Physico-chemical Properties of Kenyan Made Calcined Clay -Limestone Cement (LC3)

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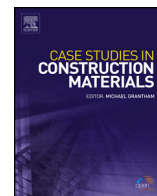Meru University of Science and Technology
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Physico-chemical properties of Kenyan made calcined Clay -Limestone cement (LC3)

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A B S T R A C T

In Kenya fired clay bricks are mainly used as construction materials. However, vast quantities of these Fired Rejected Clay Bricks (FRCB) generated are rejected annually as a result of improper calcination or demolition of housing units made of clay bricks. These FRCB are largely disposed off in open fields leading to land pollution. This paper reports the experimental findings on the performance of Limestone Calcined Clay Cement (LC3). The test cement was prepared by blending and inter-grinding of clinker, FRCB, limestone and gypsum. Saturated lime test was used to assess the pozzolanic activity of LC3. Mortar prisms measuring 40 mm x 40 mm x 160 mm were cast using LC3 at a water/cement (w/c) ratio of 0.50, 0.55 and 0.60. The casted mortars were cured in water for a period of 2, 7 and 28 day separately. Compressive strength tests were conducted at each of the testing ages on the cured mortar prisms. The cured mortars were also subjected to porosity and chloride ingress tests. Compressive strength measurements were also taken after exposure of 28-day cured mortar prisms in 3.5% sodium chloride solution in accelerated chloride ingress in a laboratory set-up. For comparison purposes, all the aforementioned tests were also conducted using commercial Ordinary Portland Cement (OPC) and Portland Pozzolana Cement (PPC). The results showed that LC3 and PPC were pozzolanic while OPC was non-pozzolanic. Furthermore, there was significant difference in terms of compressive strengths between LC3 and OPC at all the curing ages. In addition, LC3 exhibited lower porosity, chloride ingress in terms of chloride diffusion coefficients compared to PPC and OPC. Increased w/c ratio resulted in increased porosity, chloride ingress while compressive strength decreased. In conclusion, FRCB was found to be potential raw material for the production of LC3 in Kenya.

1. Introduction

Cement is considered as the primary material for use in housing and general construction worldwide [1]. Ordinary Portland Cement (OPC) is the most common type of cement used in construction especially where civil structures such as dams and bridges are needed. There is a growing demand for production and use of cement in most construction activities globally to meet the ever increasing demand for housing and general infrastructure. The production of OPC requires massive use of natural raw materials and energy [2]. The OPC manufacture process also results in significant emission of carbon dioxide (CO_2) in the atmosphere. Studies estimate that the cement industry is responsible for 5–8 percent of global man-made CO_2 emissions [2]. CO_2 is the greenhouse gas mainly responsible for global warming and climate change [3]. Additionally, during the production of Portland cement, argillaceous and calcareous materials are inter-ground, either in a wet or dry form and clinkerized in a rotary furnace at a temperature in excess of 1300 °C, fuelled by petroleum oil or coal. The resultant clinkers are inter-ground with about 5 percent gypsum ($CaSO_4.2H_2O$) to give Portland cement [1]. The process is

quite expensive, especially due to the high energy demand for fuel during clinkerisation process and grinding. The resultant Portland cement is therefore expensive and unaffordable to many, especially in developing countries [4–6].

The need to meet sustainable development calls for stringent measures aimed at the reduction of carbon footprint in cement industry is a key priority worldwide. There is a growing concern in the construction industry to reduce the amount of clinker in cement [7]. Therefore, reducing the clinker content in cement by replacement with calcined clay and limestone has been reported as a good alternative to lower the cost of the cement and reduce the amount of CO_2 emissions [30]. In Kenya, volcanic ash is mainly used in the manufacture of commercial Portland Pozzolana Cement (PPC). However, the geological distribution of volcanic ash is limited to some areas around Athi River in Kenya. This has resulted to massive agglomeration of cement industries in Athi River town due to its proximity to volcanic ash deposits [8]. Transportation of packaged cement to other parts of the country is one of the causes of increased prices of cement. Therefore, the cement is mainly unaffordable to a majority of Kenyan population.

On the other hand, fired clay bricks have been used in building and general construction purposes [9–14]. The fired clay bricks are commonly used in construction activities mainly due to the widespread availability of clays in most parts of Kenya and low cost of production of the bricks [15,16]. However, the fired clay bricks, when used in construction exhibits short service life. This has also led to mushrooming of slums in most regions where fired bricks are used. This calls for frequent repair or replacement of fired clay brick structures. This subsequently results in the generation of enormous Fired Rejected Clay Bricks (FRCB) generally considered as a waste material leading to: misuse of manpower, financial loss to contractors, significant impacts on health, aesthetics and environmental degradation. In addition, vast quantities of FRCB are annually generated as a result of improper calcination or demolition of housing units made of clay bricks. The FRCB are largely disposed off in open fields leading to land pollution. The present study therefore aimed to evaluate the use of FRCB in cement production. This has the potential to effectively lower the cost of cement, reduce the carbon foot print in cement industry and provide an eco-friendly means of waste disposal to ensure sustainable development.

Limestone Calcined Clay Cement (LC3) is innovative blended cement that is produced by blending of limestone, calcined clay, clinker and gypsum at specified proportions [2]. The cement is potentially affordable in Kenya due to low clinker content and abundance of raw materials such as clays and limestone [2]. LC3 is also eco-friendly since it can effectively reduce the CO_2 emissions by 30 percent [18]. Additionally, the production of LC3 cement does not require massive capital investments since a modification of existing cement plants can be done. Extensive studies have been carried out on the use of clays obtained from mines and low grade clays from industries, where such clays are considered not pure enough for use in their products. However, little attention has been paid on the potential of using broken fired clay bricks as a source of calcined clay for use in LC3 production. The main objective of the study was to evaluate the physico-chemical performance of LC3 made using FRCB, limestone and gypsum. Incorporation of ground FRCB and limestone is envisaged to reduce the proportion of clinker in the blended cements.

