples were cast at a water-to-binder ratio of 0.45 in a cylindrical plastic mould 100 mm high, with a radius of 20 mm. XRD scans were carried out on disc specimens sliced from the cement paste samples at various ages of hydration using a Bruker D8 Advanced Eco model without stopping the hydration. The scans were done in the range from 5 to 70° with a step size of 0.0167° and a time step of 30 s.

Mortar cubes of size 70.6 mm  $\times$  70.6 mm  $\times$  70.6 mm were cast to measure the compressive strength of different blends. The mortar samples were cast at a water-to-binder ratio of 0.45

with a constant sand-to-binder ratio of 3. The samples were demoulded 24 h after casting and were subsequently placed for underwater curing at a temperature of  $27 \pm 2^\circ\text{C}$  until the age of testing. The compressive strength was measured after 1, 3, 7 and 28 d. The rate of loading was kept constant at 35 (N/mm<sup>2</sup>)/min.

Prisms of size 100 mm  $\times$  100 mm  $\times$  250 mm were also cast at 15, 30 and 45% cement replacement level. The mortar prism samples were used to measure the carbonation resistance of the blends. After 28 d of underwater curing, the prism samples were preconditioned at a temperature of 27°C and 60% relative humidity for 14 d prior to exposure to carbon dioxide. Epoxy was applied to the square surface of the prism samples to induce unidirectional carbonation. The prism samples were placed in an accelerated carbonation chamber maintained at 3% carbon dioxide concentration, a temperature of 27°C and 40% relative humidity. The microstructural changes occurring on carbonation in samples exposed to 3% carbon dioxide concentration is similar to samples exposed in natural conditions (Cui *et al.*, 2015; Shah *et al.*, 2018). The rate of carbonation in concrete is slower in a higher relative humidity; hence, the relative humidity of 40% was selected for the study (Shah and Bishnoi, 2018b). The carbonation depth was measured by spraying 1% phenolphthalein indicator solution on the freshly broken surface of prism samples at different ages of exposure (Rilem CPC-18, 1988).

### Concrete

The concrete was cast according to the procedure described in the relevant Indian standards (IS 456 (BIS, 2000); IS 10262 (BIS, 2009)). Concrete was cast at a water-to-binder ratio of 0.40 at 0, 10, 15 and 20% cement replacement levels. Polycarboxylic ether (PCE)-based water-reducing admixture was used to improve the workability of the concrete. The details of the mix design for 1 m<sup>3</sup> of concrete for different mixes is given in Table 2. The admixture requirement of the concrete was adjusted to get a slump of 100 mm. Crushed stones were used as the coarse aggregate, having a nominal size of 10 and 20 mm mixed in a proportion of 0.66:1, whereas river sand was used as the fine aggregate. Owing to the high fineness and cohesive nature of the calcined clay particles, the admixture dosage required to obtain a slump similar to the control blend increased with the increase in replacement level of cement with LCCP.

Concrete cubes of size 150 mm  $\times$  150 mm  $\times$  150 mm and cylinders 100 mm high with a radius of 50 mm were cast. The compressive strength of the concrete was measured after 1, 3, 7, 28 and 90 d of curing. After 90 d of curing, the cylindrical samples were cut into discs with a height of  $50 \pm 2$  mm. The porosity of the concrete samples was determined by boiling water test, conducted in accordance with ASTM C642 (ASTM, 2008), on the disc samples. The rate of water absorption of the concrete was also measured on the disc samples

Table 2. Details of concrete mix design for 1 m<sup>3</sup>

	Cement: kg	LCCP: kg	Coarse aggregate: kg	Fine aggregate: kg	Admixture: kg	Water: kg
OPC	405	0	1193	673	2.4	162
10LCCP	364	41	1188	671	2.8	162
15LCCP	344	61	1186	670	3.2	162
20LCCP	324	81	1183	668	3.6	162

Note: xLCCP, x per cent of cement replaced with LCCP

according to the guidelines provided in ASTM C1585 (ASTM, 2004). Only the primary absorption rate was measured. The ionic movement and permeability in the concrete disc samples were measured using the rapid chloride permeability test (RCPT) as described in ASTM C1202 (ASTM, 2012). The RCPT values give an indirect approximation of the chloride resistance of the system.

**Results**

**Isothermal calorimetry**

The energy released during the hydration of the cement was measured using isothermal calorimetry. Figure 2 shows the isothermal calorimetry curves of OPC and blends containing different percentages of LCCP. The total energy released increases with the addition of LCCP. Figure 3 shows the cumulative energy released during the first 24 h of the hydration. The peak corresponding to aluminate hydration appears early and distinctly as the amount of LCCP is increased in the system, whereas at lower replacement levels the aluminate hydration peak is difficult to differentiate from the main peak of cement hydration. The peak around 8 h in 50LCCP shows the aluminate reaction.

**Setting time**

Table 3 shows the standard consistency and initial setting time values of different blends. The standard consistency value increases with the increase in cement replacement level by LCCP, implying that to obtain the same flow (workability) the amount of water required in blends containing LCCP is more as compared to OPC. The initial setting time of the cement paste marks the point at which the paste starts to lose its plasticity – that is the beginning of hardening of the cement paste (Dave *et al.*, 2017). A slight increase in the initial setting of LCCP blends is observed as compared to OPC at lower replacement levels, whereas a notable reduction in setting time is observed for the blends containing higher amounts of LCCP.

**Phase assemblage**

The phase assemblage of hydrated cement systems was studied using XRD. Figure 4 shows the XRD pattern of 7 d hydrated samples of OPC and LCCP blends. Ettringite and portlandite were the major crystalline phases present in the OPC sample. In LCCP blends, along with ettringite and portlandite, peaks corresponding to hemicarboaluminate and monocarboaluminate are observed. With the increase in replacement level, the intensity of the hemicarboaluminate peak increases,