2. Materials and methods

2.1. Materials

Both limestone and FRCB were obtained from Kitui County in Kenya. FRCB were obtained from the demolition wastes at different damp sites within Kitui while limestone was obtained from Ngaaine, Kyuso Sub-County in Kitui County. The various FRCB obtained from various damp sites were mechanically mixed to obtain an homogenous mixture. The chemical composition of clinker, limestone, ground fired clay (broken clay bricks), PPC and gypsum are shown in Table 1 In addition, Table 2 gives the description of various cements used.

The description of various materials used in this study is given in Table 2.

Table 1
Chemical Composition of Clinker, Limestone, FRCB and Gypsum.

Chemical composition	Clinker	FRCB	Limestone	Gypsum	PPC
SiO_2	21.78	58.13	1.85	2.44	31.59
Al_2O_3	4.55	15.55	0.98	0.87	6.23
Fe_2O_3	3.97	9.88	1.63	0.79	3.29
CaO	62.97	1.66	68.63	34.25	45.77
MgO	1.05	0.83	1. 86	1.79	1.25
SO_3	2.07	0.04	0.02	40.82	1.66
K_2O	0.6	4.78	2.79	0.05	0.57
Na_2O	0.17	3.18	2.15	0.05	0.18
H_2O	2.33				2.13
Cl^-	0.01				0.047
Sum (SiO_2, Al_2O_3, Fe_2O_3)		83.56			
Loss on Ignition (LOI)	0.96	2.92	10.26	12.99	0.88
Blaine fineness, m^2/Kg	339	445			425

Table 2

Description of Various Cements used.

Cement Type	Description
OPC	Ordinary Portland Cement (OPC) [42.5 N/mm]. OPC was prepared by blending and inter-grinding of clinker and 5 % gypsum in a laboratory ball mill.
PPC	Commercial Portland Pozzolana Cement (PPC) [32.5 N/mm^2]. It is locally manufactured using volcanic ash as pozzolana.
LC3	A blend of 50 % of clinker, 30 % of ground fired clay bricks, 15 % limestone and 5 % gypsum inter-ground in a laboratory ball mill.

The mineralogical composition of FRCB obtained from X-Ray Diffraction (XRD) analysis is given in Fig. 1. The absence of kaolinite peak indicates that the FRCB was completely amorphous.

### 2.2. Methods

2.2.1. Pozzolanicity

Saturated lime test method was used to evaluate the pozzolanic activity of LC3, PPC and OPC. In this test, 100 ml of freshly boiled water was pipetted into a 250 ml plastic container. The container was sealed and placed in the thermostatic enclosure at $40 \pm 2\,^\circ$C until equilibrium was reached (about 1 h). The container was removed from the thermostatic enclosure. 20.00 g of the blended cement under the test was added to the water in the plastic container and shaken vigorously for 20 s to avoid formation of lumps. A horizontal rotary motion was used which prevented any part of the sample or liquid from being thrown up and remaining separated from the rest of the solution. The container was placed immediately into the thermostatic enclosure to avoid any appreciable decrease in temperature. After a period of 3, 8, 15, 21 and 28 days in the thermostatic enclosure, the container was removed from the thermostatic enclosure. The solution was then filtered immediately under vacuum through the Butchner funnel into the vacuum flask using a dry Whatman filter paper number 41. The flask was sealed immediately to avoid any appreciable carbonation by atmospheric carbon dioxide and allowed to cool to room temperature.

Determination of the concentration of hydroxyl ions was conducted by first shaking the vacuum flask to homogenize the filtrate. 50 ml of the filtrate were pipetted into a 250 ml conical flask. Five drops of methyl orange indicator were added. The resulting solution was titrated against the 0.1 M HCl to determine total alkalinity. The hydroxyl concentration in millimoles per liter was calculated according to Eq. 2.1.

$$[OH^-] = \frac{1000 \times 0.1 \times V}{50} \tag{2.1}$$

where V the volume of the 0.1 M HCl solution used for the titration.

In addition, the determination of the concentration of calcium oxide was done by adding 5 ml of sodium hydroxide solution and 50 mg of the murexide indicator solution that remained after completing [OH-] determination. The resulting
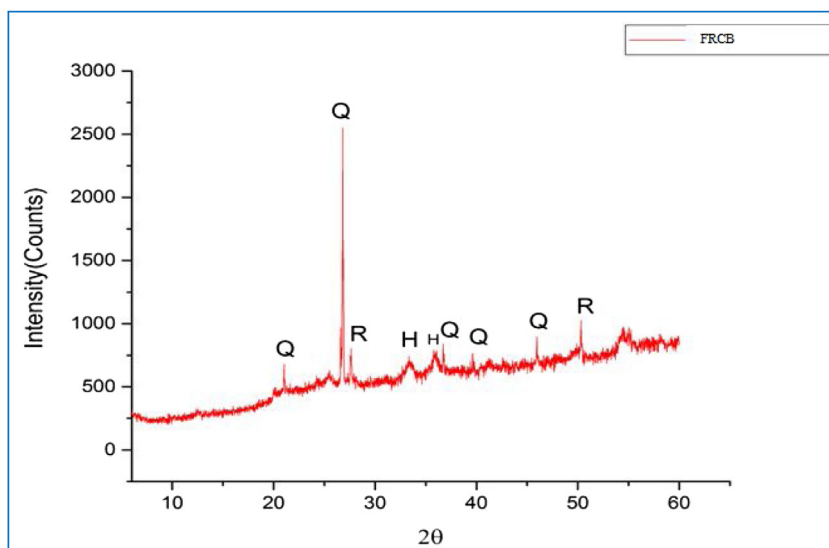
Fig. 1. XRD Spectra for FRCB.

solution was titrated against 0.025 M EDTA solution by means of burette until the color changed from purple to Violet. Before and during titration, the pH value of the solution was always confirmed to be 13 by means of a pH meter. In case the pH deviated from this, it was adjusted by addition of a requisite amount of the sodium hydroxide solution. To facilitate this, the EDTA was slowly added. Calcium oxide concentration, [CaO], in millimoles per liter was calculated using Eq. 2.2.

$$[CaO] = \frac{1000 \times 0.025 \times V}{25} \qquad (2.2)$$

where V, is the volume of the 0.025 M EDTA solution used for the titration.