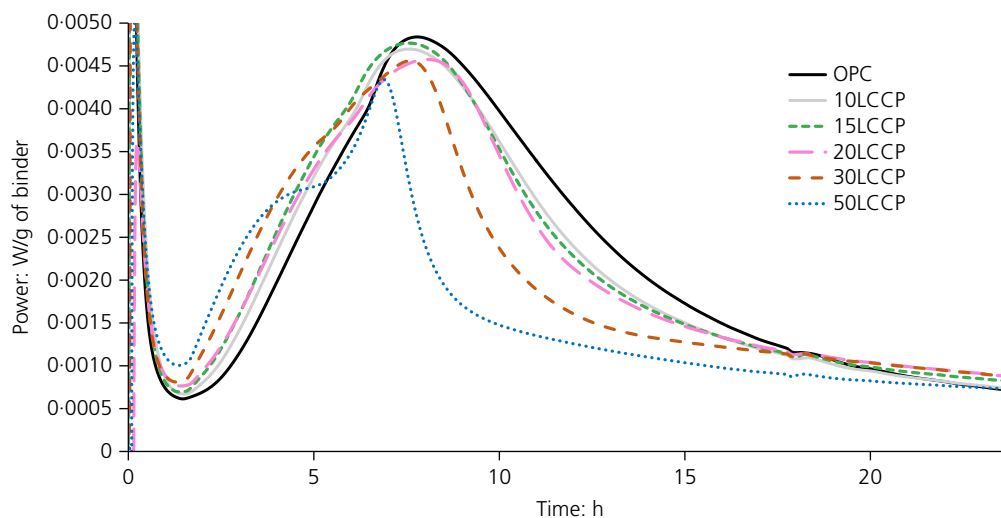


Figure 2. Isothermal calorimetry curve of cement at different replacement levels

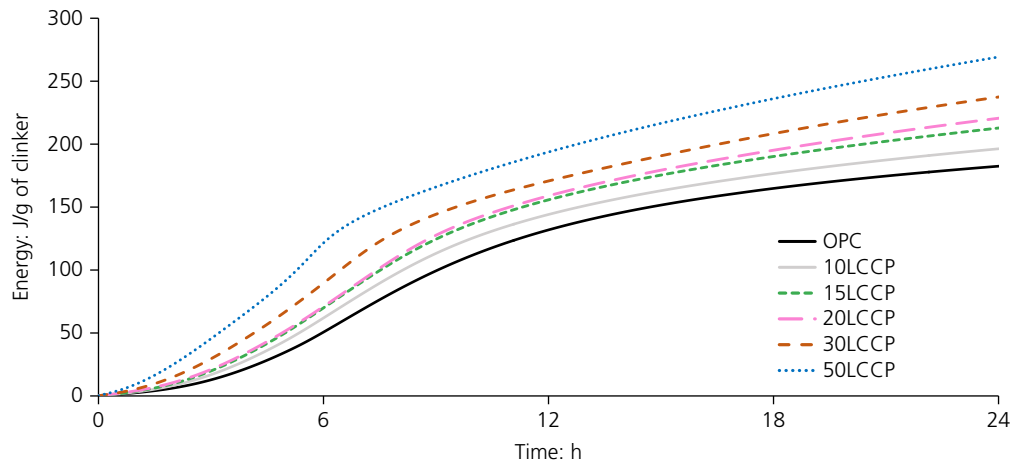


Figure 3. Cumulative energy released per gramme of OPC for all the blends

Table 3. Consistency and initial setting time of different blends

Material	Standard consistency: %	Initial setting time: min
OPC	31	140
10LCCP	34	145
15LCCP	36	155
20LCCP	37	145
30LCCP	38	125
50LCCP	43	120

whereas the intensity of the portlandite peak reduces. Rietveld analysis was used to quantify the XRD data using the external standard method. Rutile was used as the external standard. It was observed that the quantity of portlandite in the system reduces with an increase in the LCCP replacement level, as

shown in Figure 5. The reduction in the amount of portlandite is due to the pozzolanic reaction of calcined clay present in LCCP. The formation of carboaluminate phases is observed in 1 d hydrated samples of all the LCCP blends. Figure 6 shows the amount of carboaluminate phases in different blends at different ages. With hydration, the amount of carboaluminate phases present in the LCCP blends increases; the higher the replacement level, the higher is the amount of carboaluminate phase present in the system. The formation of carboaluminates is observed in OPC systems as well, owing to the presence of a small quantity of limestone in the cement as mineral additive.

Compressive strength

Figure 7 shows the compressive strength values of the cement mortar samples measured at different ages. An increase in

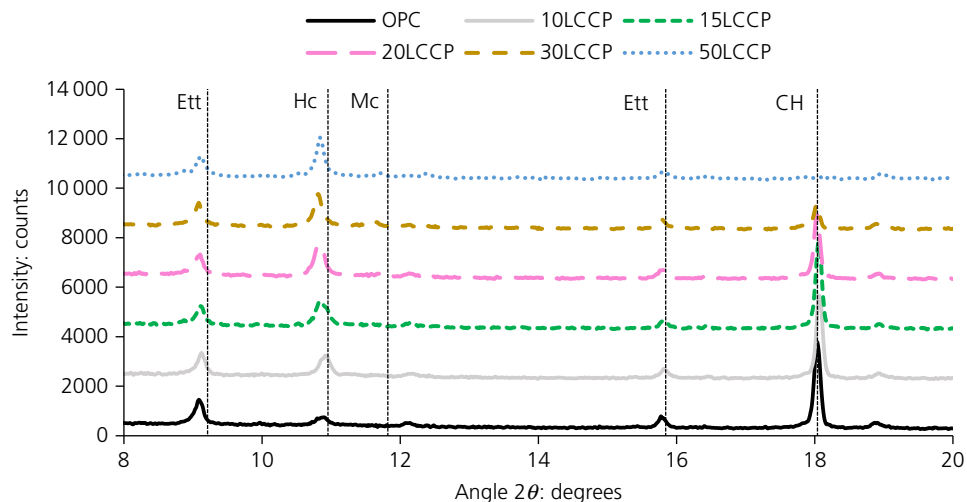
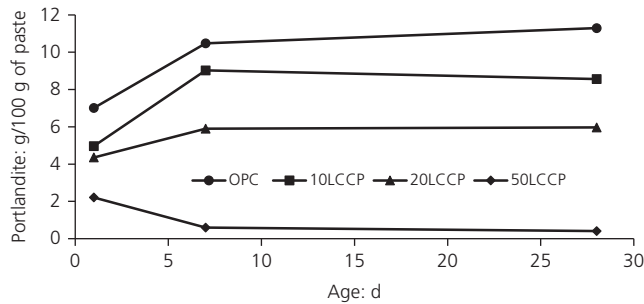
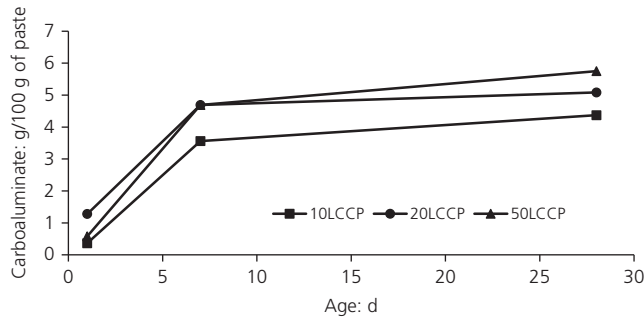


Figure 4. XRD scans of 7 d hydrated cement paste samples (Ett, ettringite; Hc, hemicarboaluminate; Mc, monocarboaluminate; CH, calcium hydroxide)

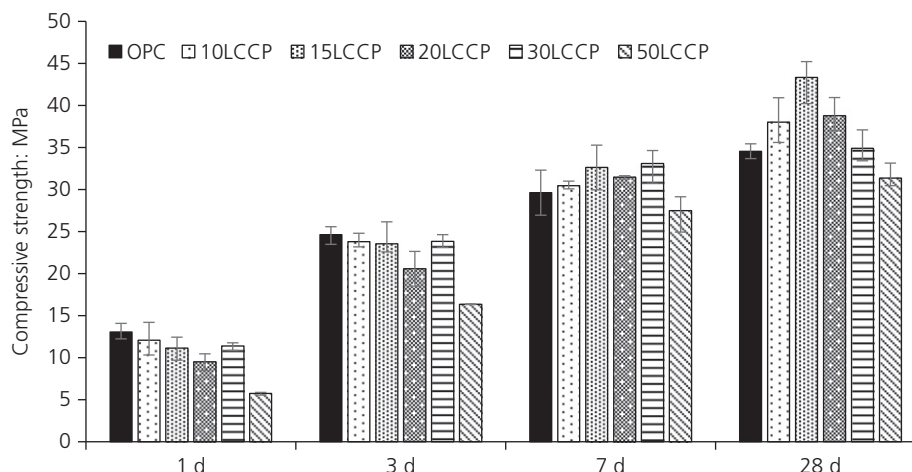


**Figure 5.** Amount of portlandite present per 100 g of paste quantified from XRD data using Rietveld analysis for OPC, 10LCCP, 20LCCP and 50LCCP at different ages



**Figure 6.** Amount of carboaluminate present in per 100 g of paste quantified from XRD data using Rietveld analysis for 10LCCP, 20LCCP and 50LCCP at different ages

compressive strength is observed until 30% replacement of cement with LCCP, whereas at 50% replacement a compressive strength similar to OPC is observed. The highest 28 d compressive strength is observed for the blend containing 15% LCCP. Figure 8 shows the compressive strength of the concrete



**Figure 7.** Compressive strength of mortar samples at different ages for different cement replacement levels

samples. Compressive strength higher than or similar to OPC is observed for all the replacement levels of cement.

**Transport properties**

The transport properties of concrete samples were accessed using porosity, sorption and rapid chloride ion permeability tests. Figure 9 shows the results for water accessible porosity of the concrete samples. The porosity of the concrete reduces on the addition of LCCP. The capillary suction was measured by the rate of water absorption in the concrete. The rate of water absorption of concrete reduces on replacing cement with LCCP, as shown in Figure 10. The ionic permeability of different concrete blends measured using RCPT at 90 d is shown in Figure 11. It is observed that the use of LCCP reduces the permeability of the concrete. The control mix OPC shows the highest chloride ion permeability among all the blends.

**Carbonation depth**

The carbonation depth in mortar prism samples was measured after 30, 60 and 90 d of exposure. Increase in the replacement level was observed to lead to an increase in carbonation depth. However, mortar cast with 15% cement replacement level shows carbonation resistance similar to OPC. Figure 12 shows the measured carbonation depth values for the mixes at different ages of exposure. The representative error bar shows the average variation in the carbonation depth values.