2.2.2. Mortar preparation and compressive strength test

Mixing, casting and pre- curing of mortars was done in accordance to EAS 148-1:2000 standard with slight modifications. In this regard, 450 g of the LC3 cement was placed in the mix basin of an automatic programmable mixer. 1350 g of the standard sand was placed in an automatic pour-trough and automatically added a little by little until all the 1350 g was added while the mixer was still running at a speed of 30 rpm. The mix basin and its contents were clamped onto the automatic programmable mixer and allowed to run for three minutes. Requisite amount of 250 ml of water was added. The machine was left to run for ten minutes.

By using a trowel, the mortar paste was scooped from the automatic programmable mixing basin and placed in a compaction mould of a vibration compaction machine. Leveling of the paste was done with a mould trowel in each of the three chambers of the mould. This was done repeatedly until each mould chamber was half full. The compaction mould was then clamped onto the vibration compaction machine. The machine was set to automatically vibrate for 60 - blows at a speed of 30 - blows per minute. More mortar was scooped and placed onto the mould to fill. The compaction mould machine was again set to run at the same speed and blows per minute. A trowel was then used to level so as to achieve a smooth finish at the top of the mould. Where the mortar was seen to be leveling below the mould fill, mortar paste was added as the compaction proceeds. Excess mortar was cut off from the mould using the sharp edge of the trowel and the top surface of the mortar paste smoothened off using the same trowel.

The vibration machine mould clamps were then loosened to release the mould. The mould with mortar was placed into a temperature controlled room maintained at a temperature of $21 \pm 2\,°C$ and relative humidity above 90 percent for $24\,h \pm 30$ min. The above process was repeated using commercial PPC and OPC cements instead of LC3. Mortars were de-moulded within $24\,h \pm 30$ min and marked accordingly for identity purpose. The mortars were placed in a curing tank for 2, 7 and 28 days. At each testing age, mortar prisms from each cement category were removed from the curing tank, wiped and allowed to drain for 10 min. Each prism was placed in a compressive strength test machine following the instructions on the instrument manual in order to determine its compressive strength. The compressive strength results were presented in Megapascals (Mpa) for each curing period.

2.2.3. Porosity

Porosity of mortar was determined with a prism of 40 mm × 40 mm × 160 mm in size of specimens based on the study of [19]. The 28 day cured mortar prisms were oven dried at $100 \pm 5\,°C$ to a constant weight. Thereafter, the samples were immersed in water until they achieved full saturation and their weights in water were also recorded. Thereafter, the specimens were taken out and their surfaces wiped quickly with a wet cloth. The samples were weighed in air immediately. The porosity of the mortar specimens was approximated using Eq. 2.3.

$$P = \frac{W_a - W_b}{W_a - W_c} \times 100 \qquad (2.3)$$

where P is the porosity, W_a is the specimen weight in the saturated surface-dry condition, W_b is the specimen dry weight until reaching constant weight in oven and W_c is the weight of saturated specimen.

2.2.4. Chloride ingress

Chloride ingress test was conducted in accordance to ASTM C 1556 (2004). The cement mortar cured for 28 days were reduced to 100 mm length using cutting machine. An electrochemical cell was set-up in accordance with [19]. The mortar specimen were placed between two cells and covered with a fabric material. The anodic compartment was filled with 500 ml of water. An equal volume of 3.5 % NaCl was placed in the cathodic compartment. Stainless steel electrodes were placed on two sides of the specimen as the electrodes. The electrodes were connected to a 12 ± 0.1 V direct current (DC) power source. Current between the electrodes through the mortar was recorded using a milli-ampere ammeter after every 30 min. The top of the container was then covered with a polyethylene paper and the entire set up maintained at $22 \pm 1\,°C$ for thirty six hours. During the experimental period, the solutions were stirred periodically using a glass rod.

The mortar sample were removed from the electrochemical cell set up and allowed to drain for 30 min. Three mortar cubes for each ingress ion were sliced into 10 mm slices along the length using a water-lubricated cutting machine. Each slice was brushed using a 25 mm pure bristles brush and dried at 50 °C to a constant mass. A rotary hammer drill was used to drill through a circular portion of 25 mm from the center of each mortar slice. The mortar obtained was ground to pass through a 76 μm mesh sieve using a pulverizer. The ground mortar was placed in a 20-ml glass sample holder and shaken to mix. Before another sample is ground, the pulverizer-basins should thoroughly be cleaned with water and dried to avoid cross-

contamination. The ground samples were then subjected to chloride analysis. Triplicate analyses were done for every cement mortar category. Apparent diffusion coefficients (D_{app}) for each cement category were approximated from solutions to Fick's 2nd law using the error function.

3. Results and discussions

3.1. Pozzolanicity

Pozzolanic activity was used to measure the degree of reaction between a FRCB and Ca^{2+} or $Ca(OH)_2$ in the presence of water. Pozzolanic materials such as FRCB contain active amorphous silica and alumina which react with $Ca(OH)_2$ at ambient temperature. The quantity of $Ca(OH)_2$ in the cement solution in terms of the concentration of CaO and OH^- was determined. In practice, the lower the resulting quantity of $Ca(OH)_2$ or CaO and OH^-, the higher the pozzolanicity. In this study, a comparison on the quantity of CaO and OH^- in different cement types were conducted over time. Fig. 2 show the changes in concentration of CaO with time while the results on the concentration of OH^- at different curing durations are given in Fig. 3 at different curing durations for LC3, OPC and PPC cements.