**Discussion**

The hydration process of cement consists of several stages: pre-induction or dissolution, induction, acceleration and deceleration (Bishnoi and Scrivener, 2009). A rapid dissolution of ionic species into the liquid phase and the formation of hydration products get underway on contact of the cement with water. After the short initial period of rapid dissolution, the overall hydration rate slows down significantly for a period of a few



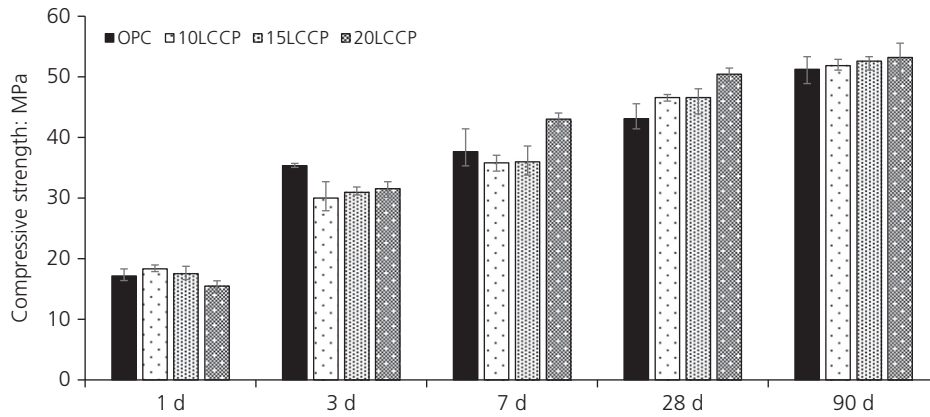


Figure 8. Compressive strength of concrete at different ages for different cement replacement levels

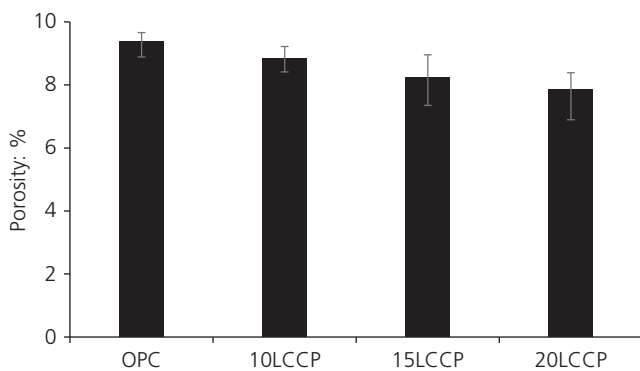


Figure 9. Percentage porosity in concrete samples measured using boiling water test

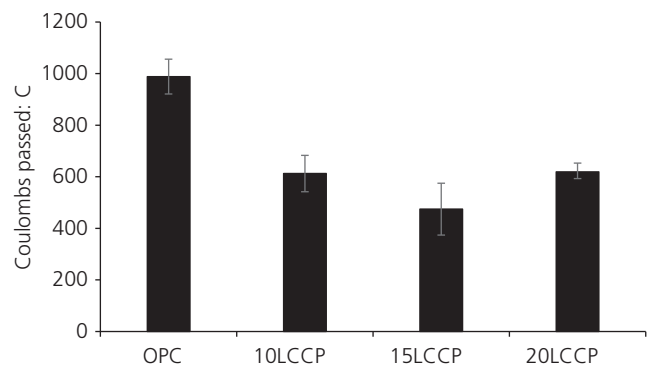


Figure 11. Chloride diffusion in all the blends measured using RCPT

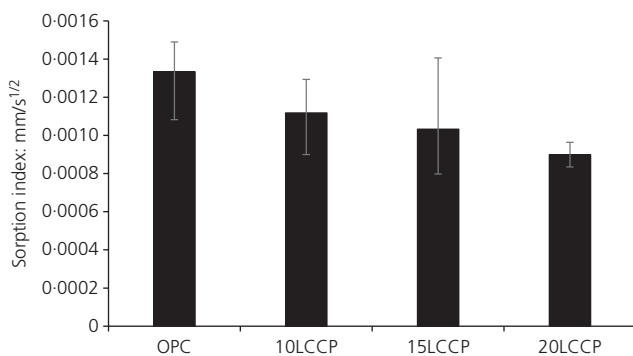


Figure 10. Rate of water absorption in concrete

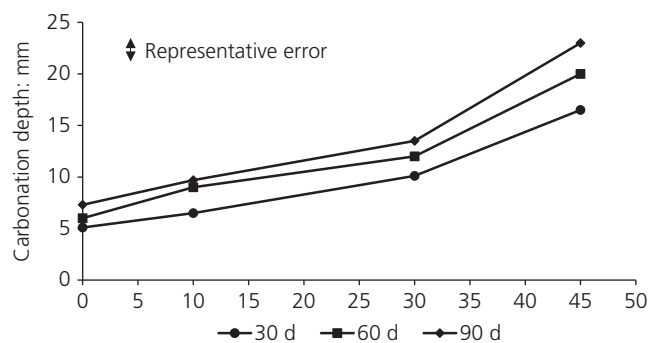


Figure 12. Carbonation depth measured after 30, 60 and 90 d of exposure in 3% carbon dioxide concentration, 40% relative humidity and a temperature of 27°C

hours. The induction period or dormant period reduces on replacing cement with LCCP. The isothermal calorimetry curves in Figure 2 show that the region where the energy released is at a minimum reduces on the addition of LCCP. Subsequently, the slope of the acceleration stage of the hydration process is observed to increase on increasing the

replacement level of cement with LCCP. The particles of LCCP provide extra nucleation sites for the growth of hydration products of cement, resulting in an enhanced reaction of the clinker phases. The beneficial effect of fillers on hydration has been reported in the literature (Choudhary *et al.*,

2016; Elgalhud *et al.*, 2016; Knop *et al.*, 2014; Thomas *et al.*, 2009). The peak corresponding to aluminate hydration occurs earlier and with higher intensity on increasing the amount of LCCP present in the system. The value of total energy released per gramme of OPC increases with the addition of LCCP. The hydration of aluminates from LCCP also possibly contributes to the heat released during the early hydration.

A slight increase in initial setting time is observed in blends containing up to 15% LCCP as compared to OPC. However, for cement paste samples containing 30% and 50% LCCP, a reduction in the setting time is observed. The setting time results are in agreement with isothermal calorimetry results that show a shorter induction period and faster acceleration in blends containing 30% and 50% LCCP. This contrasts with the setting time characteristics of cement replaced with the most widely used SCMs such as limestone, fly ash, slag and so on, which usually result in an increase in the initial setting time of the cement (Dave *et al.*, 2017; Siddique, 2008). The lower setting time of LCCP blends at higher replacement can be attributed to the additional reaction of calcined clay particles along with clinker grains. Owing to the high fineness and the structure of calcined clay, the water demand of LCCP blends is higher as compared to OPC blends to obtain a similar flow (consistency). Limestone particles in LCCP help to mitigate the demand for extra water to a certain extent. However, the higher water demand did not have any significant influence on the setting time characteristics of the LCCP blends. The implications of admixtures in terms of the setting time characteristics were not investigated in this study.

The pozzolanic reaction of calcined clay results in formation of additional C–S–H and carboaluminates and consumption of portlandite produced on hydration of clinker. The higher the replacement level of cement with LCCP, the lower is the amount of portlandite present in the system. For 50LCCP blend, no peaks corresponding to portlandite are observed after 7 d of hydration, implying consumption of all the portlandite produced on cement hydration by calcined clay. The amount of carboaluminates formed increases with hydration in all the LCCP blends. The compressive strengths of mortar and concrete of LCCP blends are either similar or greater when compared to OPC. The pozzolanic reaction of calcined clay and the formation of carboaluminates helps to improve the compressive strength of the system. The positive effect of the interaction of limestone with SCMs on the mechanical and durability properties have been reported in the literature (Antoni *et al.*, 2012; Emmanuel *et al.*, 2016). The carboaluminate phases formed are more stable as compared to that of monosulfoaluminate, which forms in the absence of carbonate ions during the decomposition of ettringite (Klieger and Hooton, 1990). Cements containing SCMs are generally known to have lower early strength due to the dilution effect and limited pozzolanic reaction of the SCMs during early age. However, in the present study, even at 50% cement replacement

with LCCP, no significant difference is observed in the compressive strength as compared to OPC at 28 d. At lower replacement levels, the compressive strength of LCCP blends is higher as compared to OPC, even at 7 d.