It was observed that the blended cements (LC3 and PPC) showed a progressive decrease in the concentration of CaO and OH^- while OPC showed a slight increase at all the curing ages. This can be attributed to the differences in hydration processes in both cement categories. The hydration reactions of OPC that produce CH are given by Eqs 3.1 and 3.2 [20];

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{3.1}$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{3.2}$$

In OPC, the increased concentration of OH^- and CaO can be attributed to the accumulation of CH produced during the hydration with continued curing. However in LC3 and PPC, the CH produced during the hydration of OPC is consumed during pozzolana reaction resulting to the formation of calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) as shown in Eqs. 3.3 and 3.4 [20];

$$3CH + 2S + 3H \rightarrow C_3S_2H_3 \tag{3.3}$$

$$A + H + CH \rightarrow CAH \tag{3.4}$$

The progressive consumption of CH in LC3 and PPC effectively reduces the concentration of OH^- and CaO in the hydrated cement matrix. Pozzolanic cements are known to continuously consume and hence reduce CH in hydrated cement pastes as opposed to OPC.

In LC3 and PPC, the decrease in the CH component in hydrated cement matrix is beneficial as this lowers the phase that is susceptible to attack by aggressive media. The secondary cementious materials (CSH, CASH and CAH) produced during the pozzolanic reaction have cementitious properties resulting in the strength enhancement in pozzolana based cements. In addition, CSH, CASH and CAH phases lead to the densification of hardened cement and hence less permeable and more durable structures are obtained [4]. However, in OPC, the CH produced during the hydration process does not contribute to
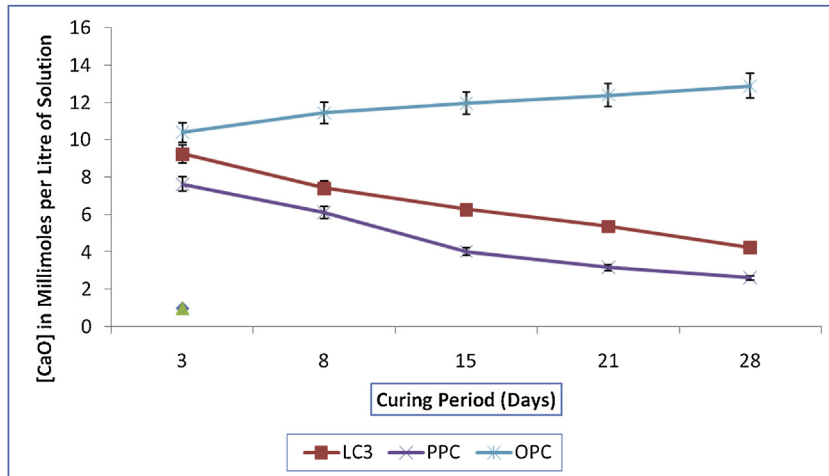

Fig. 2. Concentration of CaO in LC3, PPC & OPC Cements.
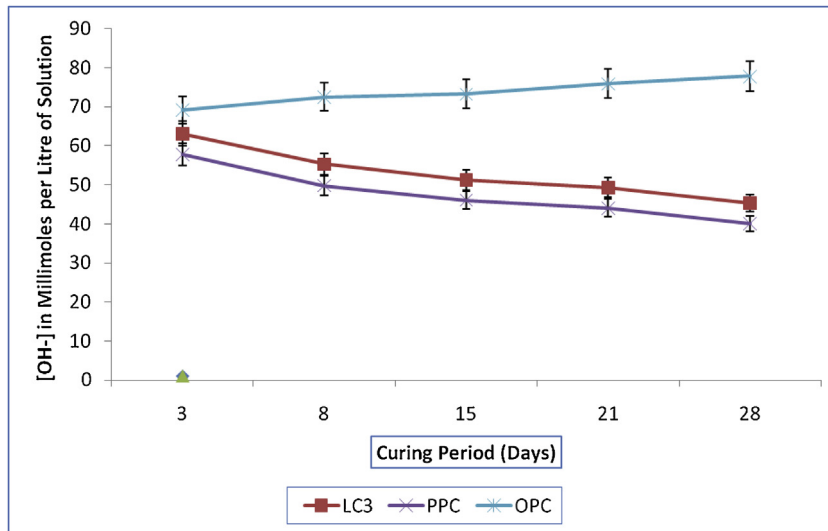
Fig. 3. Concentration of OH⁻ in LC3, PPC & OPC Cements.

the strength of the cement matrix. CH is slightly soluble in water and therefore decreases the paste amount thereby leaving behind a porous and a lower density paste in case leaching occurs. This results in lower strength and makes the system prone to attack by aggressive media. CH after dissolution travels to the surface of the cement-based system and reacts with atmospheric carbon dioxide leading to efflorescence [21]. CH has also been found to participate in alkali-silica reaction that weakens the cement-based system.

LC3 exhibited higher concentration of CaO and OH⁻ than PPC samples. This can be attributed to the fact that commercial PPC contains only volcanic ash as pozzolana while LC3 contained burnt clay and limestone as pozzolana. Limestone is calcium rich compound. Presence of limestone and burnt clay increases the concentration of CaO and OH⁻ in LC3.

In conclusion, LC3 exhibited lower pozzolanic activity than PPC. However, OPC was found to be non-pozzolanic. Generally, inclusion of limestone could have added more filler material in the hydrated cement matrix thus reducing the extent of pozzolanic activity in LC3 cements.

3.2. Compressive strength

The compressive strength results for LC3, PPC and OPC at varied w/c ratio and curing ages are represented in Fig. 4

Compressive strength increased with increased curing duration for all the cement categories. This is because curing promotes hydration reactions of the main phases of clinker phases present in LC3, PPC and OPC as shown in Eqs. 3.1 and 3.2
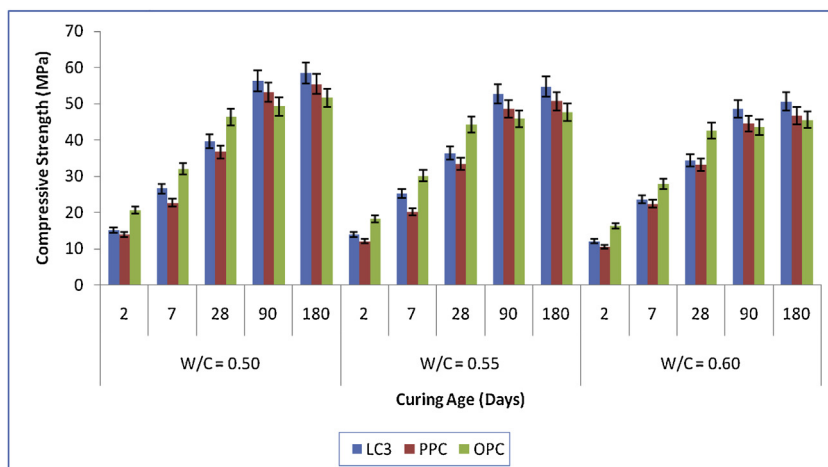

Fig. 4. Compressive Strength for LC3, PPC and OPC at Varied w/c ratios and Curing Ages.

[20]. The hydration of C_3A and C_4AF are shown in Eqs. 3.5 and 3.6;

$$C_3A + 6H \rightarrow C_3AH_6 \tag{3.5}$$

$$C_4AF + 4CH + 22H \rightarrow C_4AH_{13} + C_4FH_{13} \tag{3.6}$$

The hydration of C_3S and C_2S mainly produces calcium silicate hydrates ($C_3S_2H_3$) or simply CSH and calcium hydroxide (CH). The calcium silicate hydrates ($C_3S_2H_3$) is a cementious material primarily responsible for strength of hydrated cement based materials. However, the hydration products of C_3A and C_4AF are of no significance to the strength of cement hydrate pastes. Most of the early strength development (first four weeks) is mostly attributed to hydration of C_3S while C_2S influences the later gain in strength. In blended cements, the pozzolanic reaction takes place when CH is released during hydration of clinker phases in cement. The released CH reacts with pozzolanic materials in presence of water to form calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) as shown in Eqs. 3.3 and 3.4 [1].

Calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) are the secondary cementious materials. The pozzolanic reaction can be compared to the hydration of Portland cement since both reactions lead to the formation of calcium silicate hydrate (CSH). Both CSH and CAH from pozzolanic reaction contribute to the compressive strength of the blended cement mortars.

Commercial OPC exhibited higher compressive strength than LC3 and PPC at all the curing ages from 2 to 28 days. This could be attributed to the differences in the relative amount of C_3S and C_2S between the blended cements OPC. OPC contains a higher proportion of C_3S and C_2S that are mainly responsible for the higher strength development in OPC than the blended cements. On the other hand, the blended cements (LC3 and PPC) exhibited higher compressive strength than OPC at 90 and 180 days of curring at all w/c. This could be attributed to increased pozzolana reaction taking place in blended cements with increased curing duration [20].

It was observed that w/c ratio greatly influenced the strength of all test cements mortars at all the testing ages. The strength decreased in the order w/c = 0.50 > w/c = 0.55 > w/c = 0.60 w/c ratio is considered as the most important factor affecting mortars/concrete strength. This is because it affects the porosity of the hardened paste. The quantity of water used also affects the flow or rheology of the mixture as well as cohesion between paste and aggregate. As a result, it influences the overall strength of mortar.

In conclusion, the minimum standard requirements of compressive strength for cement mortar prisms by EAS 148-1 (2000), specifies a 28 days compressive strength of 32.5 MPa for Portland pozzolana cements. LC3 cement met this specification up to 50 per cent replacement of clinker by mass when limestone and FRCB were used regardless of the w/c taken. For the 28 days cured samples, there was a significant difference in terms of compressive strength gain between LC3 and commercial OPC at w/c = 0.50, w/c = 0.55, w/c = 0.60 as the T- calculated values were 45.29, 50.95 and 39.13 respectively. The T- calculated values were far above the T- critical value of 6.314 at 95 % confidence level.

3.3. Porosity

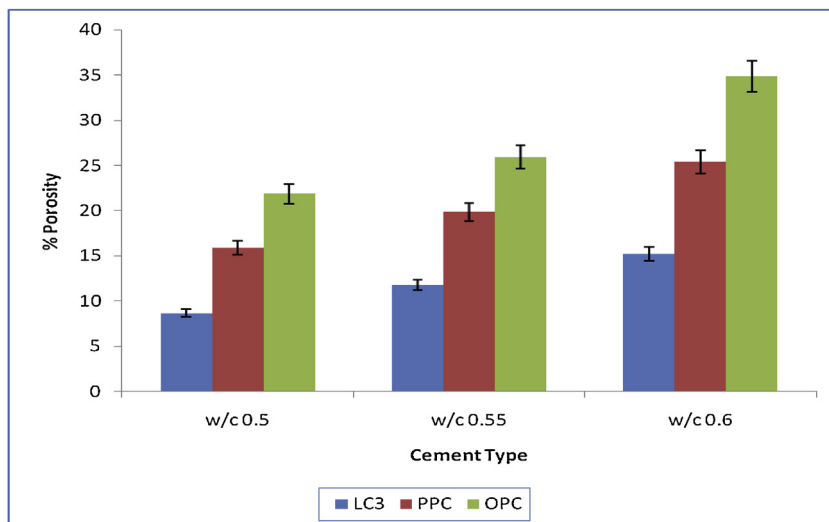The results of porosities for different mortars used are given in Fig. 5;

Fig. 5. Porosity of Hydrated LC3, PPC and OPC at Varied w/c Ratios.

It was observed that all blended cements exhibited lower porosity compared with OPC mortars. This is perhaps due to the incorporation of pozzolanic materials in blended cements. Pozzolanic materials increase the nucleation sites for precipitation of hydration products such as CAH, CSH and AFt phases that result in pore refinement thus lowering their porosity [22–25]. Additional secondary cementitious material formed during the pozzolanic reaction results in densification of mortars thus lowering their porosity. The presence of pozzolanic materials leads to a greater precipitation of cement gel products in blended cement than in OPC, which more effectively block the pores more effectively and therefore help to reduce permeability. The water-soluble CH liberated by hydrating cement may leach out of hardened cement and leave voids which increase porosity in OPC mortars. In blended cement, the pozzolanic reaction, by reaction of SiO_2 and Al_2O_3 with the CH, directly reduces the amount of CH and minimizes the leaching of CH subsequently reduces porosity of mortars. The additional secondary hydration products arising from the pozzolanic reaction, fills the voids, which result in more dense hydrated cement microstructure and consequently reduce the permeability of cement based materials from a pore refining process point of view.