The higher the replacement level of cement with LCCP, the lower is the water-permeable porosity. The hydration products formed on pozzolanic reaction in blends containing LCCP are deposited in the pores and help to reduce the capillary porosity of the system. The rate of water absorption is found to be lower in all the LCCP blends studied as compared to OPC. The rate of water absorption in concrete is mainly governed by the capillary pores present in the concrete and their connectivity. The number of pores corresponding to smaller size increases in blends containing LCCP due to the pozzolanic reaction of calcined clay assisting in refinement of the pore structure. Refinement of the pore structure due to pozzolanic reaction of SCMs has been reported in the literature (Lothenbach *et al.*, 2011; Mehta and Manmohan, 1981; Sabir *et al.*, 2001; Shah and Bishnoi, 2018a). The refined pore structure increases the tortuosity of the system, thereby restricting the movement or transport of ions/fluids in the concrete. The reduction in value of the sorption index of LCCP blends could be primarily associated with the reduction in total volume of capillary pores and increased tortuosity. The rapid chloride permeation test result (Figure 11) shows a reduction in total charge passed on addition of LCCP to the cement, signifying improved resistance to chloride ingress in LCCP blends. With reduced capillary porosity and increased tortuosity, the permeability of the system also reduces. Chloride binding can occur in LCCP blends due to the higher amount of alumina hydrates. Chlorides are known to react with aluminate hydrates to form Friedel's salt. Also, physical binding of chloride ions on the surface of C–S–H is known to occur (Avet, 2017; Saillio *et al.*, 2014; Thomas *et al.*, 2012). The above phenomena can collectively result in lower chloride ingress in LCCP blends as compared to OPC. The carbonation resistance of cement containing SCMs is generally lower as compared to OPC due to lower total alkalinity (Branch *et al.*, 2016; Khunthongkeaw *et al.*, 2006; Shah and Bishnoi, 2018b). The higher the replacement level of cement with LCCP, the lower was the carbonation resistance of the cement. The lower carbonation resistance of LCCP blends can be attributed to lower calcium hydroxide content in the hydrated cement due to the pozzolanic reaction of calcined clay, which is the primary phase responsible for maintaining hydroxyl alkalinity in the system. However, the carbonation depth measured on 15LCCP mortar blend is only marginally higher than OPC, implying that, although the alkalinity of the system is reduced due to the pozzolanic reaction, the diffusion of carbon dioxide is slowed down due to the lower porosity and increased tortuosity of the system. Therefore, the formation of carboaluminates and the pozzolanic reaction of calcined clay have a significant positive influence on the transport properties of the system.



From the study carried out, it can be observed that LCCP can provide a sustainable and viable solution to the construction industry. The synergetic effect of the constituent materials of LCCP blended cement helps in developing concrete with improved mechanical and durability properties as compared to OPC. Medium-grade kaolinitic clay and limestone having purity of even 60% are found to be sufficient to make an efficient LCCP. Along with the advantage of the increased life of limestone quarries by producing low-clinker-factor cements, the use of low-grade limestone will help to consume the reject/waste limestone that is usually dumped with no useful application. The implications of using such limestone for other processes of cement and concrete production like grinding, workability and so on should be investigated thoroughly before being put into use.

### Conclusions

In this study, the feasibility of using a new type of LCCP as cement replacement was investigated. The effect of different cement replacement level with LCCP on hydration, setting time, strength development, transport properties and carbonation was investigated.

The rate of hydration of cement was found to increase on replacing cement with LCCP. The pozzolanic reaction of calcined clay and the additional sites provided by the fine particles of LCCP for the growth of hydration products is the primary reason for the increased rate of hydration. The higher the replacement level, the more prominent was the aluminate hydration peak, inferring participation of LCCP in the early age of hydration. No significant effect on initial setting time of cement paste was observed on replacing cement with LCCP at lower replacement levels, whereas a reduction in setting time was observed at higher replacement levels.

The XRD results show the formation of carboaluminate phases as early as 1 d after hydration, at all the replacement levels of cement with LCCP. Higher or similar compressive strength was obtained in all the LCCP blends at 28 d. Concrete prepared by replacing up to 20% cement with LCCP showed higher or similar strength as compared to OPC at all ages. The pozzolanic reaction of calcined clay resulting in the formation of C-S-H and carboaluminates helps to improve the mechanical properties of blends containing LCCP.

The water-permeable porosity and rate of water absorption were found to reduce on increasing the replacement level of cement with LCCP. The total charge passed in LCCP blends measured using the rapid chloride permeation test was found to be lower as compared to OPC. The carbonation resistance of the blends containing LCCP was lower as compared to OPC. The higher the replacement level, the lower was the carbonation resistance. However, at 15% replacement, the carbonation resistance of LCCP blend was found to be similar to OPC.

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