LC3 exhibited lower porosity than PPC. This is because LC3 is OPC- calcined clay - limestone ternary cements systems. The ternary cement blends exhibits lower porosity than neat OPC made mortars. The reduced porosity can be attributed to the fact that as the hydration of cement progresses, the hydration products fill the pores to a greater extent in ternary cements than in blended cement containing a single type of pozzolana material such as PPC [26,27]. The hydration products in ternary cement blends such as LC3 have been found to occupy more than twice the volume occupied by anhydrous cement leading to enhanced pore refinement. The increased pore refinement effectively decreases the porosity of hardened cement more in LC3 cements than PPC.
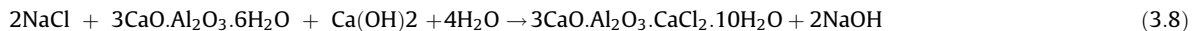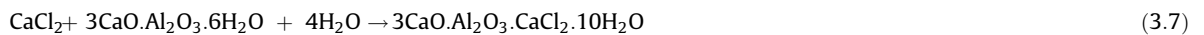
Porosity was observed to increase with increase w/c ratio. The porosity increased in the order w/c = 0.50 < w/c = 0.55 < w/c = 0.60. This is could be attributed to the increased addition of mixing water during casting. The increased w/c ratio leads to coarse pore distribution. This results in decreased pore refinement hence increasing the porosities.

3.4. Chloride ingress

3.4.1. Chloride diffusivity

Results for chloride ingress into LC3, PPC and OPC mortars at varied w/c ratio determined at different depths of cover within the mortar are graphically presented in Figs. 6–8.

It was observed that chlorides were found in mortars in all the cement categories. This can be attributed to the fact that all hydrated cements bind a certain proportion of chlorides present in the bulk of hydrated cement matrix. Chloride binding can either be physical or chemical [28,29]. The CSH phase is considered to physically bind chlorides due to its high specific surface values. Chemical binding involves the formation of Friedel's salts as shown in Eqs. 3.7 and 3.8 [28];

$$CaCl_2 + 3CaO.Al_2O_3.6H_2O + 4H_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O \qquad (3.7)$$

$$2NaCl + 3CaO.Al_2O_3.6H_2O + Ca(OH)2 + 4H_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O + 2NaOH \qquad (3.8)$$

There was a high chloride concentration at the shallow depths of cover (<20 mm), in all the cement categories. This could be attributed to the proximity of the mortars surfaces at the shallow depths of cover. Greater diffusion of chlorides could have occurred at shallow depths of cover resulting to higher chloride content than in those found in the bulk of the cement
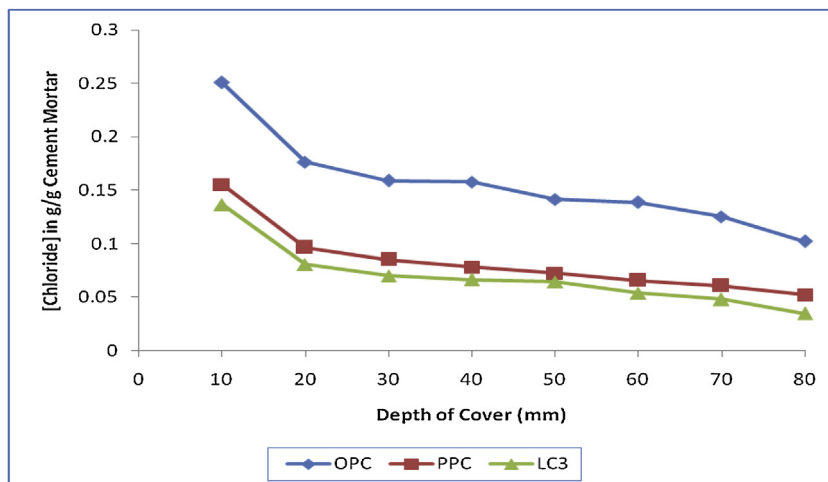

Fig. 6. Chloride Profile for LC3, PPC and OPC against Depth of Cover at w/c = 0.50.
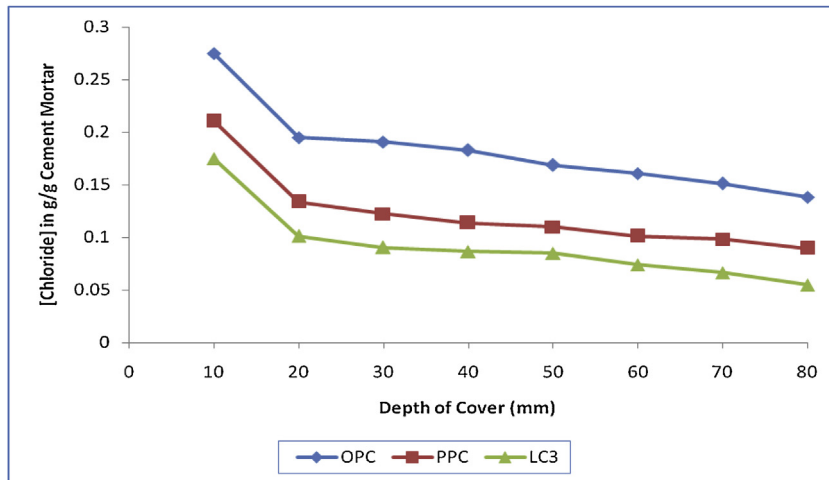
Fig. 7. Chloride Profile for LC3, PPC and OPC against Depth of Cover at w/c = 0.55.
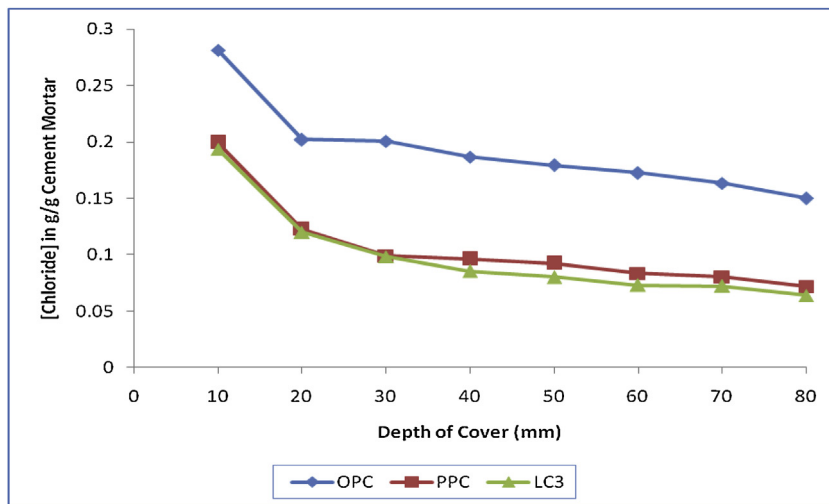

Fig. 8. Chloride Profile for LC3, PPC and OPC against Depth of Cover at w/c = 0.60.

mortars. In addition, the total chloride was observed to decrease with increase in depth of cover. This could be attributed to changes in the intrinsic diffusivity and chloride binding capacity of the cement involved. There was a sharp decrease in the amount of chlorides at the shallow depths of cover (<20 mm). This could be attributed to chloride binding capacity and diffusivity of chlorides in the cement mortar. At greater depths of cover (>20 mm), it was observed that in all the cement categories, all the cement mortars exhibited the lower chloride ingress. This is perhaps due to the fact that chloride binding increased with increased depth of cover as the chlorides diffuse inside bulk of the mortars resulting in increased chloride binding. This reduces diffusion rates of chlorides into the bulk of the cement involved.

Blended cements exhibited lower chloride ingress than OPC at all the depths of cover. This can be attributed to the fact that blended cements have lower CH than OPC in their pore solution. A low amount of CH in blended cements is as a result of pozzolanic reaction. CH, acts as the main source of OH^- hence the decreased amount of OH^- leads to a lower exchange capacity between the OH^- and the chlorides in the pore water. Lower exchange capacity between the OH^- and the chlorides in the pore water, reduced porosity result of pore refinement, denser mortar due to the deposition of more CSH from the pozzolanic reaction and higher binding capacity as a result of inclusion of pozzolana materials. These factors account for the low chloride ingress in blended cements. In addition, LC3 was observed to exhibit lower chloride ingress than PPC. This is because LC3 mortars exhibited lower porosity than PPC mortars. The low porosity in LC3 minimizes chloride ingress.

Chloride ingress was observed to increase with increase in w/c ratio. The total chlorides ingressed increased in the order w/c = 0.50 < w/c = 0.55 < w/c = 0.60. A high w/c ratio is known to contribute to a higher permeability consequently increasing the ingress of chlorides in cement pastes. When the w/c ratio increases, the porosity of the resultant mortar increases resulting in higher diffusivity of the chloride into the mortar.

3.4.2. Apparent chloride diffusion coefficients

The error fitting curve for determination of apparent chloride diffusion coefficient (D_{app}) for the test cement, OPC mortar at w/c = 0.50 is presented in Fig. 9. Similar error fitting curves were used for determination of the apparent diffusion coefficients for each cement category at w/c = 0.50, w/c = 0.55 and w/c = 0.60. Moreover, the error fitting data for each cement category is presented in Tables 3–5.

It was observed that the higher the w/c the higher was the D_{app} across all cement categories. This can be attributed to the fact that high w/c affects porosity mortars. The connectivity of the pore system depends on the amount of original mixing–water filled space and the degree to which it has been filled with hydration products. This could explain why increase in w/c ratios resulted to increased diffusion coefficients.

It was observed that the blended cements showed lower D_{app} than OPC at all w/c ratio. This is mainly because blended cements contain pozzolana materials which enhance chloride binding hence reducing the amount of ingressed chlorides. Blended cements have been found to bind more chlorides than OPC. High chloride binding ability effectively removes a large proportion of chloride ions in the pore structure of a cement mortar. This leads to low chloride ingress in the cement mortar characterized by low D_{app} as observed in this study. The chloride binding capacity is controlled by the amount of cementing materials used and the C_3A content in the hydrated cement. C_3A content of the cement influences its binding capacity, with increased C_3A content leading to increased binding.

In this study, LC3 exhibited lower D_{app} than PPC. This is because LC3 mortars were less porous than those of PPC. Highly porous cementitious materials allow greater permeability of chlorides thus resulting in increased D_{app} values. Significant decrease in the chloride diffusion coefficients is observed in ternary systems such as LC3 than in binary systems such as PPC. This can be attributed to the increased chloride binding with increase in the amount of supplementary cementitious materials added [28,29]. Addition of limestone and FRCB has been found to reduce the pore sizes leading to densification of the hydrated cement matrix thus lowering porosity and subsequently D_{app}.

The chloride diffusivity from migration tests (D_{mig}) were observed to be higher than those measured from the penetration profile [D_{app}]. This is because chloride diffusivity is dependent on the binding. In the migration test, the bound chloride is less than natural diffusion. Less chloride binding results in high diffusion coefficients and vice versa [17,30,32–34].

3.4.3. Change in compressive strength

The percent gain in compressive strength results after exposure of the mortar in 3.5 percent sodium chloride solution are given in Fig. 10;

Gain in compressive strength of mortars after exposure to 3.5 % sodium chloride was observed in all the test cements. This is perhaps due to the ingress of sodium and chloride ions in the hydrated cement matrix. The Na^+ and Cl^- are known to activate or initiate residual cement hydration or pozzolanic reaction and thus increase strength of mortar /concrete [19,31]
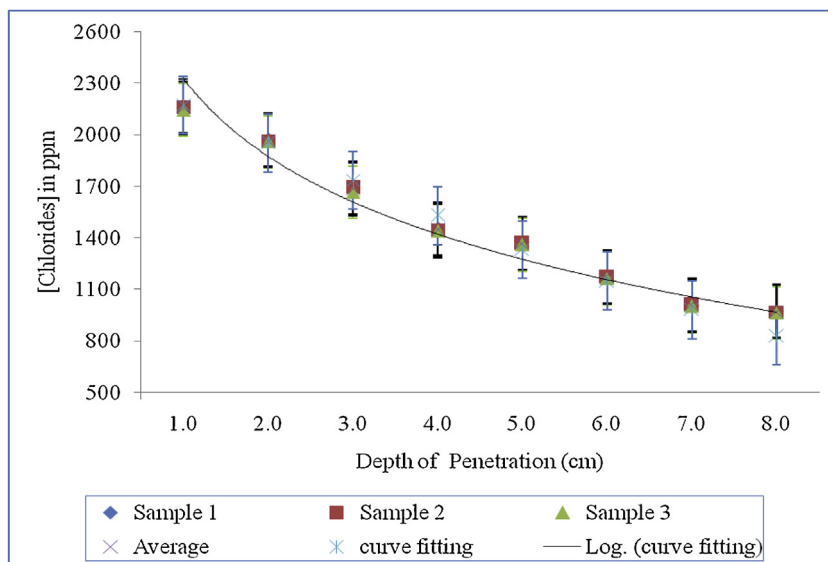

Fig. 9. Error Function Fitting Curve for OPC (w/c = 0.5, D_{app} = 15.65 × 10^{-12} m^2/s, r^2 = 0.945).

Table 3
D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/c = 0.50.

Binder type	w/c = 0.50		
	D_{mig} (m^2/s) $\times 10^{-10}$	D_{app} (m^2/s) $\times 10^{-12}$	r^2- values
LC3	1.147	4.489	0.969
PPC	1.253	6.948	0.968
OPC	2.773	15.65	0.945

Table 4
D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/c = 0.55.

Binder type	w/c = 0.55		
	$D_{mig} \times 10^{-10}$	$D_{app} \times {}_{10}{}^{12}$	r^2
LC3	1.424	5.015	0.975
PPC	1.831	7.934	0.969
OPC	3.226	18.069	0.945

Table 5
D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/c = 0.60.

Binder type	w/c = 0.60		
	D_{mig} (m^2/s) $\times 10^{-10}$	D_{app} (m^2/s) $\times 10^{-12}$	r^2- values
LC3	1.453	6.817	0.965
PPC	2.559	8.978	0.969
OPC	3.842	19.983	0.956
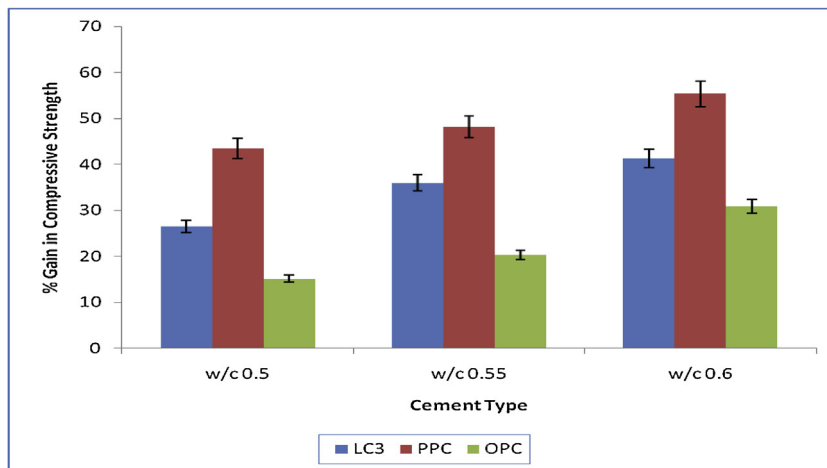
Fig. 10. Percentage Gain in Compressive Strength Verses Cement Type at Varying w/c Ratios.

It was observed that blended cements exhibited higher gain in compressive strength than OPC. This could be attributed to the fact that in blended cements ingressed chlorides activate the pozzolana reaction resulting in increased compressive strength [17]. The slight increase in compressive strength observed in OPC is possibly due to the ingressed chlorides initiating hydration reaction of residual OPC at 28 days of curing.

LC3 cements exhibited the lower gain in compressive strength compared to PPC although both are blended cements. This could be attributed to the low chloride ingress in LC3 cement mortars due their lower porosity than PPC. Low porosity in LC3 cement mortars is responsible for reduced ingress of aggressive chlorides ions. Chloride ions activate pozzolanic reaction

blended cements. Low chloride ingress observed in LC3 cements mortars therefore could have resulted in low gain in compressive strength.

Higher gain in compressive strength was observed at increased w/c. The compressive strength gain was higher in the higher the w/c ratio in all test cements. The gain was highest at w/c ratio of 0.6. High w/c ratio offers increased voids and spaces through which residual cement hydration takes place resulting in higher gain in compressive strengths.

4. Conclusion

In light of the above results and analysis, the following conclusions were made;

 i The FRCB are potential raw materials for LC3 production in Kenya.
 ii FRCB exhibited good pozzolanic activity when blended with limestone and clinker.
 iii LC3 exhibited the lowest porosity and chloride diffusivity and apparent chloride diffusivity coefficients than commercial PPC and OPC at all the w/c ratios used.
 iv Ingress of chloride ions in LC3, PPC and OPC were found to improve the compressive strength of the mortars.
 v Chloride ingress in hydrated mortars of LC3, PPC and OPC increased as porosity of their mortars increased.
 vi Porosity of the hydrated mortars increased as w/c ratio increased.
 vii Chloride ingress in hydrated cement mortars was majorly influenced by porosity, type of cement and w/c ratio.
 viii Generally, performance of LC3 in terms of its mechanical and durability indicated that it can be used in a similar construction environment as PPC and OPC.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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